

AN ABSTRACT OF THE THESIS OF

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Title: SOME FACTORS INFLUENCING THE EFFECTIVENESS OF SOIL
FUMIGANTS FOR WEED CONTROL

Abstract Approved

Major Professor

This study had two purposes:

1. To evaluate chlorinated C_3 compounds as phytocidal agents when used as soil fumigants and,
2. To determine some of the factors affecting the results of such fumigation.

It was found the chlorinated derivatives of propane and propene were very effective for the control of herbaceous perennial noxious weeds. However, the cost of these materials limit their use to high priced land and the control of small patches of these weeds. These materials are the most effective means of control of perennial weedy grasses.

The factors found to influence the effectiveness of soil fumigation were:

1. The diffusion - kill pattern of the material
This was found to be characteristic for a given material and the shape is influenced by molecular weight.
2. Adsorption of the fumigant.
In general the degree of adsorption increased with molecular weight and colloid content.
3. Soil moisture.
The optimum soil moisture is one that supports good plant growth.
4. Inherent toxicity of the material
It was found that the physical laws governing the behavior of gases must be considered in soil fumigation.

SOME FACTORS INFLUENCING THE EFFECTIVENESS
OF SOIL FUMIGANTS FOR WEED CONTROL

BY

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SOME FACTORS INFLUENCING THE EFFECTIVENESS OF SOIL FUMIGANTS FOR WEED CONTROL

INTRODUCTION

The problem of pest control is of vital (economic) concern to man. Annually the several agricultural pests - insects, diseases, rodents and weeds - exact a heavy economic toll in reduced crop yields and crop damage. It has been estimated that the combined ravages of the above mentioned four will cost the United States between ten and twelve billion dollars.

Man has long searched for suitable means of alleviating or obviating the destruction of his food crops by these factors. Entomologists and plant pathologists many years ago found that by employing certain chemicals as protectorants for economic plants or animals the ravages of insects and plant diseases could be reduced. Not many years ago it was found that certain chemicals could be used to selectively destroy undesirable plants. This was the inception of weed control. By comparison to entomology and plant pathology, weed control is still in its infancy.

It has been found that plants vary widely in their response or susceptibility to chemicals. This is true particularly when one considers the response in the light of the growth habits of different plants. For example, annual plants may readily be controlled by hypertonic solutions of salts, cytolytic agents and appropriate synthetic growth regulating chemicals; on the other hand biennial and perennial plants may often require more drastic

treatment for control.

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Temporary soil sterilants, permanent soil sterilants and selective-contact phytocidal agents have been tested extensively for control of weeds.

Because of certain obvious advantages, certain materials of gaseous nature or high vapor pressure have long been used in combatting insects, rodents and weeds. These materials, known as fumigants, have been used to control insect and weed pests in stored grain, buildings and in the soil. In the case of certain plants, fumigation is about the only means of control.

The objective of the following experiments was twofold:

- (1) First, to evaluate certain chlorinated aliphatic C_3 compounds as phytocidal agents when used as fumigants, and
- (2) secondly, to determine some of the more important factors influencing the effectiveness of soil fumigants.

Entomologists have long employed fumigants for the control of insects. Garreau (32, p. 326) reported the use of carbon bisulfide for fumigating stored grain in 1854; Thenard recommended carbon bisulfide as a soil fumigant in 1869. Marion in 1878 (19, p. 4) was cognizant of the phytotoxic properties of carbon bisulfide but it was not until 1906 that Walker (19, p. 4) employed it for control of plants. Wilcox (1909)(41, p. 2) subsequently employed the same material for weed control in Hawaii. By 1925, carbon bisulfide was being used extensively for control of noxious plants.

Meanwhile, entomologists were investigating a number of promising materials (31, p. 6; 36, p. 199) and by 1936 had introduced several new and effective fumigants (31, p. 15). Such materials as methyl bromide, ethylene dibromide, methyl thiocyanate, dichloroethyl ether and chloropicrin were being used extensively in specialized fumigant problems for insect control (31, p. 14-21; 35, p. 57,58; 37, p. 210; 33, p. 11).

Weed control workers, however, had limited their attention to three materials, namely: carbon bisulfide (28, p. 237; 30, p. 22) chloropicrin (29, p. 248), and materials producing hydrogen cyanide. This fact can be ascribed to the characteristic problems of soil fumigation (38, p. 63; 5, p. 67; 28, p. 451; 29, p. 35) that requires material of high vapor pressure combined with sufficient weight of vapor and toxicity. Many materials have been tested for toxicity to various organisms (33, p. 34; 32, p. 327;

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25, p. 72; 31, p. 15) but often are found to be lacking in one or more requirements for economical useage. Offord (25, p. 10) for example, working with Ribis spp found chloroacetamide, ethylene and ethylene chlorohydrin relatively ineffective.

It is nearly self evident that the inherent properties of a chemical will edlimit its biocidal activity (36, p. 8; 37, p. 200; 31, p. 1). Tattersfield (37, p. 221) points out that vapor pressure of an organic compound is one of the important physical properties in determining the effectiveness of a fumigant treatment for wire worms. He found that where the boiling point was above 170 degrees centigrade the material failed to reach a toxic concentration under conditions of the experiment. Conversely, however, biocidal value increased as the molecular weight increased. It would follow, therefore, that in a given homologous series a point would be reached where physical properties would limit the toxicity of the series although it could logically be postulated from theoretical consideration that the higher molecular weight compounds would be most toxic. Crafts (10, p. 418) in his work with dinitro phenols found that when the alkyl side chain reached five carbon atoms in length, the solubility of the compound in the cytoplasm of the plant was the limiting factor with respect to toxicity.

It should be pointed out, however, that biological specificity often becomes a factor in consideration of toxicity of a given compound. Miller (23, p. 1035) points out that plants show a specificity with respect to growth substances.

While it may be seen that physical properties will delimit toxicity within a homologous series, chemical constitution will, in part, account for the differential activity between series. Frear (15, p. 737) in his analysis of the toxicity of 6155 organic compounds to insects found that certain groupings inherently possessed greater toxicity than others. For example, according to this author, phenolic hydroxyl groups nearly always exhibits greater biocidal effect than alcoholic hydroxyl groups. Similarly, phenyl groups and olefinic linkage generally made for greater toxicity than did aliphatic groupings.

Hatfield and Rogers (30, p. 23) found carbon bisulfide an effective fumigant for control of perennial weeds but Davis and Hawkins (13, p. 16) as well as Offord and Van Atta (26, p. 12) found that not all perennial plants responded to this material. However, Ball (3, p. 37) et al considered carbon bisulfide sufficiently effective to recommend for field useage. Cook and Halferdahl (9, p. 78-79) found in a survey of the literature of weed control that carbon bisulfide was generally quite effective. Crafts and Raynor (11, p. 98) felt that both carbon bisulfide and chloropicrin were effective in the control of perennial plants.

No single fumigant has been found to be entirely satisfactory for all problems of fumigation (25, p. 68). The search for new fumigants has seen the introduction of methyl bromide, ethylene dibromide, ethylene dichloride and other halogenated materials. Carter (6, p. 384) in 1943 announced that a mixture of dichloropropane and dichloropropene had been found to be very effective

in controlling root knot nematode in pineapple. This mixture was termed DD mixture, taking the first letters of the name of the two ingredients. However as early as 1937 Shepard et al (31, p. 7) reported on the use of propylene dichloride.

The mixture of chlorinated propanes and propenes is a by-product of the manufacture of allyl alcohol and allyl chloride (14, p. 146). Propane is chlorinated under pressure in presence of violet light in the preparation of chlorinated propanes and propenes. However, after Carter's discovery of the value of this mixture, production was shifted to produce the mixture of dichloropropane and dichloropropene. Since the reaction is exothermic, there resulted a so-called heavier end that consisted of more highly chlorinated products.

Andrews and Kepner (2, p. 2236) found some confusion existing in the nomenclature of chlorinated propenes. They also cite evidence to indicate existence of various stereo-isomers.

Since soils possess a large interfacial surface, it is logical to assume that it would adsorb gaseous material. Hanningsson (19, p. 56) and Newhall (25, p. 70) et al found this to be the case. However, Fuhr et al (16, p. 275) under conditions of their experiments did not find an appreciable adsorption except in the case of reactive gases. The sorption of the reactive gases may be explained on the basis of reaction with the ionic shell of the soil colloid. A possible explanation of the apparent lack of sorption of the unreactive gases will be offered later. Newhall (25, p. 70) found that as the interfacial area of the soil

increased - that is, as the particles became smaller - adsorption⁷
of a given gas increased.

When a gas molecule (23, p. 152) impinges on a surface they do not rebound elastically but condense on the surface, being held by the field of force of the surface atoms. These molecules may subsequently evaporate from the surface. The time lapse between condensation and evaporation depends on the intensity of the surface forces. Adsorption is a direct result of this time lag.

If the surface forces are relatively intense, evaporation will take place slowly. The surface of the absorbent will, therefore, become covered with a layer of molecules. Usually as in the case of true absorption the layer will be unimolecular, for as soon as the surface becomes covered by a single layer, the surface forces are satiated.

Conversely, if the surface forces are weak, the evaporation may occur so rapidly that only a small fraction to the surface becomes covered with a unimolecular film. In any event, evaporation of the material from the surface will be at a rate commensurate with the surface forces.

It is important to keep in mind the concept that regardless of the attractive forces the absorbed material will evaporate. While the rate of evaporation varies from one absorbent to another, it also varies between absorbed materials depending on their vapor pressure.

Since the surface forces are chemical in nature, the range

of these forces are small, of the order of 10^{-8} centimeter. The effective range of the forces, therefore, is usually much less than the diameter of the molecules. Thus the impinging molecules orient themselves in a definite manner in the surface layers since they are held by forces acting between the surface and particular atoms or groups of atoms in the adsorbed molecule.

Adsorption decreases as temperature increases or as pressure decreases (23, p. 156). Thus, removal of adsorbed material from the adsorbent may be accomplished by lowering the pressure or raising the temperature. It might be safely predicted therefore, that as the temperature increases there would be less adsorption in the soil.

