The Effect of Temperature on the Dispersion of 1,2-dibromo-3-chloropropane in Soil

D. E. JOHNSON AND BERT LEAR[1]

Abstract: A study was conducted to evaluate the effect of temperature on the dispersion of 1,2-dibromo-3-chloropropane (DBCP) in soil. The facility of solution of DBCP in water was also investigated. Results of these studies show that the movement of DBCP from an injection site is temperature dependent. These data also indicate that DBCP dissolves readily in water and that dissolved chemical serves to limit the rate of outward dispersion once the liquid DBCP which was added has changed state. The mechanics of DBCP dispersion following soil injection are discussed.

Injection of chemicals into the soil for pest control has been used for a long time. Numerous studies have used a bioassay (organism survival) to estimate the movement of these materials following injection. Improved analytical techniques have recently provided a means of studying the movement of volatile nematicides in soil. Data developed using these techniques provides more precise information with respect to concentrations present and the persistence of a particular material in soil.

Johnson and Lear (2) presented data on the distribution of 1,2-dibromo-3-chloropropane (DBCP) in soil treated by the so-called "flooding method." This paper reports experiments designed to evaluate the distribution patterns of DBCP in soil columns which had been injected with the chemical.

MATERIALS AND METHODS

Soil columns were formed by joining plexiglass rings 4.5 cm in diameter by 5 cm tall with masking tape to form a tube of appropriate length. The center plexiglass segment of each column was drilled to permit the insertion of a hypodermic needle. The plexiglass columns were packed with moist soil in 50 ml increments. Each increment was tamped with a circular plunger driven by a 240 g weight dropped from a height of 12.5 cm three times. When the column was packed to the desired height, the uppermost ring was removed and the soil struck off to provide a flat surface.

The tops of the columns were sealed by attaching a small plastic petri dish to the column top with masking tape. Sealed columns were then stored at the temperature required for a particular experiment for at least 24 hr prior to use to permit temperature equilibration.

The moist soil was prepared by weighing the quantity of air dry soil required for a single column into a polyethylene bag. The volume of water required to bring the soil to the desired moisture content was added with preliminary mixing done in the bag. The moistened soil was mixed for 5 min in laboratory twin shell blender, with intensifier bar. The mixed soil was then returned to the plastic bag and stored until used. A minimum post-mixing storage period of 3 days was used to permit additional moisture equilibration.

One soil type, Yolo fine sandy loam, was used throughout this study. After air drying, the soil was screened through a 6 mm square hole sieve. The screened soil was mixed thoroughly in a twin shell blender so that representative subsamples would be obtained. Mechanical analysis of the soil showed it to contain 53%, 25%, and 22% sand, silt, and clay, respectively.

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[1] Department of Nematology, University of California, Davis 95616.

The 1,2-dibromo-3-chloropropane (DBCP) used was technical material obtained from commercial sources. The chemical was formulated to contain 40 mg DBCP /ml in redistilled hexane. The formulated material, when not in use, was stored at –13 C to limit vaporization losses.

Each column was injected with 0.1 ml of formulated DBCP (equivalent to 4 mg DBCP) using a hypodermic syringe and needle. The chemical was injected through the hole in the center plexiglass annule into the center of the soil column. After injection, the hole was sealed with masking tape. Treated columns were stored in a constant temperature box.

At the appropriate time interval after injection, the columns were sectioned by cutting the taped joints with a razor blade. Cores were removed from the center of each column segment with a cutter 1.5 cm in diameter and placed in glass-stoppered bottles for DBCP extraction. The soil cores used for analysis were cylinders of moist soil 1.5 cm in diameter by 5 cm tall. The balance of the soil in each segment was used for moisture determination by drying at 105 C for 24 hr.

DBCP was extracted from the soil by adding 10 ml of distilled water and 25 ml of redistilled hexane to each bottle. The bottles and contents were shaken vigorously for 30 min on a reciprocating shaker. The supernatant hexane was decanted into smaller containers, also glass stoppered, and stored for analysis. Analyses were made within 4 hr of extraction to reduce evaporation losses of DBCP. The analysis was performed using the gas chromatographic method described by Johnson and Lear (3). Concentrations reported are μg DBCP per gram of water (μg/g). This expression requires that the moisture content of the extraction sample be known. This was accomplished by determining the wet weight of the extraction sample and calculating the quantity of water present based upon the moisture and the wet weight of the soil taken for the moisture determination.

