Distribution of 1,3-Dichloropropene over the Phases in Soil

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An investigation was carried out on the distribution of *cis*- and *trans*-1,3-dichloropropene over the phases in soil with the purpose of obtaining data for mathematical models describing the movement of these fumigants in soil. The measurements included three types of soils and were taken at 2°, 11°, and 20° C. Concentrations in the vapor and water phases were measured with a gas chromatograph. From these results, the amount adsorbed was calculated. The adsorption isotherms appeared to be linear in the important concentration range. The *trans*-isomer was considerably stronger adsorbed than the *cis*-isomer. The value of the adsorption coefficient was proportional to the organic matter content of the soils. The amount adsorbed at a certain concentration in the vapor phase at 2° C was about three times higher than the amount adsorbed at 20° C.

The use of soil fumigants, containing *cis*- and *trans*-1,3-dichloropropene, for the control of plant parasitic nematodes in arable framing is still increasing. In view of the harvest, this fumigation has to be performed in the autumn. During this season, soil temperature is decreasing and the precipitation surplus is increasing. A considerable part of the fumigated soils contains high amounts of organic matter. As a result of this, the percentage mortality of parasitic nematodes may be inadequate. In addition, there were cases in which considerable residual amounts of *cis*- and *trans*-1,3-dichloropropene were still present in spring.

It is therefore desirable to describe and predict the relation between time and concentration in the soil under different circumstances. The movement of fumigants in the soil is mainly a result of diffusion in the vapor phase. During this diffusion process there is a tendency to establish an equilibrium between the concentrations in vapor, water, and adsorbing phases. It is assumed that the biological effect of these pesticides in soil is correlated with the concentration in the water phase (Goring, 1962, 1967).

Movement of fumigants like *cis*- and *trans*-1,3-dichloropropene in soil is affected by a complex of factors concerning properties of the compound, properties of the soil, climatic conditions, and mode of application. Mathematical models can be used to study the single and combined influence of these factors. Hemwall (1959, 1960) started with this in the field of soil fumigation by using numerical solutions of the so-called diffusion equation with constant diffusion coefficient. The data used in these calculations concerned 1,2-dibromoethane (EDB) of which Call (1957) had measured a number of physical properties.

It was impossible to carry out computations for *cis*- and *trans*-1,3-dichloropropene because the data concerning the distribution over the soil phases were lacking, except for an estimation of the distribution ratio for the water/air system at 20° C, mentioned by Goring (1962). The investigation reported in this paper is an attempt to fill up this gap in knowledge. The measurements were carried out under circumstances that may occur during and after soil fumigation in the autumn. In view of the analogies that could be expected, the results of Wade (1954) and Call (1957) concerning the "sorption" of 1,2-dibromoethane in moist soils were important. They obtained good results with the supposition that the equilibrium establishment between the concentrations in the soil phase is very rapid. For this reason data on the

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equilibrium distribution are very important for the investigation of the movement of fumigants in soil.

Castro and Belser (1966) found that, in a soil under laboratory conditions, a few percent of the amount of *cis*- and *trans*-1,3-dichloropropene present was hydrolyzed per day. From results of Williams (1968) it can be deduced that under field conditions this rate may be much lower. This holds particularly for fumigation in the autumn, as is borne out from analyses in our laboratory. In anticipation of further data concerning the rate of decomposition under different circumstances, it is therefore useful to look at the original compounds.

METHODS AND MATERIALS

The concentration measurements were carried out with an Aerograph gas chromatograph, Model A-600-B, provided with an electron capture detector with tritium source. The stainless steel column had an inner diameter of 1.5 mm, and a length of 5 meters. The filling consisted of 10% (w/w) Carbowax 20M on 70 to 80 mesh Anakrom ABS. The carrier gas was pure nitrogen and the flow rate was 25 ml per min. The temperature of the injector was 170° C, and of the column and detector it was 118° C.

The recorder used was a Honeywell 1 mV with integrator. The injection liquid was *n*-hexane, 5 μl being injected at a time. The retention times for *cis*- and *trans*-1,3-dichloropropene were 3.2 and 4.4 min, respectively. The standard solutions in *n*-hexane were made from *cis*-1,3-dichloropropene 99% and *trans*-1,3-dichloropropene 99% (obtained from Shell Nederland Chemie N.V.). The concentrations ranged from 0.2 to 2.0 μg per cm^3. Solutions of known and unknown concentration were injected alternately, through which the unknown concentrations could be inferred from the calibration line.

