1954

Contamination of food and air by lindane vapor.

Aristotle Nicholas Siakotos
University of Massachusetts Amherst

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CONTAMINATION OF FOOD AND AIR
BY LINDANE VAPOR

ARISTOTLE N. SIAKOTOS

1954

CONTAMINATION OF FOOD AND AIR BY LINDANE VAPOR

Aristotle N. Siakotos

Thesis submitted in partial fulfillment of the
requirements for the degree of

Master of Science

University of Massachusetts, Amherst.

1954.

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INTRODUCTION

In the period following World War II a great demand arose for newer and better insecticides. The new organic insecticides came into general use in unprecedented amounts. This demand was partially a result of the publicity given to DDT and other new insecticides. Also, great refinements and improvements of equipment resulted.

Insecticides are classified as materials that kill or repel insects by their chemical or physical action. Insecticides may be grouped into two classes: contact and stomach poisons. Contact poisons kill by contacting the body wall and penetrating into the circulatory system or the nervous system. Fumigants are also considered to be contact insecticides since they penetrate through the body wall or insect trachea, which may be considered as part of the body wall. Stomach poisons are taken in through the insect digestive system.

METHODS OF INSECTICIDE APPLICATION

Fumigation (or vaporization) is said by Hensil (1952) to be one of the oldest methods of applying insecticides, started perhaps by the ancients with the burning of sulfur. Dusts were also applied very early, for example, hellebore and pyrethrum powders. Later sprays came into general use starting with the soaps and oils and later with the arsenicals.

Recently continuous vaporization has entered the insect control field and has proved to be effective for controlling a wide variety of insect pests.

INTRODUCTION TO VAPORIZATION

Bourcart (1913) vaporized nicotine at high temperatures in closed areas. Hartzell (1926) fumigated greenhouses with naphthalene vapors. Gnadinger (1936) mentions an early use of pyrethrins, placing powdered flowers on a hot stove resulting in volatilization of the active insecticidal agent. Frear (1942) reports the application of rotenone by burning rotenone bearing roots. The above mentioned methods all have one thing in common. They are methods of discontinuous vaporization and high concentration treatments. The concentrations employed are usually in excess of the concentrations toxic or noxious to man and animals. Continuous vaporization employs a light dose of an insecticide over an extended period of time.

Continuous vaporization in the post war period was applied to insecticides with considerable success. British workers (Stammers, Whitfield, 1947; Fox-Wilson, 1949) had originated the concept of continuous space treatment. American workers further developed the idea of continuous vaporization. Spear and Sweetman (1952) vaporized DDT successfully. Christopher and Spear (1951) tested Lindane and found it capable of continuous vaporization.

According to Spear (1952) the concentration of Lindane vapor must be lethal to insects within a reason-

able period of time. However, the lethal concentration to insects must not be harmful to humans and other mammals occupying the area. To date, with properly operating vaporizers in enclosed areas, Lindane has not been shown to be harmful to humans exposed up to ten hours daily (Spear, 1952) excepting in a few cases of probable allergic individuals. However, in some cases (Conley, 1953) certain degradation products from contaminated Lindane may have been injurious (hydrogen chloride and trichlorobenzenes). As a result of the marked success with Lindane, vaporizers were widely sold for insect control in stores, theaters, restaurants, warehouses and other enclosed areas.

Spear (1952) states the advantages of using continuous vaporization over conventional methods of insect control to be as follows: (1) there are no diluents, (2) there are no stains on furnishings or equipment, (3) there is no dust and (4) the odor problem is negligible. The process is economical and requires a minimum of labor.

The disadvantages of such a method are, according to Spear (1952): (1) experienced and skilled men are needed to install the vaporizers in the correct position, (2) the breakdown of insecticide due to accidental contamination produces bad odors and a loss of insecticidal activity necessitating the use of very pure insecticides to prevent decomposition, and (3) as with any mechanical device, vaporizers are subject to mechanical defects and accurate rates of vaporization must be maintained under

varied conditions.

The insecticide commonly used in continuous vaporization is Lindane (the gamma isomer of hexachloro-cyclohexane). This insecticide lent itself readily to vaporization, (Spear, 1952; Spear & Sweetman, 1952). Christopher and Spear (1951) patented the use of Lindane for continuous vaporization. Lindane, when vaporized at the rate of approximately one gram per 24 hours per 15,000 cubic feet, remains as a vapor.

A CONTINUATION IN A SERIES OF STUDIES

This study is a continuation in a series of studies made at the University of Massachusetts. Spear (1950, 1952a) investigated vaporization characteristics of insecticides and toxicity of insecticide vapors to insects. Toczydlowski (1952) applied continuous vaporization to fabric pests and Moore (1951) employed continuous vaporization for the control of other structural insects. Decareau (1950) was interested in animal toxicity of Lindane vapor. Tatro (1952) was concerned with food contamination resulting from exposure of foods to vaporized Lindane.

This work is a continuation of Tatro's thesis problem with added emphasis on Lindane vapor concentrations, food package penetration by Lindane vapor, and food contamination by several methods of applying Lindane residues.

IMPORTANCE

Considerable interest has arisen in the past few years on the possible health hazards of insecticide residues in foods. According to Oser (1951) this interest, in many instances, is heightened by the lack of specific information regarding health hazards and documented case reports of ill-effects. Oser (1951) states that one must realize that no chemical is completely safe under all conditions and concentrations. Accordingly harmlessness should be evaluated only under the conditions employed. Oser (1951) also states that "ultimate proof of safety demands knowledge of all possible deleterious effects and is predicated on the demonstration of safety not merely in man but in all men irrespective of age, sex dietary habits, physical environment, physiological stress, health or disease. The day is not in sight when such ultimate proof will be possible." Hueper (1953), on the other hand, has stated that benign and malignant tumors have been produced in rats by prolonged ingestion of DDT. Arsenic cancers have been found among arsenic ore miners, smelter workers, arsenic insecticide manufactures, dusters and consumers of wine where grapes were sprayed with arsenical insecticides. Of course one must realize that both authorities are more or less stating opinions. Supporting data are not given.

At this point the dilemma of the public health authorities with regard to establishing safe residue tolerances becomes evident. What would be a safe tolerance?

Until considerably more reliable information can be furnished, the problems stated above will be in a state of flux. The Miller Bill (H. R. 7125) will provide some much needed clarification and revision of some of the present confusion in present statutes pertaining to insecticide contamination.

The same sort of confusion exists with the real and unreal hazards of vaporized Lindane. Some authorities (California State Board of Public Health, 1952) would ban all vaporizers and others permit their use under certain specific conditions (Haller and Simmons, 1951). The American Medical Association (Conley, 1953) does not prohibit or recommend the use of vaporized Lindane, but warns of excessive exposure to vaporizers and does not recommend their use in private homes and other small capacity areas.

PURPOSE

The purpose of this study was to determine the Lindane contamination of food resulting from several methods of application of Lindane as used commercially and in households. The methods of application employed were continuous vaporization, fumigation-residue, spraying of surfaces with an aqueous emulsion and painting surfaces with an oil solution.

With continuous vaporization the prime requisite is that a nearly constant concentration of the insecticide remains in the atmosphere being treated. The air concentration should be toxic to insects and non-toxic to humans. This method is used primarily for flying insects

although it is also effective on some crawling species. The fumigation-residue application utilizes the heat from a modified electric bulb to rapidly vaporize the insecticide into an enclosed unoccupied area. It produces a super-saturated atmosphere resulting in the deposition of a Lindane residue which is effective primarily against crawling insects. Any flying insects present in the space during or shortly after the treatment are also killed.

The paint and spray applications are used commonly in applying insecticides for crawling insects in households.

DESCRIPTION OF AEROVAP

One of the devices employed in this study to vaporize Lindane continuously is commercially known as the Aerovap* (Plate 1).

A detailed description has been given by Underwriters Laboratories, Inc. (1947, 1950). This device (Model C-20) is an electrically heated, thermostatically controlled wall bracket mounted vaporizer intended for insect control. It is essentially composed of four open-top cylindrical receptacles. The outer receptacle, of black bakelite, is attached to a bracket arm assembly for wall mounting. Within this outer receptacle fits a cast aluminum receptacle filled with heating elements and a thermostatic control. The innermost cup, of pyrex glass, is the container for the insecticide. The outer cup into

*A vaporizer produced by American Aerovap, Inc., New York City

Plate 1

The Aerovap, A Continuous Vaporizer

which the pyrex glass cup fits is of anodized aluminum. The pyrex glass cup has a capacity of about 150 grams of insecticide. Provision is made for the insertion of a thermometer for measurement of well temperature. Temperature is thermostatically controlled and accurate to $\pm 3^{\circ}$ C.

DESCRIPTION OF THE BUG BULB, A FUMIGATOR

The "Bug Bulb" (Plate 2) is a modified electric lamp with a depression at the top to provide a container for Lindane tablets. The upper half of the Bug Bulb is aluminized to concentrate the heat at the depression and so vaporize the insecticide at a maximum rate. This vaporizer can be screwed into any convenient electric socket that can be adjusted so that the vertical axis of the bulb is perpendicular to the floor. With each bulb twenty-four $1/3$ gram Lindane tablets are included.

The operation of the "Bug Bulb" lies entirely in the hands of the home-owner or other user. Because of this, the possibilities of misuse are infinitely great.

*A fumigation vaporizer produced by American Aerovap, Inc., New York City.

Plate 2

The Bug Bulb, A Lindane Fumigator

REVIEW OF LITERATURE

CHEMICAL PROPERTIES OF LINDANE

In 1825 Michael Faraday first synthesized the compound benzene hexachloride or 1,2,3,4,5,6 hexachlorocyclohexane. Its insecticidal properties were discovered in France in 1941 (Raucourt, 1945) and also independently in England in 1942 (Haller and Bowen, 1947).

There are sixteen possible isomers of hexachlorocyclohexane, six of which are known. The Greek letter prefixes do not denote spatial arrangement, but the order of discovery (Shepard, 1951).

The insecticidal activity of benzene hexachloride was discovered by Slade (1945) to be due, almost completely, to the gamma isomer content although the alpha isomer shows some slight toxicity to insects. Metcalf (1947) reports the insecticidal activity of the gamma isomer is one thousand times the insecticidal activity of a mixture of isomers (12 percent gamma isomer content).

Hexachlorocyclohexane may be produced by bubbling chlorine gas through benzene under ultra-violet light.

If the reaction takes place in the absence of ultra-violet light, hexachlorobenzene is produced.

Many modifications now exist which give an increased yield of the gamma isomer content; for example, Gunther (1946) states that the gamma isomer content is increased from 12 to 42% by adding 2% aqueous sodium hydroxide to the chlorination mixture.

Metcalf (1948) reports that in 1946 hexachlorocyclohexane contained the following constituents:

alpha isomer	=	65 - 70%
beta	"	= 5%
gamma	"	= 10 - 12%
delta	"	= 6%
epsilon	"	= 4%
heptachlorocyclohexane	=	4%
octachlorocyclohexane	=	0.6%

The heptachlorocyclohexane and octachlorocyclohexane are formed by the chlorination of monochloro and dichlorobenzenes.

The mixture of isomers is very stable and can be recrystallized from hot concentrated nitric acid, but in the presence of alkali three moles of hydrogen chloride are removed to give principally 1,2,4 trichlorobenzene and lesser amounts of 1,2,3 and 1,3,5 trichlorobenzenes (Christol, 1947). The gamma isomer may be separated from

the mixture by dissolving hexachlorocyclohexane in methyl alcohol which dissolves the gamma and delta isomers only. Upon concentrating the solutes the gamma isomer crystallizes out first. It is then recrystallized several times from chloroform (Slade, 1945). Another method is by use of chromatographic adsorption (Metcalf and Flint, 1951).

Lindane is the common name given to the gamma isomer of 1,2,3,4,5,6 hexachlorocyclohexane with a purity of not less than 99 percent of the gamma isomer (Rohwer, 1949). The compound was named in honor of Van der Linden, the Dutch scientist who originally described the gamma isomer.

Commercial Lindane has a melting point of 112° C. The calculated boiling point is 313° C. Its molecular weight is 290.85. It is a white crystalline material and is soluble in water to ten parts per million. It is also quite soluble in most organic solvents (Slade, 1945).

Gunther (1948) states that Lindane is stable to 110° C. and consequently Lindane can be employed for vaporization at or near that temperature without polymerization or rapid breakdown, as is the case with other insecticides such as pyrethrins and DDT.

The structure of the gamma isomer is according to Van Vloten (1948):

A musty taste is often produced when crops are treated with technical benzene hexachloride but the gamma isomer does not cause any appreciable altering of taste to food crops. The other isomers contribute the musty taste (Shepard, 1951).

