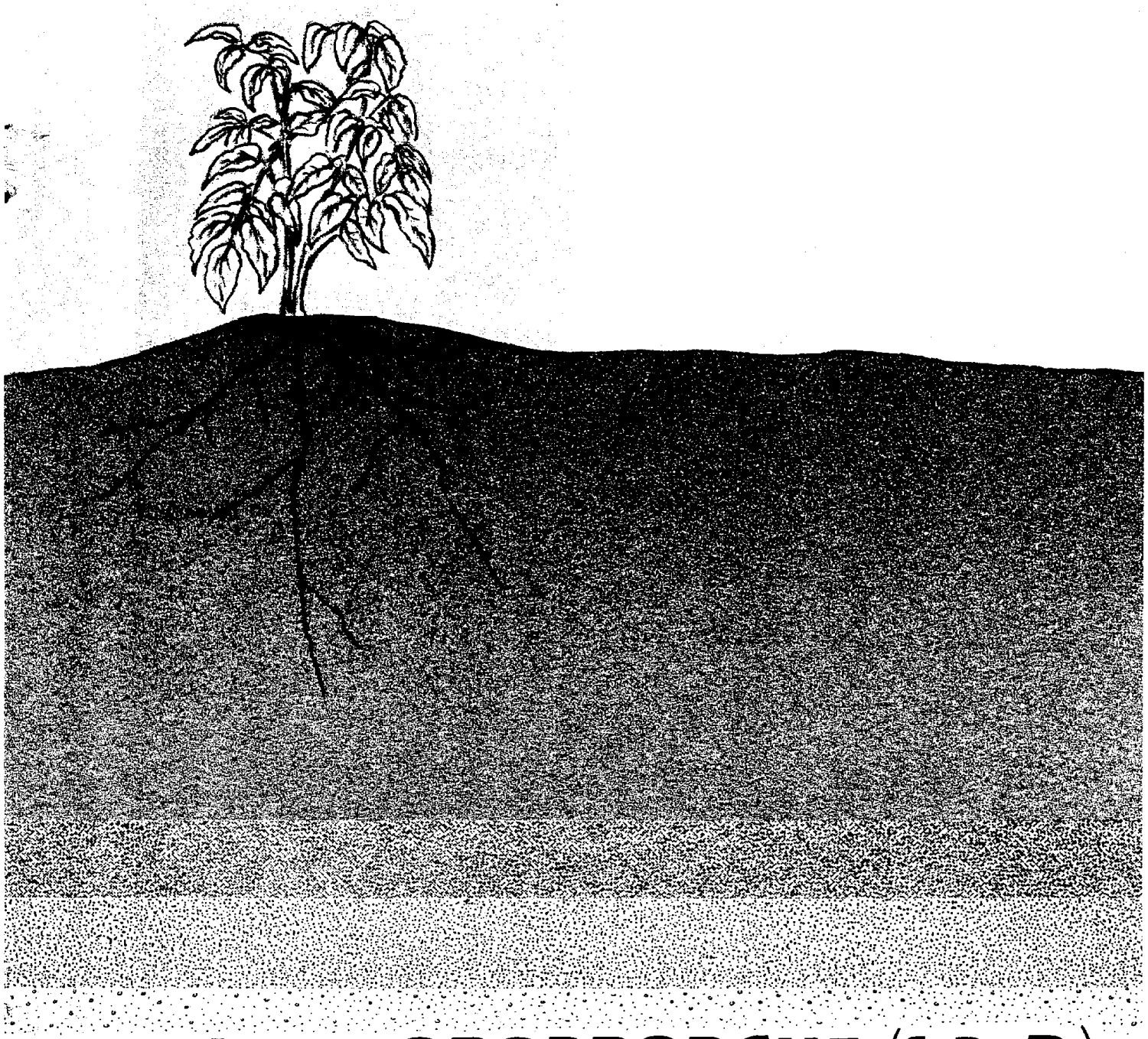
California State Water Resources Control Board
TOXIC SUBSTANCES CONTROL PROGRAM



1,2-DICHLOROPROPANE (1,2-D)
1,3-DICHLOROPROPENE (1,3-D)

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1,2-DICHLOROPROPANE (1,2-D)

1,3-DICHLOROPROPENE (1,3-D)

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PREFACE

This is the third in a series of reports issued by the State Water Resources Control Board (SWRCB) on agricultural and industrial chemicals. These reports deal with priority chemicals of concern to water quality and the protection of beneficial uses of water in California. On January 26, 1982, the State Board issued a Pesticide Guidance Document based on the premise that agricultural production and water quality protection can be compatible goals.

Chronic effects of persistent pesticides (e.g., impaired growth and reproduction) may be more devastating in the long run to the environment than immediately apparent acute effects. Preventive measures are invariably less costly to society than corrective actions required after toxic chemical pollution has occurred.

Some current practices may have an adverse impact on water quality. These activities can usually be modified to minimize adverse environmental effects. Where existing or potential water quality problems have been identified, the State Board will recommend appropriate measures to correct or prevent adverse impacts.

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LIST OF ABBREVIATIONS AND TERMINOLOGY

Agencies

Federal:

NIOSH	National Institute for Occupational Safety and Health
NTP	National Toxicology Program
U.S.D.H.H.S.	United States Department of Health and Human Services
U.S. EPA	United States Environmental Protection Agency

California:

ARB	Air Resources Board
DFA	Department of Food and Agriculture
DHS	Department of Health Services
DWR	Department of Water Resources
RWQCB	Regional Water Quality Control Board
SWRCB	State Water Resources Control Board

Units:

°C	Degrees Celsius
cc	Cubic Centimeter (milliliter)
Kg	Kilogram (1000 grams)
l	Liter (1000 milliliters)
lb	Pound
mg	Milligram (10^{-3} gram)
ml	Milliliter (10^{-3} liter)
mm Hg	Millimeters of Mercury
pH	Measure of Acidity
ppb	Part Per Billion
ppm	Part Per Million
ppt	Part Per Trillion
torr	Unit of Atmospheric Pressure Equivalent to Millimeters of Mercury
ug	Microgram (10^{-3} milligram)
ul	Microliter (10^{-3} milliliter)

Chemicals:

3-CAA	3-Chloroallyl alcohol
DBCP	1,2-Dibromo-3-Chloropropane
1,2-D	1,2-Dichloropropane
1,3-D	1,3-Dichloropropene
2,3-D	2,3-Dichloropropene
D-D	Soil fumigant (D-D Mixture)
ECH	Epichlorohydrin
EDB	1,2-Dibromoethane (Ethylene dibromide)
NBP	4-(p-Nitrobenzyl) pyridine

Miscellaneous:

ACGIH	American Conference of Government and Industrial Hygienists
ADI	Acceptable daily intake
C_3	Three bonded carbon atoms to which functional groups may be attached
cis	Designating an isomer with functional groups attached to the same side of a carbon-carbon double bond.
DNA	Deoxyribonucleic acid
EC_{50}	Effective concentration of a toxicant that severely affects normal function of 50 percent of a test population within a specified time.
EUP	Experimental use permit
FIFRA	Federal Insecticide, Fungicide and Rodenticide Act
GC MS	Gas Chromatography Mass Spectrometry
GLC	Gas-liquid chromatography
HSL	Hanford sandy loam
IPM	Integrated Pest Management
in vivo	Within the living organism
in vitro	An artificial environment outside the living organism
$K_{w/v}$	Henry's Law Constant (water phase:vapor phase)
$K_{om/v}$	Distribution coefficient (organic matter:vapor)
LC_{50}	Lethal concentration of a toxicant that kills 50 percent of a test population within a specified time
LD_{50}	Lethal dose of a toxicant that kills 50 percent of a test population within a specified time
MCL	Maximum contaminant level
NA	Not available
ND	Not detected
SNARL	Suggested no adverse response level
trans	Designating an isomer with functional groups attached to opposite sides of a carbon-carbon double bond.

1,2-DICHLOROPROPANE
1,3-DICHLOROPROPENE

SUMMARY

The State Water Resources Control Board (SWRCB) investigation of 1,2-dichloropropane (1,2-D) and 1,3-dichloropropene (1,3-D) was prompted by a concern about the long-term use of these soil fumigants: like DBCP (1,2-dibromo-3-chloropropane), the banned chemical they had replaced, 1,2-D and 1,3-D could contaminate ground waters in California. The major factors which led to selection of this chemical group include: (1) their chemical similarity to DBCP and possible persistence in soil of 1,2-D; (2) the recent dramatic increase in their reported use in California from four million pounds in 1977 to over 16 million pounds in 1981; (3) potential mobility in soil; and (4) potential mutagenicity and carcinogenicity.

This investigation is part of the priority chemical program which established a system of criteria to identify, to search out, locate and monitor for specific chemical pollutants of surface and ground waters. In the past the process of identifying pollutants was random or accidental: samples were taken for any number of chemicals; often one substance was found in the search for another. The State Water Resources Control Board's program instead set up a precise plan to examine, locate and monitor for 1,2-D and 1,3-D. Available technical literature was first reviewed for information on the use, environmental fate and toxicology of these chemicals. Areas were selected for monitoring that had historic and recent 1,2-D and 1,3-D use and soil conditions with a high potential for chemical migration to shallow ground water. Monitoring was then implemented to examine "worst case" situations which could lead to ground water contamination.

PROPERTIES AND USES

Short-chain chlorinated hydrocarbons, 1,2-D and 1,3-D are water soluble, highly volatile liquids widely used as chemical intermediates in industry, as components of paint removers, degreasing agents and dry cleaning fluids, and as soil fumigants to control nematodes. The major biologically active ingredient in soil fumigants is 1,3-D; 1,2-D is a manufacturing by-product.

D-D and Telone II are trade names of the two most widely used soil fumigants in California. D-D contains from 30 to 35 percent 1,2-D, from 50 to 60 percent 1,3-D and 5 to 20 percent other halogenated three-carbon compounds. Telone II contains less than 2 percent 1,2-D, about 92 percent 1,3-D and 6 percent other halogenated three-carbon compounds. Some fumigant formulations have contained small amounts of epichlorohydrin, a known animal carcinogen. Over the last 25 years, numerous soil fumigant formulations have been used in California. Until its ban in 1977, DBCP was the most heavily used. By 1981 the fumigants 1,2-D and 1,3-D were the second most heavily used pesticides in California, exceeded only by sulfur.

ENVIRONMENTAL FATE

Volatilization of 1,2-D and 1,3-D from soil and water and diffusion of the vapors are the most significant mechanisms for environmental dispersion and attenuation. Rapid transformation of 1,3-D can occur in soil as a result of hydrolysis. The primary hydrolysis product, 3-chloroallyl alcohol (3-CAA), does not appear to move rapidly in soils. This may be related to its ability to bind to some soils. Rapid biodegradation of 3-CAA in some soils has been reported.

Transformation and degradation of 1,2-D occurs by microbial action. The rate of biodegradation is primarily influenced by chemical concentration, the presence of appropriate microbial species and their population density in the soil. Diffusion of 1,2-D is rapid in porous sandy soils and movement is greater than for either 1,3-D or 3-CAA. Downward migration can increase 1,2-D persistence due to a reduction in microbial population with soil depth. Under these conditions 1,2-D migration to ground water is possible.

TOXICOLOGY

Very little information is available concerning acute and chronic toxicity of 1,2-D itself. Most literature references describe studies with formulations containing both 1,2-D and 1,3-D and often lack information on compound purity. Both 1,2-D and 1,3-D are moderately toxic to mammals and aquatic life, 1,3-D being more toxic than 1,2-D.

In Ames tests 1,2-D exhibits marginal mutagenic activity and 1,3-D strong mutagenic activity. A recent National Toxicology Program (NTP) draft report concluded that 1,2-D increased liver adenomas in mice; 1,3-D carcinogenicity data are currently under review by NTP. As with many other halogenated short-chain hydrocarbons, 1,2-D and 1,3-D are skin and eye irritants. Overexposure to vapors, particularly from 1,3-D, can lead to headache, nausea, pulmonary edema and, ultimately, death. In animal studies overexposure is typically characterized by eye irritation and severe injury to lungs, liver and kidneys.

CRITERIA AND STANDARDS

Toxicity to aquatic life occurs at concentrations of 244 ug/l (ppb) for 1,3-D and 3,040 ppb for 1,2-D according to the Environmental Protection Agency's (EPA) 1980 water quality criteria for dichloropropanes/dichloropropenes. The ambient water quality criterion for protection of human health from ingestion of 1,3-D in water and fish is 87 ppb. No criterion was set for 1,2-D due to insufficient data. The California Department of Health Services (DHS) and EPA, Office of Drinking Water, has set an informal SNARL (suggested no adverse response level) advisory of 10 ppb for 1,2-D in drinking water when the water is consumed for a period greater than ten days.

DETECTION OF 1,2-D and 1,3-D IN CALIFORNIA GROUND WATER

An increasing number of wells, sampled from Kern County in the south to Del Norte County in the north, have been shown to contain 1,2-D. Although it is a major component of the nematicides D-D and Telone II, 1,3-D was not detected in wells where 1,2-D was. Past monitoring programs had concentrated on 1,3-D and overlooked the need to analyze for the more persistent 1,2-D component, first detected in California well water in 1979. Seven (7) wells located near Occidental Chemical Company in Lathrop, San Joaquin County, were found to have residues of 1,2-D (between 0.2 to 5.0 ppb) that apparently were caused by manufacturing and storage processes at the factory. In subsequent sampling of these wells four (4) years later, 1,2-D was not found. The second reported finding of 1,2-D in California ground water occurred in 1982 in conjunction with EPA's National Ground Water Monitoring Program. Two (2) community wells in Visalia, Tulare County, were sampled and found to contain 1,2-D (2.9 and 25.9 ppb). Investigation of the sites suggested an industrial point source. The more highly contaminated well was shut down. Community well water in Reedley, Fresno County, was also found to be contaminated with approximately one (1) ppb of 1,2-D. The source was not identified.

The State Board Toxic Substances Control Program began its ground water sampling program in the spring of 1982. High use areas for D-D and Telone were identified from computer generated use data obtained from the University of California, Davis. Potable well water was sampled at homes in close proximity to field application sites. Wells located in areas with porous sandy soil and/or high water table (shallow wells) were sampled preferentially. All sampling and analysis were conducted according to standard EPA procedures.

San Joaquin, Fresno and Merced Counties were chosen for initial ground water sampling of private domestic wells based on high documented use of D-D and Telone in these regions. None of the 23 wells sampled in Fresno County had detectable levels of 1,2-D or 1,3-D. Of 37 wells sampled in Merced County, three (3) contained 1,2-D residue ranging from 0.4 to 0.9 ppb. No 1,3-D was detected in any of these samples. In San Joaquin County, nine (9) out of 35 domestic wells sampled (26 percent) had levels of 1,2-D ranging from 0.4 to 16 ppb. Two (2) wells had concentrations above the SNARL (suggested no adverse response level) of 10 ppb; the persons using them were advised by DHS to seek an alternate source of drinking water until the problem was resolved.

An attempt was made to determine whether agricultural use of fumigants containing 1,2-D was related to ground water contamination in this area. Soil core samples were collected at a field site with a documented history of 1,2-D and 1,3-D nematicide use. Soil core analysis identified 1,2-D from just below the surface to a depth of about 10 feet. Although not detected between 10 and 14 feet, 1,2-D was detected again between 15 and 24 feet. Sampling was discontinued at 24 feet because of water intrusion. The highest 1,2-D residue levels were detected within the first eight feet of the surface and ranged from 1.8 to 12.2 ppb. Between 15 and 24 feet, trace concentrations of 1,2-D ranging from 0.03 to 2.2 ppb were detected. Water at 24 feet contained 4.6 ppb of 1,2-D. 1,3-D was only detected within the top 6.5 feet of soil at trace levels (0.3 to 1.1 ppb).

This was the first field evidence showing that 1,2-D migrated through the soil. Evidence from the core study suggests agricultural use of fumigants as the source of this contamination.

In early 1983 1,2-D was discovered in Del Norte County well water in the community of Smith River. As of June 1, 1983, 68 percent (25 out of 37) of the wells sampled had detectable levels of 1,2-D, and five (5) of these were above the SNARL advisory limit of 10 ppb. The absence of any known industrial sources of 1,2-D in this area strongly suggests that the Smith River well water contamination is caused by application of soil fumigants containing 1,2-D. In an attempt to mitigate this problem, both DFA and the local County Agricultural Commissioner have followed the State Water Resources Control Board's recommendation to avoid further use of soil fumigants having unacceptably high levels of 1,2-D, that is more than 2 percent.

The highest concentrations of 1,2-D and 3-CAA in California were recently detected in monitoring wells at an abandoned pesticide storage site in Crescent City. Levels ranged as high as 1,200 ppb for 1,2-D and 1,410 ppb for cis- and trans-3-CAA. 1,3-D was not detected. This contamination is most likely due to improper storage and disposal of these materials.

More recent findings of 1,2-D include one (1) well in Sutter County (4.5 ppb) and 17 wells in Kern County near Bakersfield. At the latter site, concentrations of 0.1 to 7.9 ppb have been detected in both shallow and deep wells. Agricultural use of soil fumigants is the suspected source of this contamination also.

In summary the finding of 1,2-D in over 60 California wells appears to be associated primarily with agricultural use of 1,2-D and 1,3-D type nematicides. Agricultural areas where ground water contamination occurred are typically characterized by porous soil and/or shallow unconfined ground water. Soil core analysis at one (1) contaminated site in San Joaquin County has shown that 1,2-D can travel through soil to depths of at least 24 feet.

RECOMMENDATIONS

After weighing the evidence concerning 1,2-D and 1,3-D, several important facts stand out:

1. Initial surveys have discovered 1,2-D in California ground water in an increasing number of shallow and deep wells in eight (8) counties from Kern County in the south to Del Norte County in the north.

2. None of the sites sampled contained detectable concentrations of 1,3-D.

3. Most of the 1,2-D findings appear to be related to agricultural use of nematicides rather than from point source (e.g., industrial) discharge.

4. A recent National Toxicology Program draft report indicates that 1,2-D causes an increase in liver adenomas in mice and chromosomal aberrations in Chinese hamster ovary cells.

5. Repeated exposure to 1,2-D causes liver and kidney damage in experimental animals.

6. The 1,2-D component is much less effective than 1,3-D as a soil nematicide and, therefore, is not essential.

Because of these findings and because of the difficulty and the prohibitive cost of rehabilitating these aquifers once they are contaminated, every effort should be made to prevent further contamination of ground water by 1,2-D in California. To accomplish this objective, the following actions are recommended to the appropriate state and federal agencies:

California Department of Food and Agriculture (DFA)

1. Reevaluate registration and use conditions for nematicides containing 1,2-D, whether as a major contaminant or active ingredient, in accordance with California Administrative Code, Title 3, Chapter 4, Subchapter 1, Group 2, Section 2367.

2. Request that EPA and registrants of products containing 1,2-D take immediate action to reduce the 1,2-D content of all registered soil treatment products to the lowest practical level (i.e., less than two percent as an initial goal).

3. Notify county agricultural commissioners that permits should not be issued for restricted materials:

   a. Having unacceptably high levels of 1,2-D; and

   b. In areas having a high potential for ground water contamination (e.g., areas with sandy soils and shallow unconfined aquifiers). County agricultural commissioners should consult with Regional Water Quality Control Boards for information concerning locations where the risk of ground water contamination is high.

4. Accelerate research on alternative methods, including Integrated Pest Management, to control soil-borne parasites, for example, by breeding nematode resistant plants. Use of nematicides for "insurance" purposes should be discouraged.

5. Improve the DFA Pesticide Use Report system so that:

   a. Data for both major components (1,2-D and 1,3-D) of fumigant pesticides are separately and accurately listed in the DFA Pesticide Use Reports.

   b. Information on time, place and rate of both 1,2-D and 1,3-D application is stored in the computer data base to allow easy generation of:

      (1) County maps of application sites, and

      (2) Monthly use figures.

   c. Sales data supplied by registrants can be used to validate user-supplied data in Pesticide Use Reports.

National Toxicology Program (NTP)

1. Accelerate issuance of final report on 1,2-D carcinogenicity studies.
2. Accelerate issuance of final report on 1,3-D carcinogenicity studies.

3. Conduct reproductive and teratogenic studies on 1,2-D.

U.S. Environmental Protection Agency (EPA)

1. Accelerate cancer risk assessment for 1,2-D in drinking water.

2. Develop maximum contaminant levels (MCL) for 1,2-D in drinking water based on present knowledge of 1,2-D toxic effects.

3. Accelerate issuance of toxicology data for 1,3-D transformation products, specifically 3-CAA.

4. Revise label description for all soil fumigants to include:

   a. Identification of active and "inert" toxic ingredients; and

   b. Carcinogenicity and other chronic toxicity information for all ingredients whether active or inert.

State Water Resources Control Board (SWRCB)

1. Adopt maximum contaminant levels as ambient water quality objectives for ground water.

2. Coordinate with Regional Boards to delineate critical ground water protection areas within agricultural regions.

Regional Water Quality Control Boards (RWQCB)

1. Incorporate SWRCB ambient water quality objectives into RWQCB basin plans.
2. Continue compliance inspections of possible point sources (non-agricultural uses) of 1,2-D.

California Department of Health Services (DHS)

1. Develop drinking water maximum contaminant level based on present knowledge of 1,2-D toxic effects.

2. Develop criteria for locating of domestic wells in:

   a. Areas with existing ground water contamination; and

   b. Areas where ground water may reach the cultivation zone. This should be done in cooperation with Department of Water Resources, county health departments, and Regional Water Quality Control Boards.

3. Implement statewide monitoring program for large and small community water systems to determine the source and extent of 1,2-D ground water contamination.

4. Sponsor legislation that would give DHS authority to monitor private, individual wells where the risk of ground water contamination is high and which are not now monitored by state or local agencies.

Air Resources Board (ARB)

Include 1,2-D and 1,3-D in air quality investigations.

Department of Water Resources (DWR)

Sponsor legislation that would require mandatory statewide application of DWR criteria for (a) preparation of accurate and retrievable well logs; and (b) closure and abandonment of wells.

University of California (UC)

Support research to reduce environmental losses of 1,3-D and 1,2-D, thereby reducing application rates.

I. INTRODUCTION

Soil-borne, plant parasitic nematodes are a major agricultural pest. These organisms, often microscopic in size, proliferate in warm, porous, sandy soils typical of many agricultural regions of California. Large populations of these organisms can destroy developing root systems, restrict plant vigor and reduce crop yields. For some crops, losses in yield can exceed 50 percent in the absence of proper control measures.

A major nematicide prior to registration suspension in 1977, 1,2-dibromo-3-chloropropane (DBCP), was banned not only because it proved to be a potent carcinogen and human sterilant but also because it had entered ground waters. This regulatory decision imposed a severe hardship on agriculture. DBCP was the only nematicide registered for general use in post-plant treatment, providing protection for perennial crops. At the present time, Aldicarb is the only chemical fully registered for post-plant use on selected crops. Since DBCP was banned, the use of other registered nematicides has increased significantly. These control agents include fumigants such as D-D, Telone II, methyl bromide, chloropicrin, EDB and formulated products such as Nemacur, aldicarb, oxamyl, Mocap and Dasanit. Several of these chemicals are under study to determine their efficacy in post-plant use.

Agriculture depends upon these chemicals for nematode control. Characteristics which make soil fumigants and other nematicides effective, however, are the same characteristics which make them possible contaminants of ground water. These characteristics include the ability to diffuse rapidly through the soil profile and to remain stable for extended periods of time.

