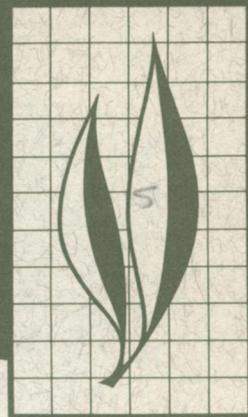


# HILGARDIA

A JOURNAL OF AGRICULTURAL SCIENCE PUBLISHED BY  
THE CALIFORNIA AGRICULTURAL EXPERIMENT STATION



*Volume 42, Number 11 · May, 1974*

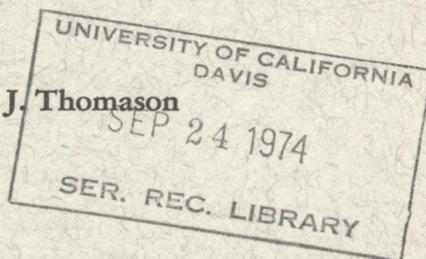
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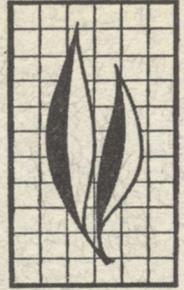
## 1,3-Dichloropropene and 1,2-Dibromoethane Compounds:

I. Movement and Fate as Affected by Various  
Conditions in Several Soils

II. Organism-dosage-response Studies in the  
Laboratory with Several Nematode Species

M. V. McKenry and I. J. Thomason





## Part I. Movement and Fate as Affected by Various Conditions in Several Soils

The approximate movement and fate of 1,3-dichloropropene (Telone,<sup>®</sup> D-D,<sup>®</sup> or Vidden-D<sup>®</sup>) and 1-2-dibromoethane (EDB) in two soils were predicted using extrapolations from laboratory experiments and soil-vapor phase concentrations obtained from simulated field experiments. The most far-reaching diffusion patterns in mineral soils are those obtained in soils whose moisture content is nearest the wilting point of plants (15 bars moisture tension). As the moisture content of the soil is increased, the diffusion pattern gradually becomes more limited. This effect is most striking when fine-textured soils have moisture contents in excess of  $\frac{1}{2}$  bar moisture tension (at the 30.5 cm depth).

Fumigation of warm soils (25°C) results in a faster rate and greater distance of nematicide diffusion. In colder soils (5°C), the rate of diffusion is slower, and the persistence of the chemical is longer, but the total distance of diffusion of an effective dosage is decreased. Increased soil temperatures result in increased rates of hydrolysis of cis- and trans-1,3-D. The same is not true of EDB.

The soil texture and type determine to a large extent the amount of soil moisture present and the size of the connecting air spaces. Soil-air space and size of pores are important, because these chemicals move primarily in the vapor phase and the smaller pores are most easily blocked when water is present. It is important that fumigant applicators are successful in sealing the soil surface and chisel shank hole after an application. Failure to do this results in significant losses to the atmosphere especially, if the subsoil is in a moist to wet condition.

(continued inside back cover)

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## Part I. Movement and Fate as Affected by Various Conditions in Several Soils<sup>1</sup>

### INTRODUCTION

SINCE 1943, pesticides containing 1,3-dichloropropene (1,3-D), which is sold as Telone,<sup>®</sup> D-D,<sup>®</sup> or Vidden-D,<sup>®</sup> and 1,2-dibromoethane (EDB) have been widely used because of their behavior in soil and their toxicity to various plant-parasitic nematodes. Concurrently, a great deal of field research with these two fumigant-type nematicides has produced considerable information concerning methods and timing of application, dosage requirements for specific crops or pests, and theories as to how these chemicals behave in soils. Previously, workers noted control or lack of control by these materials and have speculated on the soil factors responsible for results. However, they often neglected to identify, or even to control in some cases, many of the soil or environmental variables.

The purpose of the work reported here, therefore, was to develop new techniques to study quantitatively as well as qualitatively the movement and persistence of 1,3-D and EDB in soil, so that their behavior might be predicted on the basis of some known soil properties or conditions.

Kolbezen and Abu-El-Haj (1972*a,b*) developed techniques to monitor the movement of methyl bromide in field soil. It appeared that the same techniques might be applicable to the study of other fumigant-type pesticides. Thus, we began work monitoring the diffusion

of Telone, D-D, and EDB in field situations. The techniques proved useful in the field, and much information was obtained. However, the variability and lack of control encountered in the field left many questions unanswered. Youngson and Goring (1962) had previously used large iron boxes in which they studied diffusion and toxicity of nematicides. Their experiments were static rather than dynamic, however, and movement and dosage were determined by the percentage kill of nematodes at the time the test was terminated. We used similar equipment, but we monitored the dynamic flow of gas concentrations at various points in the soil from the time of treatment until the test was terminated.

Aspects of soil, water, and air contamination by these nematicides were also studied. Using laboratory data, approximate rates of hydrolysis were calculated for the individual toxicants. The sorptive capacity of the soil-water and mineral fraction was also determined for varying soil conditions. Losses to the atmosphere were determined experimentally. This information combined with knowledge of the diffusion pattern and total soil-vapor phase concentrations enabled us to achieve an integrated picture, which resulted in the development of an approximate material balance.

Hemwall (1960), Goring (1962), and

<sup>1</sup> Submitted for publication April 12, 1973.

Leistra (1972) have all studied the fate of these nematicides in soils and have established principles and theories on the subject of soil fumigation based on field and laboratory results and mathematical models. Recently, Leistra

(1972) reported on diffusion and adsorption of 1,3-D in soils of the Netherlands. The reader is referred to Leistra (1971) and Goring (1962) for a more extensive literature survey of the subject.

### MATERIALS AND METHODS

#### Sampling techniques for soil-vapor phase

The soil-vapor phase was sampled directly by removing a quantity of air from a given undisturbed area in the

soil profile. This technique is much faster and has less inherent variability than does a direct sampling of the water phase. Also, the same areas in the soil may be sampled repeatedly.

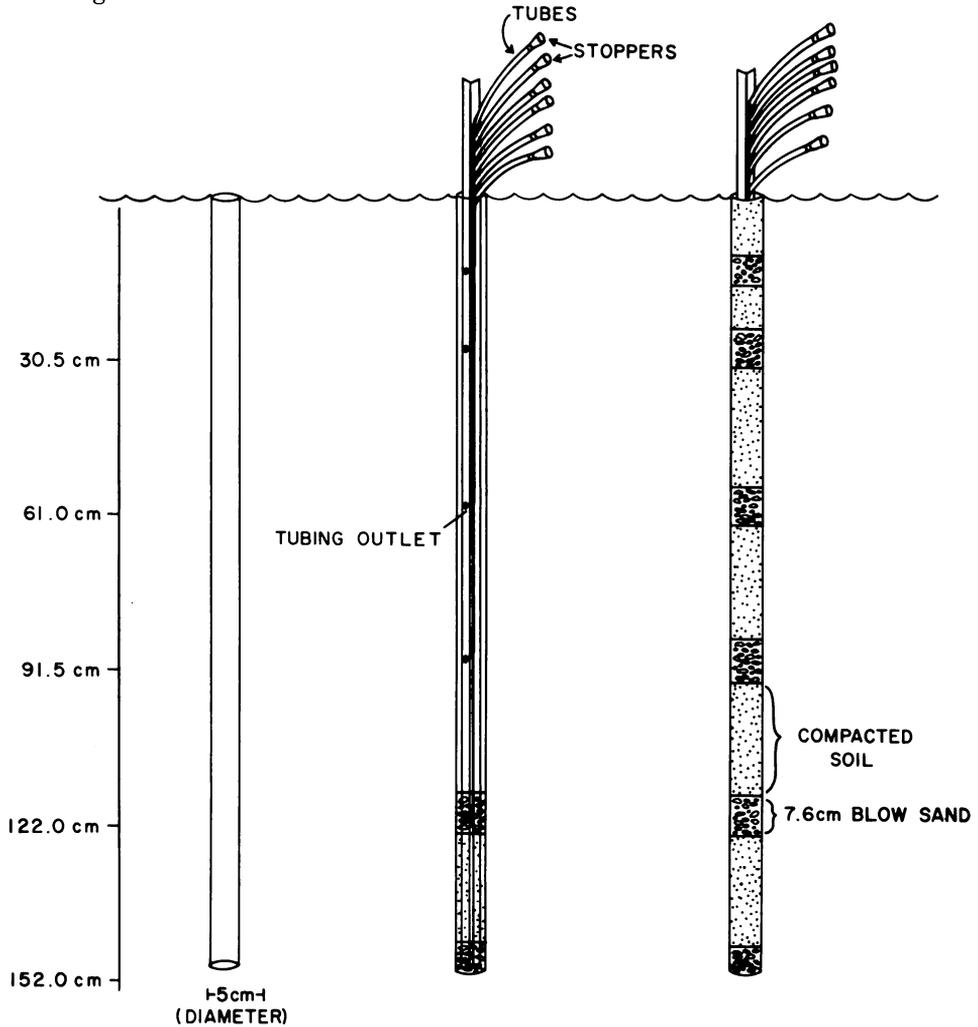


Fig. 1. Diagram of the probe constructed with outlet tubes at various depths. After placement in a hole, soil was carefully added and tamped around the probe with a 7.6 cm sand filter around each subsoil outlet.

**Field experiments.** Samples of the soil-vapor phase were obtained by using a slight variation of the technique of Kolbezen and Abu-El-Haj (1972*a,b*). Stainless steel tubing (0.318 cm outside diameter) was mounted onto 1.9 cm × 1.9 cm L-shaped steel (fig. 1). This was done in such a way as to allow sampling at 15.2, 30.5, 60.9, 91.4, 122 and 152 cm depths. In one set of experiments, the sampling probes were set at a depth of 305 cm. A sampling site usually consisted of a set of four probes, each one at a different distance (7.62, 15.2, 30.5 and 45.7 cm) laterally from the line of injection.

Holes were dug with a 5 cm can auger usually to the 152 cm depth. The probes were placed in the hole, and soil was carefully tamped into place around the probe. A layer of

sand surrounding each subsurface outlet was tamped into place to a distance of 3.8 cm above and below the probe opening. Above the 7.6 cm of sand, the soil was replaced and carefully tamped back into the hole to a point of 3.8 cm below the next tubing outlet where the procedure was repeated (fig. 1). Tamping also insured that no excess gases would move along the probe from one outlet to the next. The above-ground outlets were sealed with small, rubber septum caps. The sites were then ready for application of the fumigant.

For some treatments, a hand fumigator (Maclean gun) was used to make injections every 5.0 cm along a line. In other experiments, actual commercial and experimental tractor-drawn chisel applicators were used.

After the chemical was applied, soil-vapor phase samples were drawn at various times, and the gas concentration was analyzed at each point in the soil, until only trace amounts could be detected. Typically, samples were taken at 2, 5, 10 and 24 hours—and 2, 3, 4, 5, 7, 10, 14, 17, 21, 25, 30, 40, 60, 90 days following application of the fumigants.