Various equations (12, p. 117) have been derived to express adsorption. Langmuir's equation (12, p. 118) can be deduced if it is assumed that the adsorption is simple. This equation is as follows:

$$\frac{a}{c} = \alpha + \beta a$$

where

a = adsorbed quantity

c = the concentration

α, β = constants

A more common but limited equation is that of Freundlich which may be written as follows:

$$\frac{x}{M} = kc^n$$

where

x = weight of adsorbed material

M = weight of adsorbing material

c = concentration

k = a constant

n = a constant from 0.1 to 0.5

To determine the constants k and n a plot of $\log x$ against $\log c$ is made and from the data from the plot these constants may be calculated.

The total pressure of a system of gases is a function of the partial pressure of each gas (23, p. 54) or expressed another way

$$P = P_1 + P_2 + P_3 + \dots + P_n$$

Therefore, in the soil where a mixture of gases and water vapor exist, it would be predicted that adsorption of a fumigant would decrease because of lowered pressure and adsorbed water vapor on the colloidal micelle. Newhall (25, p. 70) and his coworkers found this to be true. Penman (28, p. 461) and Hannesson (20, p. 509) found the adsorbed water to retard the flow of a gas through the soil.

Though considerable attention has been directed toward the movement of liquids through porous solids (1, p. 3), the movement of gases through porous solids particularly in soils has received less attention than its importance would seem to indicate (28, p. 437). However, Barrer (4, p. 1) has recently compiled a text on the solution of the equations dealing with diffusion. Most of these equations are the solution of Fick's differential equation which in itself is based on Fourier's (21, p. 7) mathematical treatise on the conduction of heat.

The two forms of Fick's equation are:

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$$(a) \quad P = -D \frac{\partial C}{\partial x}$$

$$(b) \quad \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Equation a gives the rate of diffusion in the steady state of flow, through a unit area of any medium in terms of concentration gradient and the diffusion constant, D. Equation b refers to the accumulation of material at a given point as a function of time.

To consider in more detail the aspect of diffusion in soil, attention is first directed to Graham's equation for the speed of diffusion (u) of gas (38, p. 209) which is:

$$u = \sqrt{\frac{3RT}{M}}$$

The path through the soil is at a 45° angle to the direction of the maximum pressure gradient which can be shown to be equal to $\frac{1}{2}$, (28, p. 441). Also, for any given soil, a certain portion of it consists of solid matter, gas and water, the remainder termed porosity (28, p. 437). The area of this porosity will affect the rate of flow through a column of soil. This characteristic is constant (C) for any given soil.

Then because there is a resistance to flow, the diffusion coefficient, which is a constant for any specific material, is introduced where

$$D_0 = \frac{3}{16} \frac{1}{\sqrt{\eta h}} \frac{M_1 + M_2}{M_1 M_2}$$

However in the case of porous solids, the diffusion coefficient

(D_1) may be shown to be (28, p. 441)

$$D_1 = D_0 \sqrt{\frac{1}{2}}$$

However in the "steady state" of flow the equation becomes

$$\frac{\partial N}{\partial t} = - \frac{D}{\beta} \frac{P}{L}$$

Various conditions in the soil have been found to affect the diffusion of gases. Penman found that in the initial stages of flow adsorption would account for the diminished diffusion of carbon bisulfide. Hagan (18, p. 116) noted that the textural grade of the soil had less effect on permeability of a gas than had been expected. However, Buchrer (5, p. 56) found that soil structure could be studied and classified by the movement of gases through the soil. Hannesson (20, p. 509) found that the moisture content of a soil markedly affected the flow of a gas in the soil. As the moisture content increased, the movement of the gas sharply decreased. He also found (20, p. 509) that compaction and shearing forces also effectively limited the diffusion of the gas. Of these factors, Hannesson (20, p. 509) concluded the moisture content was the most important.

Now combining these factors in an equation to express the quantitative flow in a soil (18, p. 95)

$$\frac{N}{At} = CD_1 \frac{dP}{dL}$$

Where

N = Mass of diffusing molecules

A = Cross-sectional area

t = time

$\frac{dP}{dL}$ = rate of change of pressure

C = soil constant

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D = diffusion constant

Although in the study of many problems concerned with the soil, the factor of rate of flow is important, the problem of soil fumigation is more actively concerned with the diffusion pattern (27, p. 34, 35). This factor has had little study from the theoretical standpoint. The diffusion pattern of a given fumigant will determine the success or failure of a treatment by limiting the spacings between injections.

Various empirical methods have been developed to determine the effective spacing of fumigants (7, p. 69). It may be shown from trigonometric consideration (39, p. 63) that the most effective spacing of injections is an alternating pattern. Thus drawing a line from the injection points of any three adjacent rows will form an equilateral triangle. To determine the spacing between injection points for a given fumigant the maximum distance of effective kill is determined; this is termed K (7, p. 67).

Then using the trigonometric values of the equilateral triangle the calculations become:

- (1) Distance between rows

$$D_r = K \times 1.5$$

- (2) Distance between injections in the row

$$D_i = 1.732 K$$

- (3) Distance from plot edge

$$D_e = 0.5 K$$

The field experiments on which this paper is based were conducted primarily in the vicinity of Corvallis, some of them were conducted at various other locations in the state. The laboratory and greenhouse studies were all performed at Corvallis.

Preliminary experiments were started in 1944, when the author received a sample of dichloropropane - dichloropropene mixture for experimental purposes. The initial trials of this material in comparison to carbon bisulfide on Convolvulus sepium and Cirsium arvense indicated that the mixture was very effective for herbicidal purposes.

During the winter of 1944-1945, greenhouse trials of various soil fumigants were made. The chlorinated C_3 hydrocarbons again showed up well.

The studies on soil fumigants was expanded in 1945 to include laboratory and greenhouse studies as well as field work. This work was continued through the fall and winter of 1947.

The principal materials under investigation were chlorinated C_3 hydrocarbons but other materials such as chloropicrin and carbon bisulfide were included for purposes of comparisons. For the most part, the chemicals other than the chlorinated products were of commercial grade.

Carbon bisulfide: This product was the Anchor brand activated CS_2 of Wheeler Reynolds and Stauffer Chemical Company. Molecular weight: 72.02

Chloropicrin: Eastman technical grade. Molecular weight 164.40

$\beta\beta$ Dichloroethyl ether: Eastman technical grade. Molecular weight 150.98

P_{DD}: This was a mixture of dichloropropane and dichloropropene containing some more highly chlorinated products. The earlier samples had a wide boiling range (85°-121°C for the 80% point), later ones however, were more highly purified as indicated by a narrower boiling range. Most of the P_{DD} was obtained from the Shell Chemical Company. It is labelled as containing 63.0% 1-3 dichloropropene-1 and 33.0% 1,2 dichloropropane and 4% higher chlorinated compounds.

P₅: P₅ is a more highly chlorinated C₃ product than P_{DD} and is characterized by a boiling range of 104° to 142° C for the 80% point. This and P₇ and P₉ were supplied by the Dow Chemical Company.

P₇: P₇ consisted of a 50:50 mixture of P₅ and P₉.

P₉: A mixture of highly chlorinated C₃ hydrocarbons.

TCB (Trichlorobutane): Technical grade supplied by Shell Chemical Corporation.

1-2-3 trichloropropane

2-3 dichloropropene-1

1-3 dichloropropene-1

Technical grade of each of the above three products were supplied by Shell Chemical Corporation in late 1947.

Laboratory Studies

Laboratory studies conducted in this series of investigations

included vapor pressure and molecular weight determinations, 15
boiling range and adsorption studies. Since some of the materials
used were mixtures and hence it became necessary to characterize
these mixtures by boiling range, chlorine content and other de-
terminations that would permit comparisons to be made between
two samples of the same mixture.

Determination of Unsaturation (21, p. 420): This was done
by determination of absorption of iodine from a solution of iodine
monobromide in glacial acetic acid. The usual procedure with
hydrocarbon material is to make this determination employing con-
centrated sulfuric acid (sulfonation) and expressing results in
terms of unsulfonatable residue. However, this reagent was found
unsatisfactory as it caused excessive charring.

The determination was conducted as follows:
A weighed sample of the chlorinated C_3 compounds was dissolved
in 10.0 cc. of chloroform and a known volume of iodine solution
was added. After standing one hour 100 cc. of water were added
and the excess iodine was titrated with a known normality thio-
sulfate solution. Blank determinations on the iodine solution
were made concomitantly. The calculations were made as follows:

$$\frac{\text{CC. for blank} - \text{cc. for sample} \times N}{\text{sample wt.}} \times \frac{\text{Mol. wt.}}{\text{mixture}} \times 100 = \% \text{ un-}$$

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saturates by weight.

Boiling Range Determination: This determination was conducted
according to the procedure recommended by the American Institute of
Petroleum Engineers.

250 cc. of material was introduced into a 500 cc. flask and connected to a distilling condenser through a 25.4 cm. column. The temperature was slowly raised until the material began to distill. The temperature at which the first drop came over was recorded as the initial point. Thereafter, the temperature was held so that the distillate came over at the rate of ten drops per minute. The temperature at which each ten percent increment of distillate came over was recorded until 80% of the material had been distilled, at which time the operation was terminated. It was found that it was necessary to stop at this point as destruction of the remaining material occurred.

Molecular Weight Determination (12, p. 68): Molecular weights of the materials were determined by the boiling point elevation method using a modified Cottrell apparatus. One of the standard solvents used in this determination is absolute ethyl alcohol. This solvent was found to be unsatisfactory as it apparently formed an azeotropic mixture with the chlorinated hydrocarbons. Repurified chloroform (B.P. 60.2) was found to be the most satisfactory solvent.

Adsorption Determinations (12, p. 117): Two types of adsorption determinations were made; the first had to do with the adsorption of P_{DD} from solution by two different soils and the second dealt with the adsorption of the gas of various fumigants by soils.

It was found that a solution of the mixture P_{DD} in the monobutyl ether of ethylene glycol obeys the Lambert-Beer law.

$$\frac{I}{I_0} = e^{-Kcd}$$

Hence it was possible to determine the concentration of this material at any given time. Five grams of soil were mixed with 50.0 cc. of a 20.0% solution of P_{DD} and the concentration remaining in solution was determined at intervals.