LINDANE AIR CONCENTRATIONS

Lindane may be present in an atmosphere either as a vapor, liquid, solid or as a combination of these three states. The liquid state is not necessarily an intermediate stage between the solid and vapor states; sublimation may occur quite readily. By the use of the Ideal Gas Law one can readily calculate the amounts of Lindane that theoretically would be present in a room or atmosphere. However, this calculated concentration is not necessarily a true one because of ventilation or changes of air that normally take place in all but the most tightly sealed spaces. At various levels of enclosed spaces, drafts and semi-dead air spaces may affect the concentration. Sorption of Lindane vapor on surfaces may also affect the quantity in a space.

The relationship of the Ideal Gas Law may be expressed in the following formula:

$$pv = nRT$$

p = pressure in atmosphere
 $= \frac{P}{P_0} = \frac{\text{vapor pressure}}{760}$
 v = volume, liters or cm^3
 n = number of moles of material
 R = gas constant
 $= .0821 \text{ liter-atmospheres/degree-mole}$
 $= 82.1 \text{ cm}^3\text{-atmospheres/degree-mole}$
 T = Temperature (Kelvin) = $273 + ^\circ\text{C}.$

VAPOR PRESSURE DATA FOR LINDANE (Ethyl Corp., 1953)

<u>Temperature °C.</u>	<u>Vapor pressure of Solid Lindane (millimeters of Hg.)</u>	<u>Calculated Air Concentration at Saturation (micrograms/liter)</u>
0	$1.8 \times 10^{-6}^*$	.03
10	$7.8 \times 10^{-6}^*$	.13
20	3.17×10^{-5}	.50
30	1.16×10^{-4}	1.8
40	3.92×10^{-4}	5.9
50	1.26×10^{-3}	18.2

*by extrapolation

Brown (1951) considered the vapor pressure data by Slade (1945) as too high and the data by Balson (1947) as slightly low. The data by the Ethyl Corp. (1953) are taken by this writer as being the most reliable since they agree closely with actual near saturation values determined by Hornstein & Sullivan (1953).

METHODS OF ANALYSIS FOR LINDANE

There are now several methods for determining Lindane once it has been isolated. A few are: infrared spectroscopy (Daasch, 1947), polarography (Dragt, 1948; Grass and Spencer, 1949), cryoscopic analysis (Bowen and Pogarelskin, 1948), ultraviolet spectroscopy (Frawley and Davidow, 1949), chromatography (Alepi, Munter and Gall, 1948; Misato, Fukunaga, 1952) organic chlorine determination (Carter and Hubanks, 1946; Shaw, 1949) mass isotope dilution methods (Trenner, Walker and Buhs, 1949), labile chlorine analysis (La Clair, 1948), and micro combustion of Lindane (Krause, Przybylski and Tworek, 1950; Agazzi, Peters and Brooks, 1953).

There are also a number of bioassay methods (utilization of a sensitive test animal to estimate the concentration of a toxic material) which may be used (Hoskins, Messenger, 1950; Hoskins, Witt and Erwin, 1952).

More specific methods may be used. Generally, these methods employ the production of specific color reaction and the measurement of the intensity of this colored product as an estimate of the concentration (Fairing & Phillips, 1951; Sehechter & Hornstein, 1952; Phillips, 1952).

AIR ANALYSIS

General methods employed in air analysis (Jacobs, 1941 and Robinson, 1942) are outlined as follows:

1. Scrubbing or Washing Devices
2. Heated Traps
3. Freezing Traps
4. Adsorbers

An example of a scrubbing or washing device is the use of some relatively less volatile liquid in which the vapors are soluble (Robinson, 1942). Following the absorption of the chlorinated hydrocarbon vapors, the concentration of insecticide may be estimated by determining the chloride ions liberated after dehalogenation of the compound (Jacobs, 1941). Also classified under this general procedure is the earlier method of Hornstein and Sullivan (1953) which employs a wash solution of glacial acetic acid. The solution of Lindane and acetic acid is then analyzed according to the method for Lindane of Schechter and Hornstein (1952). The disadvantages of this method are the slow rate at which the air sample passed through the acetic acid, the loss of acetic acid through splashing and evaporation. The evaporation of glacial acetic acid was reduced considerably by Tatro (1952) who employed one Normal solution of acetic acid and water.

Heated traps have been employed by Fulton, Nelson and Smith (1950) to decompose Lindane vapors. In this method air was drawn through a quartz tube packed with platinum. The quartz tube was maintained at red heat by an electric furnace. The resulting hydrogen chloride was passed through an aqueous solution of Na_2CO_3

and As_2O_3 . The air concentrations determined ranged from .06 to 1.0 micrograms/liter. As with most organic chloride determinations there was a lack of characterization or specificity.

Other methods have employed very low temperatures to condense vapors in air. An example is the use of a liquid oxygen gas trap employed by Shepard, Rock, Howard and Stormes (1951). The materials determined were smog pollutants. The very low temperatures employed prevented the buildup of large crystals of water vapor which might produce stoppages in the flow of air. The crystals of water vapor formed are very small and are entrapped by a filter in the outgoing gas stream. This method probably could be applied to Lindane vapor analysis. Jacobs (1941) mentions the use of freeze traps to determine benzene and p-dichlorobenzene vapors.

The second method of Hornstein and Sullivan (1953) employs an adsorptive alumina (80-200 mesh) column to remove the Lindane vapors from the air sample. The column is then washed with glacial acetic acid and the wash solution is analyzed for Lindane by the method of Schechter and Hornstein (1952).

TOXICITY OF LINDANE TO MAMMALS

According to Jenkins (1945) the acute toxicity of the gamma isomer of hexachlorocyclohexane is as follows:

LD₅₀ Single Doses of gamma hexachlorocyclo-
hexane (mg/kg)

<u>Animal</u>	<u>Skin Application</u>	<u>Oral Ingestion</u>
Rabbit	300	200
Guinea Pig	400	100
Rat	500	200
Mouse	300	

The fatal single dosage for man has been estimated by Lehman (1948) to be:

<u>Intravenous</u>	<u>Skin Application</u>	<u>Oral Ingestion</u>
7 mg/kg	50 mg/kg	125 mg/kg

Later Lehman (1949) estimated that 15 grams or 65-70 mg/kg as the lethal dosage to an adult human. This figure is about half of the previous estimate.

There are two cases of acute human responses to this insecticide. The first (Kwoczek, 1950) involved accidental ingestion of about 15 cc. of a 30% solution of benzene hexachloride by a young girl five years of age and weighing about 50 lbs. It was presumed that the solvent also may have contributed somewhat to the death of the child. This dose represented approximately 4.5 grams of benzene hexachloride or 198 mg/kg. The case ended fatally. The second case (Anon., 1951) involved one of thirty-five patients under treatment for pinworms. A patient underwent an epileptic-like seizure for ten minutes after being administered 45 mg. of a hexachlorocyclohexane emulsion. He recovered shortly thereafter. Five other patients

exhibited symptoms of less severity. Later, lower dosages produced no observable effects.

Canaries died in a few days after exposure to Lindane vapor concentrations estimated to be about .2 micrograms/liter (Moore, 1951). Tropical aquarium fish have also been killed in water that was exposed to Lindane vapors (Schulze, Sweetman and Spear, 1952). Decareau (1951) observed that Lindane accumulation in rat tissues is below amounts considered to be of health significance. The air concentrations employed by Decareau were ten to twenty times commercial concentrations. Decareau (1951) also showed that canaries are sensitive but day old chicks had shown no ill effects to commercial concentrations after twelve weeks exposure. Lindane vapor concentrations ten times commercial applications produced no adverse effects on rats raised from birth to an age of 93 weeks (Spear, 1952a).

According to Lehman (1948) the health hazard of insecticides depends on their ability to penetrate the skin, solutions being far more dangerous than dry or wettable powders. Repeated exposures may also multiply the hazards two hundredfold to a single exposure.

Chronic ingestion toxicities for the rat have been investigated by Fitzhugh, Nelson and Frawley (1950) who found that no histopathological changes were noted in any organ at a 50 p.p.m. Lindane daily intake in the diet. Storage of Lindane occurs in the rat at intake levels below 20 p.p.m. (Laug, 1948). Laug reported (Table 1) the storage levels in the various organs of the rat.

TABLE 1

Micrograms Toxicant per Gram Wet Tissue (Laug, 1948)

<u>Rat No.</u>	<u>Sex</u>	<u>(Days) Period of Exposure</u>	<u>(Mg.) Gamma Isomer Content</u>	<u>Fat</u>	<u>Kidney</u>	<u>Liver</u>	<u>Blood</u>	<u>Spleen</u>	<u>Adrenals</u>	<u>Muscle</u>	<u>Brain</u>
Diet contained 20 p.p.m. gamma isomer benzene hexachloride											
19	M	36	15.5	trace	13	1.3	.38	4.3	0	0	0
20	M	79	30.7	9.2	34	.36	.20	0	0	0	0
21	M	114	44.8	0	35	.31	0	0	0	0	0
24	F*	36	15.7	22.0	5.7	.81	.29	1.8	0	trace	trace
23	F*	79	24.9	10.0	0	.54	0	0	0	0	0
22	F*	114	40.5	14.0	0	.52	0	0	0	0	0

*Castrated female

Accumulation of the insecticide varied considerably with sex. Storage of Lindane was greatest in the fat tissues, but also occurred in the liver and kidneys in significant amounts. Lindane also may be stored in the brain (Laug, 1948). Other organs stored or carried less significant amounts. Maximum accumulation occurred in six weeks; the gamma isomer is stored at the same rate as taken in (Lehman, 1948). Maximum storage occurs in the younger animals (Anon., 1951). Elimination is by the urine, feces and milk of lactating animals. In rats on a diet of 100 and 500 p.p.m., the compound disappears from the body in one to two weeks after ingestion is stopped. The maximum rate of excretion in milk was reached 24 hours after ingestion had ceased.

The routes of absorption in mammals are in the gastro-intestinal tract, the respiratory tract and the skin. The predominant injury is liver and kidney necrosis (Anon., 1951).

On a comparative basis (Anon., 1951) the gamma isomer is thought to be about one-fourth as toxic as DDT to man although on a mg./kg. basis (weight basis) Lindane is twice as toxic to man as DDT. The reason for this conclusion is that Lindane is thought to have a decreased disposition to tissue damage, is stored in smaller amounts and is eliminated more rapidly than DDT. Pathologically, benzene hexachloride is similar to DDT in that liver damage is extensive.

The alpha isomer induces hyperexcitability. The beta and delta isomers act as depressants, the delta being more depressant. The gamma acts as a central nervous stimulant, the principal symptom being convulsions. The order of symptoms of poisoning with benzene hexachloride with a high gamma concentration or Lindane are as follows:

1. restlessness
2. micturition
3. intermittent muscular spasms
4. loss of equilibrium
5. convulsions
6. collapse
7. death

The immediate cause of death is functional disturbances of the central nervous system, especially of the respiratory center.

The chronic symptoms are:

1. nervousness
2. lack of coordination
3. nausea
4. weight loss
5. general emaciation

Antidotes are phenobarbital or sodium pentobarbital. Upon recovery the patient is kept on a fat-free diet.

Some adverse effects of Lindane vapors to humans have been reported (Anon., 1951). Headaches, nausea, and

mucous membrane irritations have been the predominate symptoms. Most of these cases were accidental, probably due to excessive vaporization rates of Lindane or other insecticides brought about by malfunctioning of unsatisfactorily constructed or poorly adjusted vaporizers. Other instances of ill effects are probably due to allergic responses to Lindane and Lindane vapor (Anon., 1952). Within the limits of commercial vaporization rates there are few if any well documented cases of chronic or acute effects of Lindane vapors at the rate of one gram per 15,000 cubic feet per twenty-four hours.

A statement on the health hazards of continuous thermal generators has been advanced by the Interdepartmental Committee on Pest Control (Haller, and Simmons, 1951). The committee recommended the following:

1. "The insecticide shall be released at the rate not to exceed 1 gram per 15,000 cubic feet per 24 hours.
2. Installation shall be made only in commercial or industrial premises, mess halls, and similar locations where human exposure will be on a working day basis - not continuous.
3. The device should not be used in homes or sleeping quarters.
4. Devices shall be so constructed that output in excess of that recommended is impossible. Fuses to protect against overloading and high temperatures, and a pilot light to indicate whether or not the unit is operating should be a "built in" feature.
5. Units should be mounted above head height and 3 feet or more from the ceiling.

6. Installation shall be such that any material which might fall cannot be dislodged and fall into or otherwise contaminate food.