For the determination of the coefficient K(w/v) concerning the distribution of *cis*- and *trans*-1,3-dichloropropene over water and vapor phases, use was made of solutions in distilled water. The concentrations ranged from 100 to 1000 ppm. About 40 ml of these solutions were put in 120-ml flasks, which were subsequently closed by a septum enfolded in aluminum foil. During 24 hr, the flasks were placed in a water bath at the required temperature and shaken a few times.

After this, 50-μl samples were taken from the vapor phase in the flasks with a gas-tight 100 μl syringe. These samples were transferred to 0.5 or 1 ml of hexane in small glass tubes. From these solutions 5 μl was injected into the gas chromatograph to measure the concentration. An amount of 5 ml of

the water phases was extracted with 5 ml hexane. The distribution ratio n-hexane/water for cis- and trans-1,3-dichloropropene is about 100. The solution in hexane was diluted and injected.

The adsorption investigations were carried out for three types of soils, humous sand [5.5% (w/w) organic matter], peaty sand [18% (w/w) organic matter], and peat [95% (w/w) organic matter]. The sands were taken from plough layers, and the peat from a layer underneath the plough layer of blank spots. These were situated in experimental fields where, in the autumn of 1969, soil fumigation was carried out. At some points of time the concentrations of cis- and trans-1,3-dichloropropene were measured at various depths in the soil. Besides, for model computations these distribution data are required for the calculation of the concentration in the water phase from the concentration in the soil samples.

To measure the adsorption on soils, the 120-ml flasks were filled three-quarters with loose moist soil. After the adsorption measurements the amounts of dry soil, organic matter, and water in the flasks were determined exactly. With a small pipette the desired number of small drops of approximately 10 mg of the pure liquids of cis- and trans-1,3-dichloropropene were added. These amounts were weighed exactly on an analytical balance. After this the flasks were closed by the septum and put in waterbaths at the required temperatures. These were 2°, 11° and 20° C. The equilibrium establishment was accelerated by occasionally rolling the flasks. By sampling the vapor phase at some intervals of time, the rate at which in this way the adsorption equilibrium was established could be determined. For the soils and temperatures studied, a period of 24 hr appeared to be more than sufficient. This is in agreement with the rates determined by Wade (1954) and Call (1957) for the adsorption of 1,2-dibromoethane on moist soils in flasks. Therefore, the concentrations in the vapor phase were measured after 24 hr. In the range of soil moisture contents from wilting point to almost saturation, the adsorption of 1,2-dibromoethane appeared to be independent of that moisture content (Wade, 1954; Call, 1957). During soil fumigation the soil is in the range around field capacity. For practical purposes adsorption measurements at only one soil moisture content are therefore sufficient. The moisture contents of the humous sand, the peaty sand, and the peat were 0.17, 0.41, and 1.20 g per g, respectively.

The amount of water in the flasks, Ww, was determined by drying the flasks with the moist soil at 105° C. After subtraction of the tare weight of the flasks, the amount of dry soil, Ws, was obtained. The amount of organic matter per flask, Wom, was determined with the loss-on-ignition method that is usable for these types of soil. The weight of the mineral parts is then: Wmp = Ws − Wom. For the density ρ mp of the mineral parts, one has: ρmp = 2.66 g per cm³; and for that of the organic matter: ρom = 1.47 g per cm³. The volumes, V, of the phases in the flasks were calculated with: Vmp = Wmp/ρmp, Vom = Wom/ρom, Vw = Ww/ρw, and Vv = 120 − (Vmp + Vom + Vw).

The concentration in the water phase could be inferred from the concentration in the vapor phase and K(w/v). The total amounts in the vapor and water phases were calculated from the products of concentration and volume. The amount adsorbed was then found by subtracting the amounts in the water phase and vapor phase from the amount added.