**Laboratory (simulated field) experiments.** Large, stainless steel boxes were constructed and carefully filled with soil to simulate a soil profile (fig. 2). Each box represented a 10.2 cm slice of a soil profile 122 cm deep and 76.2 cm wide, perpendicular to the line of injection. This enabled us to run closely controlled experiments to study the effects of soil temperature, moisture, porosity, organic matter content and texture. The boxes were constructed of 0.318 cm stainless steel plates bolted to 0.64 cm × 10.2 cm channel iron. The box had no top or bottom but was placed upright on a cart to facilitate handling. All metal-to-metal surfaces were separated by

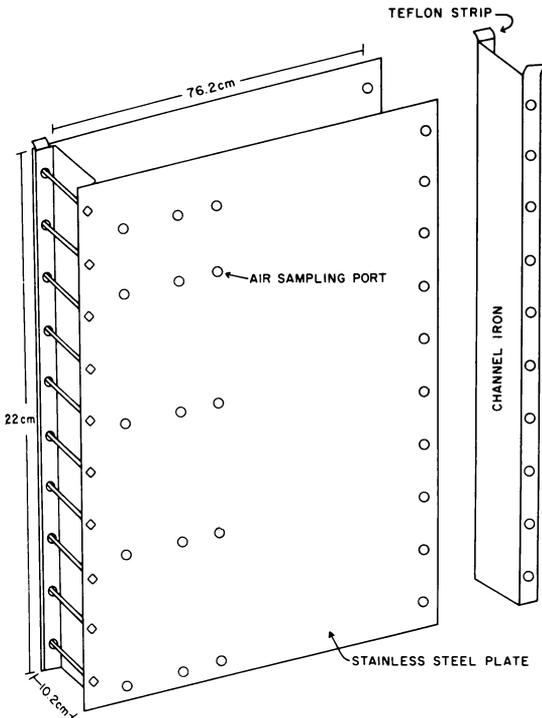


Fig. 2. Diagram of the large steel box in which laboratory (simulated field) experiments were carried out. The soil in the box represents a 10.2 cm slice of soil profile fumigated as a line injection with 76.2 cm chisel spacings.

Teflon strips. At various positions along the side of the box, 1.2 cm holes were drilled to insert stainless steel tubes (0.318 cm outside diameter) from which air samples could be withdrawn. The boxes could be taken apart without disturbing the soil profile to make bulk density and porosity measurements.

A single line injection was made at the 30.5 cm depth. In both the field and laboratory experiments the usual amount of chemical applied was equivalent to 234 liters/ha (25 gal./acre) of Telone or 40 liters/ha (4.25 gal./acre) EDB (equivalent to 47 liters/ha or 5 gal./acre of Dowfume W-85®). In the field experiments, at least four lines of injection were made in order to more closely represent a normal field application. Point injections were made in some experiments carried out in the field.

In the field, air was drawn from the individual probe and the first 20 cc discarded, then a 25 to 30 cc sample was drawn and taken to the laboratory, and two to three successive 8 to 10 cc volumes of gas were injected into the gas chromatograph. In laboratory tests, a 5 cc air sample was withdrawn and discarded. Then several 10 cc samples were removed and analyzed.

Air samples were taken with 30 cc syringes lubricated with a thin film of glycerin, after which the needles were sealed with a piece of polyurethane foam until analyzed. Generally the samples were analyzed within five hours. Note that EDB dissolves into glycerine to a certain extent (1 to 2 per cent/hour), but this is not a significant problem with the components of Telone.

### Gas chromatography equipment

The gas chromatography equipment included a Varian Aerograph Model 600-D with a flame ionization detector. An attached gas-sampling valve with

a 1 cc loop permitted consistent sampling from an air phase. When the water phase was sampled, a 5/ $\mu$ l sample was used. A 183 cm stainless steel column containing 20 per cent diisodecylphthalate on Chromosorb W (Hannon, Angelini, and Wolford, 1963) was used throughout the experiments. The Aerograph was operated at 102 to 105°C with flow rates of 20 cc/min hydrogen and 30 cc/min nitrogen. With these operating conditions one obtains the following emergence times: 1,2-dichloropropane (1,2-D)—2.7 minutes; cis-1,3-D—3.5 minutes; trans-1,3-D—4.6 minutes; 1,2-dibromoethane—6.1 minutes.

### Standards

Primary standards were made employing the use of 26.5-liter glass jars closed with a Teflon-lined lid. The standard lost 20 per cent of its initial concentration in 50 days. Because of this loss, standards were made up every two to three days.

Using a known volume of air space and a known amount of purified chemical, the concentration of chemicals was calculated at constant temperature and known atmospheric pressure on the basis of peak height. A standard curve was constructed and used for comparison of unknown samples.

Secondary standards were also used. Large glass jars were fitted with a rubber stopper pierced by a stainless steel tube through which the air phase could be sampled. A few milliliters of chemical toxicant (nematicide) were added to several liters of mineral oil present within each jar. The jars were kept at 22°C  $\pm$  2°. Concentration of toxicant in secondary standards was checked against primary standards. Repeated withdrawal of samples from the air phase within the jars indicated that the same concentration of 1,3-D or EDB could be removed several months later because of the dynamic

equilibrium of toxicant in air and the mineral oil. This technique provided a known vapor phase concentration of the toxicant based on the concept of Raoult's Law (Moore, 1962). The percentages of purity for the toxicant standards were: EDB, 99.9; 1,2-D, 99.9; cis-1,3-D, 98; trans-1,3-D, 96; and cis-3-chloroallyl alcohol, 99.9.

### Toxicants studied

Telone, D-D, and EDB were the toxicants studied in this work. Telone and D-D are different formulations of the biologically active ingredient 1,3-dichloropropene. The process of making these materials results in the production of various chlorinated three-carbon components which are present in the marketed product. Gas chromatographic analysis in our own laboratory verified the work of Utako (1963), at least for the three major components. In general, Telone contained 15.5 per cent 1,2-D, 42 per cent cis- and 36.5 per cent trans-1,3-D. The D-D was 25.5 per cent 1,2-D, 28 per cent cis- and 28 per cent trans-1,3-D. Little can be reported of the minor

components of Telone (6.0 per cent) or D-D (18.5 per cent), except that they are of little practical importance with respect to biological activity. Individual toxicants move through soil independent of each other, therefore, the minor components would be present in relatively low concentrations.

### Soil analyses

Visual observations and mechanical analyses made at various soil depths enabled us to determine the variations in the soil profile. For most experiments, a uniform soil profile was selected.

In all experiments the moisture content of soils was determined before fumigation and at the termination of the experiment by oven-drying approximately 150 grams soil at 105°C for 24 hours and calculating water loss. Figure 3 shows that soils were further characterized with moisture-retention curves, which were established using a porous plate apparatus (Richards, 1948).

Porosity was determined at the termination of experiments by removing

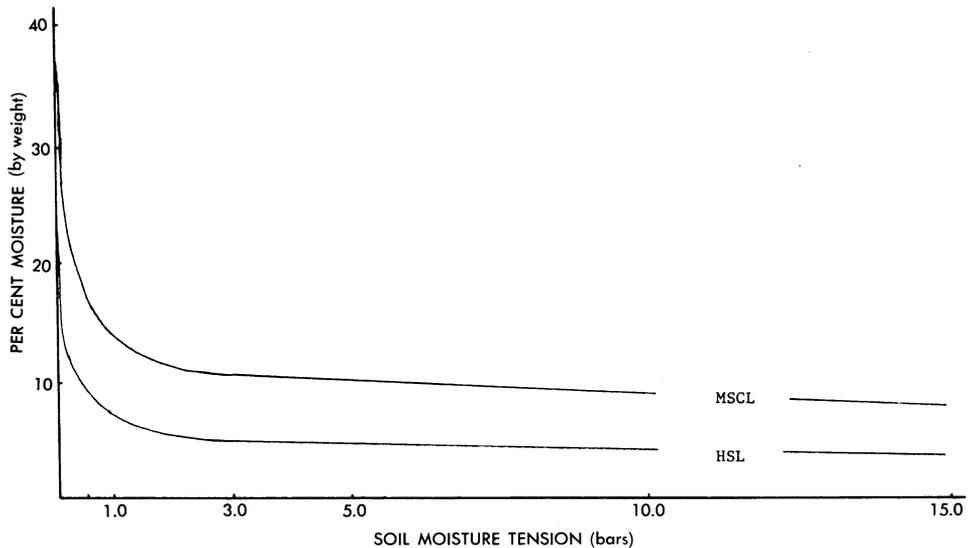


Fig. 3. Soil moisture retention curves for two soils: MSCL (Moreno silty clay loam) and HSL (Hanford sandy loam).

TABLE 1  
MECHANICAL ANALYSES OF SOILS USED IN ALL FIELD  
AND LABORATORY EXPERIMENTS

| Soil type                                  | Origin   | Sand                  | Silt                  | Clay                  | pH  |
|--|--|-----------------------|-----------------------|-----------------------|-----|
| Hanford sandy loam (HSL) .....             | NE ¼ of SW ¼ of sect. 19<br>T2S R4W, Riverside, Calif.   | <i>Per cent</i><br>63 | <i>Per cent</i><br>22 | <i>Per cent</i><br>15 | 7.1 |
| Ramona loam (RL) .....                     | NW ¼ of SE ¼ of sect. 30<br>T2S R4W, Riverside, Calif.   | 42                    | 38                    | 20                    | 6.4 |
| Moreno silty clay<br>loam (MSCL) .....     | NE ¼ of SE ¼ of sect. 14<br>T3S R3W, Riverside, Calif.   | 13                    | 62                    | 25                    | 7.3 |
| Greenfield sandy loam<br>(GSL) .....       | NE ¼ of SW ¼ of sect. 22<br>T5S R2W, Winchester, Calif.  | 60                    | 18                    | 22                    | 7.3 |
| Huerhuero sandy clay<br>loam (HuSCL) ..... | SE ¼ of NW ¼ of sect. 21<br>T2N R21W, Oxnard, Calif.     | 50                    | 26                    | 24                    | 7.2 |
| Holtville clay (HC) .....                  | NE ¼ of NE ¼ of sect. 31<br>T15S R14E, El Centro, Calif. | 10                    | 35                    | 55                    | 7.2 |

undisturbed cores of soil 30.5 cm and 91.5 cm deep. Each core, 7.62 cm in height and 15.2 cm in diameter, was removed by inserting a plastic cylinder into the soil and withdrawing. The cores were weighed and then, after sub-irrigation for several days, were reweighed to determine the saturated weight. Based on oven-dry weights, the total pore space (air-filled and water-filled) were calculated. The principles for this measurement are discussed by Vomocil (1965).

Organic matter content was determined by a method involving a sulfuric acid, dichromate reduction (Walkley and Black, 1934).<sup>2</sup>

Soil reaction was determined from a 1:2 soil paste using 0.01 M CaCl<sub>2</sub> (Schofield and Taylor, 1955) and a Beckman pH meter.

Mechanical analyses were made on all soils using the hydrometer technique of Bouyoucos (1951). Two soils, a Hanford sandy loam (HSL) and a montmorillonite-type silty clay loam from Moreno Valley, California (MSCL), were the soils most frequently used. Some field experiments were also made in clay, sandy clay loam, and loam soils. The mechanical analyses are listed in table 1.

Thermographs were used to record

temperatures at various soil depths. In the laboratory experiments, temperatures of 5, 15 and 25°C were maintained in constant temperature chambers with variations of ± 1°C.

#### Integration of the data from diffusion pattern

Table 2 is a list of laboratory and field experiments from which diffusion patterns were obtained. The data is expressed in terms of mole/liter soil-vapor phase concentrations. In order to calculate the total molar concentration, the total volume of soil-air containing the toxicant must be known. This air volume will increase with time as the material diffuses outward from the line of injection. One method of calculating the volume affected is to divide the volume of total air space in the soil profile (76.2 × 10.2 × 122 cm steel boxes) into concentric one-liter volumes emanating from the line of injection. A model of the soil profile is pictured in figure 4. Working from the line of injection outward, the linear distance required to contain one liter of soil-air was calculated, then the linear distance for the succeeding one liter of air space was calculated and so on until the total volume of soil was divided into sections based upon

<sup>2</sup> For his analysis we thank John Rible, University of California, Riverside.