Since DDT and Lindane are poisons, it is the opinion of the committee that danger will arise from deliberate or unintentional violation of these basic principles".

The recommended (Interdepartmental Committee on Pest Control, 1953) conditions under which the fumigation vaporizers are permitted to be employed are:

1. The device may be used to vaporize Lindane in a closed room in a minimum amount of 1 gram in 1,000 cu. ft. and a maximum amount of 2 grams in 1,500 cu. ft.
2. The vaporization should be complete within a period of 2 to 4 hours during which the room is kept closed.
3. The treatment may be made in homes, including bedrooms, as well as other types of premises.
4. No human, pet, bird or fish should be permitted to occupy the room during the vaporization.
5. No foods should be exposed during the treatment.
6. The room should be aired out fully before reoccupancy.
7. The treatment should not be made oftener than once in two weeks.

This ruling, although not a law, served as an authoritative opinion to guide health officers and others in administration of health laws and ordinances (National Pest Control Association, Inc., 1953). The above ruling stimulated an active interest as to the possible contamination of the foods due to the proper use and the misuse of the "fumigation" vaporizer.

APPLICATIONS OF LINDANE

Lindane is an extreme stomach poison to insects, a persistent contact insecticide and, by virtue of its relatively high vapor pressure, a fumigant (Sherman, 1948). Hensil (1951) describes Lindane as being one of the most versatile of the modern insecticides.

Lindane may be formulated as wettable powders, dusts, emulsions, oil solutions or used as pure Lindane as is employed in the continuous vaporizers. Generally, Lindane is formulated as a wettable powder with 25% Lindane or as a dust containing 0.5 to 2% of the gamma isomer. It may also be formulated as a 20 to 25% emulsifiable concentrate or as a 0.5% oil solution.

Lindane is incompatible with calcium arsenate, lime, lime-sulfur, bordeaux mixtures, the glyoxalalidines (a series of fungicides) and nicotine (American Fruit Grower, 1952). The residue problem with Lindane applications under field conditions is much less than with DDT, but under indoor conditions Lindane may last several months (Metcalf, Flint and Flint, 1950).

Lindane has been economically effective against many crop pests, including aphids, grasshoppers, cutworms, leaf rollers, web worms, twig borers, stem borers, saw flies, Japanese beetles and many others (Brown, 1952).

Lindane, because of its toxicity, has also been used as a soil insecticide for wire worms, corn seed maggot, onion maggot, white grubs and other soil inhabiting insects.

Many insects affecting animals and man may also be controlled by this versatile insecticide. In this section Lindane rapidly increases in applicability and effectiveness and because it is easily eliminated by animals its overall toxicity is less than some other insecticides. It is effective against many mites, principally sarcoptic mange mites, hog mange, chorioptic mange, chiggers and chicken mites. Ticks, biting lice, sucking lice, bedbugs, fleas, cattle grubs and other insects are also controlled. Lindane is usually applied as a wettable powder in water sprays under high pressure on animals, as dusts or as in the case of some of the mite manges, in ointments.

Lindane may also be applied for the control of household pests: houseflies, clothes moths, carpet

beetles, stored food insects, roaches, and mosquitoes (Brown, 1952). It is usually applied as a spray, dust or vapor. Under continuous vaporization control is obtained, but far more important, preventive maintenance is continued against further entries. Fumigation treatments also may be applied under this category.

Although Lindane has proved to be an excellent insecticide for an extremely large number of insects and insect allies (O'Kane, 1947) it also is under certain conditions phytotoxic (Brown, 1952). Especially sensitive are the cucurbits. Another important factor is that Lindane, although having a relatively high vapor pressure, will persist and accumulate in soils for a long time. This may affect crops grown in later years.

THEORY OF ADSORPTION

According to Brunauer (1945) if a solid was present in an evacuated space and a gas or vapor introduced, a portion of the introduced gas or vapor would be taken up by the solid.

The molecules leaving the gaseous phase may enter the inside of the solid or liquid. When the

gas penetrates into the interior of the solid or liquid, it may dissolve in the material producing a solution or it may react with the material resulting in a new compound. This phenomenon is termed absorption.

If the molecules leaving the gas phase remain on the outside attached to the surface then this phenomenon is stated to be an example of adsorption. The gas molecules do not penetrate into the field of force existing between atoms, ions or molecules. In adsorption the gas is "fixed" to the solid surface although the molecules can move in a horizontal direction (to the surface) quite freely. This "fixed" state may occur as a result of a weak attraction or interaction between solid and gas, analogous to condensation (physical adsorption) or it may result as the product of a strong interaction or attraction similar to a chemical reaction (chemical adsorption).

If the two forementioned processes occur at the same time, sorption is said to have occurred.

In adsorption the solid material on and in which the uptake of gas occurs is called the adsorbent. A general characteristic of a good adsorbent is

a very highly porous structure with an extremely large surface area. The gas or vapor adhering to the surface of the solid is termed the adsorbate.

The gas-solid (gas-adsorbent) interface provides the starting point at which adsorption takes place. Molecules and atoms making up the solid are bonded to each other by various forces: electrostatic or Coulomb forces, exchange or homopolar valences, Van der Waals forces, etc. Within solids the forces acting on an atom are equal in all directions. At the surface each atom is acted on by imbalanced forces, the inward pull of neighboring atoms being far greater than the forces tending to pull the atom outward. The very weak forces tending to pull the atom outward are to the greatest extent contributed by gas or vapor molecules at a gas-solid interface. The result of this imbalance of forces is a tendency of the solid to reduce its surface area (surface tension). Decreases in the surface energy (surface tension $\times$ surface area) occur, under these circumstances, spontaneously since relatively no energy is needed to initiate them. All adsorption processes are exothermic and thus take place with a

release of energy. This release of energy is called the heat of adsorption. Often it is equal to the heat of condensation (physical adsorption) or it may equal the heat of chemical reaction (chemical adsorption). The adsorbed molecules or atoms saturate some of the imbalanced forces of the adsorbent decreasing its surface tension (the surface tension of solids is much greater than that of liquids). It follows then, that adsorption phenomena are spontaneous and occur with a decrease of the free energy (Brunauer, 1945). It would also follow that desorption in the system would take place with an increase in energy and consequently proceed at a slower rate (Gregg, 1951).

A state of equilibrium between the gas phase and the adsorbed phase is reached at varying rates. In physical adsorption equilibrium is reached almost immediately. A time lag may be due to the time required for the dissipation of heat evolved in adsorption, the comparative inaccessibility of parts of the surface and more often, the gas or vapor molecules having to displace previously adsorbed impurities (i.e. air). Thus the quantity and rate of adsorption depends on the nature of the

solid and gas, and impurities in the system.

The following diagrams may be employed to express the concentration relationships existing between the different sorption processes:

Physical Adsorption

Ideal Solution

Absorption

Chemical Adsorption

ordinates = $\frac{x}{M}$ amount adsorbed / amount adsorbent abscissas = $\frac{P}{P_0}$ change in pressure or concentration

These diagrams are ideal conceptions not actual processes or relationships. It must be remembered that although ideal adsorption occurs in evacuated atmospheres with the introduction of a

gas or vapor, adsorption also commonly occurs under unevacuated and other less ideal conditions, but it may proceed at a far less rapid rate. Also, often under these less ideal conditions it is difficult to determine the mechanism involved in the uptake of the material since the experimental conditions cannot be as carefully controlled as under high vacuum techniques. The adsorbents or sorbents in this thesis are not as uniform in structure or as pure as materials employed under experimental high vacuum work. Many materials do not sorb by one specific mechanism; the process of adsorption may change resulting in a complex adsorption-concentration relationship.

Various theories have been advanced regarding adsorption mechanisms. Molecules of a gas or vapor collide with the surface of a solid; this collision may result in the molecule being deflected from the surface; but frequently the molecule remains on the surface for a period of time. Langmuir (1918) states that this period of time is responsible for the phenomenon of adsorption. Valence forces decrease exponentially with the distance between

the adsorbed molecules and adsorbent surface molecules. This would result in a saturated surface on the adsorbent. It is unlikely that a second layer would form, but if the forces of attraction between the adsorbed molecules and the molecules remaining in the gas phase were strong enough a second layer might form. According to Brunauer, Emmett and Teller (1938) the second layer begins before the first layer is complete, resulting in a mass of clusters of molecules on the surface. The first layer is strongly adsorbed by the surface; the second layer is adsorbed by the first layer and this continues from layer to layer. The number of layers increases with the approach of vapor saturation values (Gregg, 1951). The attraction between layers is due to Van der Waals forces (inter-molecular attraction). The capillary condensation theory of Patrick (1920) is important only if the capillaries of the adsorbent are almost several molecules in diameter and at vapor concentrations of near saturation values.

SORPTION OF INSECTICIDES IN FOOD

With fumigation the insecticide acts on insects and the material that is fumigated as a gas or vapor. This is also true of continuous vaporization. The most important difference between the two processes is the relative amounts of insecticide applied in fumigation; the dosage rate in fumigation application often greatly exceeds the dosage rate in continuous vaporization applications. It follows then, that if both processes employ gaseous or vaporized insecticides, food contamination from both processes should be similar in respect to penetration, sorption and toxicity to insects. Thus the following review of sorption of insecticides is concerned primarily with fumigation work since published data on the effects of continuously vaporized Lindane are not available to any large extent.

Shepard (1951) states that in fumigation, molecular diffusion is the principle factor which brings about gas penetration of foods and other treated products. Daniels (1948) states that in gaseous state, where the intermolecular dis-

tances are greater than in the liquid state, collisions between molecules are less frequent. The mean free path between molecules is longer, thus permitting a more rapid rate of diffusion of the substance. Two forces are acting on particles, the force of gravity which pulls them down and the kinetic force which causes them to diffuse away from the region of higher concentration at the bottom.

Page and Lubatti (1940) found that the main source of loss of a fumigant from a closed space is sorption on products or porous materials. Fisk and Shepard (1938) reported that in order to kill insects in a container it was necessary to satisfy the absorptive capacity of the medium and yet maintain a concentration toxic to the insects. They also deduced that flour sorbs large quantities of any fumigant but the extent of absorption depends on the fumigant employed. Page and Lubatti (1940) and Shepard (1951) ascertained that the most important variables were the concentration of the fumigant, temperature, humidity, pressure, free moisture and the nature of the sorbing and sorbed products. Shepard (1951) stated that the higher the concen-

tration of the fumigant, the higher the rate of sorption of the fumigant by the product, hence the higher the contamination.

The results of Fisk and Shepard (1938) indicate that the boiling point of the fumigant was related to the amounts of material sorbed. Fumigants with low boiling points and high vapor pressures were more readily sorbed or at least retained. This would tend to indicate a relationship between condensibility and sorption.

If the fumigant forms a chemical compound with a constituent of the material fumigated, then another factor is introduced. Page and Lubatti (1940) found that when dried fruit was treated with hydrogen cyanide some hydrogen cyanide was retained by adsorption or solution and some was combined with fructose to form fructose cyanohydrin. Brown (1951) states that methyl bromide is sorbed by nuts and fatty foods and it can also form a chemical combination with proteins.

Cotton, Walkden and Schwitzgebel (1944) observed that the sorbed fumigants could be used to advantage by prolonging the actual period of fumigation.

Their studies of vacuum fumigation of flour in cloth bags with liquid hydrogen cyanide indicated that the greatest kill was obtained with insects remaining in the flour 48 hours after fumigation. The sorbed gas is retained and is lethal to insects after prolonged exposure. They also found some fumigants such as carbon disulfide, chloropicrin and some other gases were very injurious to wheat germ (as determined by germination tests). The fumigants were probably dissolved in the oils of the wheat germ. This latter view has been supported by the work of Pepper, Hastings and Douglas (1947) with carbon tetrachloride on wheat. However, Shepard (1951) advises that retention of a fumigant may constitute a serious hazard to persons reoccupying fumigated spaces or handling fumigated materials. Mention is not made of the possible contamination of the foods which may be consumed as purchased. This contamination could be serious with some of the highly toxic fumigant materials.

Most methods previously mentioned are concerned with actual quantities sorbed but a

few ideas on the mechanism of sorption are also advanced. Pepper, Hastings and Douglas (1947) attempted to explain some of the phenomena of sorption of carbon tetrachloride on wheat. They determined the absorption saturation values of wheat with carbon tetrachloride. The fumigant was allowed to distribute itself between the wheat and the air so that an equilibrium concentration resulted between the wheat and air at a constant temperature. Air concentrations of carbon tetrachloride were at saturation and as long as three weeks were required for equilibrium. The final sorbed concentrations were plotted to determine the mechanism of sorption involved. It was found that carbon tetrachloride was held in unground wheat as an almost completely ideal solution and in ground wheat as a nearly ideal solution but also in some other supplementary way. This supplementary absorption was indicated to be a surface phenomena or adsorption. Carbon tetrachloride dissolved presumably in the fats and alcohols present in the wheat germ. The fat content was 2.2% and the carbon tetrachloride dissolved to the extent of 1.9%. The very slow rate

of absorption with unground wheat as compared to that of the ground wheat was attributed to the slow diffusion of carbon tetrachloride to the interior of the kernel.