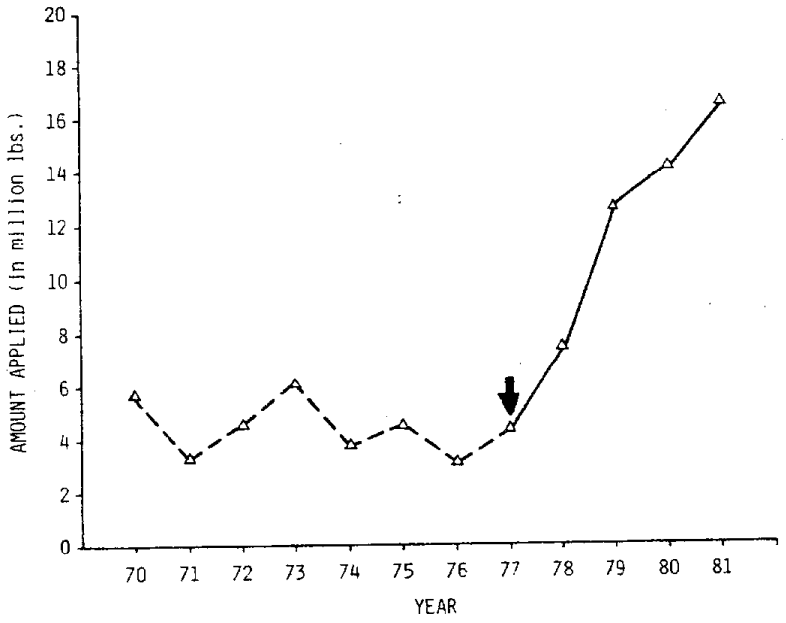
Ground water comprises approximately 95 percent of the United State's fresh-water supply (Josephson, 1980). About 50 percent of the U.S. population is dependent upon ground water for drinking. Thirty to thirty-five percent of California's population consumes ground water (McPherson, 1983). Initial findings of DBCP in California ground water destroyed a long held assumption that soil will prevent pollution of ground water by organic substances. Ground water is exceedingly difficult, if not impossible, to clean up after contamination. Prevention is the key to assuring continued beneficial use of this major resource.

Ground water pollution is emerging as a problem of major proportions. Both agricultural and industrial chemicals have been found in ground water throughout the nation. A ground water contamination study in New Jersey suggests that ground water in that state is at least as contaminated as surface water (Page, 1981). In California localized monitoring by several agencies has shown ground water contamination by several synthetic organics, including haloforms, chlorinated ethanes, ethenes, propanes and propenes, as well as by agricultural chemicals such as DBCP, EDB, simazine and carbofuran. Transport of these pollutants to shallow aquifers can occur (1) directly through wells; (2) by downward migration through the zone of aeration; (3) by induced recharge from surface water bodies; and (4) by inter-aquifer flow (Everett, 1980).

Of all the nematicides mentioned above, the compounds with the most dramatic increase in use since 1977 have been fumigants containing 1,2-dichloropropane (1,2-D) and cis- and trans-1,3-dichloropropene (cis-and trans-1,3-D) (Figure I-1). These are major components of D-D and Telone II. The historical marketing chronology of the major products with 1,2-D and 1,3-D as active ingredients is given in Table I-1. Presently marketed products are D-D and Telone II produced by Shell and Dow Chemical Companies, respectively. Today, over 54 products (listed in Appendix I) containing 1,2-D and 1,3-D are registered for use in California. In 1981 over 16 million pounds of 1,2-D and 1,3-D in 54 products were applied to California soils.

Figure I-1

ANNUAL USE OF 1,2-DICHLOROPROPANE AND
1,3-DICHLOROPROPENE FUMIGANTS IN CALIFORNIA,
1970 TO 1981



⬇ In 1977 DBCP pesticide registration was suspended. In 1978 fumigants with 1,2-D and 1,3-D were classified as restricted pesticides. These are required to be applied only by licensed pest control operators and their use reported to CDFA. Prior to 1978 the use of the fumigants 1,2-D and 1,3-D was not required to be reported except that applied by licensed operators who must report all applications.

Table I-1

HISTORY OF 1,2-DICHLOROPROPANE AND 1,3-DICHLOROPROPENE MARKETED PRODUCTS

Year Marketed	Product Name	Manufacturer	% Active Ingredients (when known)
1943	Dowfume N	Dow Chemical Co.	1,2-D:1,3-D (50:50) and related chlorinated C_3 hydrocarbons (Stark, 1944)
1944	D-D	Shell Chemical Co.	30-35% 1,2-D; 60-66% 1,3-D 5% chlorinated C_3 hydrocarbons including one or more of the following: 3,3-Dichloropropene 2,3-Dichloropropene 1,2-Dichloropropene 2,2-Dichloropropane 1,2,3-Trichloropropane epichlorohydrin allyl chloride (U. S. EPA, 1980c)
Early 1950s	Telone	Dow Chemical Co.	16% 1,2-D; 85-93% 1,3-D and related chlorinated C_3 hydrocarbons (McKenry and Thomason, 1974)
Early 1950s	Vidden D	Dow Chemical Co.	25% 1,2-D; 50-70% 1,3-D and related chlorinated C_3 hydrocarbons (Omelia, 1983)
1977	Telone II	Dow Chemical Co.	92% 1,3-D; 8% inert ingredients (inerts are defined as confidential but include <2% 1,2-D) (Omelia, 1983)

II. PROPERTIES AND USES

The physical and chemical properties of 1,2-D and cis- and trans-1,3-D regulate their mobility in soils and control of target organisms. The significance of these properties and the uses of these chemicals by industry and agriculture are discussed below.

Physical and Chemical Properties

The 1,2-D and cis- and trans-1,3-D type nematicides are highly volatile and colorless or straw-colored liquids at room temperature (Sax, 1979). Their odor has been described as 'chloroform-like' (Hawley, 1977; Hayes, 1982). Their volatility is exceeded only by methyl bromide when properties of the more common soil fumigants are compared (Table II-1). Relatively high water solubility (0.27 percent) is another significant factor common to these fumigants when compared to other pesticides. Often, to be effective, these chemicals must penetrate an envelope of water to reach the target organism. The volatility and water solubility of a chemical are factors which effect its Henry's Law Constant ($K_{w/v}$), the ratio of chemical concentration in water phase to chemical concentration in vapor phase under static conditions. A Henry's Law Constant of 11 for 1,2-D, for instance, indicates the aqueous concentration will be 11 times the vapor phase concentration. Conditions may exist in soils where movement of the vapor phase by gaseous diffusion results in continuous volatilization from the water phase. This effectively disperses the fumigant through the soil profile. The soil fraction will also affect this process by competitive partitioning (sorption) of the chemical between the soil: water: vapor phases.

Temperature significantly influences $K_{w/v}$, as shown in Figure II-1. Chemical concentration in the water phase increases dramatically with temperature decreases, and thus limits the vapor diffusion rate in soil.

Structural formulas and other available physical and chemical information for 1,2-D, cis- and trans-1,3-D, and cis- and trans-3-chloroallyl alcohol (cis- and trans-3-CAA, the primary hydrolysis products of cis-and trans-1,3-D) are given in Table II-2. Other partitioning constants such as $K_{om/v}$ (the ratio of chemical concentration in organic matter to concentration in vapor phase) have been included where available. In many prime California agricultural areas, $K_{om/v}$ will have limited significance because these soils contain much less than 1 percent organic matter.

Use Patterns

Since 1980 the 1,2-D and 1,3-D type fumigants have been exceeded only by sulfur in the total pounds applied in California.

Annual California use of 1,2-D and 1,3-D type fumigants is shown in Figure I-1. As noted in this figure (footnote), pesticide use through 1977 was required to be reported only by licensed pesticide applicators. Data are, therefore, underestimates of actual amounts used. The only comparable U.S. use data available for this period are for 1975; approximately 35 million pounds were used nationwide in this year, approximately 10 times California use alone (Stanford Research Institute, 1975).

California use data through 1977 distinguish between D-D and Telone and are presented in Figure II-2; use data from 1978 and following years do not. The fumigants are reported in three categories: D-D mixture; Dichloropropene; and 1,2-Dichloropropane, 1,3-Dichloropropene and related C_3 Hydrocarbons. As shown in Appendix I, Telone products are entered in all three categories.

The major California agricultural uses of 1,2-D and 1,3-D type fumigants from 1970 to 1981 are given in Table II-3; all uses are for pre-plant soil treatment. Application rates for open land and certain crops (Table II-4) range from 75 to 2,500 pounds per acre. An Experimental Use Permit (EUP) has been issued recently by the California Department of Food and Agriculture (CDFA) for post-plant soil treatment of vineyards with Telone II.

The 1,2-D and 1,3-D type fumigants are applied to soil by chisel (or shank) injection, usually in split application (two depths) with the majority of the fumigant injected at the lower depth. Rollerpacking is recommended immediately following injection to seal the soil surface. Product label instructions for Telone II and D-D are given in Appendix II.

Seasonal use of these fumigants depends upon local farming practices, crop and weather patterns. As shown in Figures II-3 and II-4, some counties (e.g., San Joaquin) apply this fumigant in discrete seasons, whereas others (e.g., Monterey) may apply these chemicals throughout the year. Histogram figures for each county show the overall increased use of these chemicals since the 1977 DBCP registration suspension.

The principal industrial uses of 1,2-D and 1,3-D are for oil and fat solvents and in dry cleaning and degreasing processes (Windholz, 1976). According to Fishbein (1979), U. S. production of 1,2-D was 145.1 million pounds in 1974 and 84.2 million pounds in 1975; information on 1,2-D imports to the U. S. is not available. Some industrial uses of 1,2-D described in the literature are listed in Table II-5.

Figure II-1

EFFECT OF TEMPERATURE ON HENRY'S LAW CONSTANT
OF 1,2-DICHLOROPROPANE AND 1,3-DICHLOROPROPENE
(Modified from McKenry and Thomason, 1974)

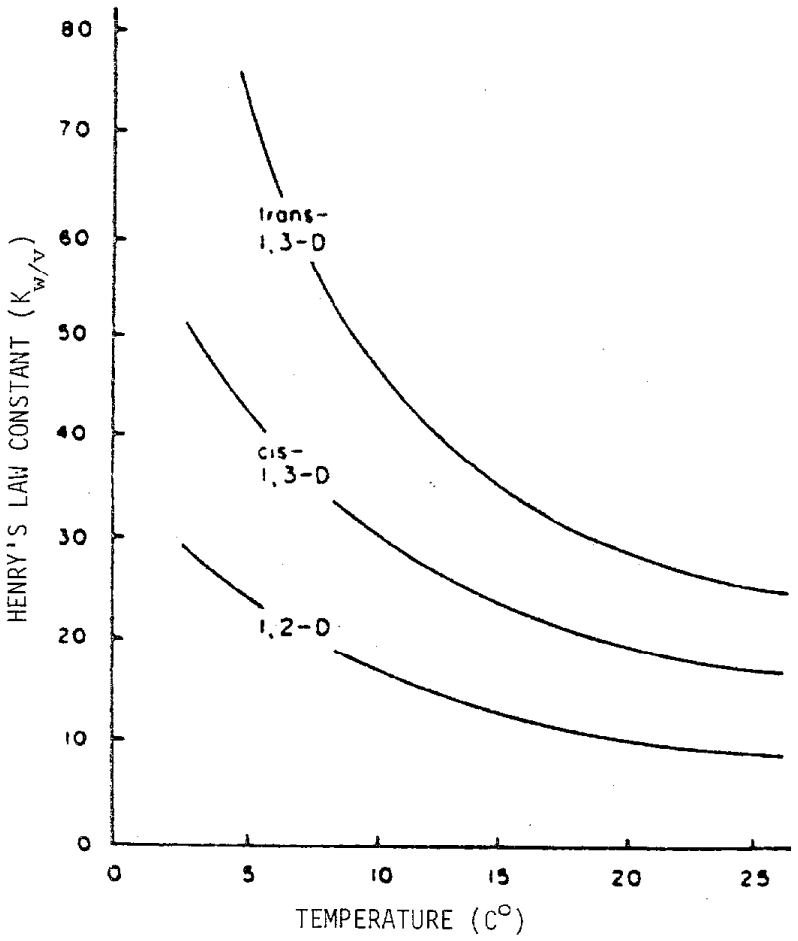
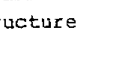


Table II-1
SOIL FUMIGANT PROPERTIES

FUMIGANT	VAPOR PRESSURE (MM HG) (20°C)	WATER SOLUBILITY (MG/L) (20°C)	HENRY'S LAW CONSTANT W/V
1,2-DICHLOROPROPANE 1,3-DICHLOROPROPENE (CIS-/TRANS-)	42 25/18	2700 2700/2800	11 18/25
METHYL BROMIDE	1380	16000	4
EDB	7.7	3370	43
DBCP	0.6	1230	164
CHLOROPICRIN	20	1950	10.8
METHYL ISOTHIOCYANATE	21	7600	88

Table II-2

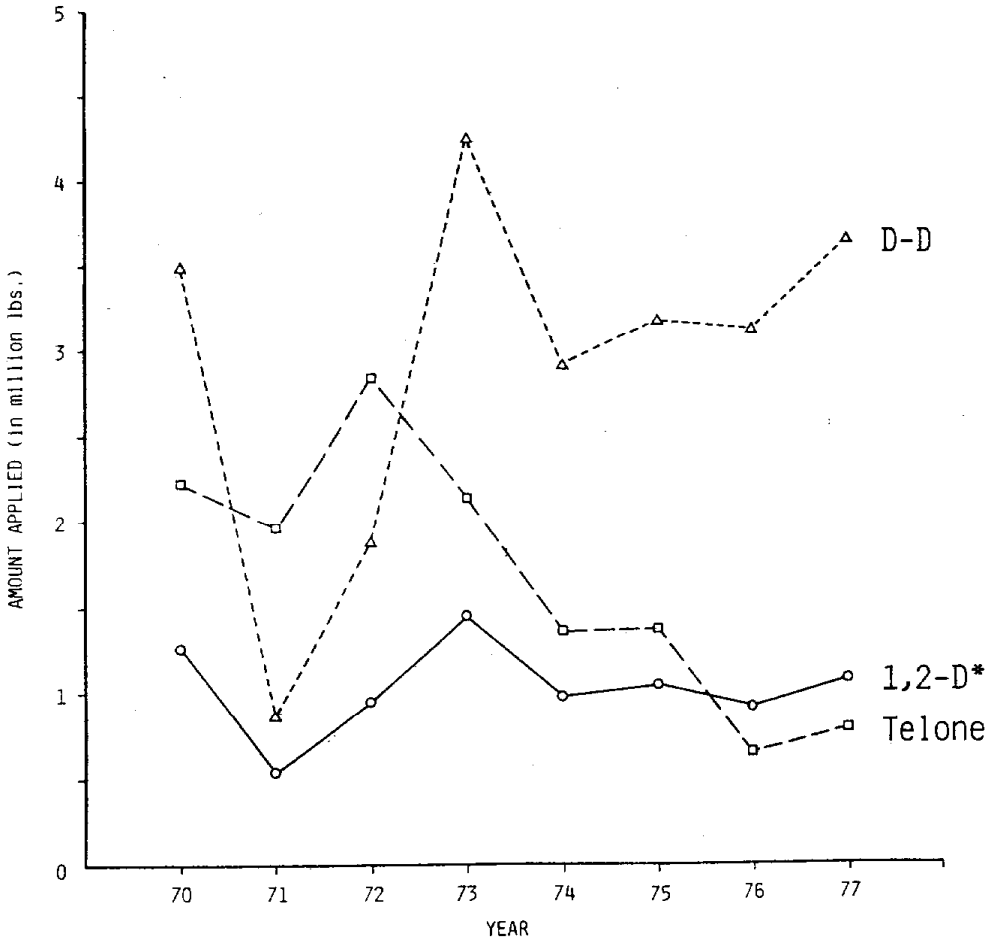
PHYSICAL AND CHEMICAL PROPERTIES OF
1,2-DICHLOROPROPANE, 1,3-DICHLOROPROPENE AND 3-CHLOROALLYL ALCOHOL

PROPERTY	CHEMICAL FORM				
	1,2-D	1,3-D		3-CAA	
		cis-	trans-	cis-	trans-
Structure					
Molecular weight	112.99	110.97	110.97	92.53	92.53
Boiling point (C^{o})	96.8	104	112	144	154
Solubility in water (mg/l)	2700	2700 760 mmHg	2800 760 mmHg	175,000	
Vapor pressure (mmHg at 20°C)	42	25	18	204	1.9
Henry's Law Constants (20°C) $Kw/_{v}$ (water/vapor) (see Figure II-1)	11	18	26	14,400 (ppm) by calculation	
$Kom/_{v}$ (organic matter/vapor)	118	240	420		
$Ks/_{v}$ (soil/vapor)		14	24		
Log P (octanol/ water partition coefficient)	2.28	1.98 (mixture of isomers)		.57 (mixture of isomers)	

(From Verschueren, 1977; Weast et al., 1977; Berry et al., 1980; Laskowski, 1983; Van Dijk, 1980; Dilling, 1977; Leistra, 1972; EPA, 1979; Berry, 1973.)

Figure II-2

ESTIMATED AMOUNTS OF D-D, 1,2-D AND TELONE
USED IN CALIFORNIA FROM 1970 TO 1977
(McKenry and Thomason, 1974)



* 1,2-D amounts are estimates based on 16% 1,2-D in Telone and 26% 1,2-D in D-D.

Table II-3

MAJOR USE OF 1,2-DICHLOROPROPANE AND
1,3-DICHLOROPROPENE FUMIGANTS IN CALIFORNIA
(DFA, 1970-1981)

COMMODITY/USE	CUMULATIVE TOTAL POUNDS ($\times 10^3$)	PERCENT OF TOTAL APPLIED
Tomatoes	10,125	11.5
Sugar beets	9,570	10.9
Fallow farm land*	8,365	9.5
Grapes	7,939	9.0
Cotton	4,942	5.6
Open land*	4,523	5.1
Broccoli	3,785	4.3
Sweet potato	3,884	4.4
Lettuce (head)	2,855	3.3
Non-ag. areas	2,753	3.1
Carrots	2,690	3.1
Potato	2,679	3.1
Other	23,715	27.1
TOTAL	87,825	100

*The selection of these categories may be based on an arbitrary decision by the pesticide applicator.

Table II-4

1,2-DICHLOROPROPANE AND 1,3-DICHLOROPROPENE APPLICATION RATES FOR FIVE CALIFORNIA AGRICULTURAL USES

TOP FIVE USES	APPLICATION RATE (Pounds/Acre*)
Open land	75 - 2500
Root vegetables	250 - 300
Grapes	400 - 2500
Cotton	75 - 600
Tomato	75 - 600

* Application rates are defined by the product label. Product density approximates 10 pounds per gallon.

Table II-5

SOME INDUSTRIAL USES OF 1,2-DICHLOROPROPANE (Souther, 1982)

Cellulose plastic products	Organic chemical synthesis
Dry cleaning	Rubber making
Fat processing	Wax making
Fumigation	Metal degreasing
Gum processing	Oil processing
Solvent systems	Scouring compound synthesis

Figure II-3

D-D AND TELONE USE IN SAN JOAQUIN COUNTY

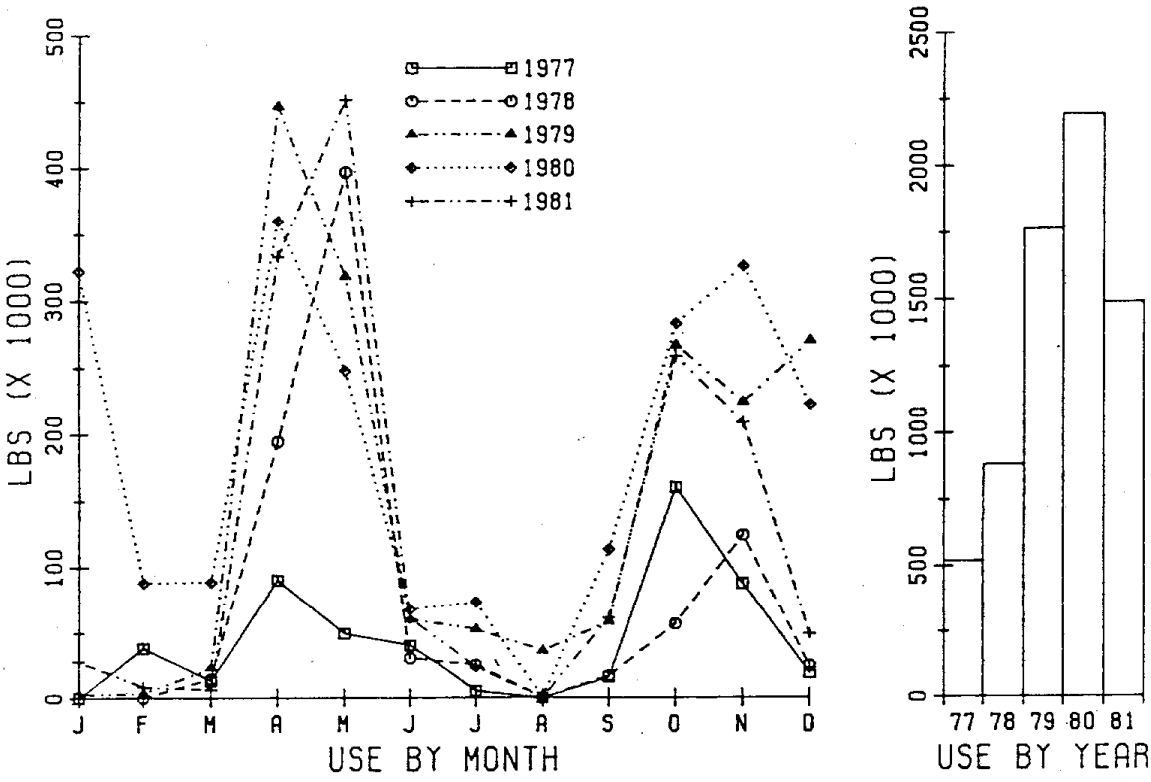
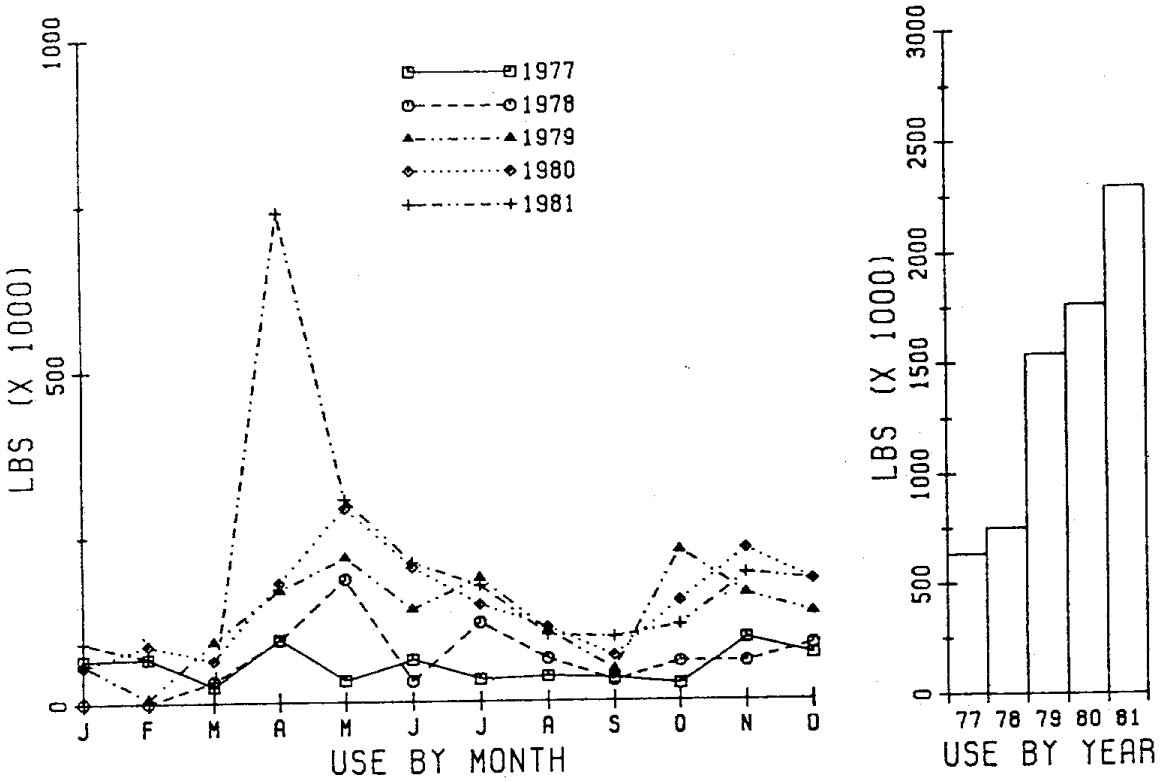


Figure II-4

D-D AND TELONE USE IN MONTEREY COUNTY



III. ENVIRONMENTAL FATE

INTRODUCTION

Initial laboratory studies evaluating the environmental fate of DBCP indicated that DBCP would not leach readily to ground water from soil, and that it would subsequently be degraded by soil microorganisms (Goring, 1967). Today field monitoring has shown that DBCP can migrate to ground water: DBCP is being found in hundreds of California wells five years after its registration and use were cancelled. Although modern laboratory methods used to study leaching and transformation have been greatly improved, the environmental fate of chemicals is best determined in the field. Soil migration studies should be conducted under "worst case" conditions (high pesticide use, porous soil, unconfined aquifer) to determine migration potential.