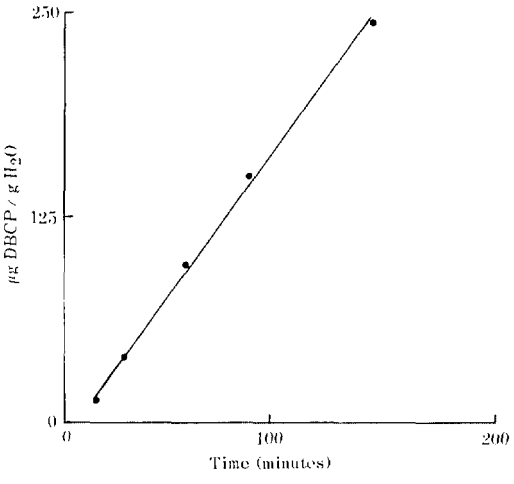

FIG. 1. The rate of solution of DBCP in water by vapor movement.

RESULTS AND DISCUSSION

Johnson and Lear (2) showed that a concentration of between 20 and 25 μg DBCP/g H_2O is lethal to *Meloidogyne* sp. Two short experiments were conducted to determine the time required for this quantity of DBCP to dissolve in water. The first experiment measured rate of movement of DBCP from a concentrated source to water. A beaker containing 200 ml of distilled water was placed in a desiccator. Small dishes, each containing 1 ml of DBCP were placed around the beaker and the desiccator closed. The water was stirred slowly during the experiment using a teflon coated magnetic stirring bar. At specified intervals, water samples were removed, diluted with distilled water and the DBCP extracted with redistilled hexane. The results are shown in Fig. 1.

The second experiment evaluated the direct solution of DBCP in water. Technical

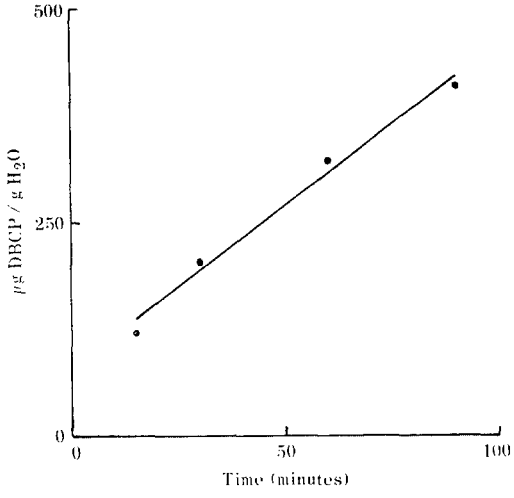

FIG. 2. The rate of solution of DBCP in water by direct mixing.

DBCP (0.5 ml) was added to bottles containing 100 ml of distilled water. The bottles were shaken gently on a reciprocating shaker. At specified times, aliquots were removed, diluted, extracted and analyzed. The results of this experiment are shown in Fig. 2.

These data indicated that the solution of a nematicidal concentration of DBCP in water occurred rapidly and that the rate of solution was not likely to be a limiting factor in controlling nematodes in soil. In the first experiment, the range of lethal concentration was reached in approximately 20 min while in the second experiment a lethal concentration was attained in less than 5 min.

In the temperature studies, columns were injected with 4 mg of DBCP at a depth of 22.5 cm. The injection point was considered to be the datum in the subsequent discussion and distances indicated are measured from this point. Each point indicated in Fig. 3 is the average DBCP concentration obtained from a 5 cm segment of the column and amount of chemical indicated was considered to be concentrated at the center of that