Desorption (Shepard, 1951) is dependent on the attraction between the material and the fumigant, temperature, moisture or other solvents, and ventilation.

Penetration and transference of the fumigant according to Page and Lubatti (1940) is due partly to diffusion and bulk movement under pressure. Both factors (Shepard, 1951) depend on the molecular weight, the concentration of the gas, the size of the pores through which the gas must pass, the distance the gas must diffuse, the moisture or solvent content of the commodity and the temperature. The energy of the diffusing gas molecules is the driving force in penetration while the sorptive capacity of the material is the resisting factor. Finely divided materials (Shepard, 1951) are the more difficult for fumigants to penetrate than granulated substances. This is due to the extremely large surface areas offered by the finer materials to the fumigant resulting in greater sorption. Also, the

smaller inter-particular spaces hinder diffusion.

Tatro (1952) exposed foods to commercial vaporized concentrations of Lindane vapor. His results are summarized as follows:

	<u>Mean p.p.m./day</u>
<u>Oleomargarine</u>	
After 1 week	2.50
" 3 weeks	.79
" 8 weeks	.43
<u>Bacon</u>	
After 1 week	1.70
" 3 weeks	1.84
<u>Bread</u>	
After 1 week	1.33
" 7 weeks	.42
<u>Pie Crust</u>	
After 1 week	3.08
" 7 weeks	.53

Tatro (1952) found that fat containing foods on long term exposure to Lindane vapor reached a fairly constant saturation value. He also

found an average of one p.p.m. Lindane in the yolk of eggs laid by chickens exposed to Lindane vapors. The average air concentration was .017 micrograms per liter.

Queen (1953) found the following contamination in products which were exposed to Lindane vapor at the rate of .98 grams per 15,000 cu. ft. per 24 hours. The foods were exposed for varying periods (2 days to one week).

<u>Food</u>	<u>p.p.m./day</u>
Sliced Bread	0.4
Sliced Bread (wrapped)	0.0166
Potato Chips	0.4
Potato Chips (cellophane pkg.)	0.10
Peanuts	0.85
Peanuts (cellophane pkg.)	0.10
Cereals in boxboard cartons	0.0143
Flour (top layer, pkgd.)	0.086

Lindane was desorbed from materials at an inverse ratio to its rate of sorption.

Muldoon and Sylvester (1951) mention that food packaging materials are usually chosen for strength, grease resistance and transfer of fixed

gases (such as nitrogen, oxygen, and carbon dioxide) and odors. Some foods such as butter and other fatty materials may undergo marked flavor changes due to absorption of foreign odors. Products such as coffee and other aromatic materials suffer from a loss of the volatile flavors. Dry cereal packaging serves primarily to prevent moisture from entering the package and thus maintain the crispness of the product. However rancid odors build up in many of these packages and must be permitted to escape.

The results of Muldoon and Sylvester (1951) with packaging materials transmitting a vapor (methyl furoate) are summarized as follows:

<u>Packaging Material</u>	<u>Grams furoic acid/ sq. meter/24 hrs.</u>
Waxed full glassine	.054
Saran 517.4 (0.0010 inch)	.925
Plain cereal glassine	2.27
Polyethylene (0.0010 inch)	6.77
450 PT cellophane	8.42
Plain Sulfite	11.9

It was also found that the effect of relative humidity on the transmission rate of most materials was quite pronounced. In all cases except polyethylene the rate of transmission was increased.

Complete protection to Lindane vapors was afforded only by a metal foil liner. Some of the results given by Queen (1953) for packaged breakfast foods exposed to commercial concentrations of Lindane vapors are as follows:

	<u>Mean p.p.m./day</u>
1. Cardboard	
14 days exposure	1.68
30 days exposure	.95
2. Cardboard - wax paper liner	
15 days exposure	.12
46 days exposure	.098
3. Cardboard - metal foil liner	
15 days exposure	0.0067

The vaporization rate was 1.19 grams per 15,000 cu. ft. per 24 hours.

PROCEDURE AND TECHNIQUES

SCHECHTER AND HORNSTEIN, (1952) METHOD OF
LINDANE ANALYSIS

The Schechter and Hornstein (1952) method is most sensitive for hexachlorocyclohexane. The authors claim a sensitivity of five micrograms. However, the results at that extreme limit are, at best, a guess with most materials.

The method of Schechter and Hornstein was followed in a modified form. An outline of the procedure follows:

A. Detection and Estimation

B. Determination

1. Sampling
2. Dechlorination of hexachlorocyclohexane to benzene and hydrochloric acid.
3. Distillation of benzene.
4. Absorption and nitration to m-dinitrobenzene.
5. Extraction of m-dinitrobenzene.
6. Reacting m-dinitrobenzene with concentrated potassium hydroxide and 2-butanone to produce a red-violet color.

7. Colorimetric measurement of color intensity at 565 millimicrons.

This procedure of analysis will also give the same color reaction with benzene and its homologs, but in this study several unexposed samples of each material were also analyzed and the results subtracted from the exposed samples.

Some difficulty was experienced regarding the size of the reaction flasks used (50 ml.) with regard to the size of sample taken. An attempt was made to utilize 500 ml. flasks. However, at concentrations beyond the mid-point of the standard transmission versus concentration curve, the results would vary by as much as 40%. The possible variables were checked (size of zinc particles, quantity of malonic acid, rate of heating and rate of refluxing of condenser). However, it was found that the nitrating column, which was packed with glass beads 3 mm. in diameter, permitted the benzene vapors to escape before being trapped and nitrated to m-dinitrobenzene. This column was then repacked with crushed 3 mm. soft glass tubing with a particle size of 0.2 to 0.5 cm. The column density was

maintained by the addition of a glass wool plug at the top. This plug prevented an alteration in column density by a surge of the vapors bubbling through the nitrating mixture. The results were then reproducible at 50% transmission with 2.0%. The percentages recovered in foods agreed quite closely with the authors 95-103% recovered. The total possible error for the modified method is estimated at about $\pm$ 5%.

The modified method of analysis for a total volume of 150 to 300 ml. is as follows:

Lubricate the nitrating column connecting joint and the stopcock with 85% phosphoric acid. Assemble. Add 6 ml. nitrating acid to the nitrating column. Lubricate the reaction flask joint with stopcock grease. Weigh the reaction flask, add sample and reweigh, the difference being the weight of the sample. Add 200-300 ml. of glacial acetic acid, 10 grams of malonic acid and 20 grams of zinc powder. (These quantities of malonic acid and zinc probably can be reduced considerably.) Connect flask and apply heat (a Fisher Hot-Spotter element in an insulated mineral oil bath wired to a plug

in the Hot-Spotter; the Hot-Spotter was used to vary the current or temperature).

Reflux for 2.5 hours. Remove heat and uncouple reaction flask. Drain acid solution into 10 ml. ice cold distilled water in a 250 ml. separatory funnel. Wash out column with 50 ml. cold water in three portions, then with 50 ml. ice cold diethyl ether, and again with 50 ml. distilled water. Shake well and allow layers to separate. Drain aqueous layer into 30 ml. ether in a second 250 ml. separatory funnel. Shake second separatory funnel well. Allow layers to separate and discard aqueous layer. To the first separatory funnel add 30 ml. 2% cold aqueous sodium hydroxide. Shake well and then drain into second separatory funnel. Shake second separatory funnel and discard aqueous layer. Add 30 ml. saturated ice cold aqueous sodium chloride solution to first separatory funnel. Shake well and drain aqueous layer into second separatory funnel. Shake the second separatory funnel and discard aqueous layer. Finally, shake both separatory funnels well and allow residual aqueous layer to separate, and then drain the aqueous layer carefully and completely.

Drain first separatory funnel through cotton wad in a Gooch crucible holder into a 250 ml. ground glass Erlenmeyer flask. Drain ether extract of second separatory funnel into the first funnel. Shake well and drain through cotton filter allowing ether solution to rinse the cotton plug thoroughly. Add 25 ml. ether to second separatory funnel. Shake well and drain into first funnel rinsing its walls. Drain first funnel through cotton filter again. Repeat rinsing of both separatory funnels and cotton wad twice more.

Add one drop mineral oil and one glass bead. Evaporate ether over a steam bath to about 0.5 ml. Remove flask and allow to cool to room temperature. Add 60.0 ml. of 2-butanone and 1 ml. 40% aqueous potassium hydroxide. Shake very well for 30 seconds. Allow to remain in dark for 10 minutes. Read transmission on Fisher Electrophotometer at 565 millimicrons using 2-butanone as the reference cell. Determine concentration from standard curve (a graph depicting a concentration versus transmission relationship) of concentration on milligrams plotted in tenths versus the transmission or

color intensity. Convert the concentration to parts per million.

The range of analysis is 0 to .5 mg. Higher concentrations may be determined by taking aliquots of the 2-butanone and m-dinitrobenzene solution and developing the color. Sensitivity with this method ranged .1 p.p.m. and higher.

After rinsing, the nitrating columns are dried as follows: attach to a water suction line and run through two 20 ml. portions of ethyl alcohol and then two 20 ml. portions of ethyl ether. Partially dry by continuing suction and allowing air to flow through apparatus for about one minute. Complete drying by placing columns in a steam heated drying oven over night. Leave door unlatched and slightly ajar. The columns must be thoroughly dried before use since the column when wet will hold several milliliters of water which will dilute the nitrating mixture and affect the results considerably.

There have been several modifications of this method by various authors (Mattson, Spillane and Pearce, 1953; Zeurner and Neuhaus, 1953) which have served to increase the reproductibility and

decrease the time required per analysis.

Some interesting information is given by Zeurner and Neuhaus (1953) regarding the determination of interference. With most other methods the recommendations usually are to run a blank (untreated) sample. Zeurner and Neuhaus (1953) recommend carrying a sample through the method of analysis, but not using any zinc in the reaction flask. This procedure will distill over the hexachlorocyclohexane and any benzene or benzene homologs or other materials in the substance being analysed. The hexachlorocyclohexane does not react with the nitrating acid but the benzene and other materials are nitrated. The resulting reading is taken as the "blank". This is a useful bit of information in view of the fact that often it is difficult to procure an untreated sample which has had the same aging and drying as the material being exposed.

The Mattson and Neuhaus modifications were made public at a date which precluded their application in this study.

An excellent feature of the Schechter and Hornstein (1952) method is the design of the

apparatus which serves to extract the reacted Lindane from the mass of material being analyzed by means of a modified fractionating condenser. Use of this by-passes the extraction, isolation and concentration procedures usually necessary with other methods. However, these procedures may be used in conjunction with the other processes of analysis thereby greatly increasing the sensitivity to detect very small quantities of Lindane in large samples.

Schechter and Hornstein (1952) claimed that their procedure is sensitive to 5 micrograms. This concentration would give a transmission reading greater than 95 percent. According to Kolthoff and Sandell (1952) the possible error at the extreme limits of a colorimetric analysis is rather high. As in the example cited by Kolthoff and Sandell (1952), the scale of the Fisher Electrophotometer can be read to ± 0.5 percent transmission. The transmission with the least possible error is about 36.8 percent. The possible error at that point is 1.4 percent. In the range of 13 to 70 percent transmission, the error is only 2 percent.

A possible error suggested by Zeurner and Neuhaus (1953) is the fact that any trichlorobenzene present will be determined as Lindane. In the Bug Bulb work this concentration of trichlorobenzene may be appreciable since the Lindane is heated to a very high temperature. According to Gunther (1948), although the gamma isomer is quite stable, it decomposes .07% in 24 hours of heating at 110° C. Since the Lindane is heated to a much higher temperature it is to be expected that a higher percentage of the Lindane will be decomposed to trichlorobenzene and hydrogen chloride. According to Brown (1951) if the isomers of benzene hexachloride are thermally generated as smokes they show 30% destruction. One would expect the decomposition of Lindane by the Bug Bulb to be higher than the .07% figure at 110° C. Considering the boiling points of trichlorobenzene (213° C.) and Lindane (315° C., estimated) it would be expected that the trichlorobenzene would not be condensed or sorbed as easily as Lindane. But, should it be sorbed or remain in the atmosphere, the error in samples taken immediately after or during the fumigation may be slight

since the trichlorobenzene would tend to remain as a vapor and be removed by normal ventilation. 1,2,4 trichlorobenzene is said by Tattersfield (1920) to be toxic as a fumigant against some soil insects.