The stability and mobility of 1,2-D and 1,3-D in air, soil and ground water are influenced by several processes as shown in Figure III-1. The role of each of these is discussed in this chapter.

PERSISTENCE IN SOIL

Cis-1,3-D, 1,2-D and trans-1,3-D appear to behave independently of each other in soil (McKenry and Thomason, 1974). Environmental transformation of these compounds is by microbial action, with the exception of the initial hydrolysis of cis- and trans-1,3-D to cis- and trans-3-chloroallyl alcohol (3-CAA). Pathways for transformation of 1,2-D and 1,3-D are shown in Figure III-2. Persistence of these compounds is primarily influenced by: (1) chemical transformation, (2) volatilization, (3) microbial transformation, (4) photochemical transformation, and (5) organism uptake.

Chemical Transformation

Little to no chemical transformation of 1,2-D has been observed in laboratory and field studies. In laboratory studies more than 98 percent of 1,2-D applied to a sandy loam soil (closed system) was recovered 12 weeks after treatment (Roberts and Stoydin, 1976). Under outdoor conditions 1,2-D did not undergo degradation and more than 99 percent was lost from soil in an open container 10 days after 1,2-D treatment.

Cis- and trans-1,3-D can be transformed rapidly in soil by hydrolysis [hydrolysis of an organic compound results with the introduction of a hydroxyl group (-OH) into the chemical structure, commonly with the loss of another group (in this case, -Cl)]. Hydrolysis rates for 1,3-D range from less than one (1) percent per day (Williams, 1968) to 3.4 percent per day (Castro and Belser, 1966). Further transformation of the resulting cis- and trans-3-CAA (Figure III-2) is thought to occur by microbial action (Van Dijk, 1974).

Hydrolysis rates for 1,3-D in soil are influenced most by temperature and moisture content. Field (McKenry and Thomason, 1974) and laboratory (Van Dijk, 1974; Castro and Belser, 1966) data show significant hydrolysis of 1,3-D to occur only at higher temperatures (15 to 25°C). Simulated field studies conducted at 5°C show similar concentrations of 1,2-D and 1,3-D in soil vapor phase 10 to 18 days after fumigant application (Figure III-3) (McKenry and Thomason, 1974). These concentrations are the result of vapor phase diffusion. There is no evidence of chemical transformation of 1,3-D at this low temperature. At 25°C concentrations of 1,3-D isomers in the vapor phase decreased with time (Figure III-3). Part of this decrease results from a higher rate of

Figure III-1

ENVIRONMENTAL FATE OF 1,2-DICHLOROPROPANE
AND 1,3-DICHLOROPROPENE SOIL FUMIGANTS

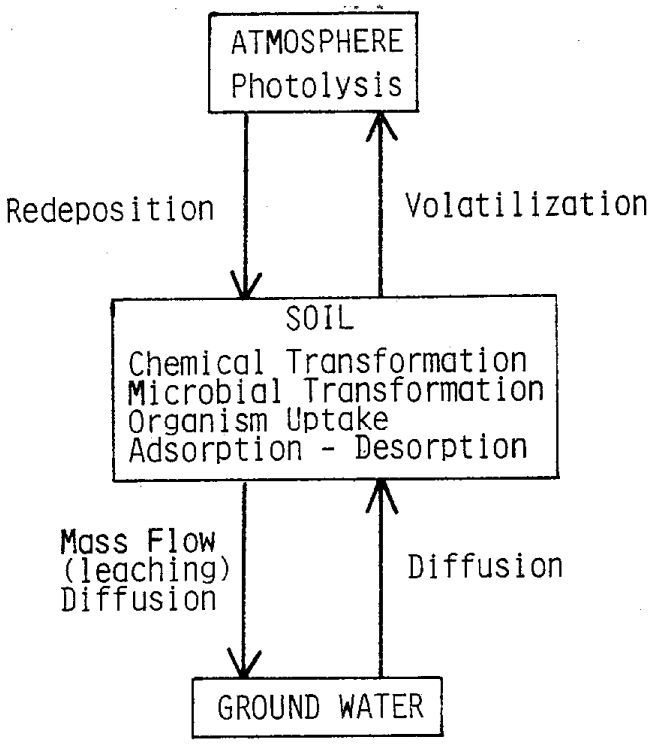
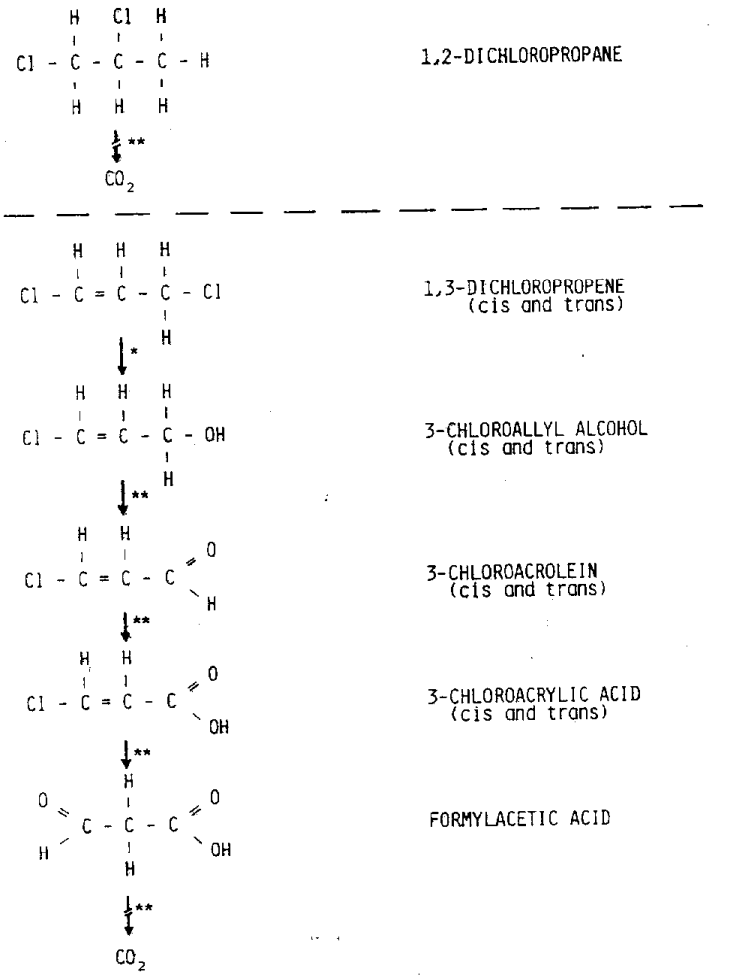


Figure III-2

ENVIRONMENTAL TRANSFORMATION PATHWAYS FOR
1,2-DICHLOROPROPANE AND 1,3-DICHLOROPROPENE



* HYDROLYSIS

** MICROBIAL ACTION

Figure III-3

EFFECT OF TEMPERATURE ON CONCENTRATIONS OF
MAJOR COMPONENTS OF TELONE IN SOIL VAPOR PHASE
(McKenry and Thomason, 1974)

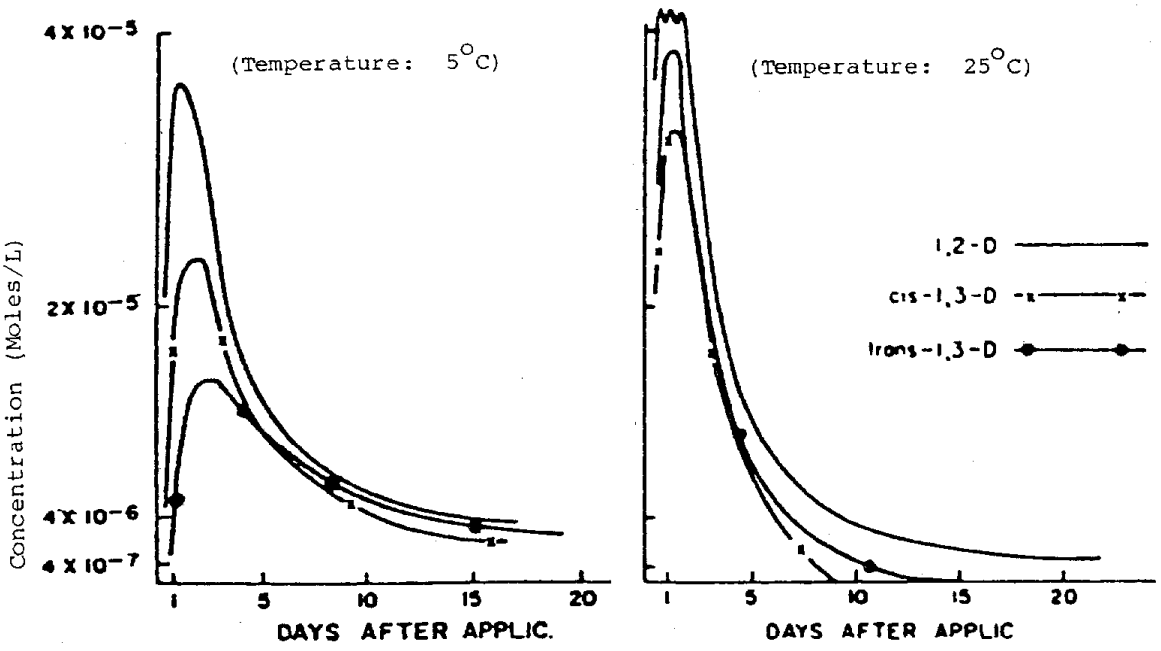
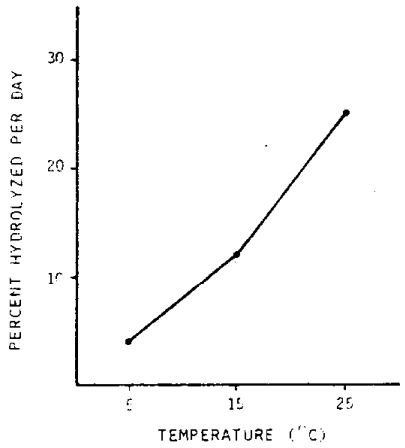


Figure III-4
EFFECT OF TEMPERATURE ON HYDROLYSIS RATE OF
1,3-DICHLOROPROPENE (SORBED PHASE) IN SOIL



diffusion at 25°C, as indicated by the lowered 1,2-D soil vapor concentration. Most of the reduction in 1,3-D concentration is the result of hydrolysis. The overall rates of hydrolysis for 1,3-D in the sorbed phase in two soils (soil descriptions are given in Appendix III) were measured from 0.3 to 15.0 bars of soil-moisture tension. The rate of 1,3-D hydrolysis increased significantly with an increase in temperature as shown in Figure III-4 (McKenry and Thomason, 1974).

Hydrolysis of 1,3-D occurs at a faster rate in dry soils (Vanachter and Van Assche, 1970; McKenry and Thomason, 1974). Chemical sorption rate increases slightly as the film of water surrounding the soil particle decreases, thus limiting hydrolysis unless the reaction is catalyzed by the soil surface. Water film thickness also decreases with increases in soil particle size. Hydrolysis rates for 1,3-D have been shown to increase as particle sizes become larger (McKenry and Thomason, 1974).

Hydrolysis rates will also vary with soil types due to differences in diffusion rate and sorption capacity. Other influential factors include the physical characteristics of the adsorbent surface, surface acidity, the nature and availability of catalytic sites, soil pH, and redox potential (Bailey, et al., 1974). However, no consistent correlation has been observed between the rate of 1,3-D hydrolysis and soil organic matter, clay content or pH (Van Dijk, 1974).

In laboratory studies hydrolysis rates have been measured in soil slurries and buffer solution. Castro and Belser (1966) applied high concentrations (10^{-2} M) of 1,3-D to very wet soil (slurries), and observed a hydrolysis rate of 3.4 percent per day. This dissipation rate does not correlate with field measurements where 1,3-D has been shown to persist from two to four months (McKenry and Thomason, 1974). The orchard soils used in these laboratory studies contained organisms that were capable of dehalogenating other substrates. The authors, however, suggest that the observed hydrolysis was chemical and not microbial. Slower rates of chloride release were observed for 1,3-D in buffer solution than in soils.

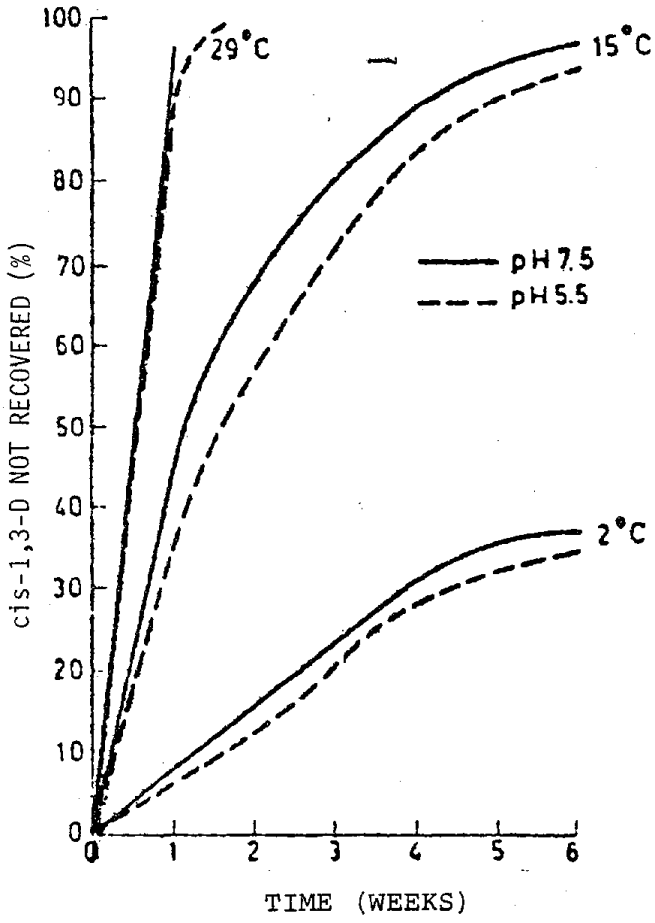
Contrary to findings by Castro and Belser (1966) with soil slurries, Van Dijk (1974) observed a longer half-life for 1,3-D in buffer solutions than in soil suspensions. In buffer solution, 1,3-D dissipation (includes nonrecovery due to the formation of bound residues) was more rapid with increases in temperature (Figure III-5). However, pH had little effect on 1,3-D disappearance rates. Dissipation rates of cis- and trans-1,3-D isomers were not significantly different in buffer solution or soil slurry studies.

Volatilization

Volatilization and diffusion in the vapor phase are the most significant mechanisms for environmental dispersal and dilution of the 1,2-D and 1,3-D type fumigants. Volatilization rates of chemicals from soil surfaces depend on their water solubility and vapor density as well as other factors such as temperature, moisture content, organic matter content and surface wind velocity (Bailey et al., 1974). Little information is available on rates of release, atmospheric dispersal, chemistry (other than laboratory chamber photolysis) and transfer of these fumigants from the atmosphere into ecosystems (Munnecke and Van Gundy, 1979).

Figure III-5

EFFECT OF pH AND TEMPERATURE ON CONVERSION OF CIS-1,3-DICHLOROPROPENE
(Van Dijk, 1974)



Estimates of cis-1,3-D loss from soil by volatilization range from 5 to 75 percent (McKenry and Thomason, 1974; Van Dijk, 1980; Leistra, 1972). In general, this is more than the loss from decomposition and diffusion to deeper layers (Table III-1).

Complete volatilization of the 1,2-D and 1,3-D type fumigants has been observed within 36 hours of soil injection (McKenry and Thomason, 1974). Extreme care in fumigation can still result in a 5 to 10 percent loss of 1,3-D from soil (McKenry and Thomason, 1974). Based on the amount of 1,2-D and 1,3-D type fumigants used in California in 1981, this could result in an estimated annual loss to the atmosphere of up to 630 tons of these chemicals (Appendix IV). An even greater percentage of applied 1,2-D could be lost from soil by volatilization (Van Dijk, 1980) since it is more persistent and volatile than the 1,3-D isomers (McKenry and Thomason, 1974; Roberts and Stoyden, 1976). 1,3-D appears to be more affected by soil hydrolysis than volatilization (Figure III-6).

Diffusion of gas molecules is greater in the air above the soil surface than within the soil system, and upward mass flow and diffusion are usually greater than downward movement (Munnecke and Van Gundy, 1979). Diffusion of 1,2-D and 1,3-D type fumigant appears to be unaffected by gravity (McKenry and Thomason, 1974; Munnecke and Van Gundy, 1979). Vapor diffusion of 1,2-D and 1,3-D occurs in soil because of their low Henry's Law Constants. The order of this diffusion in soil is, therefore, estimated (McKenry and Thomason, 1976) to be:

$$1,2\text{-D} > \text{cis-}1,3\text{-D} > \text{trans-}1,3\text{-D}.$$

Cis- and trans-3-CAA, the primary hydrolysis products of 1,3-D isomers, are not thought to be volatile due to their high water solubility even though their vapor pressures are high (Baines et al., 1977). These alcohols may be bound to soil or rapidly biodegraded. However, rapid vaporization of 3-CAA has been observed from silica gel thin-layer plates (Roberts and Stoydin, 1976).

Fumigant application method and depth can influence fumigant surface losses. For effective 1,2-D and 1,3-D fumigation (i.e., minimum volatilization losses), deeper soil should be dry and surface soil moist (McKenry and Thomason, 1974). Fumigant retention is also affected by (1) depth of tillage prior to fumigation, (2) presence of large soil aggregates (clods) (Leistra, 1972), and (3) plant roots (McKenry et al., 1978). These disruptions to the surface soil can interfere with the surface sealing after fumigant injection.

Microbial Transformation

As indicated above chemical hydrolysis is the first step in the transformation of 1,3-D. Further transformation of 1,3-D and all transformation of 1,2-D is thought to result from microbial action (Belser and Castro, 1971; Roberts and Stoydin, 1976).

Table III-1

RELATIVE CONTRIBUTION OF THE VARIOUS ROUTES OF DISSIPATION OF FIELD-APPLIED CIS-1,3-DICHLOROPROPENE FROM THE UPPER SOIL LAYER AT 12°C
(Van Dijk, 1980; Leistra, 1972)

SOIL TYPE	MOISTURE CONDITION[a]	Percent		
		VOLATILIZATION	DIFFUSION INTO DEEPER LAYERS	DECOMPOSITION[b]
Sand	pF 3	75	10	15
	pF 2	60	5	35
Sandy Loam	pF 3	55	5	40
	pF 2	20	1	80

a/ pF = 10-logarithm of the moisture tension expressed in cm of water

b/ Not estimated directly

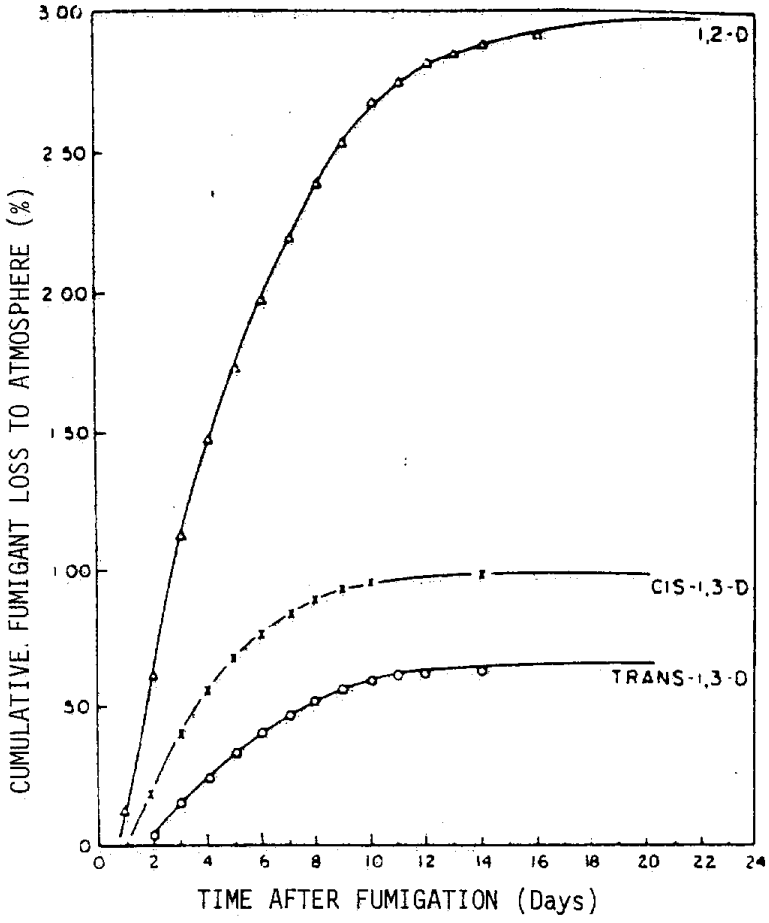
Table III-2

TOXICITY OF CIS- AND TRANS-1,3-DICHLOROPROPENE, 1,2-DICHLOROPROPANE AND 3-CHLOROALLYL ALCOHOL TO VARIOUS ORGANISMS
Moje et al., 1957

CHEMICAL COMPOUND	ORGANISM					
	Nematode		Fungi		Bacteria and Actinomycetes	
	ppm	Control	ppm	Control	ppm	Control
Cis-1,3-Dichloropropene	2.55	(95-100)	25	(85-95)	25-250	(85-100)
Trans-1,3-Dichloropropene	25	(95-100)	250	(95-100)	1000	(95-100)
1,2-Dichloropropane	250	(95-100)	1000	(95-100)	1000	(85)
3-Chloroallyl alcohol (both isomers)	25	(95-100)	250	(95-100)	250	(95-100)

Figure III-6

FUMIGANT LOSS TO ATMOSPHERE AFTER APPLICATION TO HANFORD SANDY LOAM
(McKenry and Thomason, 1974)



A number of investigations have shown the presence of diverse microbial populations in subsurface soil regions, that is, below the zone of cultivation (Dunlap and McNabb, 1973). Microorganisms such as Pseudomonas, Mycobacterium and Actinomyces, commonly found in surface soils, have also been found in subsurface samples. However, little information exists on the microbial activity in the aerated upper regions of the saturated zone (upper margin of aquifer) or vadose zone (subsurface soil). The persistence of organic chemicals such as fumigants in the saturated soil zone may result from absence or suboptimum population of microorganisms capable of transforming them. Factors which can limit organism proliferation include: (1) the absence of molecular oxygen, (2) chemical concentrations which are too low to serve as a substrate to the microorganism, and (3) the absence of an alternate energy source when the chemical is transformed by cometabolism, since not all compounds which are metabolized will support growth (Alexander, 1973).