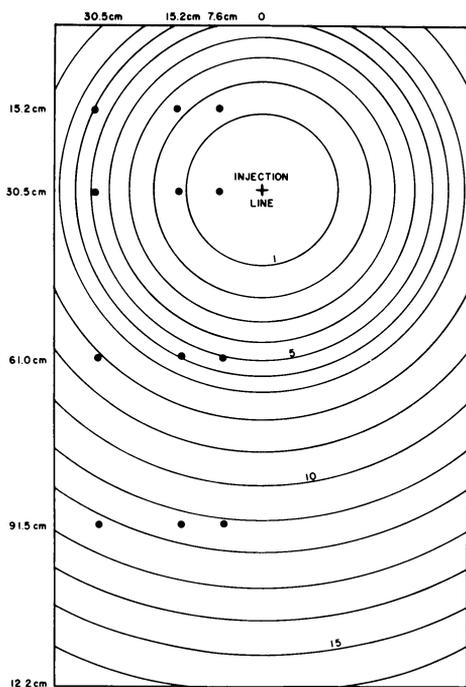


Fig. 4. A typical model (actually experiment 4) constructed to show the soil-air space within the stainless steel box (see fig. 2). Radii delimit the position of each 1 liter of air space within the box when filled with soil. Toxicant concentrations were then calculated for each 1 liter volume based upon actual measured concentrations.

the total volume of air space within the soil. This method was used for fifteen different line injection experiments listed in table 2. The model pictured in figure 4 is for experiment 4, which contains approximately 16.0 liters air space.

Superimposed upon this model were actual concentrations (mole/liter soil-vapor phase) of the toxicant. In those volumes of soil where concentrations were not established by gas chromatographic analysis, the concentrations were arrived at by integration. The sum of the concentrations and knowledge of the numbers of liters air space involved reveals the mg of toxicant present in the soil-air space at any given time. It follows that if values could be obtained for concentrations of

chemical sorbed, and if the rates for hydrolysis and loss to atmosphere could be obtained, then they should add up to the total amount of chemical added to the soil. To obtain this information, several laboratory experiments were carried out.

### Experiments to determine the amount lost to the atmosphere

To determine the amount of toxicant lost from the soil surface, a large box-type lid (15.2 cm high) was constructed of galvanized metal. This lid was bolted over the top of a large stainless steel box (of the type illustrated in fig. 2) immediately after the fumigant had been applied and the soil carefully back-filled and tamped. The stainless steel box was enlarged to accommodate a 60.9 cm profile instead of the normal 10.2 cm slice. A thick, Teflon gasket was placed between the lid and the steel box to insure an airtight seal. A constant stream of air was supplied to one end of the lid. To prevent the development of a pressure head upon the soil profile, an equal, constant stream of air was removed from the other end of the box through a manifold system. The rate of movement of air over the soil surface was approximately 0.80 km/hr ( $1\frac{1}{2}$  mi/hr). Periodically the effluent air was sampled and analyzed for the presence of toxicant. The results were expressed as per cent of toxicant naturally lost to the atmosphere. The test was carried out at a temperature of  $25^{\circ} \pm 1^{\circ}\text{C}$ .

### Experiments to determine the importance of sorption and hydrolysis

The HSL and MSCL soils containing known weights of soil particles (oven-dried basis) and water (per cent moisture by weight) were added to 26.5 liter jars similar to those used to maintain primary standards. The usual amount of soil was approxi-

TABLE 2  
TREATMENT, SAMPLE LOCATION, SOIL CHARACTERISTICS  
FOR EACH EXPERIMENT

| Experiment No. | Application rate of nematicide | Experiment situation* | Soil characteristics |                 |                 |                 |                 | Organic matter  |       |
|----------------|--------------------------------|-----------------------|----------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-------|
|                |                                |                       | Type†                | Air             |                 | Water           |                 |                 | Temp. |
|                |                                |                       |                      | v/V             | v/V             | w/W             | °C              |                 |       |
|                |                                |                       |                      | <i>Per cent</i> |       |
| 1.....         | 93 l/ha each major component   | sim-field             | MSCL                 | 33.0            | 22.0            | 15.0            | 5               | 1.1             |       |
| 2.....         | 93 l/ha each major component   | sim-field             | MSCL                 | 33.0            | 22.0            | 15.0            | 25              | 1.1             |       |
| 3.....         | 234 l/ha Telone                | field                 | HSL                  | —               | —               | 10.2            | 15              | 0.6             |       |
| 4.....         | 234 l/ha Telone                | sim-field             | MSCL                 | 16.0            | 34.0            | 21.0            | 25              | 1.1             |       |
| 5.....         | 234 l/ha Telone                | sim-field             | HSL                  | —               | 36.0            | 17.1            | 5               | 0.6             |       |
| 6.....         | 234 l/ha Telone                | sim-field             | MSCL                 | —               | 42.5            | 26.0            | 5               | 1.1             |       |
| 7.....         | 234 l/ha Telone + 47 l/ha EDB  | sim-field             | MSCL                 | 25.4            | 28.6            | 17.0            | 15              | 1.1             |       |
| 8.....         | 234 l/ha Telone + 47 l/ha EDB  | sim-field             | MSCL                 | 14.2            | 35.8            | 23.0            | 15              | 1.1             |       |
|                |                                | with lid              |                      |                 |                 |                 |                 |                 |       |
| 9.....         | 234 l/ha Telone + 47 l/ha EDB  | sim-field             | MSCL                 | 27.4            | 20.6            | 13.5            | 15              | 1.1             |       |
| 10.....        | 234 l/ha Telone + 47 l/ha EDB  | sim-field             | MSCL                 | 41.5            | 9.0             | 7.7             | 15              | 1.1             |       |
| 11.....        | 234 l/ha Telone + 47 l/ha EDB  | sim-field             | HSL                  | 28.0            | 12.0            | 8.5             | 25              | 0.6             |       |
|                |                                | with lid              |                      |                 |                 |                 |                 |                 |       |
| 12.....        | 234 l/ha Telone + 47 l/ha EDB  | sim-field             | HSL                  | 28.3            | 14.2            | 8.0             | 15              | 0.6             |       |
| 13.....        | 234 l/ha Telone                | sim-field             | HSL                  | 28.0            | 12.0            | 8.0             | 5               | 0.6             |       |
| 14.....        | 234 l/ha Telone + 47 l/ha EDB  | field                 | MSCL                 | 30.0            | 9.5             | 11.0            | 15              | 1.1             |       |
| 15.....        | 234 l/ha Telone + 47 l/ha EDB  | field                 | MSCL                 | 34.8            | 12.7            | 8.0             | 23              | 1.1             |       |
| 16.....        | 93 l/ha D-D                    | field                 | HuSCL                | 15.7            | 22.1            | 11.9            | 15              | low             |       |
| 17.....        | 47 l/ha D-D                    | field                 | HuSCL                | 15.7            | 22.1            | 11.9            | 15              | low             |       |
| 18.....        | 93 l/ha D-D                    | field                 | GSL                  | 24.5            | 11.6            | 6.5             | 15              | low             |       |
| 19.....        | 186 l/ha D-D                   | field                 | HC                   | —               | —               | 20.2            | 15              | low             |       |
| 20.....        | 234 l/ha Telone                | field                 | MSCL                 | 23.0            | 37.0            | 9.1             | 20-25           | 1.1             |       |
| 21.....        | 234 l/ha Telone + 47 l/ha EDB  | sim-field             | HSL                  | 43.0            | 4.0             | 3.2             | 5               | 2.2             |       |
| 22.....        | 234 l/ha Telone + 47 l/ha EDB  | sim-field             | HSL                  | 35.0            | 8.0             | 5.2             | 5               | 2.6             |       |
| 23.....        | 234 l/ha Telone + 47 l/ha EDB  | sim-field             | MSCL                 | 40.6            | 9.4             | 7.7             | 25              | 1.1             |       |
| 24.....        | 234 l/ha Telone                | field                 | RL                   | 43.5            | 6.0             | 8.0             | 25              | low             |       |
| 25.....        | 234 l/ha Telone                | sim-field             | MSCL                 | 28.0            | 26.0            | 16.5            | 25              | 1.1             |       |
| 26.....        | 234 l/ha Telone + 47 l/ha EDB  | sim-field             | HSL                  | 30.0            | 11.0            | 9.0             | 25              | 0.6             |       |
|                |                                | with lid              |                      |                 |                 |                 |                 |                 |       |
| 27.....        | 234 l/ha Telone + 47 l/ha EDB  | sim-field             | MSCL                 | 42.7            | 8.5             | 6.5             | 5               | 1.1             |       |
| 28.....        | 1680 l/ha Telone               | field                 | HSL                  | 20.0            | 21.0            | 4.4             | 25              | 0.6             |       |

\* Sim-field = simulated field; sim-field with lid = simulated field with lid above soil surface.

† MSCL = Montmorillonite silty clay loam soil; HSL = Hanford sandy loam soil; HuSCL = Huerhuero sandy clay loam; GSL = Greenfield sandy loam.

mately 1 kg and the amount of moisture varied with the experiment. After allowing time for the soil moisture to equilibrate with the water in the vapor phase of the jar, a known amount of toxicant was added to the jar. A single experiment usually consisted of five jars, two with soils of different moisture contents, two with similar amounts of water but no soil, and another which contained neither soil nor water. The experiments were run at 5, 15 and 25°C ± 1°. In some experiments, the soil was placed into large bags of dialysis tubing, and in others,

soil was simply added to the bottom of the jars. The soil-vapor phase concentration was inferred from the concentration of toxicant in the atmosphere of the large jar. Samples were taken from the jar periodically up to 50 days. The soil-moisture content was determined at the conclusion of the experiment.

A sampling of the vapor phase concentration within the jar provided information for the calculation of the milligrams of toxicant in the soil air spaces. By correlating that amount with the total decrease in soil-vapor

phase concentration within five hours, a constant value was obtained which indicated the relationship between the amount sorbed and the amount in the soil-vapor phase. This value is reproducible for that particular soil and moisture content and useful for predicting the per cent of toxicant sorbed by soils, if the soil-vapor phase concentration is known.

After sorption was stabilized (5 hours) in this static-type system, any further loss of toxicant was attributed to degradation or irreversible adsorption. By periodic monitoring of the vapor-phase concentration, we were able to establish rates for the loss of the toxicants based upon the concentrations sorbed to the soil. The method used to determine the amount of hydrolysis occurring was to compare *cis*- and *trans*-1,3-D to 1,2-D and EDB,

since the latter did not hydrolyze readily in these soils. Since hydrolysis was the most likely method of degradation of the 1,3-D toxicants, the water phase of the soil was extracted with water, and the presence of the chloroallyl alcohols was determined quantitatively using gas chromatography.

In the attempt to develop the material balance, it became apparent that not all of the toxicant could be accounted for. This was especially true with EDB. The actual fate of this component will not be known until <sup>14</sup>C-labeled studies are made. The grouping "chemical unaccounted for," therefore, represents (1) that toxicant which is irreversibly adsorbed, and (2) that toxicant not accounted for because of errors in the integration of data and removal of soil-vapor phase samples.

## RESULTS

### Effect of soil texture

Soil texture *per se* does not appear to be the primary limiting factor in the diffusion of chemicals. Rather, soil texture has an indirect influence upon diffusion patterns. Moisture-holding capacity, cation exchange capacity, organic matter content and percentage blocked pore spaces are generally increased with the finer textured soils. These factors should be considered individually. Blocked pore spaces occur when soil moisture is high or when soil structure is destroyed through compaction or deflocculation. The occurrence of blocked pore spaces restricts gaseous diffusion thus decreasing the chance that nematodes will be contacted by a lethal dosage of the fumigant.