Suggestions might be made concerning the analysis of trichlorobenzene in the presence of Lindane. They are (1) application of ultraviolet spectroscopy (determining the trichlorobenzene in the presence of Lindane), (2) application of hydrolysable chlorine (determining Lindane in the presence of trichlorobenzene since the end product of this dehalogenation is trichlorobenzene), (3) use of bioassay (the trichlorobenzenes being, in comparison to Lindane, relatively non-toxic), and (4) sulfonation of the trichlorobenzene and extraction with water may be also feasible (Shriner and Fuson, 1948).

With the commercial vaporization rates one then can expect less than .07% of the atmosphere samples to be trichlorobenzene but this error can be neglected. There is no reason to presume that there will be a building up of trichloro-

benzene in a treated (commercial rate) atmosphere since theoretically it will be removed at a slightly higher rate than Lindane in the normal air changes which occur in an enclosed space.

Any Lindane reacting with the aluminum foil cover resulting in trichlorobenzene will result in no appreciable error if it is determined as Lindane since it was originally so.

HORNSTEIN AND SULLIVAN (1953) METHOD OF
AIR ANALYSIS

The procedure of Hornstein and Sullivan (1953) has been employed for air analysis in this research. The sample was taken in the following manner:

————→ Alumina Tube ———→ Gas Meter ———→ Air Pump ———→

The alumina column was then eluted with glacial acetic acid and the solution analysed by the Schechter and Hornstein (1952) method for Lindane.

The pump used in these analyses was Model O, Type 1, Copeland Refrigerator Compressor with a vacuum line attached (manufactured by Copeland Products, Inc., Detroit, Mich.). The meter

employed to measure the volume of air was a Rockwell Gas Meter, No. O (manufactured by Rockwell Mfg. Co.). The rate of sample flow was about 50 to 55 cubic feet per hour.

It was noticed that the alumina column produced a considerable rise (15° C.) in temperature probable due to the heat of hydration or adsorption of water vapor on the alumina. There was no noticeable loss of Lindane from this heating effect. This was confirmed by Hornstein (1953) who ran two columns in a series. No Lindane was found in the second alumina column.

The chemical method was checked where ever possible by the use of a bioassay method (Spear, 1950). Fabric cages containing a known number of house flies were introduced in the treated atmosphere. The time required for a mortality of 50% of the population was used to establish a relationship of time versus concentration. This method has been used by other workers rather than the chemical method and it was thought that the bioassay would serve as an approximation of the air concentration employed under the conditions of the other workers for comparison.

LINDANE CONTAMINATION OF VARIOUS FOODS WITH
A FUMIGATION-RESIDUE APPLICATION

It was desirable for registration purposes with the U. S. Department of Agriculture to know what the contamination would be, if food under various forms of protection, were accidentally left in a room undergoing Lindane fumigation. Foods were exposed in packages and removed from packages as might be the case with an accidental exposure. Half of the unpackaged foods were covered with two layers of newspaper, newspapers being a common means of "protecting" exposed foods.

A corner basement room, Figure 1, with two windows and a door was employed to make the test. The volume was 984 cu. ft. including the closet. The estimated rate of air change was 1,700 cubic feet per hour (American Society of Heating and Ventilation Engineers, 1952). The exterior walls were of masonry and were about 18" thick. The interior walls and ceiling were of roughened plaster. The floor was waxed wood. All other wood surfaces were varnished. The plastered surfaces were painted.

Figure 1

The room was treated at the recommended rate of $2/3$ grams per 500 cu. ft. or four $1/3$ gram Lindane tablets.

The foods were purchased locally and were not, as far as is known, previously exposed to Lindane vapors. The foods exposed were as follows:

1. Winesap Apples - weighing 61 to 83 grams and 5 to 6 cm. in diameter. After exposure the apples were washed with 150 cc. glacial acetic acid.
2. Butter - Land-O-Lakes brand, labelled "sweet cream, lightly salted butter." Each sample represents $1/8$ of a pound or $1/2$ of a quarter. The samples were 3 x 3 x 6 cm. and weighed 48 to 65 grams each. The packaged samples were exposed in their parchment wrappers within the conventional waxed paperboard box.
3. Shredded Wheat Biscuits. Each sample represents $1/2$ of a shredded wheat biscuit, approximately 9.5 x 4.75 x 3 cm. in size and weighing 14 to 15 grams. The box was White Patent

Coated News Board with a caliper of .020 inches according to R. T. Hower of the National Biscuit Company. The package size was the 6 oz. "New Small Family Package". The test samples were taken from the top layer in the packaged samples.

4. Cookies - Ann Dale brand, manufactured by the Ann Dale Products, Inc., Fall River, Mass., named "Sugar Fingers". One half of the cookies were vanilla flavored and the other half were cocoa flavored. Each sample consisted of two cookies, one of each flavor. The cookies were oval in shape, with approximate dimensions of 8.5 x 3.5 x 1 cm., and weighed from 18 to 20 grams.

5. Sliced Bread - Wonder Bread manufactured by the Continental Baking Company. It was wrapped in waxed paper. The slices of bread measured approximately 10 x 11 x 1.3 cm. and weighed from 22 to 31 grams.

6. Bologna - sliced. The results with this material were very erratic. Consequently, this material was omitted from further study. There was not enough time to determine the source

of error. The data of Queen (1953) indicate good results with bologna.

The samples were arranged on plywood trays about 15 hours previous to the exposure. The samples were scattered at random on pieces of aluminum foil. Two samples of each food were employed to provide duplicates in the event of the loss of one sample. Blank samples were placed in wide mouthed jars with glacial acetic acid and sealed with aluminum foil covered stoppers. The plywood trays with the unpackaged samples (uncovered and covered) were placed 30 inches above the floor on a desk. The packaged samples were also placed 30 inches above the floor on a plywood tray on the bed.

The two hour samples were exposed to the Lindane concentration given off by the fumigation process into the atmosphere in the room. These samples were then removed and the room was ventilated for 1/2 hour according to the directions of the manufacturer. The exposed samples were then placed in wide mouthed jars, covered with glacial acetic acid, shaken and refrigerated

until ready to be analysed to prevent any loss of the Lindane. Analyses were completed within 24 days after the treatment.

Following the 1/2 hour airing of the room, the 24 hour samples were exposed to the vapors which originated from revaporization of part of the residual Lindane and any Lindane vapors or aerosol particles remaining in the atmosphere. Results of the exposure are shown in Table 2.

PACKAGE EXPOSURE TO CONTINUOUSLY VAPORIZED LINDANE

Packaged foods kept in storerooms, warehouses and other storage areas are often attacked by stored food insects. Roaches, houseflies and other insects also may infest the rooms. Continuous vaporization of insecticides has been employed as a control measure against the pests. Any insects gaining entrance either from infested quarters nearby or from previously infested foods or packing materials would be eliminated before new infestations could be established.

Many food packages function merely as a food container. However, others are constructed to permit the exchange of gases and vapors. It is

conceivable then, that Lindane vapor may penetrate some packaging materials under storage conditions and contaminate the enclosed products.

In this test the object was to determine if contamination of packaged foods occurred upon exposure to an atmosphere of Lindane being vaporized at the rate of approximately one gram of Lindane per 15,000 cu. ft. per 24 hours.

The storeroom selected was a basement food storage area (Fig. 2). The walls and floor were of finished concrete. The walls were about 8 inches thick. There were seven windows and two doors. The ceiling consisted of studding with a board floor which was surfaced with a floor covering. The windows were 15 x 24" and were placed at ceiling height. During the exposure two or three windows remained open continuously. One door opened to the outside serving as a loading and unloading entrance and the other door opened into a corridor leading to a kitchen. The volume of the space was 33,687 cu. ft.

Two vaporizers were installed, one near each end of the room. The vaporizers were placed

Figure 2

so that their position did not interfere with the usual movement of stored materials. The average rate of vaporization was about 2.05 grams per 24 hours per 33,687 cu. ft. or about 1 gram per 24 hours per 16,240 ft.

The foods were placed on the second shelf from the top of a typical storage rack. A distance of about 2" was maintained between packages. Samples were taken after various periods of exposure.

In nearly all cases the samples were analysed immediately after being collected. Samples not analysed immediately were stored in glacial acetic acid.

The foods were purchased at a neighborhood store and were not previously exposed to Lindane vapors, in so far as is known. Unexposed samples of each food were analysed. The foods and their packaging materials are as follows:

1. Cornflakes, Kelloggs, 8 oz. pkg.

The package was composed of two parts, an inner sack of 25 pound waxed glassine and an outer box of White Patent Newsboard having a thickness of .0175 inches (Trout, 1953). The dimensions of the package are 17.5 x 24.5 x 6 cm. The

sample was taken by carefully slitting through both packages, pouring cornflakes into a mortar and reducing the sample with a pestle. Each sample weighed about 67 to 115 grams. The sample was divided into two flasks, run separately and then the m-dinitrobenzene extracts in ether were combined and determined colorimetrically as one sample.

2. Shredded Wheat Biscuits. The box was coated White Patent Newsboard with a caliper of .020 inches (Hower, 1953). The package size was the 6 oz. "New Small Family Package". The dimensions of the package are 10.8 x 7.7 x 19 cm. Samples were taken from the top layer and weighed about 13 to 26 grams (about 1/2 biscuit). The biscuits were reduced in the same manner as the cornflakes.

3. Flako - a pastry mix made by the Flako Products Corp. The package was the standard 9 oz. size. The dimensions were 7 x 14 x 3.5 cm. The packaging materials are of two sections, an inner bag consisting of a laminated liner paper 47# basis and an outer carton consisting of

.020 stock, coated Patent Newsboard (Stolz, 1953).

Samples were taken from the top of the package and weighed 90 to 113 grams. The sample was divided into two flasks, analysed separately, and the m-dinitrobenzene extracts in ether were combined and determined colorimetrically as one sample.

4. Flour, Pillsbury's Best, 2 pound pkg.

The bag was of uncoated, unlined bleached Kraft paper, (Easter, 1953). The dimensions of the package are 11 x 7 x 16 cm. Samples taken for analysis weighed 21 to 56 grams. The samples were taken in the following manner. The package was placed horizontally on the two longest dimensions as carefully as possible so as not to allow the flour to flow. The top (side) 1 cm. layer of flour was carefully removed; then the 2 cm. layer was removed and finally a section 3.7 cm. from each side (center) was sampled. The 1 cm. layer and 2 cm. layer had 1 cm. and 2 cm., respectively, removed from the margins so that only Lindane that had penetrated to the respective depths was determined.

The untreated flour samples when analysed were variable in their apparent interference content;

therefore an average of 8 samples was taken as the mean interference. The untreated samples varied $\pm .3$ p.p.m. from the mean. It is surmised that the deviation in results were due to various degrees of charring in the sample.

5. Soup Mix, Lipton's Chicken Noodle.

The outer package was of a Boxboard with dimensions of 12.7 x 10.5 x 4 cm. There were three separate inner packages (13.2 x 10.6 cm.) of a laminated aluminum foil (aluminum to paper). Each inner package contained 2 1/8 oz. of a dry soup mix. The total sample taken for analysis consisted of two inner envelopes, a total weight of about 118 grams. The soup mix gave a high blank test but the exposed samples were higher in concentration.

6. Shredded Coconut, Lake Shore brand, 2 oz. package, distributed by W. F. Straub and Co., Chicago, Illinois. The package consisted of two cellophane bags, one within the other, heat sealed at the top and folded and cemented at the base. The samples were taken from the top and bottom of the package or a representative sample

was taken after mixing up the contents well.

7. Sugar, granulated, Domino brand, American Sugar Refining Co., 5 lb. Kraft bag. The results including the controls, were so variable that they were believed to be unreliable and so were not included.

CONTAMINATION FROM THREE METHODS OF APPLYING LINDANE RESIDUES

A great deal of speculation has been raised by Food and Drug Administration and Public Health Officials as to the possible consumer hazard from a recent method of applying Lindane as a residual treatment. With the fumigant-residual application a quantity of Lindane is heated very rapidly so that a supersaturated atmosphere of Lindane results. This excess Lindane is deposited on exposed surfaces and evaporates slowly (Queen, 1953). However, the contamination (due to sorption of vapors and the subsequent release of such vapors from the room and furniture surfaces) resulting from this method of application may, theoretically at least, be no greater than other methods of application of Lindane. The basis for

such a course of reasoning is the vapor pressure of Lindane which would allow quantities of the insecticide to be present in the atmosphere of a treated area. This air concentration will vary proportionately with the ventilation present.