The application of fumigants to soils results in a temporary, partial or complete, sterilization of the fumigated zone (Munnecke and Van Gundy, 1979). The relative toxicity of 1,2-D and the isomers of 1,3-D to nematodes, fungi, bacteria and actinomycetes is given in Table III-2 (Moje et al., 1957). In the laboratory, 62.5 to 250 ppm of 1,3-D or 320 ppm of 3-CAA can destroy microorganisms responsible for transformation of 3-CAA (Baines et al., 1977): Treatment with 1,500 pounds of 1,3-D per acre results in 1,3-D concentrations of 62 to 186 ppm in the top 2 to 24 inches of soil (Baines et al., 1977).

Control of the nematode Meloidogyne species in grape roots can require from 30 to 240 ppm day (units are a product of concentration and time) (McKenry and Thomason, 1976). Concentrations of cis-1,3-D (60 to 250 ppm per day) along with high concentrations of 1,2-D (100 to 200 ppm per day) have been measured at a soil depth of approximately seven feet after a Telone application of 1,500 pounds per acre. Pesticide label recommendations allow application up to 2,500 pounds per acre.

Destruction of soil organisms can result in the release of nutrients in the soil. Surviving or invading flora can use these nutrients and fumigant by-products for growth. The overall effect can stimulate growth of bacterial and fungal populations (Tu, 1979). Populations can reestablish rapidly in this less competitive soil environment. This stimulatory effect on bacteria was observed when soils with exceptionally high organic matter content (29 percent) were treated with D-D at the rate of 150 to 300 ppm.

Soil culture studies using media enriched with a 1,2-D, 1,3-D and D-D mixture produced abundant growth of all organisms tested (Altman and Lawlor, 1966), indicating that bacteria use the fumigants as a source of carbon. The growth of Bacillus subtilis and Arthrobacter globiformis surpassed controls with concentrations up to 100 ppm of chlorinated hydrocarbon. Several soil organisms were shown to use 1,2-D as a source of carbon at concentrations up to 1,000 ppm. Inhibitory growth was sometimes observed at low chlorinated hydrocarbon concentrations ($\leq$10 ppm), but this was overcome with further incubation. The authors hypothesize that a concentration of 10 ppm or less may not provide sufficient carbon material to maintain adequate microbial growth.

Data from enrichment culture studies of sandy soil treated with D-D suggest it may take up to 4.5 years before 99 percent of added organochlorine would be

degraded (Van Dijk, 1980). D-D was added to a field in the Netherlands (cold climate) over a nine-year period during which covalently bound chlorine (no quantification of chemical form) in the soil was monitored. The results of this study suggest that about 20 percent of the applied D-D remained in the soil at the end of nine years (Van Dijk, 1980).

The organochlorine compounds that have been isolated from metabolism of 3-CAA, the primary hydrolysis product of 1,3-D, by Pseudomonas species of bacteria include 3-chloroacrolein and 3-chloroacrylic acid (Figure III-2) (Belser and Castro, 1971). No information is available on metabolites from biotransformation of 1,2-D.

Temperature is one of the most important environmental influences controlling microbial activity (Dunlap and McNabb, 1973). In general, metabolic activity of microorganisms doubles with each 10°C rise in temperature.

Temperature has an expected, pronounced effect on the disappearance of 3-CAA (Van Dijk, 1980). In laboratory studies 3-CAA disappeared at a faster rate at a higher temperature, and the trans isomer degraded faster than the cis isomer in unsterilized soils (Figure III-7). Under these conditions the alcohol degraded faster than 1,3-D. The temperature effect in sterile soils was minimal, and disappearance of the alcohols was much slower than in unsterilized soil. In these studies 3-CAA and other chlorinated hydrocarbons were detected by measurements of chloride release, suggesting that the soil impeded degradation (Van Dijk, 1974). The author observed an initial rapid release of chloride followed by a slower rate of about three (3) percent per week. The formation of soilbound residues was not determined in this work. Other studies of 3-CAA and 3-chloroacrylic acid suggest that these compounds are bound strongly to soil (Roberts and Stoydin, 1976). It is uncertain if biotransformation of bound residues occurs, because it is not known whether these residues are physically accessible to microbes or their extracellular enzymes (Alexander, 1973 and 1981).

Soil moisture can increase soil microbial activity (Dunlap and McNabb, 1973). However, chemical hydrolysis of 1,3-D may decrease with increases in soil moisture, and may thus limit the availability of 3-CAA and further transformation of the compound (McKenry and Thomason, 1974).

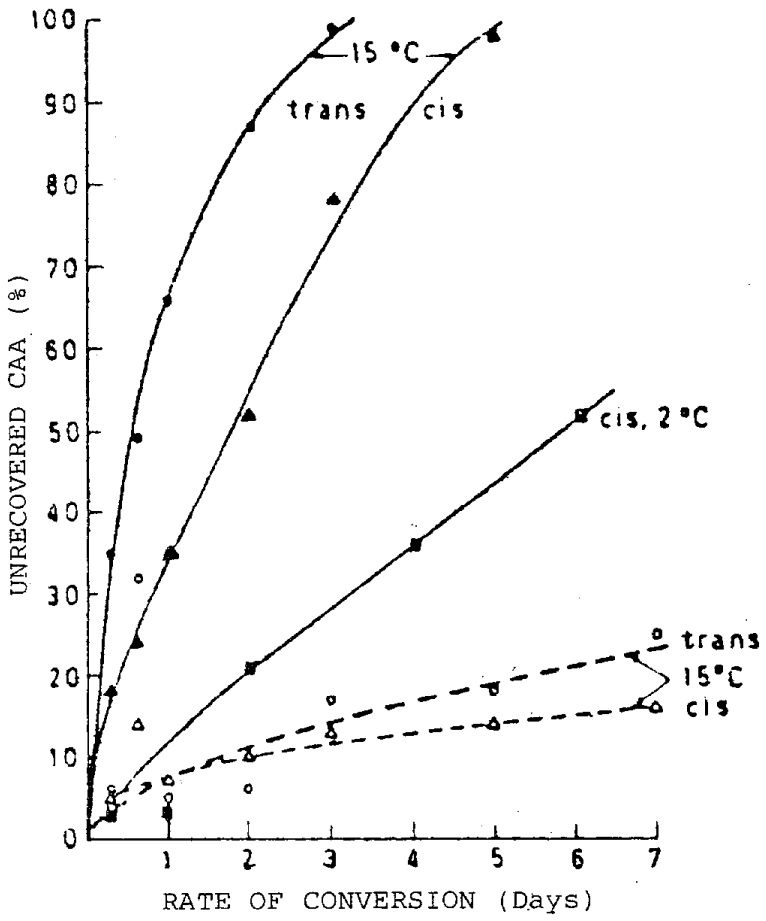
Photochemical Transformation

Vapor phase photolysis of 1,2-D and cis- and trans-1,3-D was not detected after prolonged simulated sunlight irradiation in a reaction chamber (Li et al., 1979). Photolysis of the 1,3-D isomers occurred on photoreactor surface walls suggesting surface-catalyzed reactions. The reaction products (Table III-3) isolated from these studies indicate that 12 to 13 percent of these isomers are totally degraded to CO_2 after five days of irradiation; over 20 percent 1,3-D was transformed to the toxic chemical phosgene in this study. No information has been found which identifies surface catalyzed photoproducts of 1,2-D.

Laboratory studies of homogenous gas phase photolysis of 1,2-D and trans-1,3-D suggest that photodegradation by hydroxyl radical is a rapid process compared to ozone photodegradation (Winer, 1983). 1,2-D does not photolyze readily. The estimated atmospheric half-life ($t_{1/2}$) for 1,2-D based on reaction with

Figure III-7

EFFECT OF TEMPERATURE ON CONVERSION OF CIS- AND TRANS-3-CHLOROALLYL ALCOHOL IN SANDY CLAY SOIL
(Van Dijk, 1974)



——— Unsterilized soil

---- Sterilized (autoclaved) soil

Table III-3

PHOTOLYSIS OF CIS- AND TRANS-1,3-DICHLOROPROPENE
IN A 1-LITER REACTOR
(Li et al., 1979)

IRRADIATED COMPOUND	PEAK NO.	STRUCTURAL ASSIGNMENT	AMOUNT PRODUCED (PERCENT)
cis-1,3-Chloropropene	1	cis-1,3-Dichloropropene	6.7
	2	3-Chloropropionyl chloride	56
	3	3-Chloropropionic acid	11
	1	Carbon dioxide	13
	2	Phosgene	22
trans-1,3-Chloropropene	1	trans-1,3-Dichloropropene	11
	2	3-Chloropropionyl chloride	48
	3	3-Chloropropionyl acid	8.9
	1	Carbon dioxide	11.9
	2	Phosgene	20

hydroxyl radical is 185 hours, a conservative estimate. No significant 1,2-D degradation is expected by ozonalysis. Atmospheric photolysis of trans-1,3-D by hydroxyl radical is rapid with a half-life of approximately 21 hours (Pitts et al., 1981). Photodegradation by ozone is slower with an estimated half-life of 220 hours.

Organism Uptake

The reduction of 1,2-D and 1,3-D in soil by plant and animal uptake is insignificant when compared to other dissipation processes. Under certain conditions where low concentrations of 1,3-D persist for long periods of time, plants will sorb measurable quantities of the toxicant (Williams, 1968).

Uptake has been shown to occur in potato tubers in sandy loam soil treated with (^{14}C) 1,2-D and (^{14}C) 1,3-D six months prior to planting (application rate 2.6 gal/acre) (Roberts and Stoydin, 1976). The total residue in these tubers measured by isotope emission was seven (7) ppb (measured as dichloropropenes). At the time of planting, the soil probably contained 5 to 10 percent of the applied nematicide as parent and transformation products.

Tomatoes, bush beans and carrots absorbed (^{14}C) 1,3-D from vermiculite, solution culture and sand (Berry et al., 1980). During a 24-hour period, the dichloropropenes were absorbed and translocated through the plants. All three crops also readily absorbed 3-CAA. Overall absorption and distribution of 3-CAA indicates that it was absorbed to a lesser extent than the dichloropropenes. A suggested route of plant metabolism is shown in Figure III-8. The comparative metabolism of cis- and trans-3-CAA shows that these compounds appear to be rapidly converted to normal plant products. The half-lives for 1,3-D and 3-CAA were 1.5 and 4.4 hours, respectively. Plant metabolism produces 3-chloropropanol, a compound which has not been observed in microbial transformation (Figure III-2).

Recent studies have shown the formation of 3-chloroallyl methyl sulfide ($Cl-CH=CH-CH_2-S-CH_3$) in milk after adding Telone (1,3-D, 500 ppm) and boiling (Dekker[2], 1972[3]). The detection limit for this compound was one (1) ppm by gas chromatography. The human nose can detect one (1) ppb of 3-chloroallyl methyl sulfide in tap water, a thousand-fold increase over instrument sensitivity. Bad odor has been observed in boiled milk from cows fed on D-D treated pasture. D-D components could not be detected in the milk. Off-flavor and abnormal odor have been reported in food crops such as carrots, potatoes and butter beans grown in D-D treated soils (Leistra, 1972; Dekker, 1972).

MOVEMENT IN SOIL

During the first few days after soil application, the 1,2-D and 1,3-D type fumigant moves through the soil not only by vapor phase diffusion (movement in response to concentration gradients), but also by mass flow (bulk movement with soil water or air) (McKenry and Thomason, 1974). Slower downward movement of the fumigant often results in higher losses by volatilization to the atmosphere, and lower concentrations in the deeper soil layers. According to Leistra (1972) in the initial seven hours after treatment, 1.8 times more 1,3-D diffuses upward than diffuses downward. This diffusion pattern can be caused by: (1) less soil moisture in the surface soil; (2) higher temperatures in the surface soil; and (3) looser soil above the injection line (Abdalla et al., 1974).

Figure III-8

PROPOSED PLANT METABOLISM PATHWAYS FOR CIS- AND TRANS-
1,3-DICHLOROPROPENE AND CIS- AND TRANS-3-CHLOROALLYL ALCOHOL
(Berry et al., 1980)

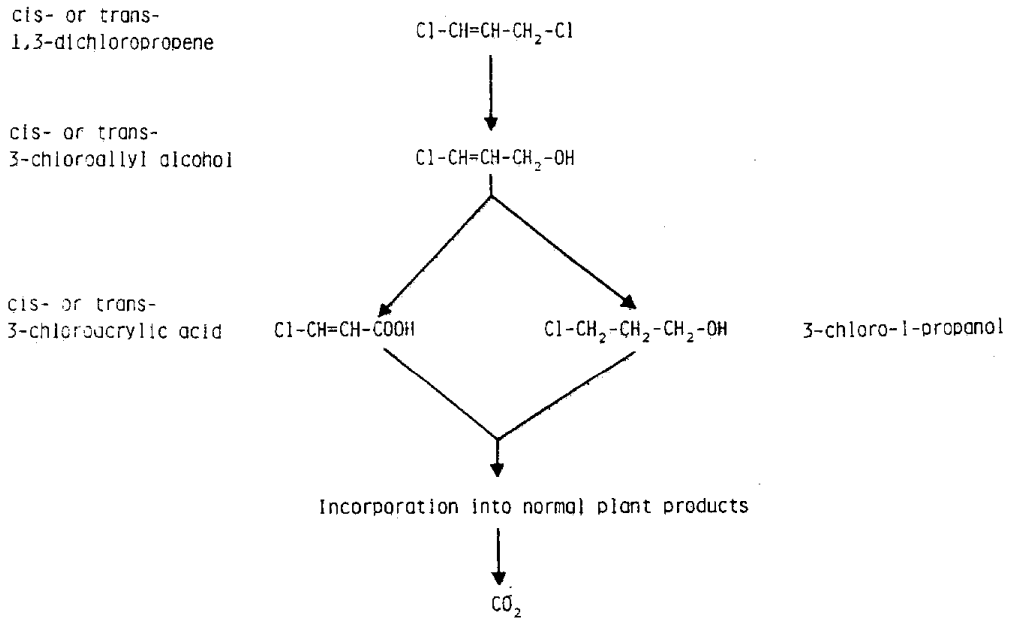
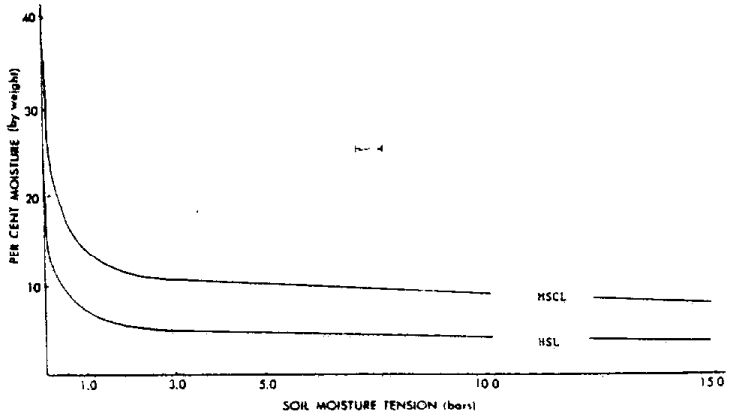


Figure III-9

SOIL MOISTURE RETENTION CURVES FOR TWO SOILS:
MORENO SILTY CLAY LOAM (MSCL) AND HANFORD SANDY LOAM (HSL)
(McKenry and Thomason, 1974)



The following discussion of the factors affecting 1,2-D and 1,3-D movement in soil emphasizes soil and climatic conditions observed in California.

Moisture

Soil moisture is the major influence on the vapor phase diffusion of 1,2-D and 1,3-D in soil. Maximum fumigant diffusion occurs in soils with 0.6 to 15 bars of soil moisture tension (Munnecke and Van Gundy, 1979). The relationship between moisture tension, expressed in bars, to the percentage of soil moisture by weight is shown for two soils in Figure III-9. Moisture tension decreases as the percentage of moisture increases. Soils wetter than 0.6 bar, 10 to 12 percent moisture, will have a number of air passageways blocked by water and will restrict fumigant movement in the vapor phase (McKenry and Thomason, 1976).

Soil fumigation at high soil moisture levels results in a slow movement of the 1,3-D fumigant vapors and uneven distribution in soil, especially in a fine-textured soil which has a higher moisture holding capacity (McKenry and Thomason, 1974). The effect of soil moisture on the lateral diffusion of cis-1,3-D is shown in Figure III-10.

Excessively dry soils, those which exceed the wilting point for vegetation (15 bars), have few or no water molecules surrounding soil particles. Under these conditions sorption of the fumigant molecules may occur directly on soil particle surfaces (Munnecke and van Gundy, 1979; McKenry and Thomason, 1974). A uniformly dry soil profile can result in a greater upward diffusion of the 1,3-D, resulting in surface loss (Leistra, 1972). Under such conditions fumigant movement to ground water is less probable.

Temperature

The second major influence on 1,2-D and 1,3-D diffusion in soil is temperature. Optimum diffusion of these compounds occurs between 15° and 20°C (McKenry and Thomason, 1976). Temperature affects the distribution ratio of the fumigant in vapor and solution phases. As temperature increases, more of the fumigant will be in the vapor phase causing an increase in vapor diffusion. The effect of soil temperature on lateral movement of cis-1,3-D in Hanford sandy loam soil is shown in Figure III-11 (McKenry and Thomason, 1974).

Soil Texture

Coarser-textured soils generally allow maximum diffusion of the 1,3-D type fumigant. With fine-textured soils, such as clay loam and clays, pore spaces are move completely blocked as increasing soil moisture increases. Soil texture will often vary with depth in the soil profile making it difficult to predict fumigant dispersion. The presence of compacted soil layers, such as plow sole or clay pan, limit downward diffusion of 1,2-D and 1,3-D (Burr, 1974; Munnecke and Van Gundy, 1979). Disruptions in these restrictive layers, such as soil macropores, can allow easy movement of air and percolating water (Buckman and Brady, 1969; Thomas and Phillips, 1979) and may serve a major role in the dispersion of fumigants.

Fumigant Characteristics

The two major characteristics of a chemical governing its rate of movement are its water solubility and vapor pressure. These two characteristics are related by Henry's Law, as discussed earlier. Henry's Law constant ($K_{w/v}$)

Figure III-10

EFFECT OF SOIL MOISTURE ON LATERAL VAPOR PHASE DIFFUSION OF CIS-1,3-DICHLOROPROPENE IN MORENO SILTY CLAY LOAM AT 15°C
(McKenry and Thomasom, 1974)

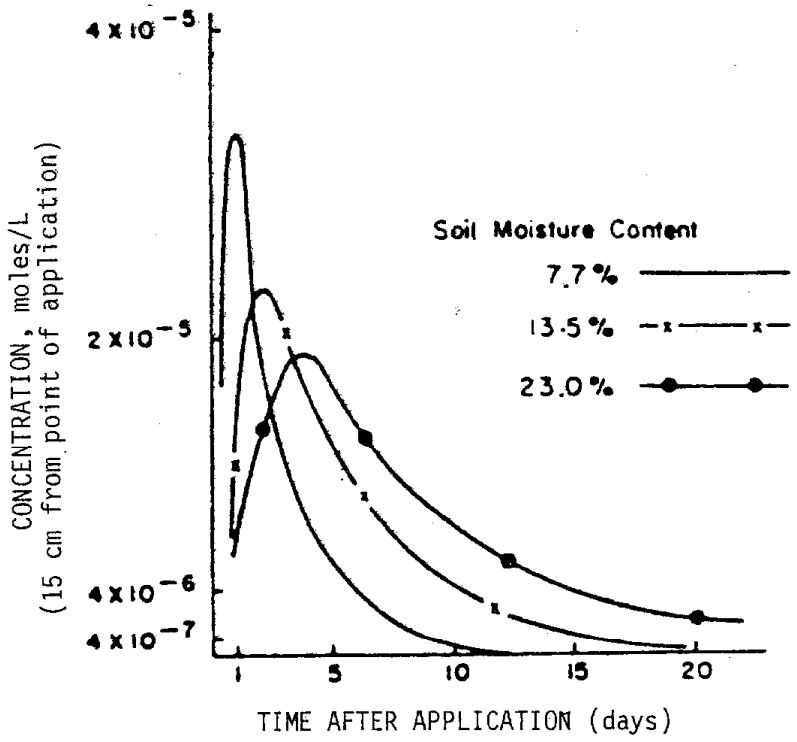
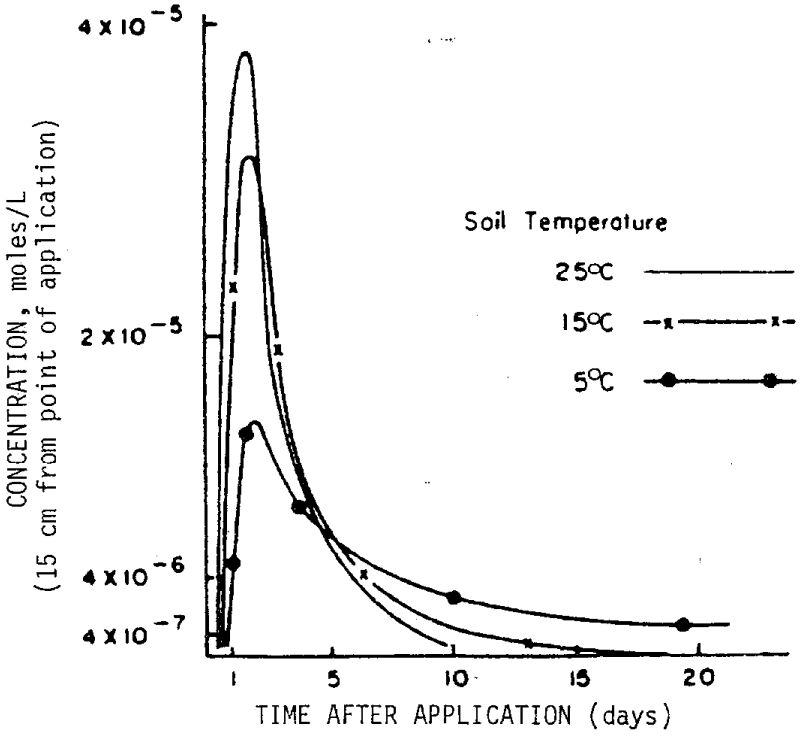


Figure III-11

EFFECT OF SOIL TEMPERATURE ON LATERAL VAPOR PHASE DIFFUSION OF CIS-1,3-DICHLOROPROPENE IN HANFORD SANDY LOAM AT 8% MOISTURE (McKenry and Thomason, 1974)



for 1,2-D is low, 11 at 20°C; at any given time, 1,2-D concentration will be 11 times higher in the water phase than in the vapor phase. The diffusion constant of 1,3-D in gas phase is 10^4 times greater than that in water phase (Leistra, 1972); therefore, their diffusion in water is negligible.