The second experiment consisted of drawing the vapors of the materials through a weighed quantity of soil for a definite period of time. Since the vapor pressures of the materials were not all the same, it was necessary to determine the vapor loss and calculate per cent adsorbed per gram of soil per gram of vapor to place all materials on a comparable basis.

Vapor pressure Determination: (12, p. 23) Vapor pressure determinations were made using the Ramsay-Young apparatus.

Chlorine Content: The percentage of chlorine was determined by the Umhoefer method using sodium isopropoxide to dehalogenate the chlorinated compounds (39, p. 384).

Greenhouse Experiments

Toxicity trials were conducted in the greenhouse with various materials to compare their phytotoxicity. This work was usually done in the winter when climatic condition precluded any field work.

The test plant used in the greenhouse trials was gray winter oats (Avena spp.). This plant has been found to be intermediate in its response to most chemicals making it, therefore, a desirable plant to use.

The plants - 8 to 10 per pot - were raised in number 2 cans

containing 485 ± 10 grams of soil. Treatments or injections of the material were made using an insulin syringe. The material was injected at a depth of one inch from the surface using a dosage of 50 to 1000 parts per million (16, p. 681).

All treatments were made in triplicate and the data reported are averages of two or more runs. In all trials comparable checks were used for comparisons.

Field Trials

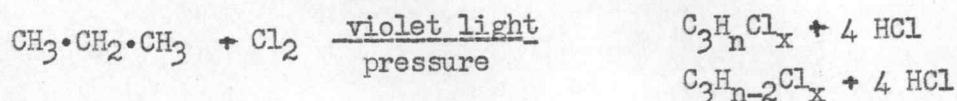
Field trials were conducted over a period of three years with soil fumigants. These trials included comparisons between materials, the effectiveness of the materials on different plants, on different soils under different moisture levels. Trials on different dosage levels, spacing and depth of injections.

The field trials were always established using randomized replicated plots. For the most part, the trials were established on land that had been worked down into a seed bed, although a few plots were established in sod. Most plots were put out using a Mack Anti-weed gun hand injector; however, a few of the plot series were put out using power driven machines. On the whole, better results were obtained with the hand injector than with machine drawn applicators.

The data taken on the plots was the re-emergence of the particular weed species from six months to one year following the application. Observations were made periodically on the treated plots. One result of these observations was the noting

of the "row effect" from the treatment. This effect was a killing of the plants for a distance from the point of injection but not extending to the next row of injections. This lack of confluency of killing zones led to more extensive observations on the pattern or zone of lethal concentration of the fumigants.

As was previously pointed out, chlorinated C_3 compounds are prepared according to the following equation:



$$\text{Where } \text{H}_n + \text{Cl}_x = 8$$

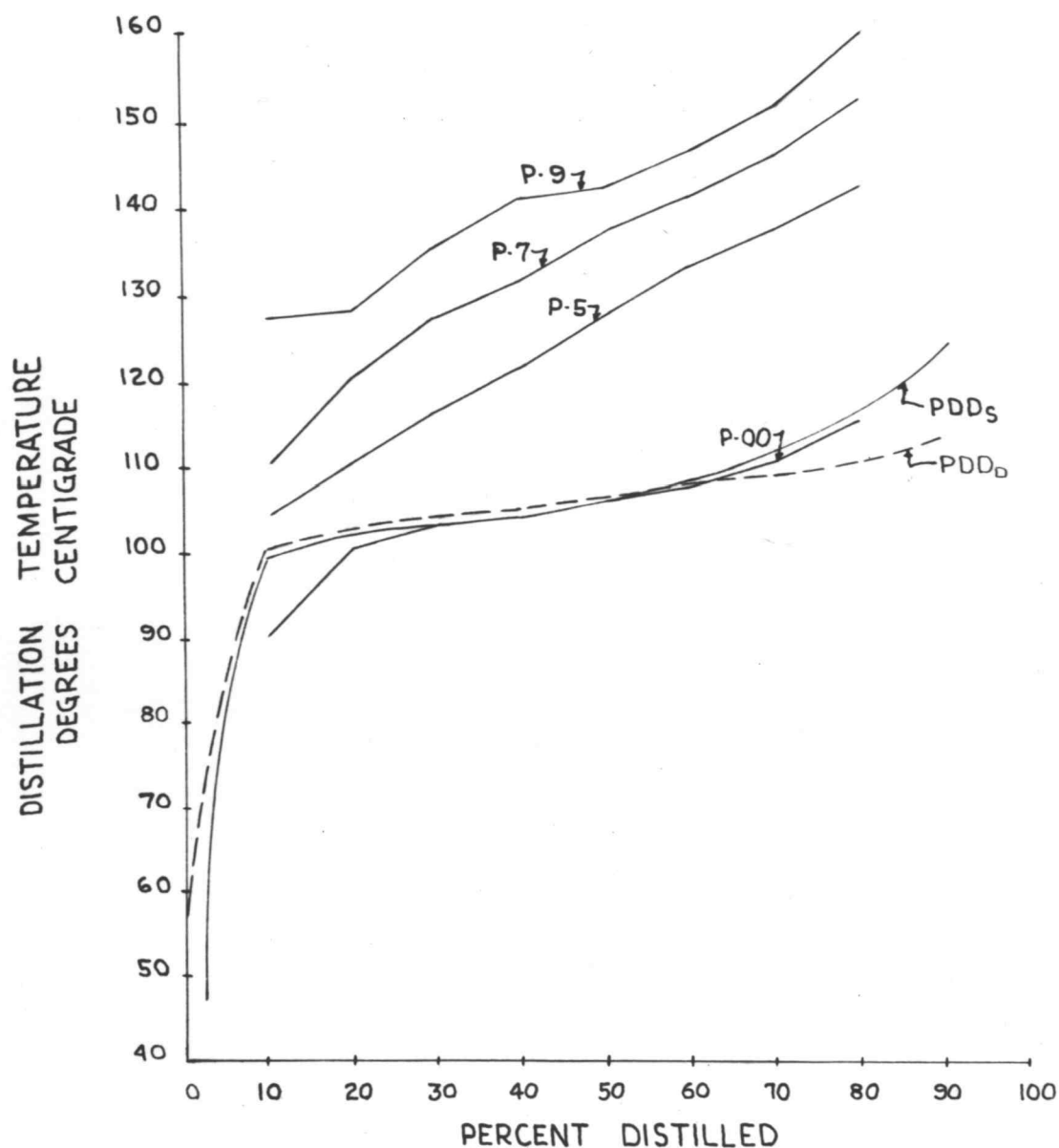
$$\text{and } \text{H}_{n-2} + \text{Cl}_x = 6$$

And where n and x may be any integer between 1 and 8.

Since the reaction occurs spontaneously, it is difficult to stop at any given point; hence there results a mixture of compounds of both saturated and unsaturated types. The lower molecular weight compounds having a high vapor pressure are the desired ones; hence the mixture is fractionally distilled. This leaves a residue of more highly chlorinated products but still possessing a low unsulfonated residue. Further fractionation results in the mixture noted in this work as P_5 , P_7 and P_9 .

Since mixtures of compounds that might vary from one sample to another were being dealt with, these mixtures should be characterized. The characterization was accomplished by determination of boiling range (see Graph 5, which is a plot of the boiling range of some of these materials), percentage chlorine and determination of unsaturate content. Limited work was done on the content of specific compounds but this was found too time consuming. It was found after analysis of a number of samples of mixtures that the P_5 , P_7 , and P_9 fractions were always about the same but that the P_{DD} mixture varied as the manufacturing process

GRAPH 5

BOILING RANGE OF SOME
CHLORINATED C_3 HYDROCARBONS

was improved.

Table I summarizes the data obtained from the characterization of the various mixtures, as well as data obtained on individual compounds. These data represent the average of two determinations of at least two or more runs.

There was some discrepancy of agreement on the molecular weight determined by the author and that found by the research laboratory of Dow Chemical Company. Consequently, the method of molecular weight determination was checked using repurified iso-amyl bromide. The determined molecular weight agreed very closely with theoretical - $150.7 \pm .14$ against the known 151.06. Since the standard error of the experiment was $\pm .02\%$ and standard deviation $\pm .14$ g. it was concluded that the method used was accurate and the values obtained correct. Table 2 presents the determined molecular weights together with the standard deviations.

The adsorption of the various fumigants was studied under two different conditions, namely:

- (1) Adsorption of the liquid phase
- (2) Adsorption of the gas phase

The first study was an attempt to study the relative adsorption of a soil low in colloids (Chehalis sandy loam) and a soil high in colloids (Cove clay). The second study was an attempt to learn something about the relative adsorption of different fumigants.

In the first experiment P_{DD} was dissolved at the rate of 20% by volume in the monobutyl ether of ethylene glycol and 50.00 cc. of this solution added to 5.0 grams of soil. Samples were withdrawn at definite intervals of time and the amount of P_{DD}

Table 1

Determination	P _{DD}	P ₅	P ₇	P ₉	TCB ¹
% Unsat. by wt.	63.1	60.0	60.1	59.9	
Mol. wt.	143.8	152.45	158.08	164.05	164.5
Vapor Pres. (mm. Hg) at					
10°C	16.9	19.8	13.0	4.8	
20°C	31.3	32.5	21.6	8.5	
30°C	51.6	51.1	34.4	14.2	
40°C	82.1				
% Chlorine	62.9	69.0	71.5	74.0	64.2
Boiling range					
Initial	69°	88°	102°	109°	95°
10%	90	103	113	128	100-117
20%	100	111	120	130	117
30%	103	116	127	135	117
40%	104	121	131	139	117
50%	106	127	137	141	117
60%	107	133	141	144	117
70%	110	138	141	146	117
80%	115	144	151	155	117
Specific gravity (20°C)	1.1770	1.2800	1.3035	1.3325	1.1210

¹ Trichlorobutane

Molecular Weights of Some Halogenated Compounds

Material	Density	Molecular wt. (Determined)	Molecular wt. (Theoretical)
PDD	1.1770	143.8 \pm .21	
P ₅	1.2800	152.45 \pm .24	
P ₇	1.3035	158.05 \pm .10	
P ₉	1.3325	164.05 \pm .10	
TCB ¹	1.1210	164.5 \pm .21	161.6
Iso C ₅ Br ²	1.2150	150.7 \pm .14	151.06

¹ Trichlorobutane (Technical grade)

² Isoamyl bromide

remaining in solution was determined with a Nesslerimeter, the difference from the original was assumed to have been adsorbed. The two soils used were Chehalis sandy loam and Cove clay. Table 3 summarizes the data so obtained from two replicated runs.