The following tests were undertaken to compare contamination resulting from such applications of Lindane. Three methods were selected, a Lindane residual applied with an electric bulb type heating device, a residual application with an aqueous emulsion of Lindane applied with a sprayer and finally the application of an oil solution of Lindane with a paint brush (as a residual). All methods were applied following recommendation of the manufacturer or the United States Department of Agriculture.

The spaces to be treated were selected as being identical in so far as possible. Three rooms of a dormitory (exterior walls were of brick) were selected; all were on the north side of the building. The walls were of plaster. The floor was of varnished wood. The tests were run during the summer months. Air samples were taken

at the following periods: two hours after the initial treatment, 26 hours after the initial treatment, and one and two weeks after the initial treatment. Food samples that had been exposed were removed at the same time. The food exposed was shredded wheat, both in packaged and unpackaged form. Rates of air change were estimated (American Society of Heating and Ventilation Engineers, 1952).

A. Fumigation-residue - A total of $2 \frac{2}{3}$ grams of Lindane or seven $1 \frac{1}{3}$ gram tablets were vaporized in about two hours in two Bug Bulbs. The concentration applied was approximately equal to $2 \frac{2}{3}$ gram per 500 cu. ft. of space. Following the two hour fumigation period the room was ventilated for $1 \frac{1}{2}$ hour according to directions of the manufacturer*. The room employed is shown in Figure 3.

The manufacturer states that flies, mosquitoes, gnats, sandflies, flying moths, wasps and spiders can be killed during the application. However, it is quite evident that most crawling insects entering the premises during and after treatment will also be killed. This would

*American Aerovap, Inc., New York City

Room 212

Floor Plan North Side of Abigail Adams House

Figure 3

include roaches, silverfish, firebrats, carpet beetles, psocids and house flies.

B. Lindane Emulsion. A total of 3 grams of Lindane as a 0.3% Lindane emulsion was sprayed on selected surfaces. These surfaces included one closet, baseboards, edges of rugs, areas around windows and doors, in corners of the room, and under furniture. The insects against which the control was aimed were carpet beetles, house spiders, clothes moths, psocids, roaches and silver fish. The procedures followed the recommendations of the United States Department of Agriculture (Henderson, 1952).

The Lindane emulsifiable concentrate used was Dow Lindane 20% Emulsifiable applied at the rate of 2/3 of a pint per gallon of total spray. A total area of 318 square feet was sprayed at the rate of 9.5 milligrams per square foot. A "Sure Shot"*** self contained air pressure sprayer using a cartridge of carbon dioxide as a propellant was employed to apply the emulsion. The room employed is shown in Figure 4.

***Manufactured by Milwaukee Sprayer Mfg. Co., Inc.
Milwaukee, Wisc.

Rooms 108 and 210

Floor Plan Northeast Side of Abigail Adams House

Figure 4

C. Lindane Oil Solution. A total of 2 grams of Lindane as 0.5% petroleum distillate solution (Black Flag, Bug Killer) was applied with a one inch paint brush to selected surfaces following the directions of the manufacturer*.

The solution contained the following ingredients: Lindane 0.5%, Technical piperonyl butoxide .10%, pyrethrins .04% and petroleum distillates 99.36%. The insecticidal material was applied to control roaches, spiders, ants, carpet beetles, silver fish, firebrats, fleas, and centipedes. The procedure of application followed the manufacturer's directions. A total of 500 milliliters of the solution was applied to baseboards, floor space under furniture, corners of the room, areas around windows and doors, cracks and crevices about the room, one closet and areas between the carpet and the wall of the room. The total area painted was 290 square feet at the rate of 6.9 milligrams per square foot. The room employed is shown in Figure 4.

*Boyle-Midway, Inc., Chicago, Ill.

Replication Tests

Following completion of the first series of comparing contamination from several methods of applying Lindane residues, a second series, Replication Tests, were carried out to check the results obtained in the first series of tests. In this series only the fumigation and Lindane emulsion tests were repeated. These tests were run in the late fall and the rooms were heated by steam radiators during the day only. A slightly different method of exposure was employed in this test. The packages of shredded wheat were exposed with their bottom side up, since it was noticed that this flap was well sealed in comparison to the top which was often poorly sealed. All samples taken in this procedure were analyzed by slightly different sampling technique. The samples were analyzed immediately and not stored in glacial acetic acid.

The rooms employed for the replication tests were unfurnished. There were two windows, one 42 x 34" and the other 20 x 28". The larger window was of two sections which opened outward. There was one door 34 x 84" in size and a closet

36 x 36". The dimensions of the rooms were 10 x 10.5' with a height of 8.5' or 1,070 cu. ft.

D. Fumigation-residue. A total of 1 1/4 grams of Lindane or five 1/4 gram tablets were vaporized in one bulb. This concentration was at the approximate rate of 2/3 of a gram per 500 cu. ft. The food was exposed on aluminum foil placed on the floor diagonally between the fumigator and the outside wall.

E. Lindane Emulsion. A total of 3 grams of Lindane were applied to the closet, baseboards, the area around the windows and door and along a two foot strip outward from the base of the walls on the floor. A total of 250 square feet was sprayed at the rate of 12 milligrams per square foot. Food was exposed as with the fumigation determinations.

TOXICITY OF LINDANE VAPOR CONCENTRATIONS TO
HOUSE FLIES

Often biological assays are more accurate for very low concentrations of a toxic material. This is most evident if the toxic material is quite toxic in minute concentrations which may be

beyond the sensitivity of available chemical methods of analysis. Although the method of Hornstein and Sullivan (1953) for air analysis of Lindane vapor is reliable at high concentrations, sensitivity at very low vapor concentrations has not been thoroughly established, as yet. Therefore bioassays of air concentrations of Lindane vapor were made as often as possible in conjunction with the chemical analysis. The object was to provide a check on the employed chemical analysis of vapor concentrations and to provide information that can be applied to residue and fumigation studies. Another factor in the employment of the bioassay of vapor concentrations was that many past workers have employed bioassay rather than chemical analysis of air concentrations of Lindane vapor making it possible for a comparison to other results.

The NAIDM 48 strain of house flies (*Musca domestica* L.) was used as the test insect. The larvae were reared by the American Aerovap Laboratory on milled oats, with added yeast, moistened with a 1:1 mixture of evaporated milk and water. The adults were fed on a 1:1 mixture of powdered

sugar and powdered milk. Water was placed in a separate container. The insects were reared at a temperature of 82.0° F. (28° C.).

All of the test insects were from three to five days old and were not fed during the time of exposure to Lindane vapors. Carbon dioxide was employed as the anesthetic in counting and caging the house flies. Fabric test cages were employed as are described by Spear (1951).

EXPERIMENTAL RESULTS

Table 2. LINDANE CONTAMINATION (PARTS PER MILLION)
OF VARIOUS FOODS WITH A FUMIGATION-RESIDUE
APPLICATION

<u>Food</u>	<u>Conditions of Exposure</u>		
	<u>Unpackaged</u>	<u>Unpackaged and shielded by two layers of Newspaper</u>	<u>Packaged</u>
A. Exposure of two hours during and after vaporization			
Apple	0.2	0.0	-
Butter	1.5	0.2	0.0
Shredded Wheat	19.9	0.0	0.0
Cookies	25.5	1.7	1.4
Bread	25.0	1.3	0.4
B. Twenty-four hour exposure followed by 30 min. ventilation			
Apple	0.0	0.0	-
Butter	0.85	0.5	0.0
Shredded Wheat	4.0	2.0	1.7
Cookies	6.7	5.9	0.0*
			1.5**
Bread	8.0	3.2	0.0
C. Air Concentrations during and after treatment (Estimated 42 Air Changes per 24 hours)			
	<u>Room Temperature</u>	<u>Vapor Concentration (micrograms/liter)</u>	
2 hrs. during treatment	23.5	0.25	
8 hrs. after 1/2 hr. ventilation	23.5	0.10	

*sample taken from center of package

**sample taken from ends of package

Table 3. PACKAGE EXPOSURE TO CONTINUOUSLY VAPORIZED LINDANE

Approximate air concentration during test =
.038 micrograms/liter.

1. Corn Flakes

<u>Sample No.</u>	<u>Days Exposed</u>	<u>Position of Sample in Package</u>	<u>Lindane found</u>	
			<u>p.p.m.</u>	<u>p.p.m./day</u>
1	106	top	.3	0.00383
2	52	top	0.0	0.0
3	52	top	0.0	<u>0.0</u>
mean p.p.m./day				<u>0.00124</u>

Estimated limit of sensitivity 0.1 p.p.m.

2. Shredded Wheat

<u>Sample No.</u>	<u>Days Exposed</u>	<u>Position of Sample in Package</u>	<u>Lindane found</u>	
			<u>p.p.m.</u>	<u>p.p.m./day</u>
1 a	104	top	21.4	0.203)same
b		bottom	8.3	0.080*)pkg.
2	104	top	20.2	0.194
3	33	top	4.6	0.140
4	33	top	5.8	<u>0.175</u>
mean p.p.m./day				<u>0.178</u>

Estimated limit of sensitivity 0.8 p.p.m.

*not included in calculation of mean.

Shredded Wheat - Unpackaged

<u>Sample No.</u>	<u>Days Exposed</u>	<u>Lindane found</u> <u>p.p.m.</u>	
1	7	6.7	} mean 10.5 p.p.m.
2	7	13.5	
3	7	11.4	
4	14	15.1	} mean 13.6 p.p.m.
5	14	11.9	
6	14	13.7	

3. Flake

<u>Sample No.</u>	<u>Days Exposed</u>	<u>Position of Sample in Package</u>	<u>Lindane found</u>	
			<u>p.p.m.</u>	<u>p.p.m./day</u>
1	107	top	0.3	0.00288
2 a	108	top	0.7	0.0065
b		bottom	0.4	0.0037*
3	50	top	0.3	0.006
4	52	top	0.2	<u>0.0038</u>
		mean p.p.m./day		<u>0.003809</u>

Estimated limit of sensitivity 0.1 p.p.m.

4. Flour, Pillsbury's Best

<u>Sample No.</u>	<u>Days Exposed</u>	<u>Position of Sample in Package</u>	<u>Lindane found</u>	
			<u>p.p.m.</u>	<u>p.p.m./day</u>
1 a	109	1 cm. layer	14.2	0.13
b		2 cm. layer	0.4	0.00367
c		center	0.0	0.0
2 a	110	1 cm. layer	17.5	0.159
b		1 cm. layer	17.5	0.159

Estimated limit of sensitivity 0.2 p.p.m.

Estimated deviation ± 0.3

*not included in calculation of mean.

5. Soup Mix, Lipton's Chicken Noodle

<u>Sample No.</u>	<u>Days Exposed</u>	<u>Lindane found</u>	
		<u>p.p.m.</u>	<u>p.p.m./day</u>
1	133	0.0	0.0
2	141	4.7	0.0334
3	141	0.0	0.0
4	141	0.4	<u>0.00284</u>
mean p.p.m./day			<u>0.00906</u>

Estimated limit of sensitivity 0.1 p.p.m.

6. Shredded Coconut

<u>Sample No.</u>	<u>Days Exposed</u>	<u>Position of Sample in Package</u>	<u>Lindane found</u>	
			<u>p.p.m.</u>	<u>p.p.m./day</u>
1 a	131	top	1.2	0.00915
		bottom	5.3	0.0405
2	131	mixed	2.7	0.0206
3	131	mixed	4.4	<u>0.0338</u>
mean p.p.m./day				<u>0.03468</u>

Estimated limit of sensitivity 0.4 p.p.m.

FOOD CONTAMINATION FROM THREE METHODS OF APPLYING
LINDANE RESIDUES

Table 4. Fumigation-Residue - 2 2/3 grams Lindane
1,568 cu. ft.
Food - Shredded Wheat

1. During 2 hr. treatment

Sample No.	Lindane found		Air Conc. (µg/l)	% Saturation*	Temperature (°C.)	Air Changes /24 hrs.**
	Unpack-aged (p.p.m.)	Pack-aged (p.p.m.)				
1		-	3.0	(3/4 hr. super-	22.5	32
2	27.5			after satura-		
3	27.9			starting tion		
4		0.0		applica-		
				tion		

2. 24 hrs. exposure after treatment following 1/2 hr. ventilation of room

5	2.7		0.060	9.7	21.5	43
6	3.2					
7		-				
8		18.5				

3. One week exposure after ventilation

9	18.5		0.015	1.5	27-28	26
10	13.8					
11		35.5				

4. Two weeks exposure after ventiaaltion

12	16.7		0.0099	.6	30	26
13	3.6					
14		1.5	} same pkg.			
15		1.7				

* Lindane air concentration

**estimated

Table 5. Lindane Emulsion - sprayed on selected surfaces -
3 grams Lindane

1,568 cu. ft.