Adsorption and Desorption

Soil sorption of 1,2-D and 1,3-D fumigants will occur on dry clay particles or soil organic matter (McKenry and Thomason, 1974; Leistra, 1972). The first molecular layer of 1,3-D adsorbed on clay is thought to be chemically bonded to the particle surface (Singhal and Kumar, 1976a,b,c and d). This form of sorption, chemisorption, involves high bonding strengths and is considered irreversible (Goring, 1967). In warm, low organic California soils, 1,3-D chemisorption is estimated to range from two (2) to five (5) percent of the total chemical present (McKenry and Thomason, 1974). Little chemisorption has been observed for 1,2-D.

Additional sorption of 1,2-D and 1,3-D type fumigants can result from weak intermolecular attractions (physical adsorption, such as Van der Walls' forces). This results in the development of several molecular layers on a soil particle surface with low binding strength (Goring, 1967). In dry soils 1,2-D and 1,3-D will sorb to clay minerals affecting chemical movement in soil. However, as the soil adsorbs moisture, the fumigant will be displaced, or desorbed, from the clay particle (Goring, 1967).

Sorption of 1,2-D and 1,3-D is directly proportional to the organic matter content of soil (McKenry and Thomason, 1974; Leistra, 1972; Seigel et al., 1951). For instance, excessive amounts (eight (8) times the normal rate of application) of 1,3-D were found necessary to obtain nematode control in a soil profile high in grape and fig roots (McKenry and Thomason, 1974). In other studies up to three times the normal application of 1,3-D was required to kill root knot nematodes when crop residues (alfalfa, cotton, peat, wheat, barley, tobacco and sugar beet crops) were added to test soils (Goring, 1967). Many prime agricultural areas in California contain less than one (1) percent of organic carbon. At these low levels, sorption to organic matter plays a minor role in the mobility of 1,3-D type nematicides. Sorption on organic matter involves partitioning, or dissolution, of the molecule into fats, waxes and other constituents. In organic matter 1,2-D is less partitionable and would be expected to be more mobile in soil when compared to 1,1,1-trichloroethane, EDB, TCE and 1,2-dichlorobenzene (Chiou et al., 1979).

Vapor phase sorption of fumigants can occur in soil. Seigel et al. (1951) observed that 1,3-D vapors were weakly sorbed by soil, and the sorption was directly related to organic matter content. Desorption was partial in high organic soil and complete in mineral soil. Other studies (Leistra, 1972) further document the role of soil organic matter in the sorption of 1,3-D vapors (Table III-4).

Sorption processes are also affected by soil temperature and moisture (Goring, 1967). Figure III-12 shows the significant effect of both temperature and soil moisture on 1,3-D sorption in Hanford sandy loam, a California soil with low organic matter content (McKenry and Thomason, 1974).

Table III-4

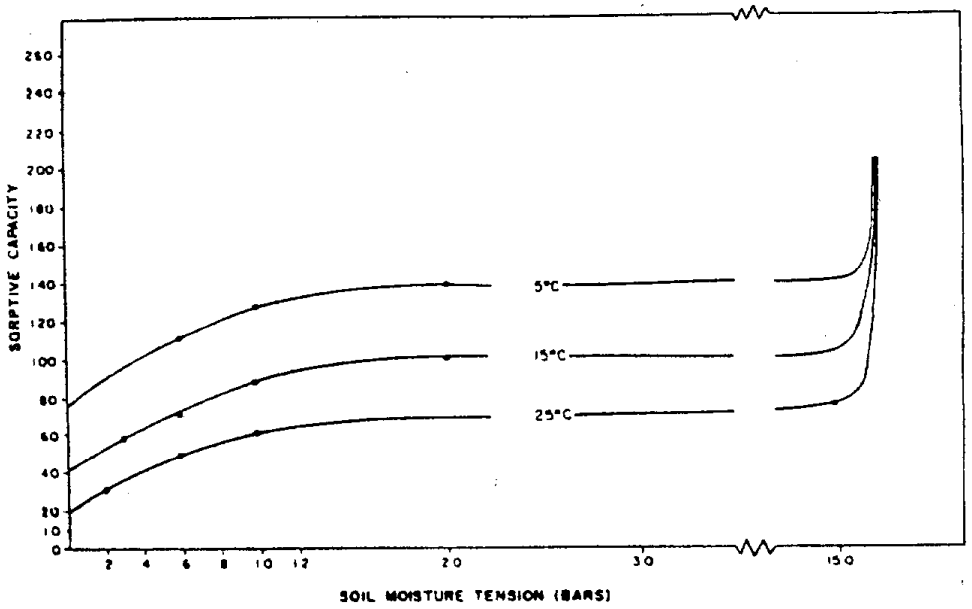
VAPOR PHASE ADSORPTION COEFFICIENTS FOR CIS- AND TRANS-
1,3-DICHLOROPROPENE IN THREE SOILS
(Leistra, 1972)

SOIL	ORGANIC MATTER CONTENT (%)	MOISTURE (%)	TEMP. (° C)	Ks/v* CIS-1,3-D	Ks/v* TRANS-1,3-D
Humic sand	5.5	17	2	38	68
			11	22	40
			20	14	24
Peaty Sand	18	41	2	130	220
			11	78	130
			20	47	77
Peat	95	120	2	680	1250
			11	430	720
			20	260	410

*Ks/v - Partition coefficient between soil and vapor phase.

Figure III-12

SORPTIVE CAPACITY OF HANFORD SANDY LOAM FOR CIS–1,3-DICHLOROPROPENE AS INFLUENCED BY TEMPERATURE AND MOISTURE
(McKenry and Thomason, 1974)



IV. TOXICOLOGY

Acute and Chronic Mammalian Toxicology

Little information is available on 1,2-D other than for acute oral studies and inhalation toxicology. Most literature references describe studies with formulations containing both 1,2-D and 1,3-D and often lack information on compound purity. Both 1,2-D and 1,3-D are moderately toxic to mammals and aquatic life, with 1,3-D being considerably more toxic than 1,2-D.

In Ames tests 1,2-D had marginal and 1,3-D had strong mutagenic activity. A recent National Toxicology Program (NTP) draft report concluded that 1,2-D caused an increase in liver adenomas in mice. Evidence for carcinogenicity in female rats was equivocal. Carcinogenicity bioassays for 1,3-D are currently under review by NTP. As with many other halogenated short-chain hydrocarbons, 1,2-D and 1,3-D are skin and eye irritants. Overexposure to vapors, particularly from 1,3-D, can lead to headache, nausea, pulmonary edema and, ultimately, death. In animal studies, overexposure is typically characterized by eye irritation and severe injury to lungs, liver and kidneys.

1-2-D

Oral: Animal experiments with rats, mice and guinea pigs show that the acute oral toxicity of 1,2-D is low in mammals. For example, the LD_{50} (see Abbreviations p. xi) for rats and mice is 1,900 to 2,200 mg/Kg and 860 mg/Kg, respectively (Table IV-1). Oral doses as low as 8.8 mg/kg 1,2-D in rats interfered with protein formation and lipid metabolism in liver. With repeated exposure to low doses, 1,2-D exerted greater toxic effects than other components of D-D (Ekshtat et al., 1975).

Inhalation: Inhalation studies also demonstrate low acute toxicity of 1,2-D in mammals (Table IV-1). Rats exposed to 1,2-D vapor had an eight-hour LC_{50} of 3,000 ppm (Torkelson and Rowe, 1981) and mice exposed for ten hours had an LC_{50} of 2,000 ppm (NIOSH, 1979). Studies comparing the aesthetic effects of short-term exposure to carbon tetrachloride and 1,2-D indicated that 1,2-D caused much less liver damage than did carbon tetrachloride, and that in mice respiratory injury rather than liver injury was the primary cause of death (Torkelson and Rowe, 1981).

In an early inhalation study (Heppel et al., 1946) 11 of 16 guinea pigs died after five 7-hour per day exposures to a concentration of 2,200 ppm 1,2-D vapor. Histological examination of the mortalities revealed fatty degeneration of the liver and kidney and necrosis of the adrenal glands. Mice exposed under the same experimental regimen showed signs of uncoordination and prostration and 10 of 11 died within the first 7-hour exposure period. Of 20 rats exposed at this concentration, five died after the fifth day of exposure. Histological examination of rats after five and eight 7-hour exposures to 2,200 ppm 1,2-D vapor also showed fatty degeneration of the liver and, occasionally, necrosis of liver cells; adrenal glands were also effected. Control rats showed no marked pathology other than spleenic hemosiderosis. Four dogs that died after 24, 27, 28 and 96 seven (7)-hours per day exposures to 1,000 ppm 1,2-D vapor also showed fatty degeneration of the liver; however, five dogs examined after as many as 128 exposures at 1,000 ppm showed no histopathological effects when compared with four control animals.

Table IV-1

MAMMALIAN TOXICITY OF 1,2-DICHLOROPROPANE, 1,3-DICHLOROPROPENE AND SOME RELATED COMPOUNDS

COMPOUND	ADMINISTRATION ROUTE	SPECIES	DOSE/RESPONSE	REFERENCE
		PROPANES		
1,2-dichloropropane	Oral	Rat	LD_{50}= 2200 mg/kg	Ekshtat et al. 1975
"	"	"	LD_{50}= 1900 mg/kg	Torkelson and Rowe, 1981
"	"	Guinea Pig	LD_{50}= 2000 mg/kg	NIOSH, 1979
"	"	Mouse	LD_{50}= 860 mg/kg	International Tech. Info.
"	"	Dog	LD_{LO}= 5000 mg/kg	Inst., 1981
"	Inhalation	Rat	LC_{50}= 8 hours= 3000 ppm	Torkelson and Rowe, 1981
"	"	"	LC_{LO}= 4 hours= 2000 ppm	NIOSH, 1979
"	"	Mouse	LC_{50}= 10 hours= 750 ppm	Torkelson and Rowe, 1981
"	"	Rat	2.16 mg/liter/week:effects ploidy of hepatocytes	Belyaeva et al., 1977
"	Air	Human	ACGIH Recommendations	Sittig, 1980
"		"	TWA= 75 ppm (350 mg/m^3) 8h/day/40 hour week	"
"		"	STEL= 110 ppm (510 mg/m^3)	"
"	Skin	Rabbit	LD_{50}= 8750 mg/kg	NIOSH, 1979
"	"	"	Severe Irritation= 500 mg/24h	
"	Eye	"	Severe Irritation= 5 mg	
1,1-dichloropropane	Oral	Rat	LD_{50} = 6500 mg/kg	NIOSH, 1979
"	Inhalation	"	LC_{LO} = 4 hours=4000 ppm	"
"	Skin	Rabbit	LD_{50} = 14,000 mg/kg	"
1,3-dichloropropane	Oral	Dog	LD_{LO} = 3000 mg/kg	NIOSH, 1979
1,1,1 -trichloropropane	Inhalation	Rat	LC_{LO}=4 hours=8000 ppm	NIOSH, 1979
1,1,2-trichloropropane	Oral	"	LD_{50} = 1250 mg/kg	"
"	Inhalation	"	LC_{50} = 2000 ppm	"
1,2,2-trichloropropane	Oral	"	LD_{50} = 1230 mg/kg	"
1,2,3-trichloropropane	"	"	LD_{50} = 320 mg/kg	"
"	Inhalation	"	LC_{LO} = 1000 ppm	"
"	Skin	Rabbit	LD_{50} = 1770 mg/kg	"
"	Air	Human	TLV = 50 ppm; TWA (OSHA)=50ppm	"

Table IV-1

MAMMALIAN TOXICITY OF 1,2-DICHLOROPROPANE,
1,3-DICHLOROPROPENE AND SOME RELATED COMPOUNDS

COMPOUND	ADMINISTRATION ROUTE	SPECIES	DOSE/RESPONSE	REFERENCE
		PROPENES		
1,3-dichloropropene	Oral	♂ Rat	LD_{50} = 713 mg/kg	Torkelson and Oyen, 1977
92% cis-/trans-isomers 8% other compounds (Telone formulation)	"	♀ Rat	LD_{50} = 470 mg/kg	"
"	Dermal	Rabbit	LD_{50} = 504 mg/kg	"
"	Inhalation	Rat	LD_{100}=2 hours=1000 ppm	"
"	"	"	severe injury-no mortality } 400 ppm, 7 hours	"
"	"	Guinea Pig	100% mortality }	
"	Air	Rat	Brief exposure, 2700 ppm-eye irritation, severe lung, nasal, liver, kidney injury	"
"	Inhalation	♀Rat, Guinea Pig Rabbit, Dog }	~185 days exposure, 3ppm-no effect	"
"		♂ Rat	" -renal tubular swelling	"
"	Eye	Rabbit	severe conjunctival irritation from 30 second exposure	"
"	Air	Human	7/10 volunteers could detect 1 and 3 ppm	"
1,3-dichloropropene	Air	Human	ACGIH Recommendations TWA = 1 ppm (5 mg/m^3) STEL = 10 ppm (50 mg/m^3)	Sittig 1980
2,3-dichloropropene	Oral	Rat	LD_{50} = 370 mg/kg	Ekshtat et al., 1975
"	"	"	LD_{50} = 320 mg/kg	NIOSH, 1979
"	Inhalation	"	LC_{LO}=4 hours = 500 ppm	"
"	Skin	Rabbit	LD_{50} = 1580 mg/kg	"
D-D	Oral	Rat	LD_{50} = 140 mg/kg	NIOSH, 1979
"	"	Mouse	LD_{50} = 300 mg/kg	"
"	Inhalation	Rat	LC_{50} = 4 hours= 1000 ppm	"
"	Skin	Rabbit	LD_{50} = 2100 mg/kg	"

Table IV-1

MAMMALIAN TOXICITY OF 1,2-DICHLOROPROPANE, 1,3-DICHLOROPROPENE AND SOME RELATED COMPOUNDS

COMPOUND	ADMINISTRATION ROUTE	SPECIES	DOSE/RESPONSE	REFERENCE
		MISCELLANEOUS		
3-chloroallyl alcohol	Oral	Rat	LD_{50} = 102 mg/kg	NIOSH, 1979
"	"	Mouse	LD_{50} = 175 mg/kg	"
"	Inhalation	Rat	LC_{50} = 1 hour= 370 ppm	"
"	"	Mouse	LC_{50} =1 hour = 540 ppm	"
"	Skin	"	LD_{LO} = 170 mg/kg	"
Allyl chloride	Oral	Rat	LD_{LO} = 64 mg/kg	NIOSH, 1979
"	Inhalation	"	LD_{LO} =8 hours = 290 ppm	"
"	Intravenous	Dog	LD_{50} = 7.2 mg/kg	"
"	Skin	Rabbit	LD_{50} = 2200 mg/kg	"
epichlorohydrin	Oral	Rat	LD_{50} = 90 mg/kg	NIOSH, 1979
"	"	Mouse	LD_{LO} = 250 mg/kg	"
"	Inhalation	Rat	LC_{LO} =4 hours=250 ppm	"
"	Skin	Rabbit	LD_{50} = 515 mg/kg	"
DBCP (1,2-dibromo-3-chloropropane	Oral	Rat	LD_{50} = 173 mg/kg	NIOSH, 1979
"	"	Mouse	LD_{50} = 257 mg/kg	"
EDB (1,2-dibromoethane	"	Rat	LD_{50} = 108 mg/kg	"
"	"	Mouse	LD_{LO} =250 mg/kg	"
1,2-dichloroethane	"	Rat	LD_{50} = 680 mg/kg	"
"	"	Mouse	LD_{LO} = 600 mg/kg	"

LC_{50} - lethal concentration 50 percent kill

LC_{LO} - lowest published lethal concentration

LD_{50} - lethal dose 50 percent kill

LD_{LO} - lowest published lethal dose

PPM - parts per million

TLV - threshold limit value

TWA - time-weighted average

mg/kg - milligrams of chemical per kilograms body weight

ACGIH - American Conference of Governmental Industrial Hygienists

STEL - Short-Term Exposure Limit

In a similar study (Heppel et al., 1948), rats, guinea pigs, dogs and mice were exposed to 1,2-D vapor at 400 ppm for seven hours/day, five days/week for up to 140 exposures. Rats, guinea pigs and dogs showed little ill effects. However, most of the exposed mice died during the experiment; histological examination of these animals showed slight fatty degeneration of the liver and kidney.

A Russian study (Sidorenko et al., 1976) reported that continuous inhalation of 1,2-D by rats (1 and 2 mg/liter for seven days) caused changes in cholinesterase activity and blood catalase. In addition, histological examination of the liver showed damage to small blood vessels, signs of protein-fat dystrophy and impairment of enzyme activity; impairment of oxidizing enzymes and phosphomonoesterases was indicated in kidney tissue.

An added hazard of 1,2-D is that, when heated to decomposition, highly toxic phosgene fumes are released (Threshold Limit Value (TLV) for phosgene in air is 0.1 ppm) (Sitting, 1980; Dreisbach, 1977).

Dermal: 1,2-D appears to be a mild skin irritant on short exposure. Enclosure of the contact site by cloth, shoes or boots intensifies the skin reaction. The dermal LD50 in the rabbit for 1,2-D is 8750 mg/kg. In addition to dermatitis, 1,2-D also is an eye irritant (Torkelson and Rowe, 1981; NIOSH, 1979). Little information on dermal absorption of 1,2-D is available.

1,3-D

Oral: Most of the 1,3-D data are based on formulations of Telone which contained about 92 percent of the cis- and trans-1,3-D (Table IV-1). The acute oral LD_{50} of 1,3-D for rats was determined to be 713 mg/Kg (male) and 470 mg/Kg (female) (Torkelson and Oyen, 1977). While these numbers suggest moderate lethal toxicity, gross examination of survivors of this study showed effects to liver, kidney and lung tissue.

In a chronic ingestion study, no behavioral or pathological changes were noted in rats receiving 1 to 30 mg/Kg 1,3-D over a 13-week period. However, kidney weight increased in female rats exposed to 30 mg/Kg 1,3-D and in male rats receiving 10 and 30 mg/Kg (Torkelson and Rowe, 1981). Rats fed low levels of 1,3-D (0.1 to 2.5 mg/Kg) over a six-month time period showed a permanent increase in lipase activity (Strusevich and Ekshtat, 1974). In a study designed to evaluate cumulative effects of 1,3-D in rats (Kurysheva and Ekshtat, 1975), normal excretory functions of the liver were reported to be altered after exposure to 2.2 mg/Kg 1,3-D for 30 days. In addition, there was little body accumulation of 1,3-D, 2,3-D and allyl chloride in orally dosed rats (Ekshtat et al., 1975).

Inhalation: Most information on inhalation effects of 1,3-D come from a study (Torkelson and Oyen, 1977) that used a formulation containing 46 percent cis- and 53 percent trans-1,3-D and 1 percent of other materials (primarily epichlorohydrin added as a stabilizer and anticorrosive agent). In short-term studies these investigators observed irritation to the eyes and noses of rats after brief exposure to concentrations above 2,700 ppm; severe lung, kidney and liver damage also was noted. Rats exposed to 1,000 ppm for two hours died, while those exposed for one hour to this air concentration survived. In addition, animals exposed to levels above 700 ppm had a peculiar garlic-like odor. A single seven-hour exposure to 400 ppm of this cis-/trans-1,3-D mixture was lethal to guinea pigs but not to rats. Rats, however, suffered loss of weight and lung injury. Recovery of weight loss was achieved in eight days, but not recovery from lung injury.

In chronic 1,3-D inhalation studies (46 percent cis-, 53 percent trans- and 1 percent of other materials) animals were exposed seven hours/ day, five days/ week to one (1) or three (3) ppm for 185 days. In experimental animals such as rats, rabbits, guinea pigs and dogs, no adverse effects were observed in any species (except rats) after prolonged exposure to three (3) ppm 1,3-D based on "demeanor, general appearance, growth, mortality, hematologic examination, final body and organ weights, and gross and microscopic examination." (Torkelson and Oyen, 1977). Cloudy swelling in kidneys of male rats was observed at three (3) ppm; female rats had a higher liver to body-weight ratio than controls. Since this study was conducted with a recently produced 1,3-D formulation, the authors concluded that the minor effects and low toxicity observed probably reflect maximum toxic effects of the newer product.

In a behavioral study, Rhesus monkeys were exposed to a soil fumigant containing 92.4 percent cis- and trans-1,3-D and 7.6 percent of other propenes and propanes (Talley and Rosenblum, 1979). Inhalation concentrations ranged from 25 to 600 ppm for a single (1) hour period with one (1) week recovery between exposures (the number of exposures was not stated). No behavioral effects were observed below 200 ppm. Failure to respond in training sessions, a central nervous system effect, was observed in one of four animals exposed to 200 ppm and in four of four animals exposed to 600 ppm; rapid recovery was observed in the post exposure period.

Dermal: A dermal LD_{50} (rabbit) of 504 mg/kg (Table IV-1) was reported for 1,3-D by Torkelson and Oyen (1977). However, another report (Sax, 1979) gives the dermal (rabbit) LD_{50} for 1,3-D as 2,100 mg/kg, suggesting different animal test strains, formulations or application methods were employed. Torkelson and Oyen (1977) covered the application site, inhibiting evaporation and maximizing exposure; Sax (1979) did not state whether or not this was done.

Liquid 1,3-D applied to the skin of rabbits caused necrosis and edema; absorption through the skin was enhanced if the liquid was confined or in a solution (propylene glycol) which retards evaporation. Caution is advised in handling because this chemical can cause blisters and burns (Torkelson and Rowe, 1981). Administration of a few drops of 1,3-D (92 percent cis and trans isomers) to the eyes of rabbits followed by a water rinse produced severe conjunctival irritation in four out of six animals and slight to moderate effects in two others within 24 hours. The injury subsided eight days after exposure (Torkelson and Oyen, 1977). Information on the extent of exposure causing permanent eye damage was not found.

Limited data show that 3-CAA (the major transformation product of 1,3-D) is approximately two times more acutely toxic than the parent 1,3-D (Table IV-1), and that it can cause severe skin blisters (Dow Chemical Company, 1981). For these reasons, additional toxicological data should be developed for this compound.

Metabolism

Both 1,2-D and cis- and trans-1,3-D undergo metabolic transformation in the rat (Hutson et al., 1971). Excretion is rapid with approximately 89 percent or more of a single [^{14}C] administered dose eliminated via urine,

Table IV-2

METABOLISM OF 1,2-DICHLOROPROPANE, CIS- AND TRANS-1,3-DICHLOROPROPENE BY RAT IN FOUR DAYS (Hutson et al., 1971)

		RECOVERY OF RADIOACTIVITY (% of Administered Dose)					EXHALED AIR		TOTAL RADIOACTIVITY RECOVERED (% of Administered Dose)
Compound	Sex	Urine	Feces	Gut	Skin	Carcass	Carbon dioxide	Other volatile radioactivity	Including volatile radioactivity
1,2-D	M	51.1	6.9	0.5	1.7	4.1	--	--	--
	F	54.4	4.9	0.5	1.4	3.2	19.3	23.1	106.8
cis-1,3-D	M	84.0	3.3	0.1	0.5	0.8	5.3	--	--
	F	82.3	1.8	0.1	0.5	0.5	2.4	1.4	89.0
trans-1,3-D	M	55.6	2.1	0.2	0.6	1.1	22.7	--	--
	F	60.4	2.3	0.5	0.5	0.9	24.4	3.5	92.1

expired air, and feces within 96 hours (Table IV-2). The major elimination route for these compounds was via urine. Average radioactivity recovered after four days for males and females was as follows: 1,2-D, 52 percent; cis-1,3-D, 83 percent; and trans-1,3-D, 58 percent. Exhaled air (females) accounted for approximately 42 percent of the 1,2-D dose, 28 percent of the trans-1,3-D dose, and 4 percent of the cis-1,3-D dose. Elimination through feces (males and females) was minor. Only minimal incorporation in tissues was evident.