RESULTS AND DISCUSSION

The ratios for the distribution over water phase and vapor phase for cis- and trans-1,3-dichloropropene are shown in Figure 1. These results are mean values of determinations
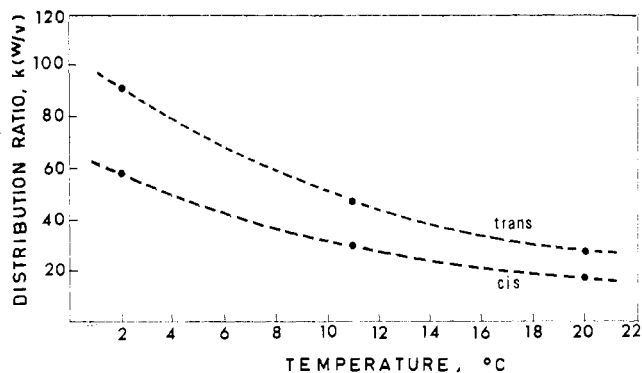

Figure 1. The ratio K(w/v) between the concentration in the water phase and the concentration in the vapor phase for cis- and trans-1,3-dichloropropene at 2, 11, and 20° C

in duplicate. The standard deviation is less than 5% of the average in all cases. In some instances this ratio was measured for a number of concentrations in the range of 100 to 1000 ppm in the water phase. The ratio K(w/v) at a certain temperature appeared to be independent of the concentration. This means that Henry's Law is valid: $C_w/C_v = K(w/v)$, in which K(w/v) is Henry's constant, and C_w and C_v are the concentrations in water phase and vapor phase.

The value of K(w/v) is substantially higher for the trans-isomer. This correlates with the lower vapor pressure and the slightly greater solubility in water (Goring, 1962). The isomers of 1,3-dichloropropene belong to the group of soil pesticides with a comparative low distribution ratio K(w/v). This means that the movement over greater distances in the soil profile is a result of diffusion in the vapor phase. In this respect, the diffusion in the water phase is negligible (Goring, 1967).

The results of the adsorption measurements at 20° C are shown in Figure 2. In the concentration range used, they can be presented as linear adsorption isotherms. The same holds for the results at 11° C and 2° C. The slope of the
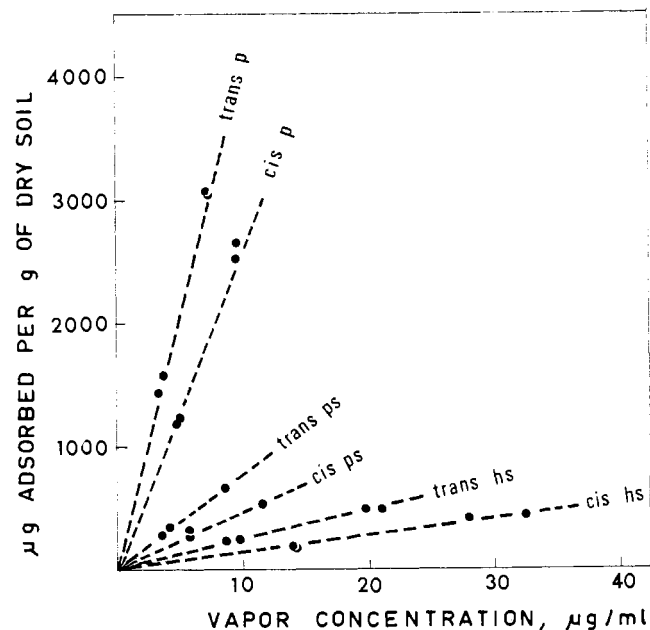

Figure 2. Adsorption isotherms for cis- and trans-1,3-dichloropropene at 20°C. hs = humous sand, ps = peaty sand, p = peat

Table I. The Adsorption Coefficients K(s/v) for *cis*- and *trans*-1,3-Dichloropropene

Soil	Temp. °C	K(s/v) *cis*	K(s/v) *trans*
Humous sand	2	38	68
	11	22	40
	20	14	24
Peaty sand	2	130	220
	11	78	130
	20	47	77
Peat	2	680	1250
	11	430	720
	20	260	410

adsorption isotherms can be expressed in an adsorption coefficient:

$$K(s/v) = \frac{\mu g \text{ absorbed per g of dry soil}}{\mu g \text{ vapor per ml vapor phase}} \quad (1)$$

The values of $K(s/v)$ for the examined cases are recorded in Table I. These results are averages of four observations at different concentrations. The standard deviations were less than 5% of the average values. The adsorption of one isomer was not measurably affected by the presence of about the same amount of the other isomer. From estimating computations and analyses of soil samples from fumigated experimental fields, it became evident that the concentration range investigated here is by far the most important one.