Food - Shredded Wheat

1. Food exposed 2 hrs. during and after spray
treatment of surfaces

Sample No.	Lindane found		Air Conc. ($\mu\text{g/l}$)	% Satura- tion*	Temper- ature ($^{\circ}\text{C.}$)	Air Changes /24 hrs.*
	Unpack- aged (p.p.m.)	Pack- aged (p.p.m.)				
1	0.6		0.096	16.6	21	32
2	0.0					
3		0.7	}			
4		0.0				

2. 24 hrs. after application

5	0.3		0.033	5.3	21.5	43
6	1.2					
7		0.0	}			
8		3.1				

3. One week after application

9	2.9		0.0085	.7	27	26
10	3.8					
11		2.8	}			
12		2.2				

4. Two weeks after application

13	4.1		0.0058	.4	28.5-29	26
14	9.7					
15		3.5				

*Lindane air concentration

**estimated

Table 6. Oil Solution - applied with paint brush on selected surfaces - 2 grams Lindane

1,568 cu. ft.

Food - Shredded Wheat

1. First two hrs. after application

Sample No.	Lindane found		Air Conc. (µg/l)	% Saturation*	Temperature (°C.)	Air Changes /24 hrs.**
	Unpack- aged (p.p.m.)	Pack aged (p.p.m.)				
1	0.2		0.059	3.7	29	32
2	0.9					
3		0.2				

2. 24 hrs. after application

4	9.4		0.018	1.2	28	32
5	4.4					
6		1.0	} same pkg.			
7		1.1				

3. One week after application

8	6.2		0.0035	.28	27	26
9	4.1					
10		0.8				
12		-				

4. Two weeks after application

13	2.1		0.0010	.2	20-21	26
14	1.3					
15	-					
16		-				
17		0.4				

*Lindane air concentration

**estimated

FOOD CONTAMINATION FROM THREE METHODS OF APPLYING
LINDANE RESIDUES - REPLICATION

Table 7. Fumigation-Residue - 1 1/4 grams Lindane
1,070 cu. ft.
Food - Shredded Wheat

1. During 2 hr. treatment

Sample No.	Lindane found		Air Conc. ($\mu\text{g}/\text{l}$)	% Saturation*	Temperature ($^{\circ}\text{C.}$)	Air Changes /24 hrs.**
	Unpack- aged (p.p.m.)	Pack- aged (p.p.m.)				
1	20.4		4.03 (1/2 hr. super-		20	63
2		2.1	after starting	satura-		
3		.6	pkg. applica-	tion		
4	14.7					

2. 24 hrs. exposure after treatment following
1/2 hr. ventilation of room

5		.3	same	0.019	2.0	25	37
6		.3	pkg.				
7	3.0						
8	4.2						

3. One week exposure after ventilation

9		0.0	same	0.0071	1.1	22	22
10		0.0	pkg.				
11	4.4						
12	4.5						

4. Two weeks after ventilation

13		9.4	same	-	.9	20.5	15
14		6.8	pkg.	0.005(est.)			
15	22.8						
16	25.6						

*Lindane air concentration

**estimated

Table 8. Lindane Emulsion - sprayed on selected surfaces -
3 grams Lindane

1,070 cu. ft.

Food - Shredded Wheat

1. Food exposed 2 hrs. during and after spray treatment of surfaces

Lindane found						
Sample No.	Unpack- aged (p.p.m.)	Pack- aged (p.p.m.)	Air Conc. (ug/l)	% Satura- tion*	Temper- ature (°C.)	Air Changes /24 hrs.**
1	0.5		0.028	5.6	20	63
2	0.5					
3		0.5				
4		0.5				

2. Twenty-four hrs. after application

5	0.9		0.0058	1.5	18	37
6		0.3	} same } pkg.			
7		0.0				

3. One week after application

8	0.0	} same } pkg.	0.0036(est.) 0.4	23-28	22
9	0.0				

4. Two weeks after application

10	0.0	0.0011(est.)	0.2	21.5	15
11	0.0				
12		0.0)	} same		
13		0.0)			

*Lindane air concentration
**estimated

TOXICITY OF LINDANE VAPOR TO HOUSE FLIES

Table 2.

<u>Test No.</u>	<u>Total No. of Flies*</u>	<u>Air Concentration (micrograms/liter)</u>	<u>Temperature °C.</u>	<u>LT₅₀ (hours)</u>
1	500	.001	20-21	8.1
2	150	.004	27-28.5	4.5
3	250	.005	21.0	3.4
4	100	.006	28-27	3.9
5	250	.006	28.5-29.0	4.3
6	300	.007	29.5	3.1
7	250	.010	29.5	2.5
8	500	.010	28.0	2.3
9	450	.018	28.0	1.8
10	250	.020	21-24.0	2.4
11	100	.022	29.5	2.4
12	550	.059	29.0	2.2

*House flies - *Musca domestica* L.

ANALYSIS OF DATA

LINDANE CONTAMINATION OF VARIOUS FOODS WITH A
FUMIGATION-RESIDUE APPLICATION

Lindane contamination resulted primarily from the precipitation of Lindane in the tests using the uncovered unpackaged samples during the two hour fumigation. A comparison of horizontal surface area of the material exposed against the concentration of Lindane found in the sample (Table 10) indicates this relationship. Horizontal surface area is the area enclosed in the horizontal dimensions of the body. Although the parts per million per unit horizontal surface area (mean parts per million per sq. cm.) of all samples, excepting the apple, are not equal, they are of about the same magnitude. Theoretically, of course, with a strict precipitation phenomenon the deposit per unit horizontal area should be equal. However, in this test all samples were not of an equal distance from the source of the deposit.

Table 10. A Comparison of Lindane Deposit per Unit Horizontal Surface Area

<u>Food</u>	<u>Approximate Horizontal Surface Area (sq. cm.)</u>	<u>Lindane found</u>	
		<u>Mean p.p.m.</u>	<u>Mean p.p.m./ sq. cm.</u>
Apple	19.8-28	.2	.01
Butter	18	1.5	.1
Shredded Wheat	37	19.9	.5
Cookies	60	25.5	.4
Bread	110	25.0	.2

Air Concentration = saturation to .25 micrograms/liter

With the ensuing twenty-four hour exposure, following ventilation of the room, the samples were exposed primarily to remaining vapors and vapors from residual Lindane although there may have been some particulate matter remaining in the atmosphere. A comparison of the uptake of Lindane per unit area is as follows:

Table 11. Deposit of Lindane Per Unit Total Surface Area

<u>Food</u>	<u>(sq. cm.) Total Area (estimated)</u>	<u>Lindane found</u>	
		<u>Total p.p.m.</u>	<u>p.p.m. sq.cm.</u>
Apple	-	-	-
Butter	64	.85	.01
Shredded Wheat	100	4.0	.04
Cookies	84	6.7	.08
Bread	253	8.0	.03

Air concentration = approximately .01 micrograms/liter

In comparing the two sorption of Lindane per unit area tests, one can conclude, that under the conditions of supersaturation obtained during the two hour fumigation (Table 10), contamination results primarily from precipitating Lindane and probably from some adsorption of Lindane vapor. In the second series (Table 11), contamination resulted primarily from sorption of Lindane vapor during the twenty-four hour exposure where 1/2 hour ventilation followed the fumigation. It must be remembered that the air concentrations of the two hour exposure and the twenty-four hour exposure are vastly different and thus the relative amounts of Lindane per unit area sorbed in each test are considered and not the total concentrations.

Although two layers of newspaper do not constitute perfect protection against Lindane vapors and particulate matter they reduced contamination during fumigation by 95.4% over that of the unprotected unpackaged foods. The packages reduced the contamination by 97.9% over that of the unprotected unpackaged materials.

During the twenty-four hour exposure to vapors of Lindane the two layers of newspaper

gave 41% protection as compared to the unpackaged and unprotected sample. The packages gave a reduction of 87.2% contamination as compared to the unprotected samples.

The shape of the apple, as compared to the other products, may have affected the deposition of Lindane during the fumigation period. The apple sample was not large enough to permit a representative sample to be taken at all concentrations.

PACKAGE EXPOSURE TO CONTINUOUSLY VAPORIZED LINDANE

The corn flakes package showed no appreciable transmission of Lindane vapor.

Results of 24.4 p.p.m. at the top of the shredded wheat package and 8.3 p.p.m. or 34% at the bottom as compared to the top indicates that penetration was greatest at the top. Perhaps this is a consequence of having the bottom of the package resting on the shelf and thus not permitting an equal penetration of the surfaces both at the top and bottom. The total surface area of the package minus the bottom area is 785 sq. cm.; the bottom area is 83 sq. cm. If it follows that penetration through the bottom area was the primary cause of the strati-

fication of the Lindane concentration in the package, then the lower 1/2 of the package should have a concentration of approximately 21% less than the top half of the package. The actual difference is almost twice the estimated theoretical concentration. This indicates that the lower concentration at the bottom was due perhaps partly to the decreased surface offered by the bottom half of the package and partly due to the factor that the top flap was not as well sealed. This latter case was observed in many of the packages. The packages would often exhibit an erratic top seal while the bottom seal was often more uniform.

The rate of sorption exhibited by the exposed shredded wheat is a characteristic adsorption phenomenon: an extreme initial high rate of sorption followed by a very gradual rate of sorption. Evidently the exposed shredded wheat after two weeks of exposure had not reached an equilibrium state since the concentration of Lindane was below that in the packages. The high concentration of Lindane found on shredded wheat is indicative of the very large surface area offered by this substance.

The Flako packages again exhibit the stratification phenomena observed in the shredded wheat although the concentrations are considerably less than those of the shredded wheat samples. The bottom flap constitutes 7.5% of the total area of the bottom half of the package. The concentration in this half of the package is .04 or 57% of the top concentration. Evidently some other factor is involved - perhaps a disruption of the air flow over the package brought about by the shelf being adjacent to the bottom half since this package was well sealed.

The packages of flour exhibited a high concentration at the flour surface adjacent to the bag wall. The concentration rapidly decreased towards the center of the package. This is to be expected since flour is stated (Shepard, 1951) as being very sorptive. It follows that the high concentrations sorbed at outer limits of the mass would decrease the rate of vapor diffusion toward the center. Another factor that may account for this phenomenon is that flour is a fine particulate material, capable of being packed quite firmly. The spaces between particles are reduced considerably affording little space for the gas molecules to penetrate into the mass.

TABLE 12

LINDANE VAPOR PENETRATION OF PACKAGES

<u>Food</u>	<u>Packaging Materials</u>	<u>Mean p.p.m./day</u>
1. Shredded Wheat	Box, .020 inch box-board	.178*
2. Flour	Uncoated, unlined, bleached Kraft paper	.149 1 cm. layer .00367 2 cm. layer 0.0 center
3. Shredded Coconut	Two bags of cellophane, one within the other	.03468
4. Soup Mix	Outer box, boxboard; Inner pkg. laminated aluminum foil	.00906
5. Flako	Outer box, .030 coated boxboard; Inner box laminated liner paper 47# basis	.003809*
6. Cornflakes	Outer box, .0175 inch boxboard; Inner liner, 25 pound glassine	.00124*

*top

TABLE 13

LINDANE VAPOR PENETRATION OF PACKAGING MATERIALS

<u>Packaging Material</u>	<u>Total Exposed Surface Area* (sq. cm.)</u>	<u>Mean p.p.m. per day</u>	<u>Mean p.p.m. per day per sq. meter</u>
1. Boxboard (.020 inch)	785	.129	.164
2. Kraft paper	653	.149 (1 cm. layer)	.228
3. Two layers of cellophane	225	.03468	.154
4. Aluminum laminated to paper	209**	.00906	.0435
5. Outer box, box-board (.020 inch) Inner bag, laminated liner paper 47#	306	.00325	.0106
6. Outer box, boxboard (.0175 inch) Inner bag, 25 pound glassine	1,259	.00124***	.00099***

* bottom surface of package disregarded

** disregarded outer boxboard package

*** top

Although aluminum foil is reputed by Queen (1953) to be almost impermeable to gases or vapors, variations occurred in concentrations of Lindane in the packages sampled. Two samples of soup mix had no detectable Lindane while another sample had a slight amount and the fourth sample had a significant quantity. These variations in penetration may be due to pinholes in the aluminum foil.

