to the customary boiling and frying methods. After 10 minutes in an open pan held at 375° F. or 15 minutes in boiling water, no significant reduction of toxaphene levels was observed.

The data gathered here may have some value in estimating the hazard of other chlorinated organic pesticides to fresh water fish. Various studies of the relative toxicity of pesticides to seven species of fish (*2, 5*) have shown that toxaphene is approximately 1/10th as toxic as endrin, three times as toxic as dieldrin, and five times as toxic as DDT. On this basis it might be expected that fresh water lakes and streams would be nontoxic if they contained less than 100 parts per trillion of endrin, 3 p.p.b. of dieldrin, and 5 p.p.b. of DDT.

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SOIL FUMIGANT HYDROLYSIS

Hydrolysis of *cis*- and *trans*-1,3-Dichloropropene in Wet Soil

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***cis*- and *trans*-1,3-dichloropropene are hydrolyzed in wet soil to *cis*- and *trans*-3-chloroallyl alcohol, respectively. Solvolysis rates in the presence of massive amounts of soil are enhanced at most threefold as compared to the rates of solvolysis in water.**

Alkyl halides are widely employed as soil fumigants to combat the destructive action of plant parasitic nematodes and other soil organisms. Lack of knowledge of the fate of these substances in a soil matrix precludes serious considerations of their toxicity, mode of action, and residue analysis. As a part of our studies of the cleavage of carbon-halogen bonds by soil and soil organisms (*2*), we report the nonbiological hydrolysis of *cis*- and *trans*-1,3-dichloropropene in wet soil.

The disappearance of these dihalides from soil has recently been noted; however, no conversion products could be detected (*3*). The present findings portray the first step of what may be a series of biological and nonbiological transformations of these substances.

Experimental

Materials. Pure *cis* - (b.p. 101° C.) and *trans*-1,3-dichloropropene (b.p. 111° C.) were obtained by careful repeated fractionation of the commercial nematocide mixture, Telone, through a helices-packed column. The isomers were shown to be pure by gas chromatography on a 6-foot Dow Corning −710 column at 90°. The corresponding *cis*- and *trans*-3-chloroallyl alcohols were obtained from the pure chlorides by refluxing in 10% Na_2CO_3 (*4*). The *cis*- and *trans*-3-chloroallyl alcohols had boiling points of 143–44° (735 mm.) and 153–55° C. (760 mm.), respectively, upon fractionation through a spinning band column. Isomer purity was shown by gas chromatographic assay on a Carbowax 20M column at 190° C.

Soil from a lemon grove was employed in the present work because it had been found to contain organisms capable of dehalogenating other substrates. The results of this study, however, should be independent of the organismic content of a soil.

Methods. Chloride was determined by direct potentiometry employing a Ag–AgCl electrode and a calomel reference electrode (*6*). The working electrode was prepared by anodizing a clean spiral of silver wire in a solution of $1M$ KCl and $0.1M$ HCl with a current of 10^{-3} ampere for 12 hours. Direct pCl measurements were made with a Leeds & Northrup pH meter after the solution or suspension to be analyzed (usually 2 ml.) was diluted with an equal volume of a solution of $1.75M$ KNO_3 and $0.25M$ HNO_3 in order to maintain a high constant ionic strength (1.0) and proton concentrations. It was later found that this precaution was not necessary and samples were analyzed directly. The potentiometer was standardized daily at

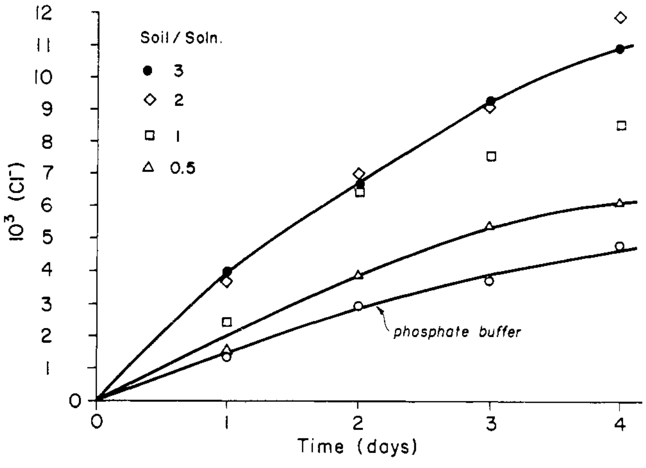


Figure 1. Rates of Cl^- release from $0.01M$ *cis*-1,3-dichloropropene in $0.1M$ phosphate buffer at pH 6.9 or 7.5 and rates in soil-solution ratios of 0.5, 1, 2, and 3

pCl = 6.5. This corresponded to a chloride concentration of $10^{-2}M$ in our system.

Under these conditions standards containing various amounts of soil gave reliable readings.

cis- and *trans-*1,3-dichloropropene and *cis-* and *trans-*3-chloroallyl alcohol were qualitatively monitored during a run by direct, flame ionization gas chromatography on a 5-foot 1/8-inch glass column of 5% diethylene glycol succinate on HMDS-treated Chromosorb W at 110°. Each dichloride isomer was examined separately. The respective emergence times were: *cis-*1,3-dichloropropene 0.5 minute, *trans-*1,3-dichloropropene 0.6 minute, *cis-*3-chloroallyl alcohol 1.3 minutes, and *trans-*3-chloroallyl alcohol 1.7 minutes. No peaks other than water and these materials were discernible.