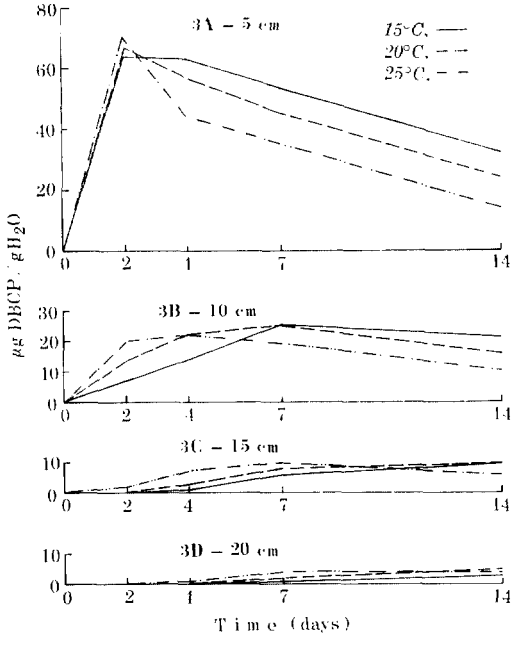

FIG. 3. The effect of time and temperature on the movement of DBCP in soil from the site of injection.

segment. Thus each point is 5 cm from the preceding and succeeding points.

These results, Fig. 3A–D, show that the rate of DBCP movement from the site of injection was proportional to the temperature. The concentration of chemical increased rapidly in the segments closest to the injection site, 5 and 10 cm segments. In the first 5 cm segment (Fig. 3A), the chemical reached a maximum concentration on day 2 and then fell rapidly to day 14. After the maximum concentration was attained, the 15 C and 25 C curves exchanged positions indicating that the movement of DBCP out of this segment was also proportional to the temperature.

In the 10 cm segment (Fig. 3B), the rate of DBCP increase was less than in the 5 cm segment. At 25 C the maximum concentration was attained on day 4 and then fell, crossing the other temperature curves

to the lowest level of the three temperatures studied. The 15 and 20 C columns reached maximums on day 7, although the 20 C curve approaches the maximum at a greater initial rate than the 15 C curve. After the maximum was reached by the 15 and 20 C columns there occurred a decrease in concentration with time. However, at 15 C the decrease did not occur as rapidly as at the higher temperatures.

In the 15 cm and 20 cm segments (Fig. 3C and 3D), the rate of concentration increase was relatively slow. The temperature effect can be seen in the 15 cm segments, however, a maximum is present only in the 25 C columns. At the other temperatures, the DBCP concentration increased to day 14 at this distance from the datum. The 20 cm segment showed a very slow increase in DBCP concentration to day 14. The presence of DBCP in this segment was not detected until day 4 and it remained at a low level until day 14.

In addition to showing the distribution of DBCP in the columns, these data (Fig. 3) also provided an indication of the mechanics of fumigant movement through soil. Consider a hypothetical model in which a continuous source of DBCP is delivered into a soil mass at a point. From this point, the DBCP diffuses outward into the soil mass. This model may consist of moist soil in a column. The application point is placed in the center of the column. At several intervals of time after the introduction of DBCP, the soil is sampled for chemical analysis at various distances from the site of application. From the data collected, a series of curves similar to Fig. 3 could be developed. We would expect the hypothetical curves to follow the initial pattern of Fig. 3A in the sampling site nearest the application site to the maximum and thereafter flatten out, maintaining a constant value. The next sampling site, more removed from the injection point would show a slower rate of concentration increase with time. Ultimately, this site would attain the same concentration of DBCP as the first. A third zone, more distant from the site of injection, would show the same pattern as the second, but the initial rate of concentration increase would be lower than the one preceding. Eventually, the entire mass of soil would reach a uniform level of DBCP content. The more distant the sampling site, the lower the initial rate of concentration increase to the maximum or steady state condition. The work of Hagan (1) supports this hypothesis. Although Hagan used carbon disulfide instead of DBCP, his data on the time required to attain a steady state with different column lengths are in accord with this hypothesis.

The data in Fig. 3 are also in accord with this hypothesis only for a limited period of time. Examination of Fig. 3A shows 3 zones. The first occurs between day 0 and day 2. During this time, the movement of DBCP from the site of injection into the 5 cm segment follows a pattern suggesting that the chemical was diffusing from a concentrated source in response to a partial pressure gradient. This is indicated by the high entry rate of DBCP into this segment. Zone 2 occurs between day 2 and 4 as indicated by the maximum. In this region, the partial pressure gradient has flattened as a result of DBCP depletion at the injection site and a concentration increase in the receiving segment. This gradient flattening is further indicated by the decrease in DBCP concentration between day 2 and 4, i.e., the rate of DBCP entry into the segment was lower than the rate of movement outward. From day 4 onward, zone 3, the rate of DBCP loss from the 5 cm segment appears to approach a constant value as indicated by the absence of any substantial changes in the slope of the curve.