Graph 1 is a plot of the logarithm of the material adsorbed per gram of soil against the logarithm of the material left in solution. Since this plot is approaching a linear function, it can be assumed that Freundlich's isotherm applies and this is a case of true adsorption.

An attempt was made to determine the comparative adsorption of different materials in the second experiment. A gas train apparatus was used in this determination (See Plate 1). A stream of air was drawn through a bottle of fumigant and the vapor so drawn off was led through a weighed quantity of dry soil. The increase in weight was taken as being adsorbed gas.

It can readily be perceived that the same amount of vapor of each of the materials did not pass through the soil because of the differences in vapor pressure at the temperature of the experiment ($20^{\circ} \pm 2^{\circ}$). Therefore, no comparison can be made between runs.

Table 4 summarizes the data of two replicated runs of each material on all three soil types.

Graph 2 is a plot of molecular weight of chlorinated C_3 compounds plotted against the percent of vapor adsorbed per gram of soil. It was found that comparison between materials could be made only by means of the % of vapor given off adsorbed per gram of soil.

Table 3.

ADSORPTION OF DD BY TWO DIFFERENT SOILS¹

Time in Minutes		Remaining in 50.0 cc.		Adsorbed per gram of soil	
		cc's	gms.	cc's	gms.
0.00	Chehalis S. L.	10.0	11.71	0.0	0.0
	Cove Clay	10.0	11.71	0.0	0.0
20.0	Chehalis	9.5	11.125	0.1	.1171
	Cove Clay	8.5	9.954	0.3	.3513
40.0	Chehalis	8.5	9.954	0.3	.3513
	Cove Clay	6.0	7.026	0.8	.9368
70.0	Chehalis	8.0	9.368	0.4	.4684
	Cove Clay	5.5	6.440	0.9	1.0539
100.20	Chehalis	7.5	8.783	0.5	.5855
	Cove Clay	5.0	5.855	1.0	1.171

¹ Data average of two replicated runs

Graph 1
Chehalis Soil

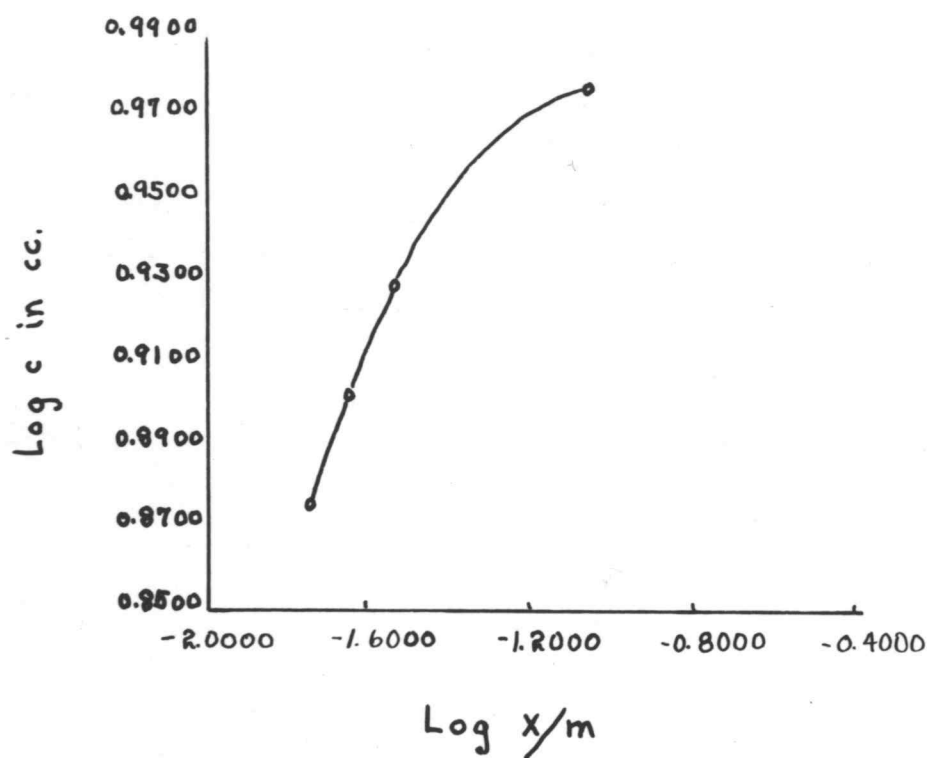
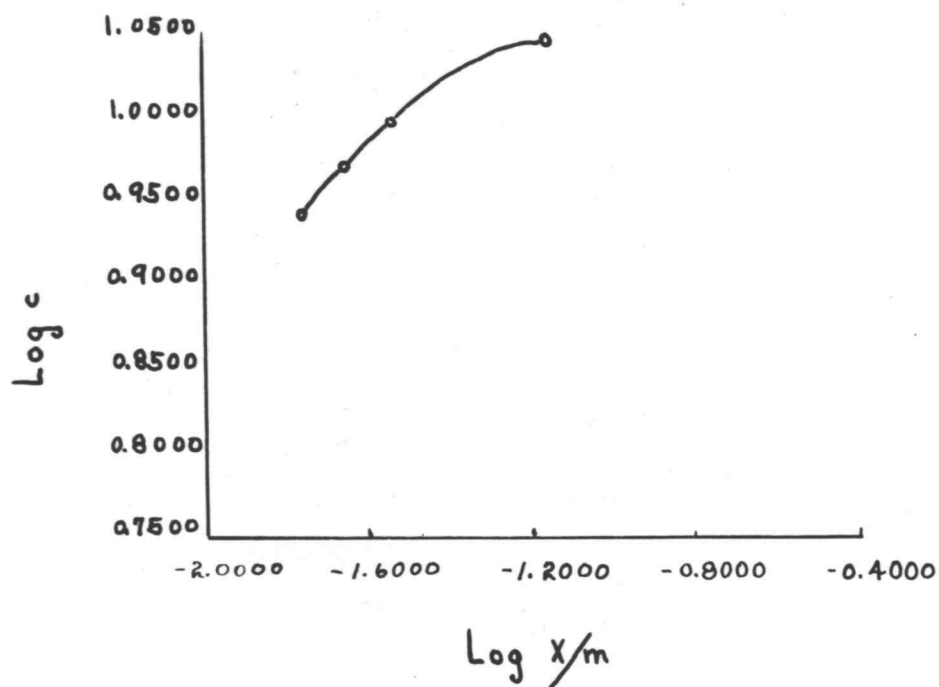
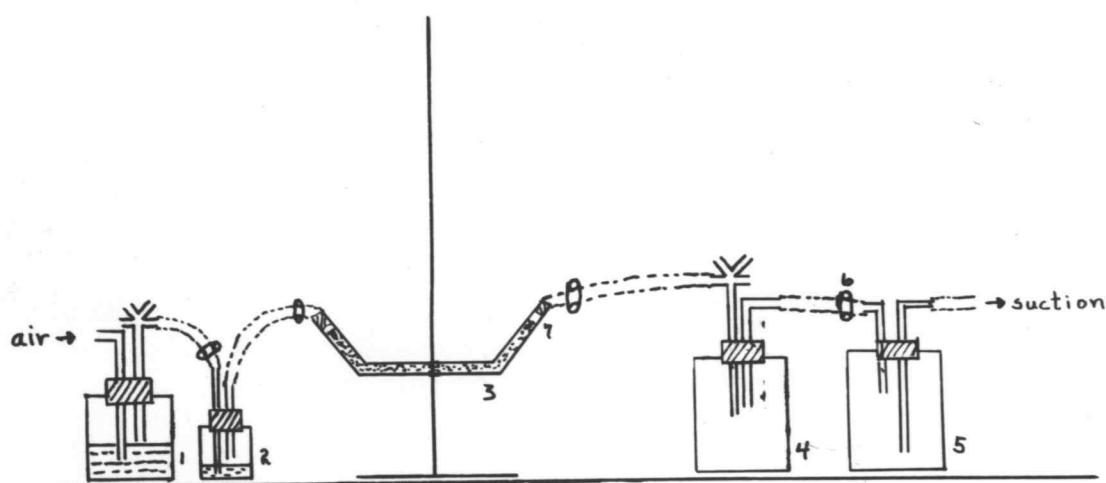


Plate 1

Adsorption Train



One unit of a 4 series setup

Legend

- rubber tubing
- == glass tubing 3+8 mm
- ▨ rubber stoppers
- 1.- 1000 ml. bottle con H_2SO_4
- 2.- 250 ml. bottle for material
- 3.- 18 mm. x 35 dm adsorption tube
- 4.- distributor chamber
- 5.- Safety chamber
- 6.- Clamps
- 7.- cotton retainer-wad