The silty clay loam used in our experiments was of the montmorillonite-type 2 to 1 expanding lattice. Soil cracking did occur in this soil under field conditions, yet overall diffusion

patterns were not affected greatly when the soil surface was tilled and compacted before application of the fumigant.

### Effect of soil moisture

High soil moisture was a major limiting factor in the total diffusion of the fumigants. This was especially true when soil moisture in the field approached field capacity, as in experiments 3 through 8. The effect of moisture level in a silty clay loam (MSCL) at 15°C is shown in figure 5. The data is taken from experiments 8, 9 and 10. The percentage numbers indicate the per cent moisture content on a dry-weight basis. Note that this graph only shows the dosages obtained at a point 15.2 cm horizontal to the line of injection. None of Telone's components were found at the 45.7 cm depth in a wet soil (23 per cent moisture dry-weight basis, experiment 8), whereas in the dry soil (experiment 10) the 1,2-D and *cis*-1,3-D were found

MOLES/L cis-1,3-D  
Soil Vapor Phase

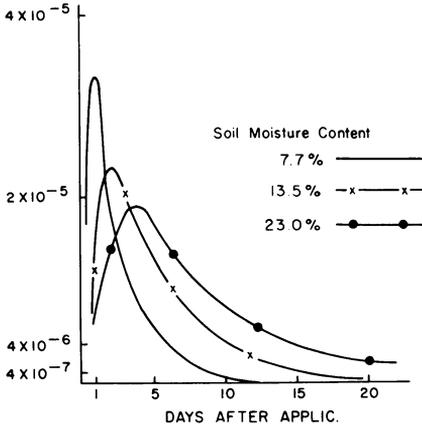


Fig. 5. Effect of soil moisture content (dry-weight basis) upon the concentration of cis-1,3-D detected 15.2 cm horizontally from the line of injection for the MSCL soil at 15°C.

MOLES/L cis-1,3-D  
Soil Vapor Phase

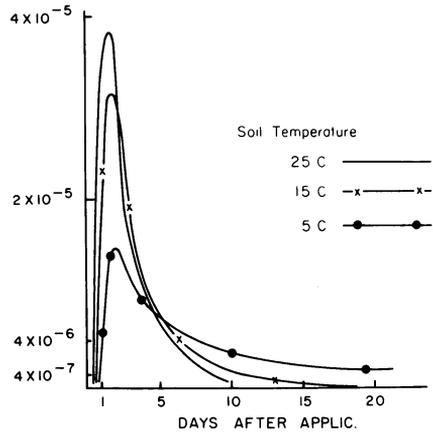


Fig. 7. Effect of soil temperature on the concentration of cis-1,3-D detected 15.2 cm horizontally from the line of injection for the HSL soil at 8 per cent moisture by weight.

at depths of greater than 122 cm. In order to better understand these effects, soil moisture retention curves

were established for the clay loam and sandy loam soils. The results are reported in figure 3, which relates the soil moisture on a dry-weight basis as compared to the amount of soil suction (bars tension) required to achieve that moisture content. The soil moisture tension values are more meaningful than values for per cent moisture content when comparing the effects of soil moisture in various soils.

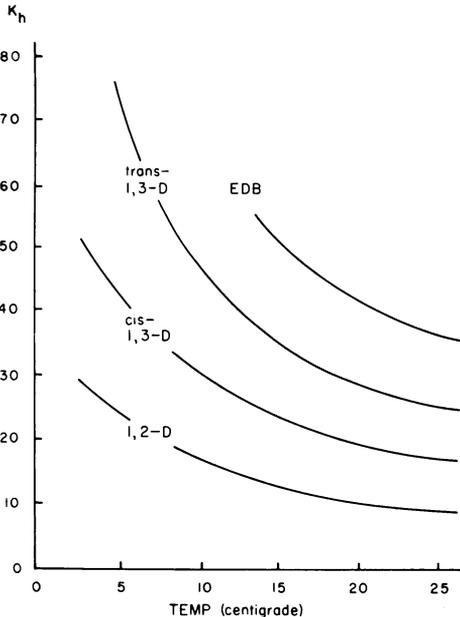


Fig. 6. Diagram indicating the Henry's Constant values for the components of Telone and EDB at various temperatures. Data compiled from the work of Leistra (1970), Goring (1962), and our own laboratory.

**Effects of soil temperature**

Increases in chemical solubility with decreased temperature also limit total diffusion distance. A three-fold increase in the value for Henry's constant (K<sub>h</sub>) as the soil temperature is decreased from 25°C to 5°C is depicted in figure 6. This effect of lowered temperature upon solubility of the chemical in the soil water and accompanying reduction of chemical in the soil-air phase is reflected in a decreased rate and distance of soil diffusion. The effect of soil temperature on diffusion as it occurs in soil is shown on a quantitative basis in figure 7. The data is taken from experiments 11, 12, and 13. Temperature

MOLES/L TOXICANT  
Soil Vapor Phase

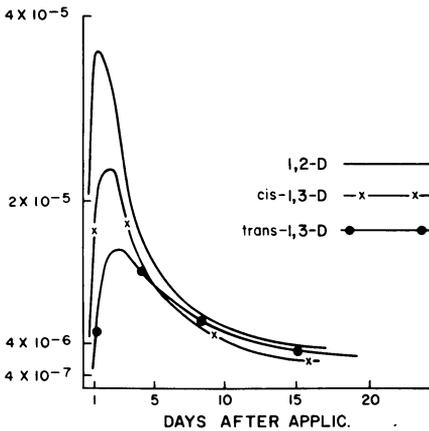


Fig. 8. Concentrations detected at a point 15.2 cm horizontally from the line of injection after an application of equivalent amounts (93.5 liters/ha) of the major components of Telone in the MSCL soil at 5°C and 15 per cent moisture by weight.

MOLES/L TOXICANT  
Soil Vapor Phase

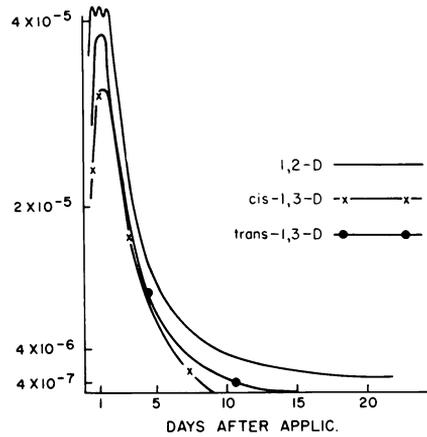


Fig. 9. Concentrations detected at a point 15.2 cm horizontally from the line of injection after an application of equivalent amounts (93.5 liters/ha) of the major components of Telone in the MSCL soil at 25°C and 15 per cent moisture by weight.

also affects the rate of volatilization of the chemical injected into the soil. This does appear to be a limiting factor as far as diffusion is concerned. In all experiments carried out in field situations (experiments 3 and 15 to 20), complete volatilization appears to have occurred within 36 hours.

Another important effect of temperature is its influence on the rate of hydrolysis of cis- and trans-1,3-D. This may be seen by observing the differences in the 1,2-D and 1,3-D peaks in figures 8 and 9 (experiments 1 and 2). Note that at 5°C, the curve between 10 and 18 days for 1,2-D and 1,3-D is similar, while at 25°C the 1,3-D components do not persist. The effect is even more noticeable at deeper soil depths. This correlates well with laboratory data showing that significant hydrolysis of the 1,3-D components occurs only at higher temperatures (15 to 25°C). Though the amount hydrolyzed does not at first appear to be large, one must consider

that the data is only in terms of vapor-phase concentrations and reflects a large amount of hydrolysis occurring in the water phase.

MOLES/L cis-1,3-D  
Soil Vapor Phase

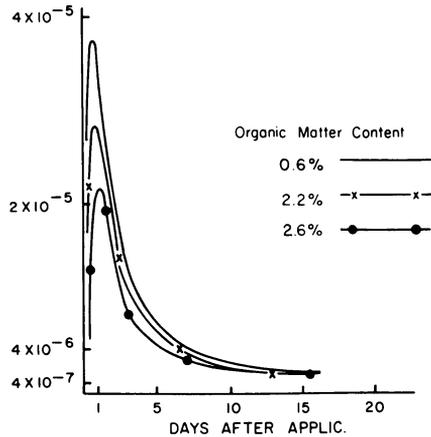


Fig. 10. Effect of organic matter (dry chopped grasses) on the concentration of cis-1,3-D detected 15.2 cm horizontally from the line of injection is shown for the HSL soil at 5°C and 4 per cent moisture.

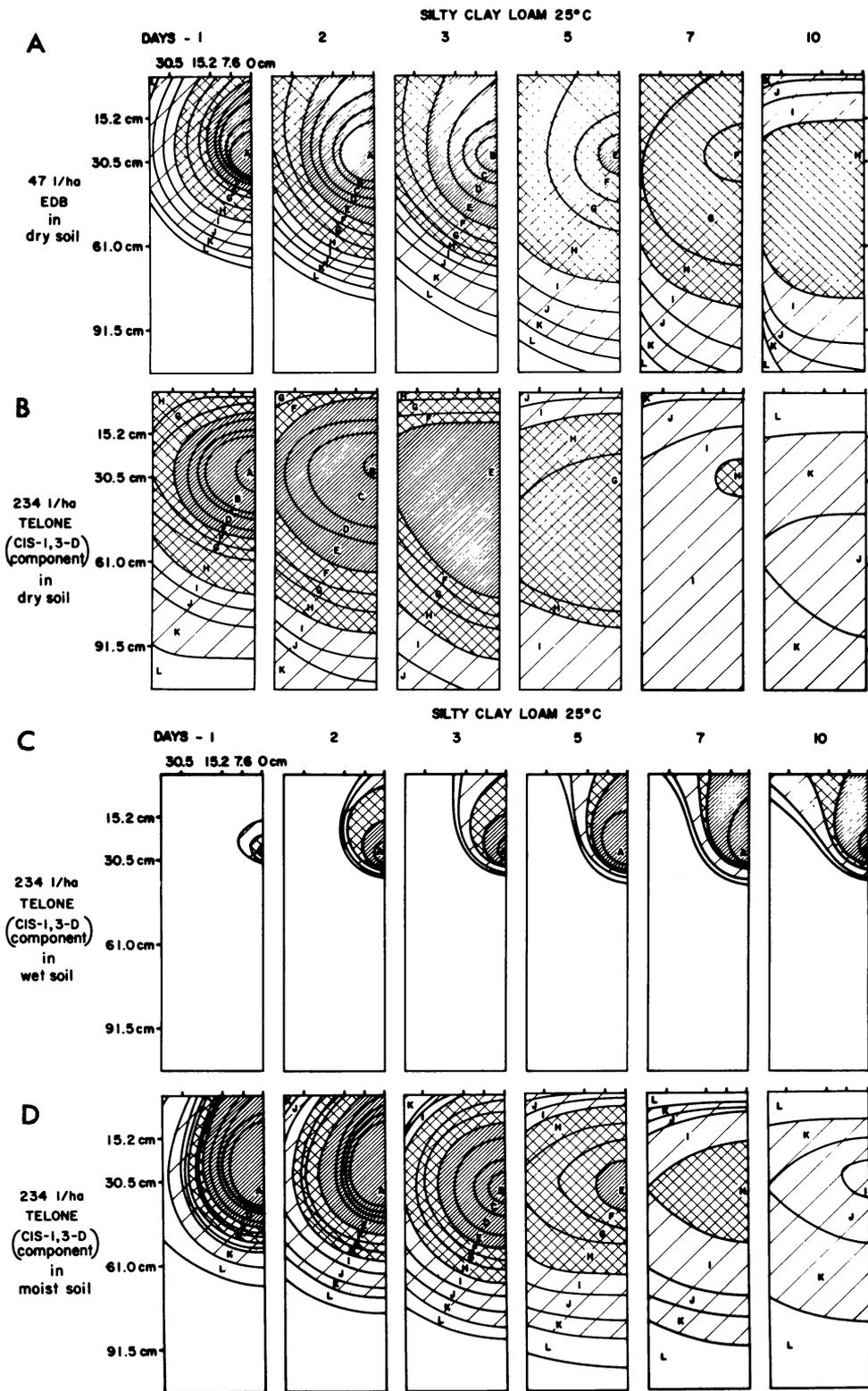


Fig. 11. (See opposite.) Total diffusion patterns through time of EDB and Telone in soils of different moisture contents and at various depths. Below is the legend. Values for ppm are calculated as liters.