Zones 1 and 3 can be observed in Fig. 3B

and 3C, while only zone 1 is to be seen in Fig. 3D. The absence of zone 2 in Fig. 3B and 3C is due to the absence of free DBCP at the site of injection by the time concentration maxima are reached. This is attributed to the limited quantity of chemical introduced into the system as compared with the hypothetical system in which the quantity of chemical was assumed to be very large.

In studies such as those reported here, the soil fumigant system never reaches a steady state. The DBCP molecules moving from the site of application outward into the soil mass will be found to exist in 4 states: liquid DBCP, vapor DBCP, as solute in soil water, and sorbed by the surface active soil fractions. DBCP in the liquid state will be found only at the point of application. In zone 1, DBCP will occur in all 4 states. The principal condition required for the existence of zone 1 is the presence of liquid DBCP. As a consequence of this there will be a large quantity of DBCP in the vapor phase. Entry into zone 2 is initiated at the time liquid DBCP disappears and the high vapor phase concentration begins to decrease. When the concentration of DBCP in the vapor phase approaches an equilibrium condition with dissolved and sorbed chemical, entry into zone 3 is indicated.

Throughout this process, DBCP has moved rapidly outward from the injection site in the vapor phase by diffusion. At the same time that the vapor dispersion process has been proceeding, some of the chemical has been entering the aqueous phase. Under the conditions described, and considering the data on the solution of DBCP in water (Figs. 1 and 2), it appears that the solution process can limit the rate of chemical movement. This factor is probably not important in zone 1 since the partial pressure gradient consideration will be dominant. However, the existence of relatively high concentrations of DBCP in the vapor phase, particularly in the region closest to the injection site, creates a partial pressure gradient with respect to the soil water. Consequently, in this region the quantity of DBCP dissolved will be proportional to the quantity of chemical present in the vapor phase. Unpublished data from this laboratory indicates that the quantity of DBCP sorbed under moist conditions by the surface active soil fraction is proportional to the quantity of chemical present in solution. Therefore, in the solution phase, as the DBCP dissolves, a fraction of the chemical is sorbed and effectively removed from solution. The process of solution from the vapor phase and the subsequent sorption will reduce the quantity of DBCP in the vapor phase. Although this may not be significant in limiting DBCP movement in zone 1, it may be of importance in limiting the chemical movement from this zone.

Zone 2 occurs only in Fig. 3A because its presence is predicated upon the rapid decrease in DBCP concentration in the vapor phase as the result of vaporization/solution/sorption of all of the liquid chemical at the injection site. Had there been a greater quantity of DBCP injected into the system, the curves of Fig. 3B might have demonstrated zone 2 characteristics. In support of this, the change in slope of the 20 C curves is not as abrupt as that observed for the 25 C curve between day 2 and 4. The significance of zone 2 in this study lies in the demonstration of the effect of temperature on the diffusion of DBCP from the site of application. This indicates that all of the liquid DBCP added to the system has vaporized, thereby lowering the partial pressure gradient and reducing the rate of diffusion.

Perhaps of more importance to the process of soil fumigation is the presence of the zone 3 portion of the curves. This is the area describing the amount of DBCP present

in the aqueous and sorbed phases after the initial turmoil within the system has subsided. It is within this zone, for exposure time considerations, that effective nematode control is dictated. The partial pressure of dissolved DBCP is substantially lower than that of the liquid chemical. Consequently, the concentration of DBCP vapor over the solution is lower than it is over pure liquid. Therefore, the rate of movement of chemical from one point to another within the soil system is retarded. For nematode control, this phenomenon is important for two reasons: i) the rate of toxicant loss from the system is reduced and ii) the effective concentration of toxicant remains longer in the soil. The volume of this region will be determined by the quantity of DBCP applied initially. In effect, the dissolved and sorbed DBCP slows the departure of the chemical from the system.

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