TABLE 4: ADSORPTION OF MATERIALS¹ USED AS SOIL FUMIGANTS

Soil	Material	Hrs. run	Liquid loss grams	Adsorbed by soil in grams	Soil wt. in tube grams	% Adsorption per gram of soil	grams adsorbed/ gm. of soil	Acre adsorp. ⁴ lbs. based on 2,000,000 lbs.
Lake Labish peat (oven dry)	P _{DD}	47:10	51.40	0.81	20.79	0.076	0.0390	171.50
	P ₅	" "	33.20	0.57	20.94	0.082	0.0272	120.00
	P ₇	" "	30.70	0.72	21.43	0.109	0.0336	148.00
	P ₉	" "	13.90	0.53	23.82	0.160	0.0222	97.60
Chehalis Fine sandy loam (oven dry)	P _{DD}	56:00	8.66	2.20	55.00	0.462	0.0400	176.20
	P ₅	" "	8.74	2.01	" "	0.412	0.0365	160.80
	P ₉	" "	22.69	0.99	" "	0.669	0.0180	72.29
	CS ₂	" "	68.16	1.85	" "	0.0491	0.0336	148.00
Cove Clay	BB ²	50:30	0.92	0.00	32.50	0.000	0.0000	0.00
	CS ₂	" "	109.18	0.41	" "	0.012	0.0126	55.50
	DO	" "	27.36	0.87	" "	0.098	0.0267	117.61
	P ₇	" "	14.10	0.51	" "	0.111	0.0156	68.71
Cove Clay	P _{DD}	50:00	17.14	0.91	32.50	0.163	0.0280	123.78
	P ₅	" "	9.68	0.66	" "	0.210	0.0203	89.42
	P ₉ ³	" "	3.68	0.41	" "	0.347	0.0127	55.94
	TCB	" "	3.47	0.52	" "	0.461	0.0160	70.92

1 Factor

$$4405 \times \frac{\text{gms adsorbed}}{\text{gms soil}} = \text{lbs ads/acre}$$

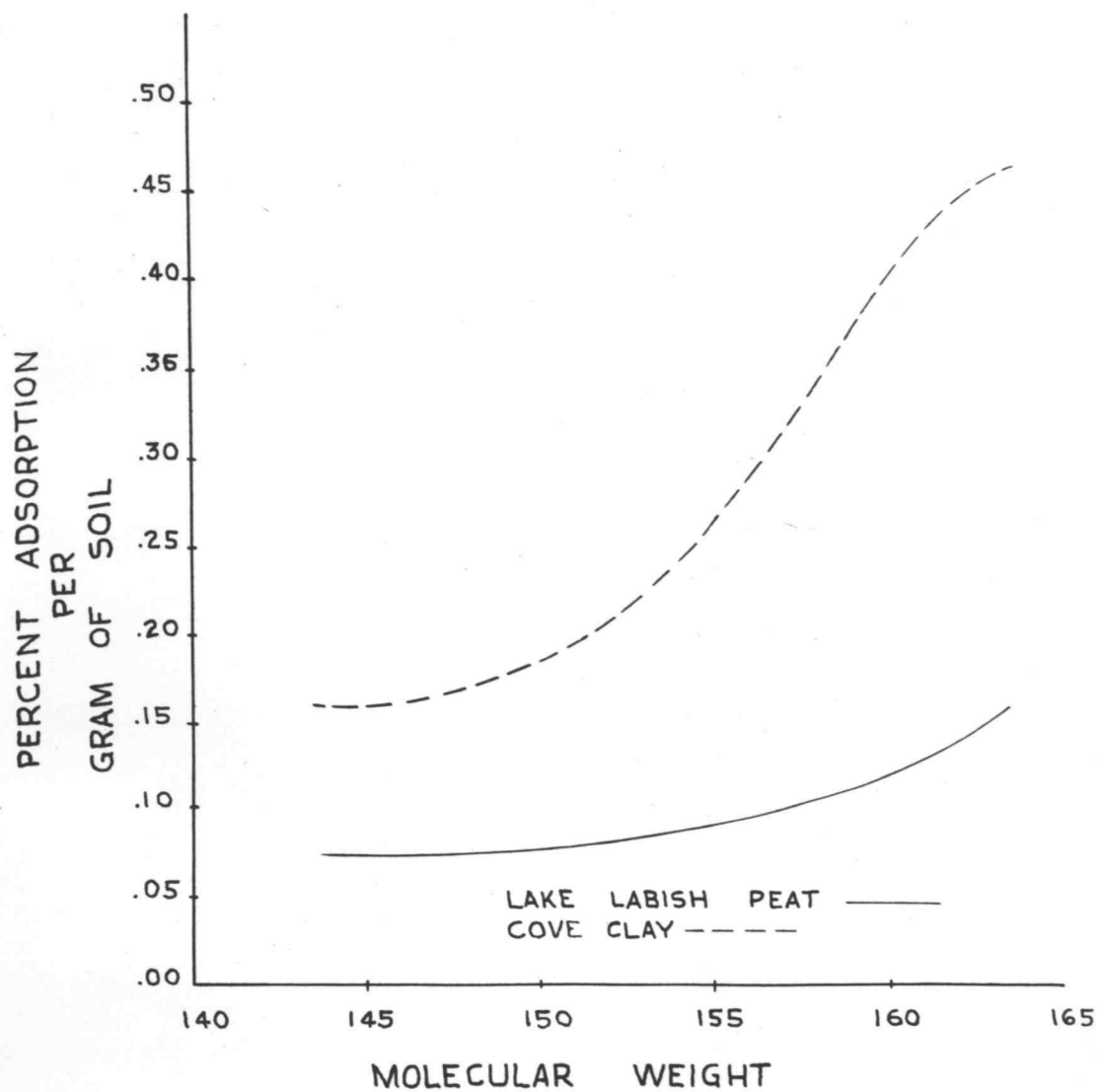
2 dichloroethyl ether

3 Trichlorobutane

4 Based on acre foot of soil (weight =
 2,000,000 lbs.)

GRAPH 2

ADSORPTION OF CHLORINATED
HYDROCARBONS BY TWO DIFFERENT
SOILS



It was found in preliminary studies that the maximum adsorption or saturation point was reached in 45-50 hours. Hence the adsorption train was run at least 45 hours and in some cases longer. Each run with a given soil was as nearly as possible a replicate of the first run.

Greenhouse Trials

Most of the greenhouse trials were concerned with the comparative toxicity of various soil fumigants or distillate fractions. These trials were conducted on gray winter oats planted in number 2 cans containing approximately 485 grams of soil. Treatments were made when the plants were 6 inches in height. Evaluation of results were made by visual estimate of the extent of necrosis and kill and the comparison to the growth of a corresponding check.

Table 5 summarizes the earlier comparison of various chlorinated C_3 mixtures and carbon bisulfide and $\beta\beta'$ dichloroethyl ether. Table 6 gives a further comparison between these mixtures and chloropicrin.

These tables are the combined averages of two or more trials in one or more winters. In general, good agreement was obtained between trials.

Table 7 presents information from trials where P_9 was fractionally distilled and the various fractions were tested for toxicity.

It may be seen from the boiling range data that the molecular weight of the fraction increased from fraction one through fraction seven and conversely the vapor pressure decreased. Analysis for

Table 5

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COMPARATIVE TOXICITIES OF FUMIGANTS IN GREENHOUSE TESTS
AS EXPRESSED IN PER CENT KILL AND PLANT HEIGHT¹

Material	ppm					
	50	100	200	300	400	500
CS ₂	0	0	0	0	0	0
ββ'DCE	0	0	10	50	75	90
P _{DD}	20	30	50	80	90	95
P ₅	10	60	75	80	95	100
P ₉	75	90	95	98	100	100
Height of Plant (Inches)*						
CS ₂	7	7	6	7	5	5
ββ'DCE	5	4	3	2	0	0
P ₅	4½	2	1	½	0	0
P ₉	3½	1½	1	0	0	0
Check	8	7½	8	8 ¾	7	7 ¾
P _{DD}	4	4	2	1½	0	0

¹ Ave. 4 replicates.

* Ave. height of all plants

TABLE 6: RELATIVE TOXICITY OF SOIL FUMIGANTS

Material		Results	
Name	ppm	% Kill	% Growth Inhibition
Chloropicrin	50	100	
	100	"	
	150	"	
	200	"	
	300	"	
	400	"	
	500	"	
	1000	"	
P _{DD}	50	35	50
	100	50	75
	150	90	95
	200	100	
	300	"	
	400	"	
	500	"	
	1000	"	
P ₉	50	50	50
	100	60	75
	150	75	90
	200	90	90
	300	100	
	400	"	
	500	"	
	1000	"	
P ₅	50	25	75
	100	60	80
	150	75	90
	200		90
	300	100	
	400	"	
	500	"	
	1000	"	
P ₇	50	10	50
	100	25	80
	150	50	95
	200	60	98
	300	90	99
	400	100	
	500	"	
	1000	"	

Material		Results	
Name	ppm	% Kill	% Growth Inhibition
PTB (Trichlorobutane)	50	—	—
	100	—	30
	150	8	50
	200	16	50
	300	20	55
	400	60	90
	500	90	95
	1000	95	99

Table 7
THE TOXICITY OF SOME DISTILLATE FRACTIONS OF P₉ AT 100 ppm

Fraction	Boiling Range	Ref. Index	% Kill ¹
1	105-115°C	1.4605	65
2	115-120	1.4701	72
3	120-125	1.4731	75
4	125-130	1.4763	100
5	130-135	1.4819	100
6	135-140	1.4839	90
7	140-145	1.4837	85

¹ By visual estimate

Table 8
THE COMPARATIVE TOXICITY OF SOME CHLORINATED C₃
COMPOUNDS TO PLANTS AT 100 ppm

Material	% Toxicity	Rank of Toxicity
PDD	79.5	2
2,3 dichloropropene-1	100.0	4
1,3 dichloropropene-1	87.5	3
1,2,3 trichloropropane	45.0	1

unsaturation showed a higher percentage of unsaturated compounds in the fourth and fifth fractions although there was not much difference between the highest and lowest fractions. Graph 3 is a plot of the upper temperature of the boiling range of the fraction against the toxicity.

Table 8 is a comparison of toxicity between some chlorinated C_3 compounds and P_{DD} mixture.