KEY

|   | ppm   | Moles/liter<br>(soil vapor phase) |                       |
|---|-------|-----------------------------------|-----------------------|
|   |       | cis-1,3-D                         | EDB                   |
| A | 5+    | $4.51 \times 10^{-5}$             | $2.66 \times 10^{-5}$ |
| B | 4     | $3.60 \times 10^{-5}$             | $2.13 \times 10^{-5}$ |
| C | 3     | $2.70 \times 10^{-5}$             | $1.60 \times 10^{-5}$ |
| D | 2     | $1.80 \times 10^{-5}$             | $1.07 \times 10^{-5}$ |
| E | 1     | $9.01 \times 10^{-6}$             | $5.32 \times 10^{-6}$ |
| F | 0.75  | $6.76 \times 10^{-6}$             | $3.99 \times 10^{-6}$ |
| G | 0.50  | $4.51 \times 10^{-6}$             | $2.66 \times 10^{-6}$ |
| H | 0.25  | $2.25 \times 10^{-6}$             | $1.33 \times 10^{-6}$ |
| I | 0.10  | $9.01 \times 10^{-7}$             | $5.32 \times 10^{-7}$ |
| J | 0.05  | $4.51 \times 10^{-7}$             | $2.66 \times 10^{-7}$ |
| K | 0.01  | $9.01 \times 10^{-8}$             | $5.32 \times 10^{-8}$ |
| L | TRACE | TRACE                             | TRACE                 |

### Effect of soil organic matter content

Sufficient organic matter in the form of chopped dry grass was added to the entire 122 cm soil profile of a sandy loam at 5°C to bring the total amount to 2.2 per cent (experiment 21) and 2.6 per cent organic matter content for experiment 22. The diffusion pattern of *cis*-1,3-D in this soil is compared in figure 10 with a similar soil where no organic matter was added (experiment 13). The experiment was run at 5°C to limit the amount of hydrolysis which would be a confounding factor at higher temperatures. Maximum concentration of 1,3-D at 15.2 cm from the injection line occurred within 48 hours at all three levels of organic matter. However, the maximum concentration of 1,3-D in the vapor phase was reduced at 2.2 and 2.6 per cent organic matter (fig. 10).

### Total diffusion patterns

The data illustrated thus far have only shown the concentration at a single point 15.2 cm from the line of injection. It is important to view the total diffusion pattern as it develops through time and at various soil depths. This is depicted in figures 11a, 11b, 11c, and 11d which represent the data from experiments 4, 23, and 25. These soils were fumigated simultaneously using the standard application rates mentioned. The only variable in the soils fumigated with Telone was the moisture content. EDB and Telone diffusion patterns shown in figures 11a and 11b respectively (experiment 23) were run simultaneously in the same dry soil. Diffusion patterns for EDB in wet and moist soil are not shown, but tests were run. The Telone experiments gave results similar to those shown in figure 5. The diffusion of 1,3-D was very rapid in a dry soil with a detectable amount reaching the

bottom of the container within 24 hours. Diffusion of EDB is much slower than 1,3-D under the same conditions. A vapor phase concentration of  $4.5 \times 10^{-7}$  moles/liter of 1,3-D at a depth of 90 cm was reached within one day, whereas seven days were required for EDB to reach a similar concentration at this depth. The type of diffusion pattern illustrated in figures 11a, 11b, 11c and 11d can be constructed for all of the experiments listed in table 2. The pictures are helpful in illustrating that the diffusion of these nematicides is a dynamic process. They also show the effects of loss to the atmosphere, depth of penetration and persistence as they are affected by soil moisture content. The restrictive effects of high soil moisture on the diffusion of 1,3-D is dramatically illustrated in figure 11c.

### Natural loss to the atmosphere

The total diffusion pattern shows that a certain amount of toxicant is lost to the atmosphere. This amount should be known in order to achieve a material balance. This loss was measured, while a constant stream of air was passing over the surface of the soil at the rate of 0.80 Km/hr. The loss from a moist HSL soil at 25°C (experiments 11, 26) is depicted in figure 12. In a field situation, the amount lost to the atmosphere is probably increased, since it is mechanically difficult to refill and compact the chisel shank hole. Changes in soil porosity can accelerate losses of 1,3-D from 2 to 20 per cent, depending upon depth of application, moisture content, temperature, soil type, and amount of fumigant applied. The amount lost is also directly influenced by the care taken to refill and compact the narrow furrow left by passage of the chisel shank.

"Natural loss to the atmosphere" is defined here as loss due to diffusion up

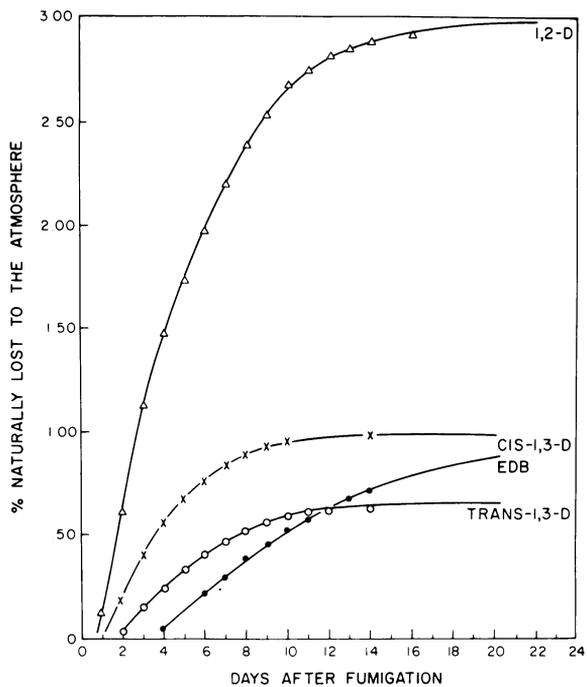


Fig. 12. Cumulative per cent of chemical initially added to the HSL soil, which is lost due to natural loss to the atmosphere.

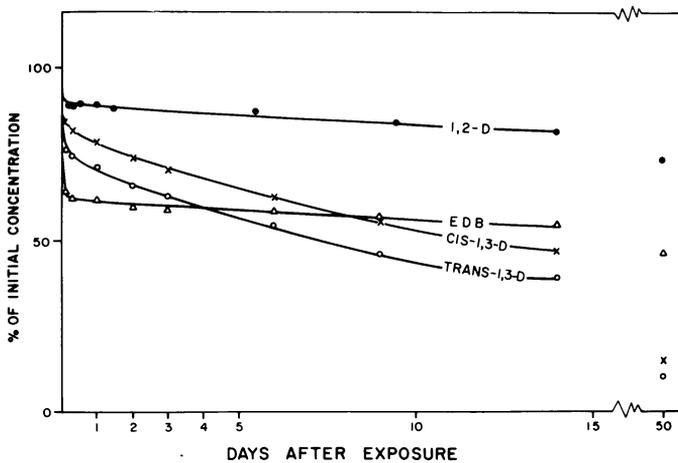


Fig. 13. Diagram illustrating the effect of the MSCL (1 kg oven dried + 310 ml water) on the vapor phase concentration of the toxicants upon addition of 50 microliters Telone and 15 microliters of EDB in the 26.5 liter jar. The sorptive capacity is determined by the fifth hour, and hydrolysis rates are determined from the concentration changes after 5 hours.

through a relatively undisturbed soil profile or a profile in which the soil from the chisel shank hole has been carefully compacted into place. The amount and rate of natural loss to the atmosphere is influenced by the  $K_h$  and the persistence of the toxicants. EDB and 1,2-D are more persistent, thus increasing the opportunity for losses to the atmosphere. EDB is not lost as readily as 1,2-D due to its highly sorptive nature. Under the conditions of these tests, less of the 1,3-D components were lost to the atmosphere, because, relatively speaking, hydrolysis was much more important than the natural loss.

### Static-type exposure system

Static-type experiments were useful in accumulating information pertaining to: 1) sorption, 2) rates of hydrolysis of cis- and trans-1,3-D to their corresponding alcohols, and 3) the relative importance of irreversible adsorption.

The general term sorption is used by Wade (1954) to include adsorption (reversible and irreversible), absorption (solution of the fumigant in the soil water) and biological decomposition by soil microorganisms. In this paper, the amount sorbed includes that fumigant in the water phase and that which is reversibly adsorbed to soil colloids or held by soil water due to surface tension. Biological degradation, chemical hydrolysis, and irreversible adsorption are not included in our definition of sorption.

Five hours after the toxicant was added to 1 kg of oven-dried soil at various moisture contents in a 26.5 liter jar, the soil-vapor phase concentration was lowered, but stabilized. (See fig. 13.) The difference in the soil-vapor phase concentration from a 26.5 liter jar with no soil and that of a jar containing soil exposed to the

toxicant for five hours was used arbitrarily as the value for the sorptive capacity (sorp. cap.) of the soil. The method of calculation and two examples—one, a wet soil (0.3 bars tension), and, two, a dry soil (slightly more than 15 bars tension)—are shown below:

#### Example 1

Fifty microliters Telone containing 42.0 per cent cis-1,3-dichloropropene with a mol. wt. of 110.98 is added to a jar containing 1 kg oven-dried soil plus 310 cc water. This calculates to be 25.56 mg cis-1,3-D added to 25.8 liter air space or a  $8.92 \times 10^{-6}$  molar cis-1,3-D concentration.

Five hours later the vapor phase concentration had decreased to  $6.93 \times 10^{-6}$  moles or 19.86 mg/jar, for a loss of 5.70 mg. The 5.70 mg has presumably been sorbed by the soil particle and water phases of the soil.

By determining the number of mg cis-1,3-D per liter of air space and making use of Henry's constant ( $K_h = \frac{\text{soil water phase}}{\text{soil vapor phase}}$ ), which is 17.7 for these experimental conditions, we can calculate the number of mg of cis-1,3-D in the soil water.

$$\frac{17.7 \times 0.769 \text{ mg/l} \times 310 \text{ ml}}{1000 \text{ ml}} = 4.22 \text{ mg/310 ml soil water}$$

then, using proportions, we can calculate the sorptive capacity for this soil using the generalized equation:

$$\frac{\text{sorp. cap.}}{\text{soil particle + soil water phase}} = \frac{K_h}{\text{soil water phase}}$$

Substituting our figures:

$$\frac{\text{sorp. capy.}}{5.70 \text{ mg}} = \frac{17.7}{4.22 \text{ mg}}$$

The sorptive capacity of cis-1,3-D for the clay loam soil at 25°C and 1/3 bar moisture tension is about 23.9 × the vapor phase concentration.