Product Analyses. Ordinary rate runs for chloride release were carried out in bottles or in stationary beakers covered with aluminum foil. Typically, for product analysis, 300 cc. of soil were added to 1 liter of an aqueous solution of 1 × $10^{-2}M$ *trans-*1,3-dichloropropene. The flask was swirled occasionally. After 66 days the chloride ion concentration was 8.9 × $10^{-3}M$. A 500-ml. sample was withdrawn from the flask after 1 hour of mechanical shaking. The mixture was saturated with ammonium sulfate and extracted five times with ether. The ether extracts were dried over sodium sulfate. The ether was removed through a small Vigreux column and the residue was dissolved in 1 ml. of *n*-hexane.

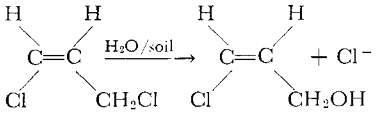
Gas chromatography of the hexane solution upon a 6-foot Dow Corning −710 column at 90° showed only one peak, which corresponded exactly with that of authentic *trans-*3-chloroallyl alcohol. The product substance was repeatedly trapped from 50-μl. injections. Its infrared spectrum was identical with that of authentic *trans-*3-chloroallyl alcohol. The amount of chloroallyl alcohol in the hexane solution was quantitated by the addition of authentic material. The over-all yield based upon chloride produced was 40%.

Under identical conditions *cis-*1,3-dichloropropene had hydrolyzed to the extent of 50% in 20 days. The product *cis-*3-chloroallyl alcohol was identified by gas chromatography and its infrared spectrum, both of which were identical with an authentic sample. The yield of alcohol was 40%.

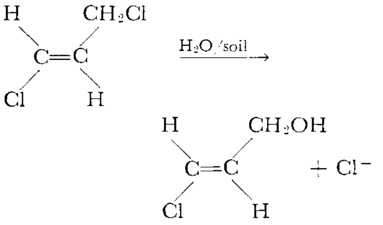
Results and Discussion

The rate of chloride release from a $10^{-2}M$ solution of *cis-*1,3-dichloropropene buffered at either 6.9 or 7.5 pH is depicted in the lower curve of Figure 1. The other points represent chloride release from $10^{-2}M$ solution of this halide when mixed with soil in the ratios: soil-solution of 0.5, 1, 2, and 3. Points represent an average of at least two independent runs. The maximum pH change during a run was from 7.5 to 7.7. Reproducibility in the soil water runs was within 10%. The points are also corrected for small blank readings of chloride in soil water mixtures of the same composition but without added dihalopropene. These amounted to, at most 0, 0.1 × 10^{-3}, and 0.2 × 10^{-3} after 1, 2, and 3 days, respectively. The rate of halide release is relatively insensitive to the amount of soil present. Thus from initial slopes the rate of hydrolysis of *cis-*1,3-dichloropropene at a soil-solution ratio of 0.5 is only 1.4 times that in the absence of soil. Moreover, a change from a ratio of 1 to 3 elicits no significant change in the kinetics. The mixtures of higher soil content enhance the rate to about the same extent and at best only threefold.

In accord with the kinetics, the only detectable organic products from either



(1)



(2)

cis- or *trans-*1,3-dichloropropene are the corresponding allylic alcohols (Equations 1 and 2). Neither the starting halides nor the alcohols were isomerized by these conditions. The yields of the alcohols determined were approximately 40% and we attribute the lack of a complete material balance to the difficulty of extracting the alcohols from soil-water mixtures.

Soil does not inhibit the normal solvolysis (*1*) of *cis-* or *trans-*1,3-dichloropropene and the biocidal properties of the chloroallyl alcohols must be considered when the dihalide fumigants are employed. It is significant that the chloroallyl alcohols are rather wide-range biocides (*5*). The fate of these alcohols in soil is under investigation.

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HERBICIDE COLORIMETRIC PROCEDURES

Evaluation of the Pyridine-Alkali Colorimetric Method for Determination of Atrazine

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The pyridine-alkali method for the determination of chloro-*s*-triazines and the reactions involved in color development have been reviewed by Burchfield and Schuldt (*2*), Gysin and Knüsli (*3*), Knüsli *et al.* (*5*), and Ragab (*7*). The mechanism of the reaction between pyridine and the chloro-*s*-triazines is probably similar to the mechanism described by Zincke (*10*) for the reaction between pyridine and 1-chloro-2,4-dinitrobenzene.

The first application of this reaction to the analysis of a 2-chloro-*s*-triazine herbicide (simazine) was by Ragab (*7*), who investigated several modifications of the pyridine-alkali reaction leading to conversion of the unstable yellow color to other more stable colors. Reaction of the yellow complex with ethyl cyanoacetate gave a red color showing maxi-