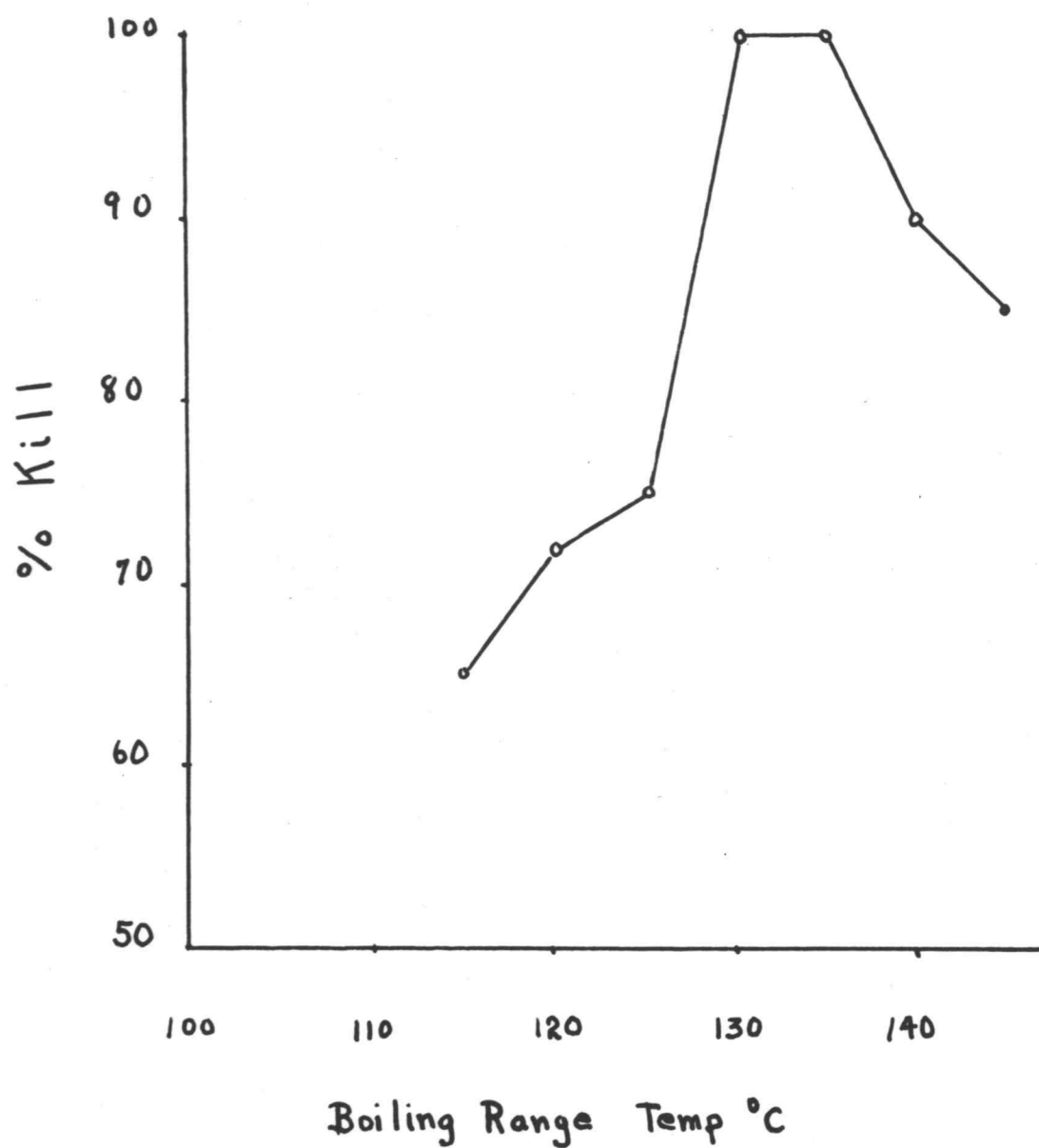
Field Trials

The field data presented in this paper comprises the results of three years investigational work. All of the plot work done with soil fumigants will not be presented here since in much of the work comparisons were made between types of toxicants rather than between specific fumigants. Later some reference will be made to some of the observational data on soil fumigants, particularly chlorinated C_3 products.

Most of the plots reported on here were applied with a Mack Anti-weed gun soil fumigant injector. This particular piece of equipment resembles an oversized hypodermic syringe with a metering pump that may be set for any desired dosage. Plots were usually one square rod in size though plots as large as three square rods were used on occasions. In all cases plots were replicated twice or more in a randomized manner. The pattern of alternating injections described by Taylor (37, p. 63) were used for hand injections. Two series of plots were applied by machine drawn equipment applying the materials in a continuous band.

Graph 3

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Preliminary trials were run to determine the relative toxicity of various materials to plants. Later trials were concerned with such factors as spacing, dosage and diffusion patterns. Some comparisons have been made between the effect of soil type and moisture on the effectiveness of the material.

Preliminary trials conducted in late 1944 and early 1945 were designed to compare the effectiveness of chlorinated C_3 compounds with other fumigants. Carbon bisulfide was most commonly used for these comparisons. Chloropicrin was not used in these trials because of its objectionable features in handling and its cost. Table 9 presents the data of the comparative trials on carbon bisulfide and P_{DD} on morning glory.

TABLE 9: COMPARISON OF P_{DD} AND CS_2 ON MORNING GLORY

Material	Depth	Spacing	Dosage	Plants/ Plot	Kill % of check ave.
CS_2	6 "	18 "	60 cc.	25	73.4
CS_2	6 "	18 "	60 cc.	4	93.8
CS_2	6 "	18 "	60 cc.	62	34
CS_2	6 "	18 "	60 cc.	47	50
DD	6 "	18 "	60 cc.	0.0	100
DD	6 "	18 "	60 cc.	0.0	100
DD	6 "	18 "	60 cc.	0.0	100
DD	6 "	18 "	60 cc.	0.0	100
CS_2	6 "	18 "	35 cc.	36	61.7
DD *	6 "	18 "	35 cc.	0	100
Check				93	
Check				102	
Check				97	
Check				92	

* Average of 4 plots

Table 10 compares the effectiveness of the two materials on canada thistle.

Table 10
COMPARATIVE EFFECTIVENESS OF CS₂ and P_{DD}
ON CANADA THISTLE

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Material	Depth	Spacing	Dosage/Injection	% Kill ¹
CS ₂	6 "	18 "	45.0 cc.	82.5
P _{DD}	6 "	18 "	45.0 cc.	100.0
CS ₂	6 "	18 "	30.0 cc.	48.7
P _{DD}	6 "	18 "	30.0 cc.	100.0
CS ₂	6 "	18 "	15	27.2
P _{DD}	6 "	18 "	15	94.9

¹ Average of 3 replications

Table 11 summarizes the studies made on the chlorinated C₃ mixtures from 1944 through the summer of 1946.

Since all plants do not respond similarly to the same material the chlorinated mixtures were tested on a number of different plants. Tables 12, 13 and 14 present the information gained on several different plants.

The moisture content of the soil appeared to affect the results of fumigant action hence it appeared desirable to determine the relationship of the two. Consequently, two different materials were tried in the field under different soil moisture levels. Table 15 presents the data obtained in this experiment.

Trials were established with the four different chlorinated mixtures to determine the optimum dosage of these materials. The plant colony was a mixture of Cirsium arvense, Agropyron repens and Equisetum arvense with an occasional plant of Equisetum hy-
menales. The percentage kill is the expression of control of all

TABLE 11: SUMMARY OF RESULTS WITH CHLORINATED C₃ PRODUCTS
1944 to 1946

Year	Season	Material	Dosage	Spacing	Depth	Plant	Kill	Remarks
1944	Fall	DD	900#/Acre	18 "	4 "	Canada thistle	99.0%	Average 6 plots
1944	Fall	DD	1600#/Acre	18 "	6 "	Morning glory	100.0%	4 plots
1944	Fall	DD	800#/Acre	18 "	6 "	" "	100	4 plots
1945	Spring	DD	300	12-18 "	2-6 "	Quack Grass	60-90%	Shallower injections
1945	Spring	DD	600	12-18 "	2-6 "	" "	75-100	Closely spaced
1945	Spring	DD	900	12-18 "	2-6 "	" "	100	Most effective
1945	Spring	DD	300	12-18 "	4-6 "	Canada thistle	50-75	Close Spacing (12")
1945	Spring	DD	600	12-18 "	4-6 "	" "	85-100	nearly always gave
1945	Spring	DD	900	12-18 "	4-6 "	" "	100	kills of 100%
1945	Spring	DD	600	12 "	5-6 "	White top	100	
		P ₅	300-900	9-15 "		Quack Grass	85-100	As material increased
		P ₇	300-900	9-15 "		" "	75-100	in mol. wt. spacing
		P ₉	300-900	9-15 "		" "	65-100	had to be closer.
1945	Summer	DD	300-750	9-15 "	2-6 "	" "	Good kills with all materials	
		P ₅				Morning glory	but lighter ones more effective	
		P ₇				Canada thistle	at lower temperatures and wider	
		P ₉				White top	spacing.	
1946	Spring	DD	450	12 "	3-4	Russian Knapweed	100%	
		P ₅	450	12 "	3-4	White tip	100%	
1946	Summer	DD	150-450	12 "	2-4	Quack Grass	60-100%	Dosage of 300-450#/A
		P ₅	150-450	12 "	2-4		60-100	seemed to be ample
		P ₇	150-450	12 "	2-4	Canada thistle	50-100	at temp. 60-80°F.
		P ₉	150-450	12 "	2-4		50-90	lighter fractions best.