The vapor phase concentration of cis-1,3-D within the jar during the next 24 hours decreased another 1.40 mg. The average vapor phase concentration of the jar during that time was 19.16 mg or 0.743 mg/liter air. Using sorptive capacity, there were 5.50 mg sorbed—which resulted in the loss of 1.40 mg, or about 25.5 per cent of that amount sorbed was lost due to hydrolysis.

#### Example 2

The addition of 50 microliters Telone to the 26.5 liter jar containing 1 kg oven dried soil + 70 cc water calculates to be 25.56 mg cis-1,3-D added to 26.0 liters air space or a concentration of  $8.86 \times 10^{-6}$  molar cis-1,3-D.

Five hours later, the vapor phase concentration had decreased to  $6.85 \times 10^{-6}$  molar or 19.77 mg/jar for a total of 5.79 mg sorbed by the soil.

Using Henry's constant (as in example 1):

$$\frac{17.7 \times 0.7604 \text{ mg}/1 \times 70 \text{ ml}}{1000 \text{ ml}} = 0.942 \text{ mg}/70 \text{ ml water}$$

Using proportions and substituting our figures (as in example 1):

$$\frac{\text{sorp. capy.}}{5.79} = \frac{17.7}{0.942}$$

The sorptive capacity of cis-1,3-D for the clay loam at 25°C and 15 bars tension is ca. 108.7 × the vapor phase concentration.

The vapor phase concentration of cis-1,3-D within the jar decreased another 1.20 mg during the next 24 hrs.

The average vapor phase concentration during that time was 19.17 mg or 0.737 mg/per liter. Using the sorptive capacity, there were 5.61 mg sorbed by 70 mg water plus 1 kg soil, which resulted in a loss of 1.20 mg or ca. 21.4 per cent hydrolyzed per day.

The calculated value for sorptive capacity includes those molecules of toxicant dissolved in the soil water and those physically adsorbed to the soil particles. (Note that the sorbed phase is in equilibrium with the soil-vapor phase concentration.)

The sorptive capacity of HSL and MSCL soils for cis-1,3-D and EDB as influenced by soil moisture and temperature is illustrated in figures 14 and 15. The results indicate that the coarse-textured soil had a higher sorptive capacity for the toxicants than did the finer-textured soil, at least in wet to dry conditions. The sorptive capacity of the soils was also increased with decreased moisture content, but it was not a straightline relationship. The sorptive capacity was greatly increased at moisture tensions above 15 bars. The values obtained for sorption were also dependent upon the type of toxicant tested. The sorptive capacity appears to be closely related to the values obtained for  $K_h$  (see fig. 6) in that EDB was sorbed to a greater extent than was 1,2-D. The steep rise in the sorption curves beyond 15 bars tension is difficult to quantitate in our system, since soil moisture tension measurements are of lower sensitivity in dry soils. For further information concerning sorption in air-dry to oven-dry soils, the reader is referred to the work of Jurinak and Volman (1956, 1957), Wade (1954), Call (1957) and Osgerby (1970).

Once the sorption process is equilibrated (five hours in this system), the same experiments may be continued to determine the relative rate of hydrolysis or degradation of the various

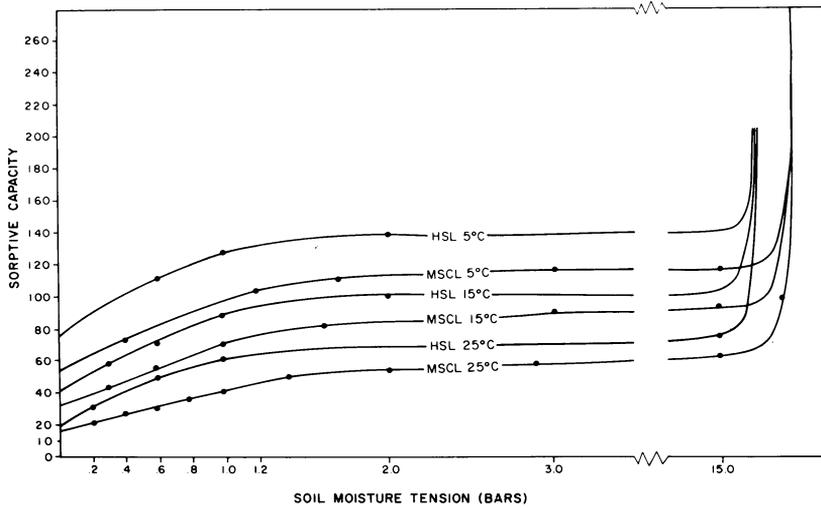


Fig. 14. Sorptive capacity of two soils for cis-1,3-D as influenced by temperature and moisture.

toxicants. Samples of the soil-vapor phase were drawn periodically over a period of several weeks. The soil-vapor phase concentrations of cis- and trans-1,3-D decreased with time, whereas the soil-vapor phase concentrations of 1,2-D and EDB remained relatively constant, with a total decrease of not more than 15 per cent in a 50-day period. This decrease in the concentration of the 1,3-D components is re-

ported as a loss due to hydrolysis. These rates of hydrolysis have been established from experiments made at various concentrations, temperatures, and moisture content for the two soils. The method for calculating hydrolysis rates has been shown, along with the two examples for calculating sorptive capacity. In a dynamic field situation, such as the MSCL soil at 7 per cent moisture, the total volume of soil par-

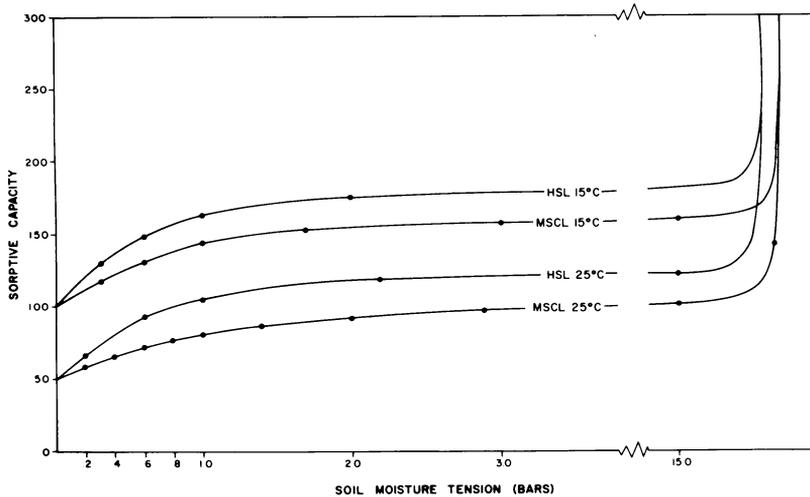


Fig. 15. Sorptive capacity of two soils for EDB as influenced by temperature and moisture.

ticles exposed to fumigant would be greater than with the same soil at 31 per cent moisture.

On an overall basis, therefore, hydrolysis occurs slightly faster in dry soils. The rates of hydrolysis for the two soils have been set as follows: 25 per cent/per day of the sorbed phase at 25°C; 12 per cent/day of the sorbed phase at 15°C, and 4 per cent/day of the sorbed phase at 5°C. As the film of water surrounding each soil particle is decreased in thickness, the rate of sorption is slightly increased (see figs. 14 and 15). Hydrolysis rates are increased with increased soil particle size. Recall that as particle size is increased, the thickness of the water film surrounding the soil particle is decreased. Therefore, the rates of hydrolysis are reported on the basis of concentrations of sorbed toxicant, rather than on just the concentrations present in the soil-water phase. The hydrolysis rates were checked for soils from 0.3 to 15.0 bars soil-moisture tension. The rates of hydrolysis will vary with different soil types due to the dynamic nature of diffusion and differences in sorptive capacity.

That sorbed concentrations of EDB and 1,2-D did not change more than 15 per cent in 50 days serves to support Wade (1954) and Call (1957) who suggest that little irreversible adsorption occurs. This may or may not be true with the 1,3-D components, since the effect of irreversible adsorption is difficult to separate from the effect of hydrolysis. (Note that dry surfaces such as the glass surfaces of the jars used to contain the primary standards are responsible for a 20 per cent loss of the toxicants in 50 days.)

### Events (or "errors") that affect material balance

Experiments were run in a static-type system in the laboratory under

carefully controlled conditions. These data were then applied to the integrated data obtained from various field and simulated field experiments (table 2). The data were not furnished by direct soil sampling and extraction of the soil-water phase, particle phase, or hydrolyzed phase. Instead, it was extrapolated from static-type experiments under controlled conditions similar to those present in the field. This type of data was not as accurate as an actual extraction of the chemical, but it should be pointed out that the undertaking of actual soil extractions throughout the soil profile at various times after a fumigation without disturbing the diffusion pattern would present a formidable task. With the information provided in this paper and the use of <sup>14</sup>C-labeled toxicant, the task should be simpler.

Using the information from this study, we are able to calculate in eight steps the approximate fate of the various toxicants in two soils as follows:

1. Integrate and convert soil-vapor phase concentrations to total mg.
2. Multiply mg soil-vapor phase by sorptive capacity to equal mg sorbed by soil-water and particle phase.
3. Multiply mg soil-vapor phase by  $K_h$  to equal mg in soil-water phase.
4. Subtract mg sorbed phase from mg soil-water phase to equal soil-particle phase.
5. Determine rate of natural loss to atmosphere from figure 12.
6. Multiply sorbed amount by hydrolysis rate to determine amount hydrolyzed for that day.
7. Estimate irreversible adsorption as a portion of that material not accounted for.
8. Re-estimate the sorbed phase—since the values obtained from the first seven steps are valid except in the early stages when mass flow and vaporization errors are prevalent.