Approximately one-half of the exhaled air from rats dosed with 1,2-D was in the form of (^{14}C) carbon dioxide, indicating extensive metabolic breakdown. The higher proportion of exhaled radioactivity (Table IV-2) detected from 1,2-D dosed rats as compared to 1,3-D dosed animals may reflect the considerably higher vapor pressure of this compound (Hutson et al., 1971).

Investigation of the metabolic fate of 1,2-D in rats has shown the mercapturic acid, N-acetyl-S-(2-hydroxypropyl)cysteine, to be a major urinary metabolite accounting for 25 to 35 percent of a single orally administered dose (Jones and Gibson, 1980). B-chlorolactate and N-acetyl-S-(2,3-dihydroxypropyl)cysteine were identified as minor products. Unchanged 1,2-D was not detected in urine, but some was eliminated in expired air (Jones and Gibson, 1980).

Information on 1,2-D metabolism in selected animals is not available, nor is a complete metabolic scheme for the rat. However, a proposed metabolic pathway is presented in Figure IV-1. In this scheme, detoxification is achieved first by formation of the polar mercapturic acid (VI) which is

readily eliminated in the urine; and, second, by the proposed conversion of the epoxide 1,2-epoxypropane (III) to propane 1,2-diol (IV) which is non-toxic and known to undergo transformation to lactate (V) and, ultimately, transfered into the tricarboxylic acid cycle where it is released as carbon dioxide. A minor pathway (Fig. IV-1) involves oxidation of 1-chloro-2-hydroxypropane (II) to B-chlorolactaldehyde (VII) which in turn forms B-chlorolactato (VIII) and possibility the oxalate (IX); this metabolic scheme also proposes that B-chlorolactactaldehyde (VII) forms N-acetyl-S-(2,3-dinydroxypropyl) cysteine (XII) through formation of intermediates 3-chloropropan -1,2-diol (X) and 2,3-epoxypropan-1-ol (XI) (Jones and Gilson, 1980).

The metabolic distributions of the cis and trans isomers of 1,3-D were different from one another in orally dosed rats (Table IV-2). For example, about 83 percent of cis-1,3-D was eliminated in urine, whereas only 58 percent of the trans isomer was detected in this phase (male and female). This trend was reversed in expired air where volatile metabolites, mainly carbon dioxide, made up approximately 28 percent of the trans-1,3-D dose and only 4 percent of the cis-1,3-D dose (females) (Hutson et al., 1971). Vapor pressure of trans-1,3-D is slightly lower than cis-1,3-D isomer, and, therefore, does not account for the difference in the metabolic behavior of these two isomers.

In metabolic fate studies, rats dosed orally with radioactive (^{14}C) cis-1,3-D were shown to eliminate 92 percent of the dose in the urine within 24 hours as the mercapturic acid conjugate, N-acetyl S-(3-chloroprop-2-enyl) cysteine; two minor metabolites were also observed. Information on the in vivo metabolism of the trans-1,3-D isomer was not reported in this study. In vitro tests, however, indicated that the glutathione-dependent detoxification of trans-1,3-D was about five times less rapid than that of the cis-1,3-D isomer (Climie et al., 1979). Both cis- and trans-1,3-D are metabolized by soil microorganisms to 3-CAA; but there was no evidence of this transformation in the rat (Jones and Gibson, 1980; Climie et al., 1979).

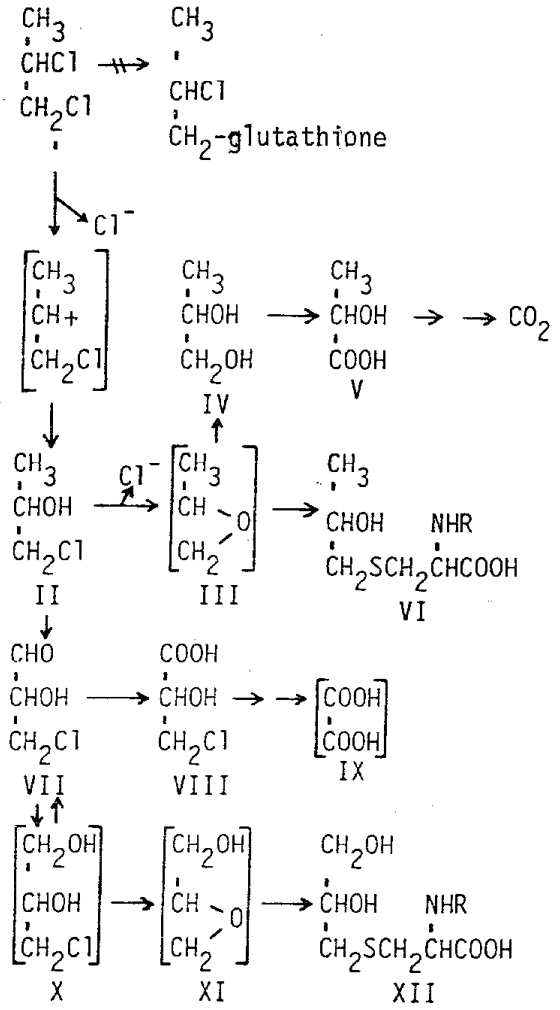
While the cis and trans isomers of 1,3-D have been shown to alkylate 4-(p-nitrobenzyl)pyridine in vitro (Neudecker et al., 1980), their rapid metabolism and elimination suggest that some effects in the intact animal could be minimized. Further study of this aspect and the extent to which metabolic detoxification might afford genetic protection are needed.

2,3-Dichloropropene, an impurity found in soil fumigants containing 1,2-D and 1,3-D, was rapidly excreted by rats within 72 hours. Following oral or intraperitoneal administration, major elimination was via urine (66 to 76 percent) followed by feces (13 to 21 percent) and exhaled air (8 percent). About 3 percent of the administered dose remained in body tissue. Results indicated that 91 percent of an oral dose was absorbed from the G.I. tract (Medinsky et al., 1983).

These data provide evidence of the rapid elimination of these short-chain chlorinated compounds by rats; they also indicate minimal residue storage in body tissue. While rapid metabolism may influence the degree of toxicity, the significance of small amounts of stored residue cannot be overlooked,

Figure IV-1

PROPOSED PATHWAY FOR METABOLISM OF
1,2-DICHLOROPROPANE IN RATS
(Jones and Gibson, 1980)



Note: Compounds in brackets are proposed intermediates.

particularly for compounds which react spontaneously with nucleic acids and proteins. These body residues may represent covalently bound adducts that lead to biochemical injury including tissue necrosis and cancer (Byard, 1983).

Occupational Exposure

No information was found on the total number of individuals exposed to 1,2-D and 1,3-D in the workplace. Widespread use of these compounds, particularly 1,2-D in the chemical industry in dry cleaning fluids, in degreasing agents, and in agriculture as fumigants, suggests that a large number of individuals would be exposed during work hours (Fishbein, 1979; USITC, 1972, -74, -76; SRI, 1975).

Case Studies:

In a Dow Chemical Company study (Venable et al., 1980), no difference in fertility was reported between unexposed employees and glycerin plant workers exposed to three carbon (C_3) compounds including 1,3-D, epichlorohydrin (ECH) and allyl chloride. In a similar study (Chemical Week, 1977) involving 864 employees at a Shell Chemical plant, cancer mortality figures for workers exposed to moderate to heavy ECH concentrations were higher than for the general population; but the mortality rate for this group was lower than for the general population.

A recent update of this study indicates that "evidence at this point to support the notion that ECH is a human carcinogen is weak, and that the highly suggestive nature of data in the previous update is not now apparent". Further, a similar report states that " epidemiological studies so far provide no evidence for an association between occupational exposure to ECH and the occurrence of malignant neoplasms in man."(Peterson, 1983).

During 1976 and 1977, California physicians reported 26 occupational injuries resulting from exposure to pesticides containing 1,3-D. Most of these were the result of spills, faulty equipment and carelessness (Maddy and Edmiston, 1978). Injury types are summarized in Table IV-3. Typical symptoms associated with these exposures included: nausea, abdominal cramps, headache, conjuctivitis, rash, blisters, difficulty in breathing, and first and second degree chemical burns.

None of the injuries are reported to have caused permanent damage. The potential hazard involved in the use of Telone II and D-D is clearly stated in the following quote from the California Department of Food and Agriculture (Maddy and Edmiston, 1978, p. 2):

> ". . . most products containing 1,3-D are toxicity category I (highest toxicity) pesticides. Inhalation can lead to headaches, nausea, vomiting, coughing and chemical pneumonia. Excessive exposure may lead to effects on the central nervous system. Skin and eye contact with this chemical can result in severe skin and eye irritations.
>
> Due to the dangers involved with this material, pesticides containing 1,3-D should be handled with closed systems. There is no protective clothing material that is completely impervious to this chemical."

In a field worker study, D-D and Telone were injected into soil and ambient air concentrations of 1,3-D were monitored during and following application (Maddy et al., 1980). The highest 1,3-D residue detected in the study was found at the loading site (Table IV-4). Within the tractor driver's breathing

Table IV-3

OCCUPATIONAL INJURIES RESULTING FROM EXPOSURE
TO 1,3-DICHLOROPROPENE, CALIFORNIA, 1976 AND 1977
(Maddy and Edmiston, 1978)

TYPE OF EXPOSURE		NUMBER RECORDED
Systemic		
Field fumigator		1
Manufacturing		1
Policeman		1
Tractor driver		1
Warehouse/truck loading		2
	Total	6
Eye		
Cleaner/repairer		7
Field fumigator		3
Manufacturing		1
	Total	11
Skin		
Cleaner/repairer		1
Field fumigator		3
Mixer/loader		2
Field inspector		1
	Total	7
Skin/Eye		
Field fumigator		1
Warehouse/truck loading		1
	Total	2

Note: These data represent exposure to chemical mixtures of which 1,3-dichloropropene was a major constituent; other constituents could contribute to toxics effects.

Table IV-4

AIR CONCENTRATIONS OF 1,3-D FOLLOWING
SOIL FUMIGATION WITH D-D AND TELONE
(Maddy et al., 1980)

SAMPLE	1,3-D CONCENTRATION (ppb)
Loading zone	3900 (highest level detected)
Tractor drivers breathing zone	380 (average)
Respirator mask (average)	
Outside	356
Inside	14
Midfield (average)	
Application time	165
24 Hours later	56
48 Hours later	37
Downwind 100 feet (average)	
During application	53
24 Hours later	60
48 Hours later	58

zone, 1,3-D air concentrations averaged 380 ppb; and only one measurement exceeded 1,000 ppb, the time weighted average (TWA) set by the American Conference of Government and Industrial Hygienists (ACGIH) for 1,3-D in soil fumigants (Sittig, 1980). Air concentrations inside the tractor driver's respirator were about 25 times below those outside the respirator (Maddy et al., 1980). Midfield and downwind, air samples were collected four feet above ground. The highest air concentration, 425 ppb, was detected midfield, but most values reported were below 100 ppb at these two sampling sites.

In a 1975 truck accident in California, a large portion of a 1,200 gallon load of Telone II (92 percent 1,3-D; 8 percent other short-chain halocarbons) spilled onto the highway. Approximately 80 people were exposed to vapors from the volatile liquid including firemen, policemen and bystanders. Of 46 persons sent to the hospital, 24 remained overnight. Twenty-eight people interviewed seven to 14 days after exposure still complained of headache, abdominal discomfort, chest discomfort or general malaise. In interviews with 21 of the exposed individuals two years later, ten complained of chest discomfort and 13 of personality changes including fatigue, irritability, difficulty concentrating, and decreased libido. These symptoms are similar to those reported by a group of individuals 13 years after exposure to methyl chloride (Flessel et al., 1978).

Carcinogenicity

Risk Assessment:

The significance of cancer to Americans is summarized in the following statistics taken from the Second Annual Report on Carcinogens (NTP, 1981, p. 5).

> "Cancer is the second most common cause of death in the United States. One in every four Americans will suffer from cancer sometime during his or her life. In 1981, about 400,000 Americans will die of cancer. In addition to the physical and emotional suffering caused by cancer, it is estimated that this disease may cost the Nation as much as 30 billion each year in lost production and income, medical expenses, and research costs."

Determining the cancer risk associated with chemical exposure by way of air, skin contact, food, or drinking water is especially difficult. Results of animal tests, whether positive or negative, do not necessarily reflect what will happen in humans. However, "All known human carcinogens with the possible exceptions of arsenic and benzene have also led to tumors in one or more animal systems." (Weisburger and Williams, 1980, p. 132)

While epidemiology studies are a useful tool in human cancer investigations, results of these studies often are difficult to interpret because human populations are exposed daily to hundreds of synthetic and naturally occurring chemicals that further complicate the problem. Chemically induced cancer as an occupational disease, however, has been demonstrated as in the classic examples of benzo(a)pyrene and certain aromatic amines (Weisburger and Williams, 1980).

Chemicals detected in drinking water are usually present only at low concentrations but pose a risk because of repeated and possible long term exposure. Carcinogenic risk assessment is different under these conditions because cancer often has a 20 year latency period that can mask the cause of disease.

In the interest of public health, federal and state agencies have established regulations designed to reduce risk by limiting the concentrations of known or suspected carcinogens in drinking water. Strong public interest in this area has resulted in passage of Public Law 95-622, Part E, 1978, that requires the Secretary of the Department of Health and Human Services (DHHS) to publish the following information annually (NTP, 1981, pp. 5-6):

> "(A) a list of all substances (i) which either are known to be carcinogens or may reasonably be anticipated to be carcinogens and (ii) to which a significant number of persons residing in the United States are exposed:
>
> "(B) information concerning the nature of such exposure and the estimated number of persons exposed to such substances:
>
> "(C) a statement identifying (i) each substance contained in the list under subparagraph (A) for which no effluent, ambient or exposure standard has been established by a Federal agency; and (ii) for each effluent, ambient, or exposure standard established by a Federal agency with respect to a substance contained in the list under subparagraph (A), the extent to which, on the basis of available medical, scientific, or other data, such standard, and the implementation of such standard by the agency decreases; the risk to public health from exposure to the substance; and "(D) a description of (i) each request received during the year involved-- "(I) from a Federal agency outside the Department of Health, Education and Welfare for the secretary, or "(II) from an entity within the Department of Health, Education and Welfare to any other entity within the Department to conduct research into, or testing for, the carcinogenicity of substances to provide information described in (ii) of subparagraph (C), and (ii) how the Secretary and each such other entity, respectively, have responded to each request".

Carcinogenesis Bioassays:
A National Toxicology Program (NTP, 1983) draft report concluded that 1,2-D (administered by gavage) caused increased hepatocellular adenomas in both male and female mice. The pathological significance of mouse liver adenomas is subject to debate. This is brought out in a draft cancer policy developed last year by the White House's Office of Science and Technology Policy which states:

> ". . . it is often necessary at least in the judgment of certain pathologists, to combine certain benign tumors with malignant ones occurring in the same tissue and at the same organ site. Examples of this are adenomas versus adenocarcinomas in the pituitary, thyroid, kidney tubules, and according to some experts, mouse liver. In all of these cases, it is argued that the pathology judgment as to whether the lesion is an adenoma or an adenocarcinoma is so subjective that it is essential they be combined for statistical purposes. It is also argued, in these specific cases, that the adenoma is related precursorally to the adenocarcinoma." (Pesticide and Toxic Chemical News, 1983. pp. 44-5)

The NTP report also concluded that in female rats there was "equivocal evidence of carcinogencity in that 1,2-dichloropropane caused a marginally increased incidence of adenocarcinomas in the mammary gland concurrent with decreased survival. . . ."(NTP, 1983, p.55). Carcinogencity in male rats was not evident.

NTP currently is evaluating carcinogenesis bioassay data for 1,3-D in rats and mice. Preliminary results suggest that 1,3-D administured by gavage may be carcinogenic. These data have not been verified by the NTP (NTP, 1983). No studies have been conducted where exposure to 1,3-D is by inhalation, the primary means of exposure for field workers. In a separate study, mice receiving repeated subcutaneous injections of cis-1,3-D developed a significant number of sarcomas at the injection site, but direct skin application did not produce malignancies (Van Duuren et al., 1979).

Both 1,2-D and 1,3-D were selected for carcinogenesis testing by NTP because data on long-term studies were not available. Further, animal tests with structurally related compounds such as 1,2-dichloroethane, 1,2-dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP) showed that these compounds were carcinogenic (NTP, 1983).

Many halogenated short-chain carbon compounds are considered to be alkylating agents. Some react directly with nucleophilic substances in DNA; others can be metabolically activated to electrophilic epoxides that readily react with nucleophilic substances in DNA (Neudecker et al., 1977; Barbin et al., 1975; Kappus et al., 1976). Chemical damage to DNA may be a significant cause of cancer (Ames, 1978). 1,2-D was judged not to be a direct alkylating agent because of its lack of reaction with 4-(p-nitrobenzyl)pyridine (NBP) (Jones and Gibson, 1980). In both in vitro (Neudecker et al., 1977) and in vivo (Climie et al., 1979) studies, cis- and trans-1,3-D were considered to be direct alkylating agents. Neudecker et al. (1980) and Eder et al. (1982) have characterized 1,3-D alkylation of NBP in vitro. While the alkylation of NBP has been correlated with mutagenicity, DNA alkylation data for 1,3-D has not been reported. Climie et al. (1979) reported that the rapid urinary eliminations of cis-1,3-D in rats is due to an efficient glutathione-dependent transformation system; the authors further suggest that this system may provide a highly effective detoxication mechanism which provides protection against direct mutagenic action from exposure to 1,3-D.

Genetic Effects

Mutagenicity

Ames Tests:

Both cis- and trans-1,3-D were strongly mutagenic (Table IV-5) with or without metabolic activation in Salmonella test strains TA1535 and TA100 (base-pair substitution), but only weakly mutagenic with or without metabolic activation in strain TA1978 (frame shift mutation). Compound purity in this study was not clearly defined (DeLorenzo et al., 1977). Neudecker et al. (1977) also reported that 1,3-D isomers are direct acting mutagens, and that the cis isomer is about twice as active as the trans isomer (compound purity: cis-1,3-D, 99.97 percent; trans- 1,3-D, 97.46 percent).

Unlike 1,3-D, relatively pure DBCP requires metabolic activation for mutagenic activity in strains TA1535 and TA100. However, low level direct mutagenicity has been observed with commercial DBCP in TA1535 and is attributed to the presence of epichlorohydrin, a stabilizer, that is also present in Telone and D-D formulations (Stolzenberg and Hine, 1980; Riles et al., 1978). Epichlorohydrin is no longer used as a corrosion inhibitor in D-D; it has been replaced by Drapex, an epoxidized soybean oil (Peterson, 1983). The manufacturer of Telone II has asked EPA for permission to remove epichlorophydrin from their product (O'mellia, 1983).

Table IV-5

MUTAGENICITY OF DICHLOROPROPANES, DICHLOROPROPENES AND SOIL FUMIGANTS IN SALMONELLA TESTER STRAINS

COMPOUND	AMOUNT PER PLATE	NUMBER OF MUTANT SALMONELLA STRAINS									
		TA1535		TA1537		TA1978		TA100		TA98	
		WO[a]	W[b]	WO	W	WO	W	WO	W	WO	W
Control[1]	0	19	21			25	28	87	89		
Cis-1,3-dichloropropene	20 µg	243	77			19	21	594	731		
" "	50 "	680	490			90	71	1800	2100		
" "	100 "	1210	990			119	131	1750	1551		
Trans-1,3-dichloropropene	20 "	235	109			27	31	362	650		
	50 "	430	381			68	75	1750	2200		
	100 "	925	828			115	91	1820	1550		
2,3-dichloropropene	20 "	190	212			31	51	531	450		
	50 "	650	451			85	97	1520	1091		
	100 "	1080	875			98	81	1900	1355		
1,2-dichloropropane	10 mg	75	81			27	27	220	185		
	20 "	210	185			38	38	480	450		
	50 "	411	312			48	48	850	920		
Control	0	17	17	15	15	8	8	71	71	22	22
Telone	100 µg	115	12	25	23	24	115	178	151	28	32
"	1000 "	75	90	18	19	45	249	263	242	27	36
"	5000 "	150	220	27	25	61	365	282	500	24	30
"	10000 "	----------Cell survival appears to be effected----------									
D-D	500 "	35	42	28	33	11	123	125	112	33	30
	15000 "	151	151	32	24	80	300	350	450	36	23
	25000 "	145	150	19	31	75	446	470	512	25	27
Control[2]	0	15	11								
Cis-1,3-dichloropropene	0.1 µl/ml	215	72								
" "	0.5 "	456	287								
Trans-1,3-dichloropropene	0.1 "	110	32								
" "	0.5 "	288	110								
Control[3]	0							78	129		
1,3-dichloropropene	10^{-1} µ moles							42	0		
" "	1 "							531	91		
" "	10 "							2215	1126		
2,3-dichloropropene	10^{-1} "							32	27		
" "	1 "							455	435		
1,2-dichloropropane	1 "							0	0		
" "	10 "							0	0		
" "	100 "							I[c]	I[c]		
1,3-dichloropropane	1 "							0	0		
" "	10 "							856	267		
" "	100 "							C	1157		
Control[4]	0	28	17	7	19			135	131	28	31
1,2-dichloropropane	100 µg	31	15	11	19			143	136	33	45
" "	1000 "	54	19	11	24			196	141	31	35

a/ wo = without metabolic activation

b/ w = activated liver microsomal fraction added

c/ Complete inhibition of bacterial cell growth

1/ Debrenzo et al., 1977

2/ Neudecker et al., 1977

3/ Stolzenberg and Hine, 1980

4/ NTP, 1983

In Salmonella strains TA1535 and TA100 1,2-D was mutagenic without activation, but only at exposure levels 500 times greater than those observed with 1,3-D (DeLorenzo et al., 1977). Stolzenberg and Hine (1980) reported that 1,2-D was not mutagenic in TA100 up to 1.1mg/plate (compound purity determined by boiling point: 95° to 96°C). They also reported complete inhibition of bacterial lawn growth at 11 mg 1,2-D/ plate. DeLorenzo et al. (1977) did not report inhibition of bacterial lawn growth up to 50 mg 1,2-D per plate. The different dose responses observed in these two studies may reflect a difference in the purity of the test compounds used.