TABLE 12: EFFECTIVENESS OF P_{DD} ON CANADA THISTLE

Rate of Application	Spacing	Depth of a Application	% Kill
6 cc./hole	18 "	5 "	60
8 " "	"	6 "	60
8 " "	"	6 "	55
6 " "	"	6 "	45
2 " "	"	6 "	25
6 " "	"	6 "	75
8 " "	"	6 "	100
8 " "	"	6 "	90
12 cc./hole	"	6 "	20
4 " "	"	6 "	30
8*	"	6 "	75
12*	"	6 "	90
4*	"	6 "	32
8*	"	6 "	85
12*	"	6 "	100
16*	"	6 "	100
900#/Acre	"	4 "	100
900#	"	4 "	100
12 cc.	"	6 "	90
4 cc.	"	3 "	65

* Soil very dry at time of application

Table 13

THE COMPARATIVE EFFECTIVENESS OF CHLORINATED C₃
COMPOUNDS ON QUACKGRASS

Material	Space	Depth	Soil	Rate lbs./Acre	% Kill
P ₅	1'	3"	Sandy	150	59.5
P ₅	1'	3"	loam	250	75.6
P ₅	1'	3"	14.7% H ₂ O	350	91.2
P ₇	1'	3"	"	150	68.1
P ₇	1'	3"	"	250	84.9
P ₇	1'	3"	"	350	90.8
P ₉	1'	3"	"	150	70.0
P ₉	1'	3"	"	250	75.1
P ₉	1'	3"	"	350	94.7

<u>Analysis</u>	dF	X ²	L.S.	Least Squares	F. value
Material	2	56.46	28.23	.44	
Dosage	2	762.21	381.10	5.92	4.46
Error	4	257.21	64.30		
Total	8	1175.88			

$$LSD_{.05} = \frac{L.S. Error \times 2}{df} \times F_{.05} = 15.13\%$$

TABLE 14: COMPARISON OF EFFECTIVENESS OF P_{DD} ON VARIOUS PLANTS 42

Plant	Spacing	Depth	Dosage lbs/Acre	% Kill
Canada Thistle	12 "	4 "	450	90.0
"	"	9 "		100
Quackgrass	12	3-4 "	450	89.5
"	9	3-4	450	100
"	9	3-4	300	95
Russian Knapweed	12	4 "	500	100
White top	12	4 "	500	100

TABLE 15

COMPARISON OF EFFECTIVENESS OF SOIL FUMIGANTS
UNDER DIFFERENT MOISTURE LEVELS*

Material	% H ₂ O	Plant	Dosage	% Kill
P _{DD}	8.21	Quackgrass	500#/Acre	52.5
	21.3	"	" "	97.6
	63.7	"	" "	65.0
P ₉	6.3	Canada Thistle	500	30.2
	18.9	" "	"	95.0
	55.6	" "	"	45.6

* Average of 3 replicated plots

of these plants. Table 16 contains the information on this trial.⁴³

Since spacing and depth of injection were felt to influence the results of fumigation, trials were initiated to study these factors. Table 17 and 18 present the data from these studies.

Table 19 is another summary of results obtained with soil fumigants during the course of these studies.

The row effect mentioned earlier, always appeared where the spacing of injections was wide. The width of the killing region was found to be characteristic of any given material; for example it has long been known that the diameter of kill zone for carbon bisulfide is 18 inches. Since vapor pressure and molecular weight was shown to affect the diffusion of gas in the soil, it was reasoned they may well affect the size of killing zone. Graham's law of gas diffusion expressed mathematically is:

$$u = \frac{3RT}{M}$$

and for a two gas system

$$\frac{u_1}{u_2} = \frac{\frac{3RT}{M_2}}{\frac{3RT}{M_1}}$$

Then using the constant 18 for carbon bisulfide

$$\frac{u_{CS_2}}{u_{unknown}} \times 18 = \text{distance of kill for unknown}$$

Table 20 presents data of killing distance of some of the Chlorinated C₃ mixtures.

Table 16

44

A COMPARISON OF EFFECTIVENESS OF DIFFERENT MATERIALS
AT DIFFERENT DOSAGE LEVELS ON CANADA THISTLE

Material	Dosage	% Kill	Ave.	Total Treatt
P _{DD}	750	100	100	(1) 200.0
	750	100		
	600	99.5	97.0	(2) 194.0
	600	94.5		
	450	86.0	92.0	(3) 184.0
	450	98.0		
	300	79.0	80.5	(4) 161.0
	300	82.0		
P ₅	750	95.0	93.8	(1) 187.5
	750	92.5		
	600	83.0	83.8	(2) 167.5
	600	84.5		
	450	82.5	79.3	(3) 158.5
	450	76.0		
	300	70.0	67.5	(4) 135.0
	300	65.0		
P ₇	750	80.9	83.2	(1) 166.5
	750	85.6		
	600	82.2	78.5	(2) 159.0
	600	76.8		
	450	67.4	69.1	(3) 138.6
	450	71.2		
	300	45.0	51.8	(4) 98.5
	300	53.5		
P ₉	750	67.5	68.0	(1) 135.9
	750	68.4		
	600	37.5	49.2	(2) 98.7
	600	61.2		
	450	50.1	51.9	(3) 103.8
	450	53.7		
	300	35.6	32.8	(4) 65.6
	300	30.0		

Table 17

45

A COMPARISON OF MATERIAL AND SPACING
ON CONTROL OF CANADA THISTLE

Material	Spacing	% Kill	Total	Ave.
P _{DD}	9 "	100	200	100.0
	9 "	100		
	12 "	80.0	158.3	79.2
	12 "	78.3		
	15 "	58.9	108.0	59.0
	15 "	59.1		
P ₇	9 "	74.6	166.0	83.0
	9 "	91.4		
	12 "	63.6	123.3	61.7
	12 "	59.7		
	15 "	47.8	96.1	48.1
	15 "	48.3		

Table 18

COMPARISON OF EFFECTIVENESS OF VARIOUS DEPTHS OF INJECTION

Material	Depth	% Kill	Total	Ave.
P _{DD}	4	71.0	145.3	72.6
	4	74.3		
	2	64.0	124.2	62.1
	2	59.2		
P ₇	4	50.9	104.1	52.1
	4	53.2		
	2	50.0	112.5	56.3
	2	62.5		

Table 19

SUMMARY OF RESULTS WITH CHLORINATED C₃
MIXTURES AS FUMIGANTS

Material	Dosage in lbs/acre	Spacing	Plant	% Kill
P _{DD}	750	18" - 4"	Morning Glory	90
"	600	18" - 4"	" "	85
"	300	18" - 4"	" "	70
"	200	12" - 4"	Quackgrass	60
P ₅	300	12" - 4"	Quackgrass	75
"	400	12" - 4"	"	90
P ₇	200	12" - 4"	Quackgrass	68
"	300	12" - 4"	"	85
"	400	12" - 4"	"	90
P ₉	200	12" - 4"	Quackgrass	70
"	300	12" - 4"	"	75
"	400	12" - 4"	"	75
P ₇	300	12" - 4"	Canada Thistle	50
"	400	12" - 4"	" "	85
"	600	12" - 4"	" "	95
P _{DD}	500	12" - 4"	Canada Thistle	95
P ₇	500	12" - 4"	Russian Knapweed	100
P ₉	350	12" - 4"	Canada Thistle	55
P _{DD}	500	12" - 4"	Canada Thistle	98.5
P ₇	500	12" - 4"	Russian Knapweed	100
P ₉	400	12" - 4"	Canada Thistle	75
P ₇	400	12" - 4"	" "	88
P ₅	400	12" - 4"	" "	97
P ₉	300	1 sq. ft.	" "	72
P ₇	300	1 sq. ft.	" "	85
P ₉	300	1 sq. ft.	" "	

Table 19 Cont.

Material	Dosage in lbs/acre	Spacing	Plant	% Kill
P ₇	300	Acre	Canada Thistle Horsetail	50
P ₇	400	"	Canada Thistle	85
	600	"	" "	95
	200	"	Quackgrass	68
	300	"	"	85
	400	"	"	90
P ₉	200	"	Quackgrass	70
P ₅	419	12" - 4"	Quackgrass	100
P ₇	416	18" - 4"	Quackgrass	80
	416	12" - 4"	"	100
P ₉	416	12" - 4"	Quackgrass	95
P ₅	700	12" - 4"	Can. thistle, lamb quarter, pig weed, horsetail	100
P ₅	700	18" - 4"	Same as above	75
P ₇	700	12" - 4"	Same as above	100
P ₇	420	18" - 4"	" " "	80
P ₉	700	12" - 4"	Same as above	100
P ₉	470	18" - 4"	" " "	77
P _{DD}	450	18" - 4"	Morning glory	90
P _{DD}	330	18" - 4"	" "	85
P _{DD}	250	18" - 4"	" "	70
P ₅₀	200	12" - 4"	Quackgrass	60
P ₅₀	300	12" - 4"	"	75
P ₅₀	400	12" - 4"	"	90

CALCULATION OF DIFFUSION OF CHLORINATED C₃ GASES
USING CS₂ AS A STANDARD
(EFFECTIVE KILLING DISTANCE)

Material	Found	Calculated	Mol. wt.
DD	10.5	10.0	143.8
P ₅	9.3	9.1	152.45
P ₇	8.5	8.28	158.05
P ₉	8.0	7.74	164.05
CS ₂	18		76.02

Excavations of the killing zone led to the discovery that the pattern of diffusion and kill was hemispherical in shape. That is to say, that the gas being heavier than air tended to settle downward in the soil and in doing so had the tendency to diffuse laterally as determined by root kill. The settling effect may be expressed in the well known barometric equation:

$$\text{Settling} = Cd \times Mg$$

In examining the cross section of such a pattern as determined by root kill, the following figures were obtained as averages of a number of such excavations. The term x applies to the vertical axis from the point of injection and term y to the horizontal axis. Graph 4 is a plot of these figures demonstrating the parabolic shape of the periphery of the kill pattern. Because of the growth habits of the roots of plants, this kill pattern is very important.