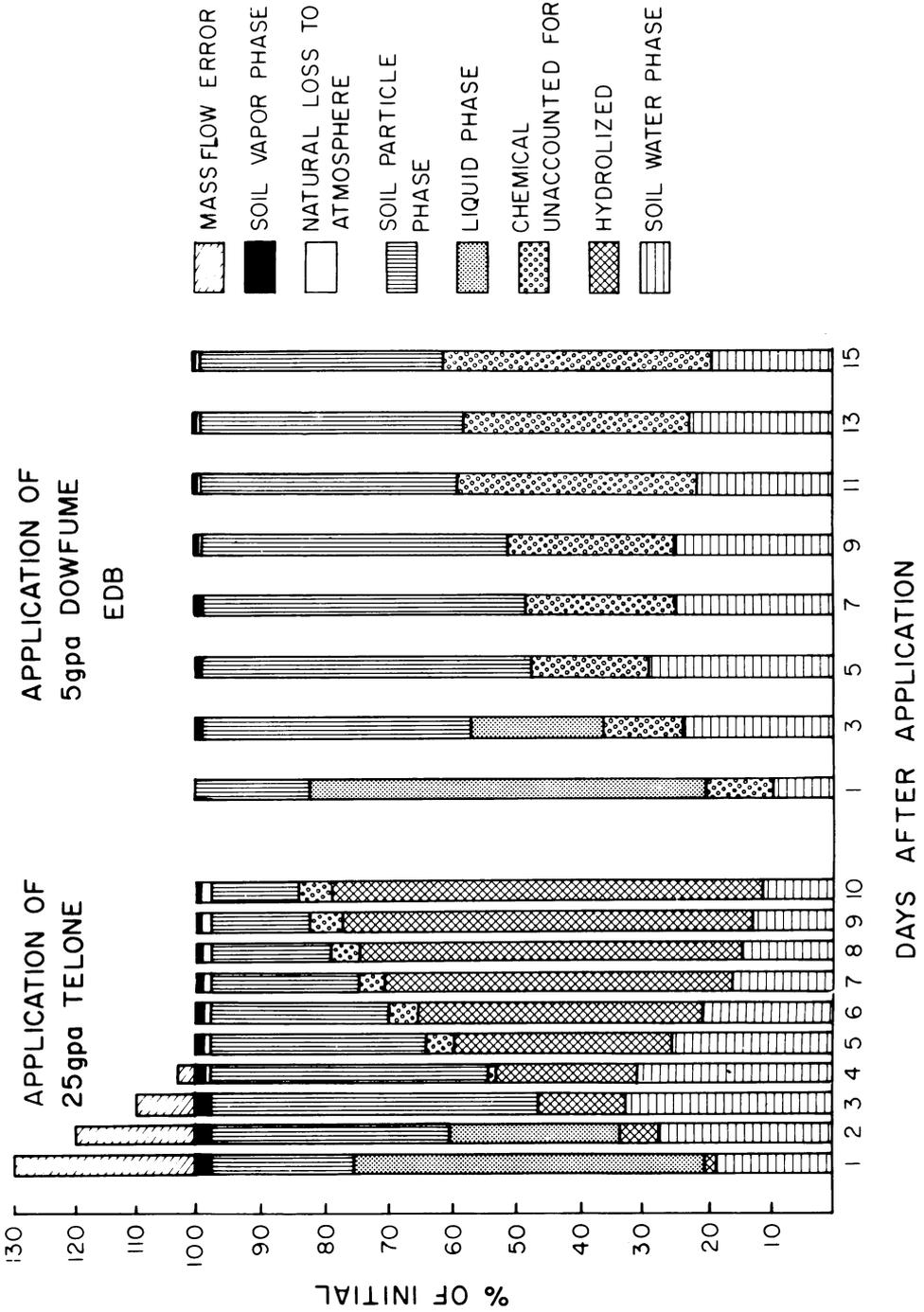


Fig. 16. Approximate material balances for cis-1,3-D and EDB in the HSL soil at 15°C.

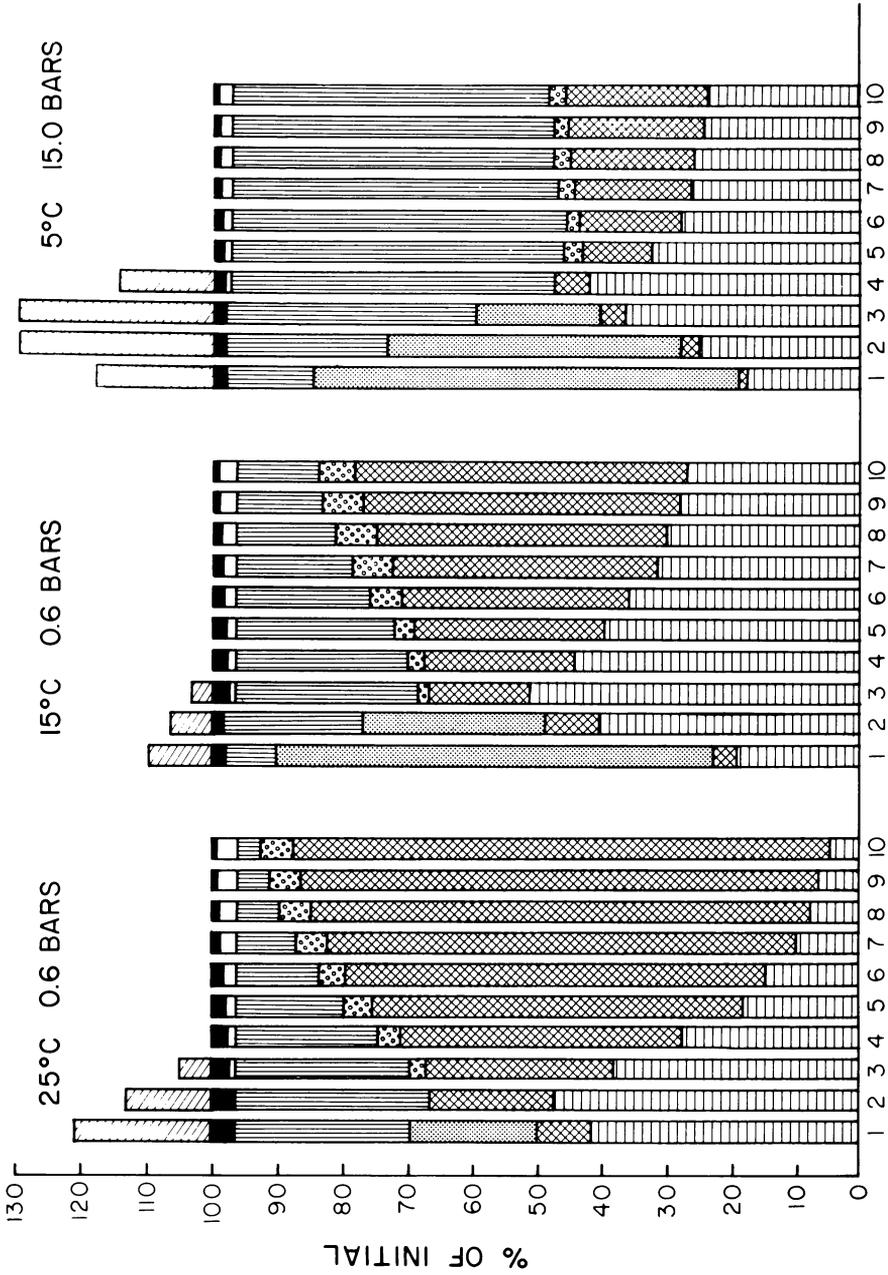


Fig. 17. Approximate material balances for cis-1,3-D in the MSCL soil treated with Telone at 5, 15, and 25°C. At 5°C the soil was drier (15.0 bars tension).

The resulting data from experiment 12 is reported in figure 16. The data from experiments 7, 25, and 27 are reported in figure 17.

We found that under certain conditions, the material balance was not achievable, and in others it was. After doing a material balance on 15 different soils with varying texture, moisture, and temperature conditions, it became apparent that one or more events were not accounted for.

We will refer to one of these events as the "error of mass flow." Those soil-vapor phase values which were achieved one to three days after application gave results approximately 5 to 35 per cent higher than that amount which was initially added to the soil. The most likely explanation for this was that in the first few days (especially in warm or dry soils), the toxicants move through soil not only by diffusion but also by mass flow. The term mass flow refers to the movement of gases at a faster rate and at higher concentrations than would be expected if they moved simply by the laws of diffusion. The error was not an error in our measurement of the gas but rather an error brought about by the utilization of soil-vapor phase concentrations to develop a material balance.

Coincidental with the "error of mass flow" is an opposing event which also distorts results. We refer to this as the "error of vaporization," and it occurs as follows: Simply, if air space is insufficient for movement of the toxicant in the soil-vapor phase, then the toxicant will not vaporize as readily. This leaves a liquid phase reservoir, which decreases with time and is undetectable by our methods. This phenomenon is especially prevalent in soils with limited air space. It is not a major problem under actual field conditions or in soils where the chisel shank hole has not been carefully sealed, because in these situations there are greater air

space and surface area in which the toxicant is able to vaporize.

Other possible explanations for the errors might be incorrect sampling or integration of the data or that the vapor phase of these toxicants is slightly heavier than air, and they might not diffuse evenly in all directions. (However, there was no indication of the latter in any of the experiments.)

Whatever the major reason for the errors of mass flow and vaporization, by the fourth day, the values for the soil-vapor phase may be taken as valid; and the values obtained in the static-type experiments are directly applicable to the data from the dynamic-type experiments (table 2). We nonetheless arbitrarily lowered the soil-water and soil-particle phase concentrations, to allow for the effects of mass flow and vaporization.

### Approximate material balance

In 15 experiments (table 2) we were able to account for  $100 \pm 35$  per cent of the toxicant at any given time after its application to these two soils. On the fourth day after application, we were able to account for  $100 \pm 20$  per cent. Figure 16 (experiment 12) and figure 17 (experiments 7, 25, and 27) show an approximate material balance for cis-1,3-D and EDB under various soil conditions.

The concentrations in the soil-water, soil-particle, and liquid phases were estimated in order to determine the approximate total amount sorbed, which, in turn, provided estimates of the concentration still in the liquid phase and mass flow—factors that were not relevant after the fourth day.

The approximate material balance (fig. 16) for EDB was typical of the data obtained from EDB experiments. The same factors affecting 1,3-D also affected EDB; however, the hydrolysis

was not as great. The degradation rate was not obtainable from our data, and only an estimate could be made. However, we can predict that since EDB is more persistent than 1,3-D, the percentage of EDB chemically adsorbed would be greater than for 1,3-D. The final answer will not be available until we are able to better distinguish chem-

ical adsorption from other forms of chemical decomposition, including hydrolysis. At this point in time, we are only able to estimate it as "chemical unaccounted for." Nevertheless, the material balance, as indicated by our studies does provide the background work for future studies in which actual soil extractions would be made.

## DISCUSSION

A fumigant applied to the soil as a stream of liquid evaporates to a vapor of individual molecules. In the vapor phase these molecules move many times faster than they move in the water phase. However, the molecules in the vapor phase do have an affinity for water, mineral, and organic phases which make up the substrate we call soil. Water is present in soils as a thin film around soil particles. Most diffusion of molecules occurs through the continuous air spaces within the soil. As a chemical moves through the air, a dynamic equilibrium is established between the molecules of toxicant in the vapor phase of soil and those in the water phase of soil. For example, at 25°C there is 17.7 times the concentration of *cis*-1,3-D in the water phase as there is in the vapor phase. It follows that if the soil-water content is increased, the overall distance of soil diffusion will be decreased as the chemical becomes more diluted—and coincidentally it will be moving through the soil more slowly. The same is true if for some reason the toxicant's affinity for water is changed. One way by which the relative concentration of nematicide in water and air is influenced is through a change of the soil temperatures, as indicated in figures 6 and 7.

The relative diffusion pattern of any fumigant-type pesticide (methyl bromide, 1,2-dibromoethane, *cis*-1,3-D, *trans*-1,3-D, chloropicrin, and the like) is somewhat predictable based on its

inherent physico-chemical characteristics. This is not the entire story, however, since certain other factors may also influence the diffusion pattern. One such factor inherent with the fumigant is its rate of degradation. If the toxicant is gradually hydrolyzed or degraded while it is in the water phase, then there is less chemical in the vapor phase available for diffusion. An example is the hydrolysis and subsequent degradation of *cis*- and *trans*-1,3-D in warm soils (25°C). With EDB, the rates of loss due to hydrolysis are not as rapid in warm soils but may be more noticeable in the more alkaline soils (Castro and Belser, 1968).

### Soil effects on fumigation

Use of the soil profile box (simulated field conditions) made it possible to study diffusion patterns and concentration gradients of nematicides as they were affected by various soil factors. Results agreed well with similar experiments in the field.