The NTP draft report (1983) shows no significant mutagenic activity in Salmonella strains TA100, TA1535, TA1537, and TA98 following exposure to 1,2-D (Table IV-5). NTP's interpretation suggests a marginal response:

> "The mutagenic activity of 1,2-dichloropropane is marginal. This compound was tested in strains TA100, TA98, TA1537, and TA1535 of Salmonella. . . in the presence or absence of S9. No clearly postive response was obtained. In the absence of activation, there was a dose-related response in TA100 and in TA1535, with marginally positive responses at the highest doses tested (1 to 2 mg/plate). The potential for impurities to have caused the marginal, mutagenic response at these doses clouds the interpretation of these data. The dose-related response was not observed in TA100 or TA98 in the presence of S9 suggesting that the DCP or the impurity (if present) may be detoxified."(p. 54)

D-D and Telone were mutagenic in Salmonella strains TA1535 and TA100 with and without metabolic activation (Table IV-5) (DeLorenzo et al., 1977). Mutagenic activity increased significantly in TA1978 following treatment with activated liver microsomal fraction which seems to have formed a metabolite with enhanced mutagenic properties. D-D and Telone exhibited considerably lower mutagenic activity in mutant strains of Salmonella than did purified 1,3-D.

2,3-D, a possible by-product of D-D/Telone formulations and other three carbon (C_3) chlorinated mixtures, was mutagenic with or without activation in strains TA1535 and TA100 (Table IV-5) (DeLorenzo et al., 1977; Stolzenberg and Hine, 1980). Allyl chloride was also mutagenic in bacterial test strains (Bignami et al., 1980; McCoy et al., 1978). It is structurally similar to 1,3-D, and is a possible by-product of chlorinated C_3 mixtures (epichlorohydrin is the epoxide of allyl chloride). Stolzenberg and Hine (1980) noted that slight structural changes of C_3 compounds could significantly alter mutagenic activity. They also concluded that brominated derivatives generally were more mutagenic than chlorinated derivatives, and that the relative positions of halogen atoms and the double bond appeared to influence mutagenic activity.

Sister Chromatid Exchange/Chromosomal Aberrations:

1,3-D induced a significant increase in sister chromatid exchange in Chinese hamster ovary cells with and without metabolic activation (Tomkins et al., 1980). The 1,3-D used in this study was 99.4 percent cis and trans isomers (Tomkins, 1983, personal communication). 1,2-D caused both sister chromatid exchanges and chromosomal aberrations in Chinese hamster ovary cells; 1,2-D purity was approximately 99.4 percent (NTP, 1983). Each test indicates the potential of these chemicals to induce changes in genetic material.

Teratogenicity/Reproductive Effects

No information on teratogenicity or reproductive effects was found for either 1,2-D or 1,3-D.

Aquatic Toxicology

In general, data show that 1,2-D and 1,3-D are less toxic to aquatic species than many other chemicals found in water. Toxicity studies indicate that 1,3-D is significantly more toxic to aquatic organisms than 1,2-D. Much of the bioassay data was developed from static test systems that did not account for the high volatility of 1,3-D and, especially, 1,2-D. Therefore, LC_{50}/EC_{50} concentrations could be considerably lower than reported. In addition, toxicity data for 1,3-D may reflect, in part, exposure to 3-CAA, its major breakdown product. Information on compound purity and product formulation are also lacking for most of the reported studies.

Acute Toxicity:

Table IV-6 summarizes aquatic toxicity data published in EPA's water quality criteria (EPA, 1980c) for dichloropropanes and 1,3-D. Acute LC_{50} concentrations of 1,3-D and the dichloropropanes for freshwater fish ranged from 6,060 to 320,000 ppb; for saltwater fish, from 1,770 to 240,000 ppb. 1,3-D was approximately 53 times more toxic to freshwater fish than 1-2-D (and other chlorinated propanes), and about 135 times more toxic than 1,2-D to saltwater fish. The freshwater invertebrate, Daphnia magna, appears to be relatively resistant to 1,2-D with a 48 hour EC_{50} value of 52,000 ppb. As with fish, 1,3-D was more toxic to Daphnia than 1,2-D. The saltwater crustacean tested, a mysid shrimp, was clearly more sensitive to 1,3-dichloropropane than any of the other fresh or saltwater organisms tested (1,2-D was not tested). In this instance, 1,3-D was about 13 times more toxic than 1,3-dichloropropane.

Related studies (LeBlanc, 1980; Heitmuller et al., 1981; and Buccafusco et al., 1981) also indicate that 1,2-D and several other dichloropropanes are less toxic to aquatic species than 1,3-D. Table IV-7 further emphasizes the "acute no observable effect concentrations" for these chemicals. Acute toxicity values for Telone and D-D are presented in Table IV-8. D-D containing approximately 55 percent 1,3-D, 35 percent 1,2-D, and 10 percent related C_3 compounds is as toxic to largemouth bass and walleye as Telone containing about 92 percent 1,3-D, and 8 percent 1,2-D and other C_3 compounds.

1,3-D was more toxic to freshwater and saltwater algae (Table IV-9) than 1,3-dichlopropane (1,2-D was not reported). 1,3-D also appears to be as toxic to the marine diatom tested (Skeletonema costatum) as it was to Mysid shrimp (Table IV-6). In agriculture, D-D and Telone are generally used before planting (unlike DBCP) because they are toxic to terrestrial plant species. This toxicity, together with the S. costatum data, points to the immediate need for more information on the potential threat of these chemicals to phytoplankton and other algae resulting from spills and runoff.

Chronic Toxicity:

Chronic toxicity studies examine the effects of low-level chemical exposure over an extended period of time. The test should include exposure of an organism's most sensitive life stage to the chemical being evaluated.

Table IV-6

ACUTE TOXICITY OF SOME DICHLOROPROPANES AND 1,3-DICHLOROPROPENE TO AQUATIC ORGANISMS (U.S. EPA, 1980c)

SPECIES	CHEMICAL	LC_{50}/EC_{50} (ppb)
	FRESHWATER	
Daphnia magna	1,1-dichloropropane	23,000
" "	1,2-dichloropropane	52,000
" "	1,3-dichloropropane	282,000
Fathead minnow	1,2-dichloropropane	139,300
" "	1,3-dichloropropane	131,100
Bluegill	1,1-dichloropropane	97,900
"	1,2-dichloropropane	320,000
"	1,2-dichloropropane	280,000
"	1,3-dichloropropene	6,060
	SALTWATER	
Mysid shrimp	1,3-dichloropropane	10,300
" "	1,3-dichloropropene	790
Sheepshead minnow	1,3-dichloropropane	86,700
" "	1,3-dichloropropene	1,770
Tidewater silverside	1,2-dichloropropane	240,000

Table IV-7

ACUTE NO OBSERVABLE EFFECT CONCENTRATIONS OF SOME DICHLOROPROPANES AND 1,3-DICHLOROPROPENE FOR AQUATIC SPECIES

CHEMICAL	SPECIES	NO OBSERVABLE EFFECT CONCENTRATION (ppb)	REFERENCE
1,3-Dichloropropane	Sheepshead minnow	38,000	Heitmuller et al., 1981
1,3-Dichloropropane	Daphnia magna	68,000	LeBlanc, 1980
1,1-Dichloropropane	" "	<6,800	"
1,2-Dichloropropane	" "	<22,000	"
1,3-Dichloropropene	" "	410	"
1,3-Dichloropropene	Sheepshead minnow	1,200	Heitmuller et al., 1981

Table IV-8

ACUTE TOXICITY OF D-D AND TELONE TO AQUATIC SPECIES
(Johnson and Finley, 1980)

SPECIES	TELONE 96-Hour LC (ppb)	D-D 96-Hour LC (ppb)
Daphnia magna	90 (48-hr EC_{50})	
Fathead minnow	4,100	
Largemouth bass	3,650	3,400
Walleye	1,080	1,000
Cutthroat trout		1,000 - 10,000
Rainbow trout		5,500
Channel catfish		4,400
Bluegill		3,900

Table IV-9

ACUTE TOXICITY OF 1,3-DICHLOROPROPENE AND
1,3-DICHLOROPROPANE TO AQUATIC PLANTS
(U. S. EPA, 1980c)

CHEMICAL	SPECIES	96-HOUR EC_{50} (ppb)
	FRESHWATER	
	Alga	
1,3-Dichloropropene	Selenastrum capricornutum	4,950
"	" "	4,960
1,3-Dichloropropane	" "	48,000
"	" "	72,000
	SALTWATER	
	Alga	
1,3-Dichloropropene	Skeletonema costatum	1,000
"	" "	1,040
1,3-Dichloropropane	" "	65,800
"	" "	93,600

Table IV-10

CHRONIC TOXICITY OF SOME DICHLOROPROPANES
AND 1,3-DICHLOROPROPENE TO AQUATIC SPECIES
(U.S. EPA, 1980c)

CHEMICAL	SPECIES	CHRONIC VALUE (ppb)
	FRESHWATER	
1,2-Dichloropropane	Fathead minnow (embryo larval stage)	60,000
"	" "	8,100
1,3-Dichloropropane	" "	5,700
1,3-Dichloropropene	" "	244
	SALTWATER	
1,3-Dichloropropane	Mysid shrimp	3,040
1,2-Dichloropropane	Sheepshead minnow	164,000 (growth inhibition)

Chronic toxicity values for 1,2- and 1,3-dichloropropanes ranged from 57,000 to 60,000 ppb in studies with the embryo-larval stages of fathead minnow (Table IV-10). As was the case in acute studies, 1,3-D, having a chronic toxicity concentration of 244 ppb, was significantly more toxic than either 1,2- or 1,3-dichloropropane. Mysid shrimp were about twice as sensitive to 1,3-dichloropropane (chronic value = 3,040 ppb) as the fathead minnow (chronic value = 5,700 ppb). No observable effects were noted in sheepshead minnows exposed to 82,000 ppb 1,2-D, but growth inhibitation was noted at 164,000 ppb (U.S. EPA, 1980c). In early life stage toxicity tests with the fathead minnow (Pimephales promelas) exposed to 1,2- and 1,3-dichloropropanes, larval weight and survival were the most sensitive indicators of chemical stress (Table IV-10). Maximum acceptable toxicant concentrations for 1,2-D was 6,000 and 11,000 ppb, and for 1,3-dichloropropane, 8,000 and 16,000 ppb (Table IV-11), based on reduced larval weight (Benoit et al., 1981).

Bioaccumulation/Biomagnification:
No data were found on bioaccumulation or biomagnification. Metabolic studies with mammals, however, indicate no appreciable accumulation of either 1,2-D or 1,3-D in tissues (Hutson et al., 1971). The Log P (octanol/ water partition coefficient) for 1,2-D and 1,3-D are 2.28 and 1.98, respectively (U.S. EPA 1980b). These values are high enough to suggest that some bioaccumulation may occur in aquatic organisms in spite of the high volatility of these compounds.

Table IV-11
EFFECT OF 1,3-DICHLOROPROPANE AND 1,2-DICHLOROPROPANE EXPOSURE TO EARLY STAGES OF THE FATHEAD MINNOW
(Benoit et al., 1982)

1,3-DICHLOROPROPANE

PARAMETER	WATER CONCENTRATION (ppb)				
	Control[a]	4,000	16,000	32,000	65,000
Percent Hatchability	85	76	78	82	82
Percent Normal at Hatch	98	100	100	100	42[b]
Percent Survival (28-day fish)	93	98	97	98	49[b]
Weight (mg) (28-day fish)	125	115	98[b]	79[b]	25[b]

1,2-DICHLOROPROPANE

PARAMETER	WATER CONCENTRATION (ppb)					
	Control	6,000	11,000	25,000	51,000	110,000
Percent Hatchability	97	96	98	98	96	96
Percent Normal at Hatch	100	100	100	100	67[b]	0[b]
Percent Survival (28-day fish)	95	92	95	58[b]	27[b]	0[b]
Weight (mg) (28-day fish)	145	140	126[b]	79[b]	18[b]	-

[a] Control had slight contamination

[b] Significantly different from controls (p=0.05)

V. CRITERIA AND STANDARDS

Several criteria and standards have been developed for 1,2-D and 1,3-D. These limits have been developed from laboratory studies of acute and chronic effects of 1,2-D and 1,3-D exclusive of potential carcinogenicity. No criteria or standards have been established for the formulated products, D-D and Telone II.

EPA developed ambient water quality criteria to protect aquatic life from acute and chronic effects of dichloropropenes and dichloropropanes. These are presented in Table V-1.

Ambient criteria to protect human health from chronic effects have been developed only for dichloropropenes, these are: 87 ug/l, based on ingested water and contaminated aquatic organisms; and 14,100 ug/l, based on consumption of aquatic organisms alone. These criteria were developed assuming that a 70 kg person would drink two liters of contaminated water and eat 6.5 grams of contaminated seafood per day. A safety factor of 1000 was applied to compute the average daily intake based on test results that 1,3-D is mutagenic.

EPA did not develop human health criteria for dichloropropanes due to insufficient data. However, EPA estimated a tenative water safety concentration of 483 ug/l based on a study that does not meet present methodology requirements and assumptions of standard water intake and fish consumption (as described above for dichloropropenes).

Table V-1

WATER QUALITY CRITERIA FOR
PROTECTION OF AQUATIC ORGANISMS
(U.S. EPA, 1980c)

	FRESHWATER		SALTWATER	
	Acute	Chronic	Acute	Chronic
	ug/l		ug/l	
Dichloropropanes	23,000	5,700	10,300	3,040
Dichloropropenes	6,060	244	790	-

Note: Concentrations given are the lowest for which toxic effects have been observed. Acute and chronic toxicity would occur at lower concentrations among species that are more sensitive than those tested.

EPA's Office of Drinking Water has developed a health advisory of 100 ug/l for 1,2-D containing water that is consumed for less than 10 days. This health advisory is based on a no-observed adverse effect level (NOAEL), a safety factor, body weight of 70 kg, and consumption of 1 to 2 liters of contaminated water per day. The California Department of Health Services (DHS) requested guidance from EPA for setting a longer term exposure 1,2-D action level(Crook, 1982). EPA made a tentative recommendation of 10 ug/l for water consumed for ten or more days (Lappenbusch, 1983). DHS has adopted both the 10 and 100 ppb concentrations for the respective time periods of consumption.

The California Department of Food and Agriculture established a temporary tolerance for 1,3-D on crops of 10 ppb in 1980. This temporary tolerance was issued as part of an Experimental Use Permit (EUP) which expired on October 1, 1982. The temporary tolerance applied to almonds, grapes, lemons, grapefruits, cherries, figs, peaches, plumb, oranges, prunes, and walnuts. Produce treated under California EUPs cannot be marketed. This temporary tolerance, therefore, has not been used to protect consumers.

VI. MONITORING STUDIES

Overview

Despite high annual production and widespread environmental dispersion of 1,2-D/1,3-D, surface and ground water monitoring studies rarely report finding these compounds. The reasons are: (1) the compounds were not in the water examined; (2) the compounds were present only at levels below detection limits; (3) analytical detection procedures were inadequate; (4) the compounds were overlooked in water analysis. According to this report, the lack of 1,2-D findings in the past is probably explained, in part, by the latter two problems. Unlike 1,2-D, 1,3-D is not persistent and appears to undergo rapid environmental transformation. As a result, 1,3-D would most likely be detected where high amounts are present, for example, shortly after field application or at storage, dump and spill sites.

The EPA has reported 1,2-D and 1,3-D in both surface and ground water. An EPA study on the frequency of organic chemicals in surface water (Table VI-1) detected 1,2-D and 1,3-D at six and three sites respectively (Shackleford and Keith, 1976). The EPA Office of Drinking Water recently completed a draft report on results of a national survey on the occurrence of volatile organic contaminants in ground water supplies (U. S. EPA, 1983). Of 945 wells sampled across the country, 13 (1.4 percent) were positive for 1,2-D (estimated median concentration = 0.90 ppb).

Table VI-1

DETECTION OF 1,2-DICHLOROPROPANE AND
1,3-DICHLOROPROPENE IN SURFACE WATER
(Shackelford and Keith, 1976)

COMPOUND	WATER TYPE	DATE REPORTED
1,2-D	Effluent (sewage treatment plant)	1976
"	" " " "	"
"	Finished Drinking Water	"
"	River	--
"	Effluent	1975
"	Seawater	1971
1,3-D	Finished Drinking Water	1974
"	" " "	1975
"	" " "	"

National

Results of a Maryland study reported in 1980 revealed that water in 13 of 36 wells sampled had detectable levels of 1,2-D ranging from 1 to 440 ppb; three of these 36 wells were also positive for DBCP (Pinto, 1980). The wells were in close proximity to sites where 1,2-D containing nematicides were being used on fields previously treated with DBCP. Well depth ranged between 30 to 50 feet in an unconfined aquifer. The soil type at these sites was conducive to leaching surface materials. Maryland scientists concluded that vertical movement in the area was probably limited to about 70 feet and lateral movement to several hundred yards, and that contamination of the ground water was related to local soil fumigation practices. Subsequent well water sampling indicated both 1,2-D and DBCP were stable and persistent in ground water.

In a Long Island, New York study conducted between 1981 and 1983, 1,2-D was detected in ground water (up to 70 ppb) following application of Telone, Telone II, D-D and Vorlex; 1,3-D was not detected. A preliminary U.S. Department of Agriculture report indicated 3-CAA was also detected in water but the finding was not confirmed. 1,2,3-trichloropropane residue was detected at low levels (Moran, 1983). The latter compound has not been frequently reported in ground water.

State of California

In 1979 1,2-D was first detected in California well water. Seven wells located near Occidental Chemical Company in Manteca, San Joaquin County, were found to have residues of 1,2-D ranging from 0.2 to 5.0 ppb (Table VI-2). The contaminated water appeared to originate from this manufacturing and storage site, a point source discharge. In subsequent sampling of these wells three years later, 1,2-D was not found (Occidental Chemical Company, 1982; SWRCB, 1982 and 1983).

In 1979, the California Department of Agriculture (DFA) analyzed 72 well water samples for 1,3-D as part of an extensive DBCP survey. 1,3-D was not present in any sample at a detection limit of 1 ppb (Peoples et al., 1980). The more persistent 1,2-D was not included in this study.

In 1981 1,2-D was again found in California ground water during EPA's National Ground Water Monitoring Program (EPA, 1983; Spath, 1983). Of 64 California wells sampled, three were positive for 1,2-D. This included two community wells in Visalia, Tulare County, where 1,2-D was found at concentrations of approximately 3 and 26 ppb; investigation of the site indicated an industrial point source problem. The third well was located in Reedley, Fresno County, where 1 ppb was detected in a commmunity well. The source of this contamination was not identified. 1,3-D was not detected in any of these water samples (Redlin, 1983).

Concurrent with findings of point source (for example, manufacturing sites) contamination, the State Water Resources Control Board recognized the need for a systematic study to determine potential 1,2-D, 1,3-D and 3-CAA contamination of ground water from non-point (agricultural) sources. Results of studies begun in 1982 showed that underground drinking water supplies in selected agricultural areas were contaminated with 1,2-D (Table VI-2). As a result of these findings, DHS and RWQCBs (Regions 1 and 5) accelerated their 1,2-D ground water studies. In Kern County at the southern end of the Central Valley and Del Norte County along the northern coast, 1,2-D was subsequently discovered in well water. Results of all California state investigations are presented in Table VI-2; these data are derived, for the most part, from unpublished sources.

Table VI-2

SUMMARY OF GROUND WATER CONTAMINATION IN CALIFORNIA:
1,2-DICHLOROPROPANE, 1,3-DICHLOROPROPENE, 3-CHLOROALLYL ALCOHOL

Date	Location	Amount Detected (ppb)	Wells Sampled: No. Sampled	Wells Sampled: No. Positive	Comments	References*
1,2-DICHLOROPROPANE						
1979	San Joaquin Co., Manteca	0.2-5.0	7	7	Near Occidental Chem. Co., private & community wells.	a
1982	"	--	7	0	" "	a,b
1981	Tulare Co., Visalia	2.9-25.9	2	2	Nat. Ground Water Study, comm. wells.	c
1981	Throughout California	--	61	0	" "	c
1981	Fresno Co., Reedley	1	1	1	" "	c
1982	Fresno County	--	23	0	Domestic wells.	b
1982	Merced County	0.4-0.9	37	3(8%)	" "	b
1982/83	San Joaquin Co., Manteca	0.4-16	35	9(26%)	" "	b
1982	"	--	7	0	Community wells.	b
1982	Yolo Co., Davis	0.7	4	1	Municipal community well.	d
1983	Del Norte Co., Smith River	0.4->10	37	25(68%)	Domestic wells.	e
1983	Del Norte Co., Crescent City	Up to 1200	1	1	Pesticide storage site monitoring well.	e
1983	Kern Co., Bakersfield	0.14-7.9	40	17(43%)	Mostly community wells.	f
1983	Sutter Co., Oswald	3.0	4	1(25%)	Domestic wells.	b
NO. COUNTIES WITH POSITIVE WELLS TO DATE = 8		TOTAL WELLS =	266	67(25%)		
1,3-DICHLOROPROPENE						
1979		--	72	0	DFA	g
1982/83		--	136	0	SWRCB & RWQCB	b,e
NO. OF COUNTIES EXAMINED = 5			208	0		
3-CHLOROALLYL ALCOHOL						
1983	Del Norte Co., Crescent City	Up to 1410			Monitoring well, pesticide storage site.	e

*References:

a - Occidental Chemical Co., 1982
b - SWRCB, 1982-83
c - U. S. EPA, 1983
d - Public Works Department, City of Davis, 1982
e - RWQCB (Region 1), 1983
f - Nelson, 1983 (Appendix X)
g - Peoples et al., 1980

SWRCB Field Studies

The objective of this investigation was to examine ground water pollution in relation to agricultural use of soil fumigants containing 1,2-dichloropropane and 1,3-dichloropropene. These chemicals were selected on the basis of (1) agricultural use practices, that is, injection into soil; (2) chemical/physical characteristics that would allow movement through soil; and (3) the potential for high toxicological risk based on structure/activity relationship with other known high risk chemicals, such as DBCP, EDB, etc. In addition, after some 25 years of use in soil fumigation, little information was available on the environmental fate of these compounds.

Sampling Protocol

Sampling sites were selected on the basis of (1) high reported D-D/Telone use between the years 1971-1980; (2) porous soil profiles; and/or (3) shallow underground aquifers. Final site selections were made with the assistance of regional geologists, and county agricultural officials who verified fumigant use within a given location and often recommended specific sites and wells to sample.

Selected areas were screened further by actual field reconnaissance. This was necessary because reported pesticide use data did not always correlate with the age or kind of crops growing in a given area. For example, 1,3-dichloropropene, unlike DBCP, is phytotoxic and most often is used for preplant applications. An area with 30-year old fruit trees and 50-year old grape vines, therefore, has not recently been fumigated with D-D/Telone even though it may be indicated on a pesticide use report.

Only private residence wells were selected for sampling. Prior to sample collection, an attempt was made to characterize each well by reviewing drillers' well logs; however, few logs were available. As a result, specific well sites were chosen at random within selected sampling areas.

Water samples were collected from faucets closest to the well head. In most instances, well water had to be sampled after it had passed through a pressure tank with approximately 200 to 500 gallons capacity rather than being tapped directly from the well casing. Water was run 15 to 30 minutes prior to sample collection in an attempt to limit chemical loss to head space within the pressure tank and to assure adequate flushing of water in the well casing. Samples were always collected from faucets, never hoses, with flow rates adjusted to minimize air bubble formation.

Duplicate water samples were collected at each well in 40 ml glass vials with Teflon-lined caps. Water samples were immediately placed in an insulated chest containing blue ice ($\sim$6°C) and 40 ml travel blanks. Samples were delivered to a commercial laboratory usually within 24 hours of collection; maximum travel time was about 80 hours. Samples were analyzed by the purge and trap method for volatile organics (EPA Method 624) using a Coulson electroconductivity detector (Appendix VIII). Detection limit for both 1,2-D and 1,3-D was 0.5 ppb. Initially, duplicate one-liter water samples were collected for 3-CAA, but this practice was discontinued because of poor detection capability (see Appendices V, VI and VII for analytical method).