From results of Castro and Belser (1966), it can be calculated that, under laboratory conditions, the decomposition rate for *cis*- and *trans*-1,3-dichloropropene in a loam soil was about 0.035 day^{-1}. From residue analysis of Williams (1968), it can be concluded that the decomposition rate in sandy and peat soils was lower than 0.01 day^{-1}. The latter follows also from analyses at our laboratory of 1,3-dichloropropene in field samples taken more than 6 months after the fumigation of sandy and peaty soils. So the neglection of the decomposition in the short period of these experiments introduces an error of at most 1% in the measured values.

It is possible to express graphically the relation between the values of $K(s/v)$, mentioned in Table I, and the content of organic matter in the soils. From these diagrams it follows that, for the adsorption of *cis*- and *trans*-1,3-dichloropropene, $K(s/v)$ is proportional to the content of organic matter. Thus it is possible to define the coefficient $K(om/v)$ for the adsorption by 1 g of organic matter as follows:

$$K(om/v) = \frac{\mu g \text{ adsorbed per g of organic matter}}{\mu g \text{ vapor per ml vapor phase}} \quad (2)$$

The mean values of $K(om/v)$ for the three soils are calculated. The relation between these averages and the temperature is shown in Figure 3. The standard deviations are less than 10% of these average values.

From the coefficients $K(om/v)$ and $K(w/v)$, one can deduce $K(om/w)$, thus indicating the distribution of the compounds over the organic matter and the water phase.
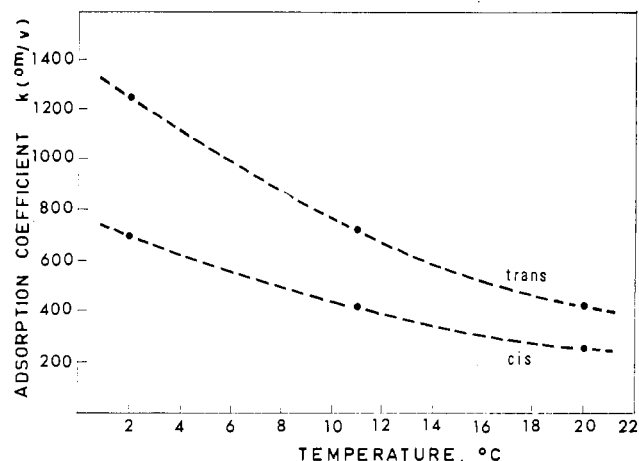

Figure 3. The relation between K(om/v) and temperature for the adsorption of *cis*- and *trans*-1,3-dichloropropene on three soils

$$K(om/w) =$$

$$K(om/v)/K(w/v) \text{ in } \frac{\mu g \text{ adsorbed per g of organic matter}}{\mu g \text{ dissolved per ml water phase}} \quad (3)$$

Calculation of $K(om/v)$ for *cis*- and *trans*-1,3-dichloropropene in the examined cases gives average values of 14 and 15, respectively. From this it follows that the difference in the $K(om/v)$ values for the *cis*- and *trans*-isomers is mainly a result of the difference in $K(w/v)$.

The temperature influence on $K(om/w)$ is not distinct, so the relation in Figure 3 is chiefly based on the temperature effect on $K(w/v)$.

The distribution coefficients discussed here can be used to calculate the percentages of *cis*- and *trans*-1,3-dichloropropene in the different phases at equilibrium. This has been done for the soils studied, simulating structure and moisture conditions that may occur during soil fumigation in the field. For the temperature range from 2 to 20° C, it was found that less than 1% is in the vapor phase, between 10 and 20% is dissolved in water phase, whereas between 80 and 90% is adsorbed.

By using mathematical analysis, the consequences of these distributions for the concentration-time relation in the water phase in soils can be predicted. In addition, the concentration in the water phase can now be calculated from the measured concentrations in the soil samples. These distribution data are indispensable when one has the intention of comparing the concentrations in the water phase resulting from measurements and from computations.

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