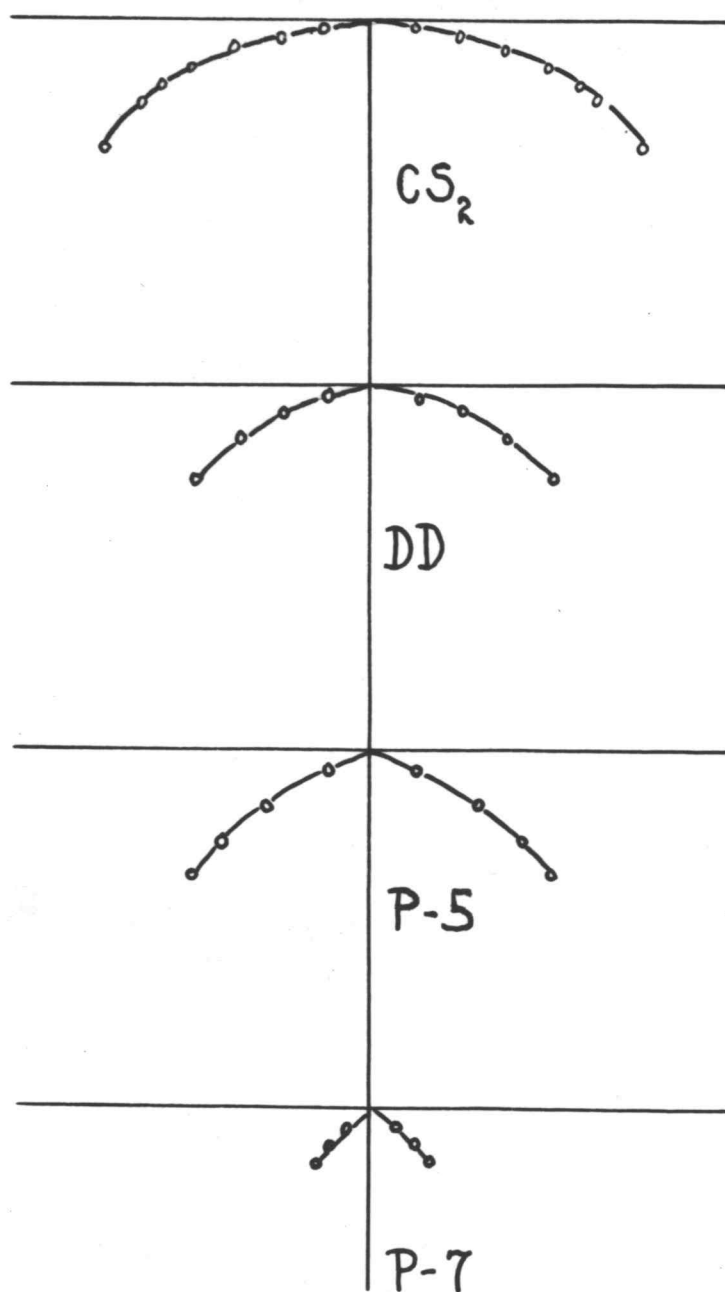
An interesting sidelight to the study on soil fumigants was the residual effect of the chlorinated C₃ compounds. A treatment was made on Canada thistle during the summer of 1946. The area

KILL PATTERN OF SOME SOIL FUMIGANTS

Material	X axis Inches from injection pt.	Y axis
CS ₂	2	12
	3	15
	4	18
	5	24
P _{DD}	22	10
	3	12
	4	15
	5	18
P ₅	2	7
	3	10
	4	12
	5	15
P ₇	2	4
	3	7
	4	10
	5	12

Soil - Fumigant Diffusion Kill - Pattern

50



Graph 4

was subsequently seeded to barley that fall.

In the spring it was observed that the grain on the treated area was much taller and thrifty appearing than the grain on the non-treated area. Protein analysis showed the grain on the treated area to be much higher in nitrogen. The following table summarizes the observations made on the area.

Treated area (P ₅)	Height of Grain 10 "	Protein 16.24 %
Non-treated	6 "	12.36

This observation has been made before on other halogenated hydrocarbons. As yet no one appears to have followed this effect to maturity to check the effect on yield. It would seem that this may have interesting possibilities.

It may be seen from the data presented that mixtures of chlorinated C_3 compounds are very effective phytocidal agents when used as soil fumigants. The effective dosages are from one-quarter to one fifth of that for carbon bisulfide. It is believed that the work cited by Newhall (25, p. 73) which purports to show that even at 1000 pounds per acre P_{DD} was not effective as a phytocidal agent may not have been done in a manner compatible with the physical properties of the material.

It has been shown that the successful use of soil fumigants entails taking into account some of the physical laws governing the behavior of gases. For example, adsorption of gases by colloidal material must be taken into account inasmuch as this process removes the toxicant from the site of toxicological activity. Therefore, since it has been shown that the MLD for toxic vapors must attain a concentration of at least 50 ppm, with a low vapor pressure material adsorption may prevent this concentration being reached. It would follow then, that in a highly colloidal soil dosages should be increased to compensate for adsorption.

The data presented clearly indicate that adsorption is a function of the molecular weight of the adsorbed material as well as the interfacial surface area of the adsorbent. Thus as the molecular weight of the compound increased a proportionately greater amount would be adsorbed as measured by weight adsorbed per gram of adsorbent.

If two basic assumptions are made, the figure cited throws an interesting light on the effect of vapor pressure on rate of

evaporation from the adsorbing surface. These assumptions are:

(1) that the size of the adsorbing surface and the attractive forces are equal per unit weight for any given soil and (2) that since there is an excess of gas the soil will adsorb the same amount of material. If these assumptions are correct, then the rate of evaporation from the adsorbing surface will be a function of the vapor pressure of the material.

It was shown that as the colloidal content of a soil increased a larger amount of material was adsorbed.

The toxicity of the chlorinated C_3 compounds was shown to increase with the molecular weight but that under field conditions the physical properties such as vapor pressure of the mixture limited its usefulness.

It was also demonstrated that toxicity of the chlorinated C_3 mixtures could be correlated in part with the percentages of unsaturates that it contained. Thus, 2-3 dichloropropene-1 was much more toxic than the saturated 1,2,3 dichloropropane.

Field trials have established that the chlorinated C_3 mixtures are effective soil fumigants for the control of herbaceous perennial noxious weeds. The price of these materials (\$1.64 per gallon) limits their use to high priced land or for control of patches of these plants. However, it should be pointed out that these materials are the most effective treatment yet for the control of noxious weedy grasses.

Field trials have shown that the practical range of molecular weight and vapor pressure to be at about that of the P_5 mixture.

Above that the killing effect is too slow and the residue too long lasting. Best results are obtained on sandy soil but very good control may be had on clay soil with proper application.

A great deal of work has been done on the rate of diffusion of gases in the soil but of vastly more importance in soil fumigation for plant control is the diffusion or kill pattern. In the rate of diffusion, time is measured in seconds whereas in field operation time is in days or even weeks. Therefore little concern is given the rate of diffusion. It has been shown that the diffusion - kill pattern of soil fumigants is hemispherical. Consideration of the pattern of the different materials shows that as the molecular weight increases that the area under the periphery decreases. That is to say, that as the molecular weight increases the horizontal diffusion becomes less. This indicates that in free diffusion in the soil the barometric law of settling becomes operable. By inspection of the data on the diffusion - kill pattern, an equation might be written to show some of the relationships of the physical properties of the material to the pattern. Final solution of the equation will have to await further information.

$$X = Y^n \frac{1}{CdxMg} F$$

where n and F are unknowns that can only be determined experimentally. An empirical equation has been developed, however, that may be used to calculate the width of effective kill at any depth using the values of a known gas.

The importance of the diffusion - kill pattern becomes readily obvious in considering the habit of plant root growth. If these hemispheres of gaseous toxicant do not become confluent above the principal rooting zone portions of the plant will remain alive to continue growth. Therefore the spacing of and depth of injection must be such that the patterns intercept in the proper region of the soil.

Field trials have shown that the effective dosage range for a 95 to 100 percent kill is between 300 to 600 pounds per acre. They have also demonstrated that the distance between injections should be about 9 inches. Moisture of the soil materially influences the results. Too little or too much moisture give very poor kills in fumigation. In general it might be said that the optimum soil moisture is one that will support vigorous plant growth but is not excessive.

An interesting sidelight to soil treatments with chlorinated C_3 compounds is the stimulating effect on the subsequent crops. Quite often in unplanted soil it has been noted that cruciferous plants predominate after treatment.

Investigations conducted on soil fumigants the past three years have established their value on control of objectionable plants. This is particularly true of chlorinated propane and propene mixtures.

The following factors have been found to affect the results obtained with soil fumigants:

1. Physical properties of the material
 - (a) Diffusion - kill pattern
 - (b) Vapor pressure and molecular weight
2. Inherent toxicity of the materials
3. Adsorption of the material by the soil.

These factors must be considered to obtain maximum effectiveness with a soil fumigant.

The following facts have been established about chlorinated C_3 mixtures as soil fumigants.

Chlorinated C_3 compounds are more effective as soil fumigants than is carbon bisulfide. This is clearly demonstrated in Table 9.

The effective dosage of the chlorinated C_3 compounds is much lower than the dosage for carbon bisulfide. Dosages of 300 to 600 pounds per acre are adequate if proper application is made.

This material is effective on any type of herbaceous noxious weed.

Hand application has proven more effective than machine (power) application.

The material is most effective in sandy soils but give complete control on clay soils when properly applied.

Moisture in the soil does not appear to influence the results. If the soil is friable enough to give an adequate seal very good control will be obtained on any soil at any time the temperature is high enough. Temperatures of 40° F and up are required for the material to evaporate rapidly enough to be effective.

Correct spacing and depth are critical in the success of a treatment. Experimental work has established the fact that for best results the spacing must be no more than 9 inches. For shallow rooted plants such as quackgrass the depth of application should be 2-3 inches and for deep rooted plants 4-6 inches.

In most of the theoretical investigations on soil fumigants the investigator has concerned himself with the rate of flow and amount of flow in a given time. Since time in diffusion experiments is measured in seconds the findings of such studies have had only limited practical application. It is the writer's contention that the direction of flow and diffusion pattern are vastly more important. These factors determine the spacing and depth of placement of soil fumigants. The time to establish this pattern, whether one hour or one day, is not important in as much as a treated area will be left much longer than this.

To gain a concept of the diffusion pattern we must assume

1. That a perfectly gas tight seal exists above the point of injection and
2. The gas formed may diffuse freely in any direction but that the direction of flow will be determined by the

density of the gas.

It has been found from experimental work that if a gas of known weight and diffusion pattern is taken as a standard, the diffusion pattern of a material of known molecular weight could be calculated approximately.

It was found in this study that the diffusion pattern was hemispherical in shape. The arc or periphery of the hemisphere in cross section varied from hyperbolic in shape to acute parabolic as the molecular weight increased.

When fumigating the soil the individual hemispheres of gas must come into confluency above the zone of infestation to be of maximum effectiveness.

It is felt that additional work on theoretical aspects of soil fumigation would be of great value.

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