The shredded coconut package again exhibits the stratification similar to the shredded wheat and Flako samples. However, in this instance, the concentrations are reversed; this factor can be explained easily when the seals at both ends of the envelope-like package are examined. The bottom seal is much less effective than the top which is a crimped heat seal, the former being a simple fold cemented on to the package wall.

CONTAMINATION FROM THREE METHODS OF APPLYING LINDANE RESIDUES

It must be remembered that in these tests the Lindane is applied once at the beginning of the test. It is not reapplied thereafter. The results obtained should indicate a relationship between the decreasing Lindane vapor concentrations and quantities of Lindane sorbed on a day to day basis.

Of course, one must take into account the fact that all amounts of Lindane present are decreasing; but it is probable that the residue with the higher rate of evaporation, and consequently the higher vapor concentration, is the residue which will remain effective for a shorter period of time. Air changes per hour during similar periods of the tests did not vary enough to be considered of value in affecting these results.

The temperatures given were taken during air sampling periods, 2 hours, 24 hours, one week and two weeks after treatment. The time to take an air sample varied from a quarter of an hour to five or six hours. Since these room temperatures were not recorded from day to day, continuously, no definite conclusions can be drawn concerning their effect on the contamination results. However, temperature changes that may affect the penetration into packages by alternate expansion and contraction of the volume of air in the package, apparently do not play a significant role in penetration of packages in these tests since penetration was least in the replication studies which had the highest temperature variation.

High rates of adsorption occur with the higher concentration of Lindane vapor present immediately after application and as the concentration of Lindane vapor decreases, the rate of adsorption per day should also decrease. The large quantities of Lindane initially adsorbed should revaporize to a considerable extent. The sorption per day rates are given in Table 14.

As the air concentration decreases in the last two weeks of exposure so does the quantity of Lindane adsorbed. It appears that during this period the higher initially adsorbed concentrations of Lindane are being revolatilized and thus the concentrations obtained at the end of the one or two week exposures were representative of a day to day sorption of Lindane. This day to day sorption gradually decreases with decreases in vapor concentration. The concentration of Lindane in the food is the result of an equilibrium of adsorption and desorption of Lindane vapor on the substrate.

If one converts all Lindane residue data to a relative basis, that is, all applications considered as being equal in the initial application

TABLE 14

SORPTION RATES OF LINDANE VAPOR ON SHREDDED WHEAT

Average p.p.m. sorbed/24 hrs.			p.p.m. sorbed % saturation		Average % Air
<u>Unpackaged</u>	<u>Packaged</u>		<u>Unpackaged</u>	<u>Packaged</u>	<u>Saturation</u>
<u>Fumigant-Residue</u>					
2 hours	330	0	3.3	0	100
24 hours	2.9	18.5	.3	1.9	9.7
1 week	2.3	5.1	.4	.9	5.6
2 weeks	.72	.1	.2	.04	3.4
<u>Emulsion-Residue</u>					
2 hours	3.6	4.2	.2	.3	16.6
24 hours	.8	1.6	.07	.2	10.9
1 week	.5	.1	.2	.03	3.0
2 weeks	.5	.3	.3	.2	1.8
<u>Oil Solution-Residue</u>					
2 hours	7.2	2.4	2.0	.7	3.7
24 hours	6.9	2.0	2.8	.8	2.5
1 week	.7	.1	1.0	.02	.7
2 weeks	.1	.03	.002	.006	.5

REPLICATES

Fumigant-Residue

2 hours	210	20	2.1	.2	100
24 hours	3.6	.3	1.8	.2	2.0
1 week	.6	0	.4	0	1.6
2 weeks	1.8	.6	1.4	.5	1.3

Emulsion-Residue

2 hours	.5	.5	1.0	1.0	5.6
24 hours	.9	.2	2.0	.5	3.6
1 week	-	0	-	0	1.2
2 weeks	0	0	0	0	.9

of Lindane, 2.55 grams each instead of the 2 2/3, 3, 2 grams actually deposited, then one should establish a probable relationship to the influence of room temperature, character and availability of the residue on the air concentrations obtained. This relative concentration of deposited Lindane was taken as the mean of the series under consideration.

In the first Fumigation-residue test there appear to be considerable amounts of Lindane adsorbed in some of the samples. This may be a result of package variability since the packaged samples exposed with the bottom side up in the Replication series (opposite of the first series) showed no large variations in uptake of Lindane vapor. Also, these variations are not present in any of the other tests.

The relative rate of Lindane sorption was highest with the brushed-oil application followed by the fumigant-residual, and least with the sprayed-emulsion application. The high rate of contamination with the oil solution may be explained in the following manner. The Lindane oil solution was applied in about 500 cc. of solvent; this solvent also evaporated and was adsorbed by the shredded wheat. The Lindane

sorbed during or after this process of oil sorption, was absorbed into the oil and shredded wheat mixture. The alteration of the surface character of the adsorbent may account for this high retentive Lindane level. In other words, there was a marked change in the adsorption process as compared to the fumigant-residue and the emulsion-residue. In the two latter applications the contamination probably resulted from adsorption.

It follows from the calculations and data expressed in Table 15 that the rates of volatilization of Lindane residues are higher with the "fumigation" type of residue than those of a Lindane emulsion and are least with a residue of Lindane applied as a solution in a petroleum distillate. These relative rates of vapor decrease appear to be somewhat independent of temperature as is established by the decrease in percent saturation values. But the relative rates seem to be dependent on changes of air that have occurred. It appears, then, that the character or availability of the residue must play an important part in the relative evaporation rate of Lindane from a surface.

TABLE 15 RATE OF DECREASE IN LINDANE VAPOR CONCENTRATIONS
RESULTING FROM LINDANE RESIDUES

Section A. Air Concentrations Expressed in Micrograms
per Liter

Test:	<u>Fumigant-Residue**</u>	<u>Emulsion-Residue**</u>	<u>Oil Solution-Residue**</u>
	<u>°C.</u>	<u>°C.</u>	<u>°C.</u>
2 hours	-3.0 22.5	.082 21	.075 29
24 hours	.057 21.5	.028 21.5	.023 28
1 week	.014 27-28	.0072 27	.0045 27
2 weeks	.0095 30	.0059 29.5-29	.0013 20-21

Replications

Test:	<u>Fumigant-Residue***</u>	<u>Emulsion-Residue***</u>
2 hours	-4.03 20	.020 20
24 hours	.018 25	.0041 18
1 week	.0068 22	.0027* 23-28
2 weeks	.0048* 20.5	.0008* 21.5

*estimated

Section B. Air Concentration Expressed in Percent
Saturation

	<u>Fumigant-Residue**</u>	<u>Emulsion-Residue**</u>	<u>Oil Solution-Residue**</u>
2 hours	✓100	14.1	4.8
24 hours	9.3	4.5	1.5
1 week	1.4	.6	.4
2 weeks	.58	.3	.3

Replications

Test:	<u>Fumigant-Residue***</u>	<u>Emulsion Residue***</u>
2 hours	✓100	4.0
24 hours	1.9	1.1
1 week	1.0	1.1
2 weeks	.9	.14

**corrected to 2.55 grams Lindane

***corrected to 2.14 grams Lindane

A possible consequence resulting from misuse of the fumigation type of vaporizer is the production of abnormally high residues in a limited area. Directions* state that if more than six $1/3$ gram tablets of Lindane are to be used ($2/3$ grams per 500 cu. ft.) one should employ two vaporizers rather than one. This example is given not to indicate increased contamination of food but to indicate the variation produced in the residue deposited. The average residue obtained on shredded wheat, if one operates it according to directions, is 25.1 p.p.m. If the fumigation apparatus is operated with an excess of the recommended dosage per vaporizer (i.e. eight $1/3$ gram tablets per vaporizer) then the average residue is 79.5 p.p.m., or three times the recommended residue. This residue is confined to a much smaller area than would be the case if directions were followed.

TOXICITY OF LINDANE VAPOR TO HOUSE FLIES

The Lethal Time values (time required for 50% of the insect population to become moribund) were calculated from data obtained at each half hour to hour of exposure. A number of variations are

*Directions state specifically that no food should be present in the room during treatment.

evident in some of the LT_{50} values. In most instances these variations may be attributed to differences in temperature or differences in fly age, weight or sex ratio. Hoffman, Roth and Lindquist (1949) and Guthrie (1950) have shown that the relative toxicity of some insecticides vary with the temperature at which the insects are held. Lindane is more effective at higher temperatures, where as DDT is more effective at lower temperatures.

All data presented in Table 9 are the result of at least one point below the LT_{50} . The author is unaware of any results that have been published to date on mortalities of house flies at the concentrations of Lindane vapor reported here.

SUMMARY

This paper is a report of investigations which should lead to a more thorough understanding of the magnitude and extent of contamination of air and foods by Lindane vapors.

1. Food contamination after use of fumigators was explored as to the possible contamination resulting from accidental exposures of foods under varied conditions. These foods were exposed in the following states: unpackaged (unprotected and protected by two layers of newspaper) and packaged. Exposures took place during fumigation and during a period of twenty-four hours following fumigation.

2. A series of packaged foods were exposed to Lindane, vaporized at the rate of approximately one gram per 15,000 cubic feet per 24 hours. The foods were exposed for varying periods of time (one to four months).

3. Tests employing three methods of applying Lindane were made in order to compare the relative contamination by these methods of application. The methods of application employed were a fumigation-residual, a water emulsion residual (spray application)

and an oil solution residual (brush application). Foods were exposed for two hours (during and shortly after application), twenty-four hours (after application) and one and two weeks after application.

4. The response of house flies (*Musca domestica* L.) to Lindane vapor concentrations of 0.001 to 0.059 micrograms per liter was observed. The lethal time for 50% mortality in a laboratory strain of house flies was determined.

5. The foods were analysed by the method of Schechter and Hornstein (1952) for Lindane. Air analyses were made following the procedure of Hornstein and Sullivan (1953). Air samples were taken at the same time the food samples were collected.

CONCLUSIONS

1. Contamination during Lindane fumigation resulted chiefly from precipitating Lindane but adsorption also occurred. Contamination after the fumigation period was probably by adsorption. Newspapers and commercial packages provide some protection to contamination under fumigation conditions. The character of the food surface was an important factor in contamination under these conditions. Foods with larger surface area, per gram of material, sorbed larger amounts of Lindane.

2. Transmission of Lindane vapor into food packages occurred predominately in the upper half of the package when the package was resting on a horizontal surface. No commercial package (box-board, kraft paper, cellophane, glassine or aluminum foil) was found to resist the penetration of Lindane vapor. In the case of the aluminum foil packages penetration was probably due to pin-holes in the foil. The effectiveness of package closures markedly affected the penetration of Lindane vapor. The order of penetration of packaging materials was boxboard, kraft paper, cellophane (two layers), aluminum foil laminated to paper, boxboard with laminated liner

paper, and boxboard with glassine.

3. When similar amounts of Lindane were applied using three methods, air contamination was greatest with the fumigation-residue application followed by the sprayed emulsion and painted oil solution applications. Food contamination was highest with the fumigation-residue during application, but after application the oil solution application surpassed the fumigation and emulsion residues.

On the basis of Lindane vapor concentrations, as a measure of Lindane residue released, the fumigation-residue was less persistent in character than the emulsion and oil solution residues. Higher Lindane vapor concentrations led to high food contamination, but as the Lindane vapor concentration decreased, the sorbed contamination was reduced considerably. This reduction of sorbed Lindane was probably due to revaporization of sorbed Lindane.

4. In general, contamination is, initially, a surface phenomenon; it should vary in a relative proportion to the vapor concentrations. Later, some of the sorbed Lindane may dissolve and slowly penetrate

into the food. The quantity of Lindane penetrating probably is dependent on the duration of exposure and the physical state of the material. If the food has no appreciable solvent content (fats, alcohols, oils, etc.) then contamination results from a surface effect.

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ACKNOWLEDGEMENTS

The writer wishes to extend his gratitude to the many people who assisted to make this thesis possible: to Dr. H. L. Sweetman whose guidance and encouragement were most stimulating; to Dr. P. J. Spear who provided considerable help and advice; to Dr. C. P. Alexander, Head of the Dept. of Entomology and the other members of the department of Entomology for their encouragement and interest; to the members of the thesis committee, Dr. W. Banfield, Dr. Levine and Dr. J. E. Roberts for their helpful criticism of this manuscript; to American Aerovap, Inc., who made this thesis possible; to the Chemistry Department who so kindly provided laboratory space and offered the use of their facilities, to my wife Dimi for typing and to many others who assisted in this investigation.

APPROVED BY:

John E. Roberts

Walter M. Benfield

Arthur S. Levine

Harvey L. Sweetman

June 1954