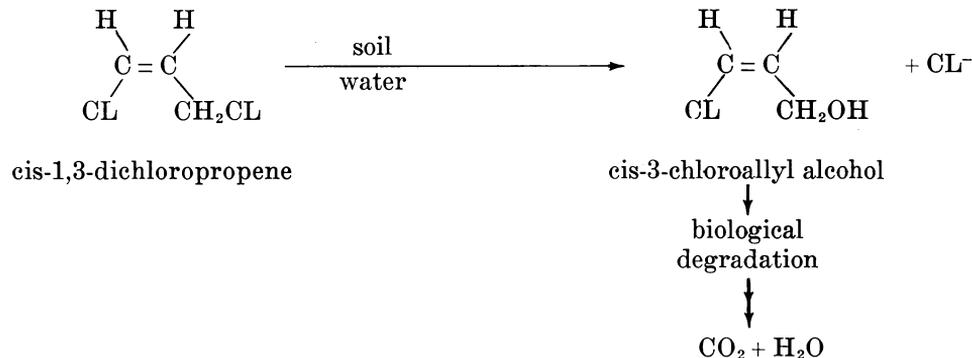
**Soil-air.** If the air space of the soil is limited and pore spaces discontinuous, the diffusion pattern will be restricted. As a general rule, a sandy loam soil should not be fumigated if the soil moisture tension is less than 0.5 bar suction at the 30.5 cm depth. Likewise, in a clay loam soil the limit would be 0.6 bar suction. At the other extreme, it is possible to fumigate sandy or clay type soils at lower moisture levels up to the permanent wilting

point (15 bars tension). For optimum movement of the toxicant, it is best to fumigate soils when they are in a drying condition.

**Soil moisture.** The greater the quantity of soil water, the greater the dilution of the toxicant and the more

restricted the total diffusion pattern will be.

Hydrolysis and subsequent degradation of 1,3-D have been shown (Castro and Belser, 1966, and Belser and Castro, 1971) to occur in moist soil in the following manner:



**Soil temperature.** The rate of hydrolysis was profoundly affected by soil temperature in our studies. It is important to note that both the parent compound (1,3-D) and the hydrolysis products are toxic to nematodes; however, the parent compound is the most toxic (Moje, Martin and Baines, 1957). The biological degradation of the hydrolysis products to carbon dioxide and water is presumably a rather fast reaction (Belser and Castro, 1971) and serves to remove the toxicant (chloroallyl alcohol) from the soil. This assumes that the *Pseudomonas* or other organisms capable of degrading the chloroallyl alcohol were not killed by the parent compound.

Theoretically, one would achieve greatest specificity of control at higher temperatures where concentrations of toxicant are low but well distributed throughout the soil profile. At lower temperatures, diffusion of the chemical through the soil profile would be restricted, and concentrations in the water would be high. The result would be the attainment of the threshold limit value for a more diverse group of soil organisms.

Temperature is, in our opinion, more important than has been thought previously. We believe that for most soil nematodes exposed to 1,3-D, the best control would be achieved between 15 and 20°C. Below 15°C the solubility of the chemical is greatly increased and thus seriously limits diffusion, while above 25°C the rate of hydrolysis could limit diffusion. However, even though hydrolysis is much slower at 5°C, significant crop responses may be achieved with the use of 1,3-D in cold soils if the soil is also dry.

The effect of temperature on volatilization from the soil surface does not appear to be important with Telone or with EDB. Since hydrolysis does not occur to any great extent with EDB, it would seem that optimum results would be achieved with this chemical at soil temperatures in excess of 25°C. In warm soil (35°C at 23 cm depth) EDB gave better control of *Meloidogyne javanica* than 1,3-D in tests carried out by the junior author.

**Soil structure.** This variable was not tested in the simulated field experiments, and it is difficult to isolate in field experiments. It is generally under-

stood, however, that diffusion of gases in very moist clay soils may be better than expected if the soil is friable as a result of aggregation of finer clay and silt particles.

Soils of uniform profile were used for the most part in these studies. However, the Ramona loam soil in experiment 24 was less uniform and indicated that the major influence of soil texture was the difference in water content in the various soil horizons. Gas will penetrate through a compacted clay layer (plow pan) if the soil and plow pan are sufficiently dry. However, pre-treatment tilling of the plow pan and/or applications of the nematicide at two depths might be in order.

Workers in certain agricultural areas with peat or muck soils will have to orient their research on methods of application almost exclusively to this problem of organic matter. Readers are referred to the work of Leistra (1970, 1971, 1972). If soils contain seasonally high residues of organic matter, it would be advantageous to plan the fumigation schedules when the organic matter content is at its lowest.

The type of organic matter which might be added after a fumigation could determine the species of organisms, particularly fungi and bacteria, which will predominate in the field in subsequent years.

Elliot and Mountain (1963) and Whitehead, Tite and Fraser (1970) report their best results with spring applications of nematicides. Other workers prefer fall application. In any case, all soil factors must be in an optimum range for fumigant movement, and application time will vary with climate, soil type, and planting date.

### Fate of the toxicant

The fumigant-type toxicants are applied to the soil, usually by means of a chisel applicator, while in the liquid

phase. Within the soil profile of dry to wet soils there are two main areas into which the toxicant will immediately move—the soil air and the soil water. If the soil is very dry (greater than 15 bars moisture tension) the chemical will sorb either reversibly or irreversibly onto the soil particle and be unavailable for diffusion. It appears that the most important factor affecting the rate of vaporization is the availability of air space. In a cooler (15°C), moist soil, or in soil where the chisel shank hole has not been properly sealed, the vaporization of the toxicant from the liquid phase may be complete within a day. If air space is limiting, it may take several days for complete vaporization from the liquid phase. As the toxicant diffuses through the soil-air phase, it is coincidentally diffusing into the soil water, and equilibrium is established between concentrations of the toxicant in the water and vapor phases of the soil. In laboratory glass jar experiments involving small amounts of soil and much air space, it reaches equilibrium in approximately three to five hours. In actual fumigation experiments simulating field conditions, however, equilibration takes longer to be achieved, especially in dry soils.

We have referred to this phenomenon as the mass flow error. In dry, warm soils one should see the fastest rate of movement of chemical, even with the increased attraction of the soil particles. It is, in fact, so fast that a material balance based on soil-vapor phase concentrations indicates more toxicant in the soil (135 per cent) than originally added. We suggest that the chemical has been vaporized at a rate much faster than it is able to diffuse. This movement by mass flow, in our experiments, was apparent for up to four days after application in some soils. After the fourth day, the concentrations within the various phases of the

soil had come to true equilibrium, and diffusion was the sole means of movement.

**Toxicant loss to the atmosphere** may occur for several reasons. Small amounts may be naturally diffused up through the soil profile. Some can escape through the inadequately sealed chisel shank hole and soil surface. The effects of temperature, moisture,  $K_h$ , depth of injection, and soil type all determine the extent of loss.

An estimate of the total amount of cis-1,3-D lost to the atmosphere after a commercial application of 234 liters/ha Telone at the 30.5 cm depth in a warm, moist, sandy loam soil would amount to approximately 5 to 10 per cent. This assumes that the operator is also pulling some surface-sealing device, which also places some soil down into the shank hole.

Toxicants are also lost from the soil profile by degradation and hydrolysis. The 1,3-dichloropropenes are especially susceptible to hydrolysis, and in a week's time as much as 75 per cent of the chemical initially added may be hydrolyzed in a dry, warm (25°C), sandy loam soil. The hydrolysis products (chloroallyl alcohols) are not as nematotoxic as the parent compound (Moje, Martin and Baines, 1957), but they are known to be highly phytotoxic. Belser and Castro (1971) have shown that a specific isolate of an unidentified species of *Pseudomonas* was capable of degrading chloroallyl alcohol.

Another pathway by which toxicants are removed from soils is through irreversible adsorption. Losses due to this phenomenon are not too important in California soils (amounting to 2 to 5 per cent of the loss of 1,3-D in warm, low organic content soils). The rates may be higher in cooler (5°C) soils, since the exposure period would be prolonged due to decreased hydrolysis rates. In soils with high amounts of fresh organic matter or in peat-type

soils, the losses due to chemical adsorption (irreversible) would be greater (Leistra, 1970). One should also be aware that reversible adsorption is greatly increased in soils of high organic matter content.

EDB, in acid soils, should persist for long periods of time. In the soils that we studied (pH of 7.0 to 7.5), the rate of degradation was quite low, indicating longer persistence than with the 1,3-D nematocides; therefore, a relatively high percentage of the toxicant initially added would be found chemically adsorbed.

### Environmental aspects

The fate of pesticides in soil, air, groundwater, and edible portions of plants should be known and understood not for the purpose of establishing zero tolerances, but rather as a guideline for using chemicals to their best advantage and for avoiding phytotoxic residues.

Within soils, the 1,3-D and EDB toxicants are distributed depending upon the soil conditions. These same conditions also influence its potential as a persistent health hazard and, as a soil contaminant, toxic to developing crop plants. Used properly, the 1,3-D nematocides are detoxified in the soil by several methods, but, in the main, hydrolysis and dilution by diffusion are primarily responsible for the decreases in concentration within the soil profile. Improper application, that is— 1) improper sealing of the chisel shank hole, 2) application to wet, cold soils, and 3) application of excess amounts that result in high (and wasted) amounts lost to the atmosphere and persistence of the hydrolysis products, may make this useful toxicant deleterious.

The toxicant may persist in soils for long periods of time (Williams, 1968); however, the concentrations at which it persists appear to have little

biological activity. With applications of 234 liters/ha Telone to a moist, warm soil, the cis-1,3-D can be expected to persist in soil atmospheres at concentrations greater than 10 parts per billion for two to four months, depending upon soil type.

The California State Department of Agriculture reports (State Pesticide Use Report, 1971) that in 1971 approximately 1,284,841 kg of pesticide containing 1,3-D were used in the state. We can estimate that approximately 72,576 kg (or 8 per cent) of actual 1,3-D would be lost to the atmosphere. It is difficult to estimate the effect this would have upon the above-ground environment, but we can point out the affinity of this toxicant for water and organic materials. A total of 14,692 kg of EDB was reportedly used agriculturally in 1971. Assuming a 5 per cent loss to the atmosphere, approximately 600 kg of EDB was lost. It should be pointed out that normally leaded gasoline contains approximately 1 kg of EDB per 4,000 liters of gas as an additive for lead removal.

The presence of these fumigants in ground water supplies would seemingly depend on how near those supplies would be to the soil surface. These fumigants move deeper and deeper into the soil with time and rains, but the dilution factor is great. In one experiment with the HSL soil in a dry, warm condition, we injected 1,683 liters/ha (experiment 28) of

Telone at the 91 cm depth. Approximately 20 parts per billion in the soil-vapor phase was detected at the 305 cm depth six days later.

The toxicant can persist in soils at low concentrations for long periods of time, and, under certain conditions, developing roots and tubers of edible plants can sorb quantities of the toxicant (Williams, 1968). Emerson, *et al.* (1969) have shown that fumigation of sandy loam soils with relatively low dosages of alkyl halide nematicides under proper conditions had no toxic residues of nematicides and had no adverse effects on the flavor or nutritional value of green lima beans, carrots or citrus. These were the only food crops tested. A significant increase in carotene content of carrots occurred in two out of three soils treated with 1,3-D. Wu *et al.* (1970) have reported similar results on carrots and sweet corn.

EDB and 1,2-dichloropropene do not readily hydrolyze and thus can persist for long periods. EDB is more persistent and should be applied at relatively low rates. In addition to the reduced nematocidal properties of EDB below 10°C, its lengthy persistence in the soil environment is another reason why EDB should not be applied to cold and wet soils. The 1,2-D has little biological activity, but it is not readily hydrolyzed and diffuses relatively fast. When compared to 1,3-D, higher percentages are lost to the atmosphere.

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## ACKNOWLEDGMENT

The advice and counsel of Dr. C. E. Castro and technical assistance of Nao Belser and H. E. McKinney are gratefully acknowledged. We thank the Dow Chemical and Great Lakes companies for generous support.