Wells with positive findings were resampled within a few weeks. Duplicate 40 ml water samples were delivered to a second laboratory for confirmation. Well water samples with 1,2-D residue approaching the 10 ppb SNARL (suggested no adverse response level) were verified by gas chromatography mass spectrometry.

San Joaquin, Fresno, and Merced Counties were chosen for initial ground water sampling based on high-documented use of D-D and Telone in these regions. Water from 23 wells sampled in Fresno County had no detectable levels of 1,2-D or 1,3-D. Of 37 wells sampled in Merced County, three (3) contained 1,2-D residue ranging from 0.4 to 0.9 ppb. 1,3-D was not detected in any of these samples. In the vicinity of Manteca, San Joaquin County, nine of 35 domestic wells sampled (26 percent) within an approximate five-square-mile area revealed detectable levels of 1,2-D in the water; concentrations ranged from a trace (0.4 ppb) to 16 ppb. Two wells had residue levels above the suggested 10 ppb SNARL set by DHS and EPA (Table VI-3). All 1,2-D positive wells were located at the edge of agricultural fields where soil fumigants containing 1,2-D were used. Wells with no detectable 1,2-D were located several hundred yards to a few miles from these fields.

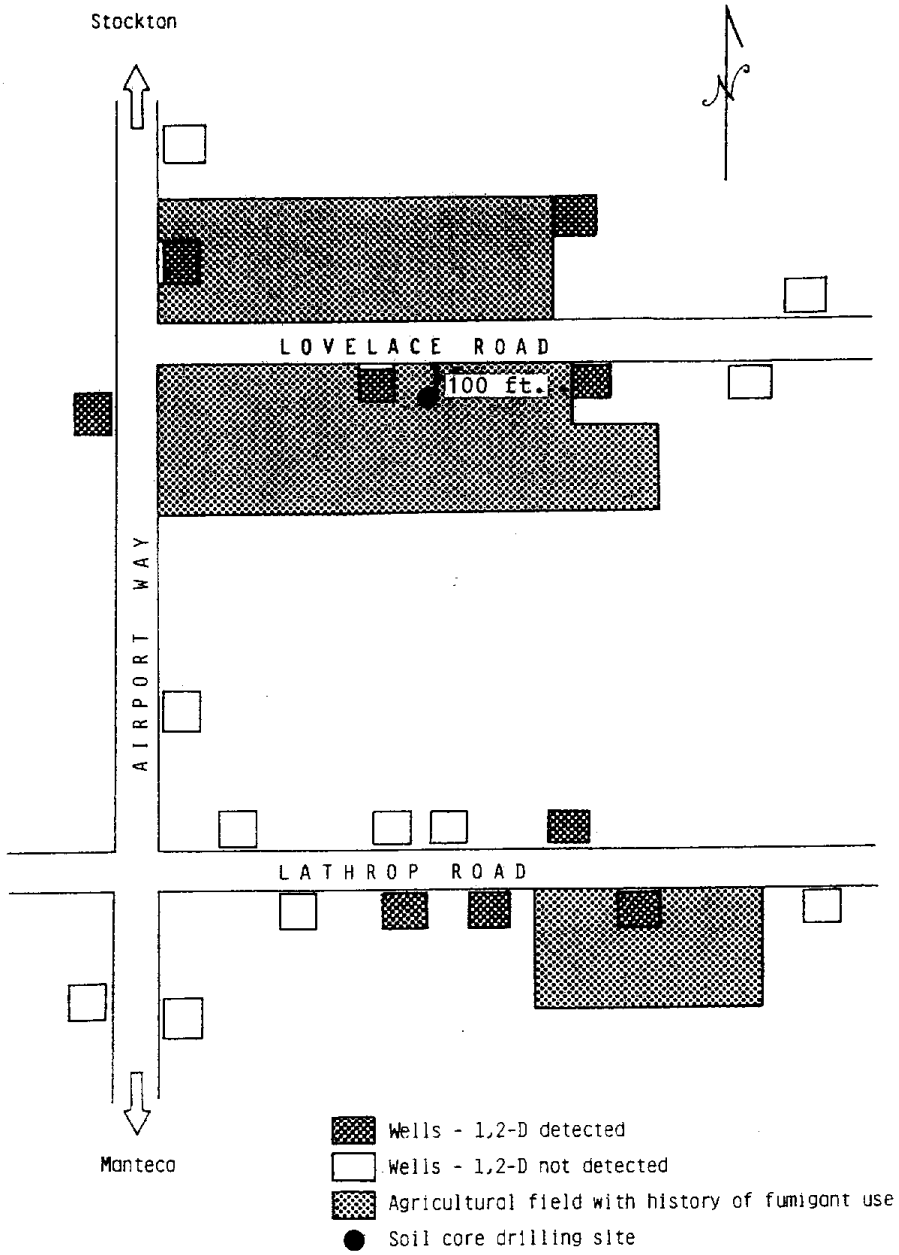
In addition to agricultural causes, it was assumed that ground water contamination could come from four other 1,2-D sources near Manteca: Occidental Chemical Company, about five miles southwest; Sharpe Army Depot, about one mile east; Forward Landfill Site (Class II-1), about 15 miles northeast; and a refuse transfer station within the immediate area. Well water was collected at various locations between these potential point sources and the 1,2-D positive well locations next to agricultural fields. Chemical analysis revealed, however, that wells located away from the fields did not have detectable levels of 1,2-D. The conclusion to be drawn is that general agricultural uses of soil fumigants containing 1,2-D, not specific sources, cause ground water contamination in the area.

In an attempt to examine the movement of 1,2-D in these agricultural fields adjacent to contaminated wells, drilling was conducted for soil core analysis. The Manteca field site selected had recent documented use of Telone II and was adjacent to the two wells where 1,2-D was found at concentrations above 10 ppb (Figure VI-1). Soil core drilling was performed by the California Department of Food and Agriculture using a truck-mounted hydraulic drill equipped with hollow-stem augers. Core samples were collected using a 20-inch split-barrel sampler containing three 6-inch stainless steel tubes; between samplings the split barrel assembly was immersed in water, scrubbed and then rinsed with pesticide grade acetone. Immediately after retrieval, a 6 to 10 gram soil sample was removed from each tube, placed in a moisture tin and weighted. These were used later to determine moisture and carbon content. The end of each 6-inch tube was then wrapped in aluminum foil, capped, taped, and immediately frozen in a chest containing dry ice. Water samples (only 2) were poured into 40 ml glass vials and capped with teflon liners and aluminum seals and placed in chests containing blue ice. Samples were transported to an analytical laboratory within 24 hours and stored at -20°C until analyzed.

Frozen samples were removed rapidly from the stainless steel tubes by slight warming. The frozen core was sawed in half lengthwise; one-half for analytical purposes and the other half for soil morphology, that is, color, texture, character, etc. After a SWRCB geologist conducted an on-site preliminary examination, soil core morphology was characterized by a consulting soil scientist (Appendix IX). Moisture was determined by subtracting dry weight from wet weight of the field collected sample; percent carbon was determined titrimetrically using the Walkley and Black Method (1934).

Figure VI-1

SOIL CORE COLLECTION SITE, SAN JOAQUIN COUNTY



Soil core samples at the Manteca site were taken at six-inch increments to an approximate depth of 24 feet where drilling was discontinued because of water intrusion. In general, soil core characterization indicated a sandy to sandy clay type soil with a reduced permeability layer at about nine feet and an aquatard at about 20 feet. Carbon content was moderate within the top four feet of soil but low throughout the remainder of the soil profile; moisture ranged from a low of about 6 percent to saturation (Appendix IX).

Chemical analysis of soil cores was performed by SRI International, Menlo Park, California and by Shell Development Company, Modesto, California (see Appendices V, VI for analytical procedures). 1,2-D was detected just below the surface to a depth of about nine feet in soil that graded from brown sand to sandy clay; the highest residue levels occurred within this zone (Table VI-3). The high 1,2-D residue detected at 7.5 feet may reflect perching above a sandy clay layer of lower permeability that was identified at the nine to ten foot depth level (Herbst, 1983). Between ten and 14 feet 1,2-D was not detected where sandy clay predominated. Soil moisture increased at this level (Appendix IX) and then dropped to its lowest point, 6 percent, at about 14 feet. Low concentrations of 1,2-D were again detected at intermittent depths between 14 and 24 feet.

A caliche aquatard was present at about 20 feet and supported a shallow, perched water table; the actual water table appeared to be present below this aquatard at 24 feet. Water samples collected below the 20-foot aquatard contained 1,2-D (4.6 ppb), m,o,p-xylenes (0.5 ppb) and were saturated with acetone; water from above the 20 foot aquatard contained 1,2-D (0.4 ppb), benzene (0.2 ppb) and were also saturated with acetone. There could be many sources of the aromatic solvents (i.e., benzene, xylene) including pesticide formulations, gasoline, etc. The presence of acetone could have been the result of inadequate drying of the split-barrel sampling device following the acetone rinse between samples.

The 1,2-D detected below the aquatard at approximately 20 feet could be the result of contamination from the perched water table via the drill hole. However, benzene which was detected in the perched water table was not detected below the aquatard. While contamination during drilling operations is possible, it apparently did not occur in the upper soil levels because 1,2-D was detected within the top 8 feet, but it was not detected in the next 6-foot section below this zone. It is possible that 1,2-D residues below 14 feet represent early soil application, while residues above ten feet reflect more recent applications that are accumulating and have not yet migrated through the sandy clay layer with lower permeability present at this depth.

While these data show that 1,2-D residue is present throughout much of the 24-foot soil profile in an agricultural field with historical use of soil fumigants, the data are, at best, preliminary. Additional drilling will be required for a more accurate picture and for evaluation and support of initial conclusions.

Trace levels (0.3-1.1 ppb) of 1,3-D were detected only within 6.5 feet of the surface. The major transformation product of 1,3-D, 3-chloroallyl alcohol (3-CAA), was detected in only one soil core two feet below the surface.

Table VI-3

RESULTS OF SOIL CORE ANALYSIS, MANTECA SITE
(SWRCB, 1983)

Depth (ft)	RESIDUE (ppb)		
	1,2-D	1,3-D	3-chloroallyl alcohol
1.5	3.6	1.0	N.A.[1/]
2.0	3.0	0.5	87
3.0	2.1	0.3	N.A.
4.5	6.7	1.1	N.D.[2/]
6.0	1.8	N.D.	N.A.
6.5	11.0	0.5	N.D.
7.5	12.2	N.D.	N.A.
8	7	N.D.	N.D.
9	1.3	N.D.	N.A.
9.5	3	N.D.	N.D.
10.5	N.D.	N.D.	N.A.
11	N.D.	N.D.	N.D.
12	N.D.	N.D.	N.A.
13.5	N.D.	N.D.	N.A.
14	N.D.	N.D.	N.A.
15	1.6	N.D.	N.A.
15.5	N.D.	N.D.	N.D.
16.5	0.2	N.D.	N.A.
17	N.D.	N.D.	N.D.
18	Trace	N.D.	N.A.
18.5	N.D.	N.D.	N.D.
19.5	0.2	N.D.	N.A.
20	N.D.	N.D.	N.D.
21	1.0	N.D.	N.A.
21.5	2.2	N.D.	N.D.
22.5	0.2	N.D.	N.A.
23	1.7	N.A.	N.A.
24	1.7	N.D.	N.A.

[1/] N.A. = Not analyzed

[2/] N.D. = None detected

The amount of 3-CAA detected (87 ppb) compared to the amount of parent 1,3-D present (0.03-1.1 ppb) indicates fairly rapid transformation of 1,3-D. This field was treated with Telone II (92 percent, 1,3-D) approximately 45 days prior to core sampling. Based on these limited residue data, it would appear that most of the 1,3-D remaining in the soil after treatment had been converted to 3-chloroallyl alcohol within this 45-day period.

This is the first evidence in a field core study displaying vertical movement of 1,2-D after its application as an agricultural fumigant. Considering the chemical and physical characteristics of 1,2-D and ideal soil properties for chemical transport here, ground water contamination could have been expected at this site.

A clear connection between agricultural use of soil fumigants and ground water contamination by 1,2-D was recently discovered in 1983 in Del Norte County. Analysis of well water in the community of Smith River Plains revealed that 25 out of 37 wells sampled had detectable levels of 1,2-D and five of these were above the 10 ppb SNARL. In none of these samples (RWQCB - Region I, 1983) was 1,3-D detected.

Smith River Plains is a relatively isolated lily bulb growing area. The soil is relatively porous and the water table shallow, particularly during the rainy season . D-D has been used extensively in the area (15,000 lbs in 1981) to control nematodes. In the absence of any known industrial sources of 1,2-D in this area, well water contamination must have been caused by application of soil fumigants. In an attempt to mitigate this problem both DFA and the local County Agricultural Commissioner have followed the State Water Resources Control Board's recommendation to avoid using any soil fumigant containing more than 2 percent 1,2-D in this area.

At an abandoned pesticide storage site in Crescent City, Del Norte County, 1,2-D and 3-chloroallyl alcohol were detected (1983) in water from two monitoring wells. Levels ranged as high as 1,200 ppb for 1,2-D and 1,410 ppb for 3-chloroallyl alcohol. No 1,3-D was detected (Table VI-3). These abnormally high concentrations are most likely due to improper storage and disposal of chemicals there. The most recent 1,2-D California findings are from Kern County in the vicinity of Bakersfield where concentration levels up to 7.9 ppb were detected by DHS in 17 wells, both shallow and deep (Appendix X). In May, SWRCB's ongoing survey discovered 1,2-D (4.5 ppb) in one of four wells sampled in Sutter County. In thes area where D-D/Telone were used in high amounts (based on pesticide use data), ground water again seems to have been contaminated by the extensive use of soil fumigants containing 1,2-D.

In summary, 67 wells in California were found to be contaminated by what appears to be the agricultural use of soil fumigants containing 1,2-D. Contaminated wells were located in agricultural areas typically characterized by porous soil and/or shallow unconfined ground water. Soil core analysis has shown that 1,2-D can travel through soil to depths of at least 24 feet.

1,3-D appears to be transformed in soil fairly rapidly to 3-CAA. Although Shell Development Company and Dow Chemical Company have analytical methods that can detect 1 ppb in water (Appendix VI and VII), detection limits for

commercial laboratories using similar methods are poor and range from 20 to 200 ppb. At these levels 3-CAA would not be detected in ground water if it were present at concentrations similar to those found for 1,2-D.

In addition to agricultural uses of fumigants, sources of 1,2-D and 1,3-D residue in surface and ground water can include household wastewater (Hathaway, 1980), chemical production, and other industrial processes (SRI, 1975; EPA 1980a). Consumer products containing either 1,2-D or 1,3-D include polishing agents, cleaning agents, and disinfectants (Hathaway, 1980). In a product release study conducted by Stanford Research Institute (1975), it was estimated that a combined total of 600,000 pounds/year out of an estimated annual production rate of 60.6 million pounds of 1,2-D and 1,3-D were unaccounted for at U.S. production sites. The report also estimated that the remaining 60 million pounds/year was being dispersed in the environment primarily through soil fumigation 1,2-D and 1,3-D were selected by SRI as two of the 80 high production chemicals having the greatest potential for environmental effects.

VII. AGRICULTURAL PERSPECTIVES

Present Practices

Soil-borne plant parasitic nematodes can seriously limit crop yield and quality. Protection of crops, particularly perennials, from nematode damage is a major challenge to California agriculture. Some of these crops must produce continuously for up to 50 years without a change in planting (Van Gundy, 1980). Until recently, effective protection of perennial crops was achieved through postplant soil fumigation with DBCP. The 1977 ban on DBCP use in California has forced agriculture to investigate alternative nematode control methods.

Nematodes are small organisms ranging in size from 0.01 to 3 mm. Crop damage by nematodes includes mechanical injury, chemico-physiological injury, withdrawal of plant nutrients, or an increase in plant sensitivity to drought and low temperatures (Leistra, 1972). The major methods presently used to reduce crop damage include cultural practices, biological control agents and chemical nematicides.

Cultural Practices: This term refers to a broad set of farm management techniques including: tillage operations, fertilization, irrigation, selection of nematode resistant plant varieties, cropping sequence (crop rotation), handling of crop residues, and timing of operations (National Academy of Sciences, 1975). These practices can be incorporated into an integrated pest management (IPM) strategy.

Crop rotation is probably among the oldest methods of nematode control. When a host crop (e.g., potatoes) is grown in soils with a low nematode density, nematode population usually increases 20 to 30 fold (Leistra, 1972). In the absence of host plants (e.g., potatoes), a decline in nematode population of up to 35 percent per year has been observed. The planting of nematode resistant plant varieties (a common practice in California) can further reduce pest populations by up to 80 percent per year. After a few years of continuous monoculture, however, a nematode "pathotype" will multiply and overcome the plant's resistance. The opportunity for development of these specific pathotypes can be reduced when resistant varieties are not grown in close crop rotation. Preplant soil fumigation will delay the appearance of new pathotypes.

Biological Control: Recent studies suggest natural enemies (predators and parasites) may reduce nematode populations to a greater extent than previously documented (Van Gundy, 1980). When an attempt is made to introduce biological agents for nematode control, problems arise, especially with regard to their introduction, dispersion, and establishment; soils are, namely, "biologically buffered" and present a serious challenge to the survival of newly introduced organisms (Thomason, 1983). In addition, farmers must maintain profitable crop production until these parasites become established in agricultural soils.

The development of new nematicides does not appear to be a high priority for the agricultural chemical industry (Van Gundy, 1980). Nematicides constitute only three (3) percent of an annual $2.6 billion pesticide market. The chemical industry estimates that approximately $15 million is required to develop and register a new product.

Chemical Control: The ban on the agricultural use of DBCP was a severe blow to California farmers. Since 1955 farmers have used this fumigant for both preplant soil treatment as well as treatment of established citrus groves, stone fruit orchards, vineyards, and many annual crops (Van Gundy, 1980). At the present time, Aldicarb is the only soil nematicide fully registered for use on selected perennial crops. Among those chemicals under study for postplant uses are:

Aldicarb (Temik)	Oxamyl (Vydate)
Nemacur	Carbofuran (Furadan)
Mocap	Telone II
Dasanit	

The problems observed in postplant treatment with presently registered nematicides such as D-D, Telone II and methyl bromide, are phytotoxicity and destruction of endomycorrhizae (beneficial symbiotic fungi) in soil. These conditions can lead to root damage (Baines et al., 1977) and severe stunting of established plants (Kleinschmidt and Gerdemann, 1972).

In some cases the phytotoxicity observed in crops treated with D-D mixture has been attributed to both the 1,3-D and 1,2-D components of this fumigant. The phytotoxic response initiated by 1,3-D is attributed to the development of 3-CAA, the primary hydrolysis product of 1,3-D (Baines et al., 1977). A soil concentration of 40 ppm (ug/g) or more of 3-CAA has been shown to be highly toxic to sweet orange seedlings in a fine sandy-loam soil. Similar studies have also shown 250 ppm of 1,2-D to be lethal to these seedlings (Moje et al., 1957). Further evidence of 1,2-D phytotoxicity has been observed in winter wheat. Ear malformation and yield reduction will sometimes occur up to the third year after fumigation (Lebbink, 1976).

Integrated Pest Management

Integrated pest management (IPM) uses a systems approach to reduce pest damage to tolerable levels. A variety of techniques are involved, including natural predators, pathogens, parasites, genetically resistant hosts, environmental modification and, when necessary and appropriate, chemical pesticides (Bottrell and Smith, 1982). Although pesticides have and will continue to play an important role in integrated pest management, IPM programs rely on nonchemical defenses against pests before altering the environment with chemical pesticides.

The use of interactive computer programs to review and weigh all the variables involved in making the best decisions for nematode control is a promising new approach (Van Gundy, 1980). Computer systems are particularly valuable in the quantification of the economic aspects of crop production and pest management. At the University of California, Riverside, a system has been developed to relate the critical injury threshold to the crop value. A data base for sugar beet pest management (Roberts and Thomason, 1981; Thomason, 1982) includes the development of methods for estimating soil nematode populations prior to planting (Ferris et al., 1981). In these studies, techniques have been developed to measure initial soil populations, predict the role of seasonal and geographic effects on injury thresholds, and determine the relationship of these variables to reduction in crop yields. From these data, an "economic threshold" can be established, that is, the density of a pest population or threshold below which the cost of applying control measures exceeds

losses caused by the pest (Bottrell and Smith, 1982; Ferris, 1978). A major environmental and economic benefit of this approach may be the ability to reduce the number of nematicide applications. Decisions to treat would not be based on the presence or absence of a particular nematode, but rather on the potentially threatening population density (Van Gundy, 1980).

The major factors limiting full implementation of an IPM program for plant parasitic nematode control are: (1) inadequate numbers of commercial laboratories capable of soil sampling and analysis for nematode population assessment; (2) limited number of crop-specific injury thresholds for growing districts and planting dates; and (3) limited grower confidence in the program. The latter factor is extremely important since errors could lead to substantial yield losses.

VIII. REMEDIAL OPTIONS

Remedial actions are required when potable well water is contaminated with organic chemicals. An aquifer receiving a continuous supply of contaminants is extremely difficult to renovate; decontamination of ground waters is often uneconomical and in some cases technically infeasible (Josephson, 1980). At the present time, the consumer is usually advised by the state or local health agency to seek an alternative water source if the level of contamination exceeds a defined action level (EPA Health Advisory Levels, 1982; see Chapter V of this report). This discussion focuses on measures to be taken when ground water has been contaminated by the use of chemical nematicides such as D-D/Telone and DBCP. Some alternatives are:

1. Use of bottled or shipped water, that is, an alternative supply after the well(s) has been abandoned.

2. Recovery and use of contaminated water for nonpotable purposes. A secondary benefit of this process is that the physical influence of pumpage will cause the flow of "cleaner" ground water to the contaminated well area, and will reduce contaminant concentrations.

3. Redrilling the well to a deeper aquifer.

4. Water treatment to remove the contaminant in the ground or at the soil surface. Better cleanup can be achieved at the surface, where organics can be stripped by aeration if volatile; oxidized with oxygen or ozone; adsorbed on activated carbon, polymers or resins; or decomposed by waste-specific microorganisms (Josephson, 1980).

Activated carbon is often the treatment method of choice for compounds with low, between 100 and 140, molecular weight (Stover, 1982). The capability of carbon to remove these compounds effectively is dependent on the quality of the water being processed. With good water quality, approximately 2.0 mg/l of total organic carbon or less, activated carbon has been shown to be effective. In poorer quality water, the low molecular weight organics can be desorbed by preferential adsorption of higher molecular weight compounds (carbon adsorption data for 1,2-D is given in Figure VIII-1). At an initial concentration of 1 mg/l, the carbon adsorption capacity is 5.9 mg 1,2-D per gram of carbon, a limited capacity when compared to DBCP which has a carbon adsorption capacity of 53 mg/g under similar test conditions (U.S. EPA, 1980a).

The Department of Health Services (DHS) has found carbon adsorption systems to be superior to air-stripping for removal of DBCP from private water systems when conditions had been optimized for carbon contact time and exhaustion rate. One (1) cubic foot of activated carbon will decontaminate up to 600,000 gallons of water with use of a flow restrictor to ensure a two-minute residence time on the carbon. Filters of this type are installed alongside a dwelling at the entry point of the water source. A standard activated carbon filter having a capacity of two cubic feet can treat over one million gallons

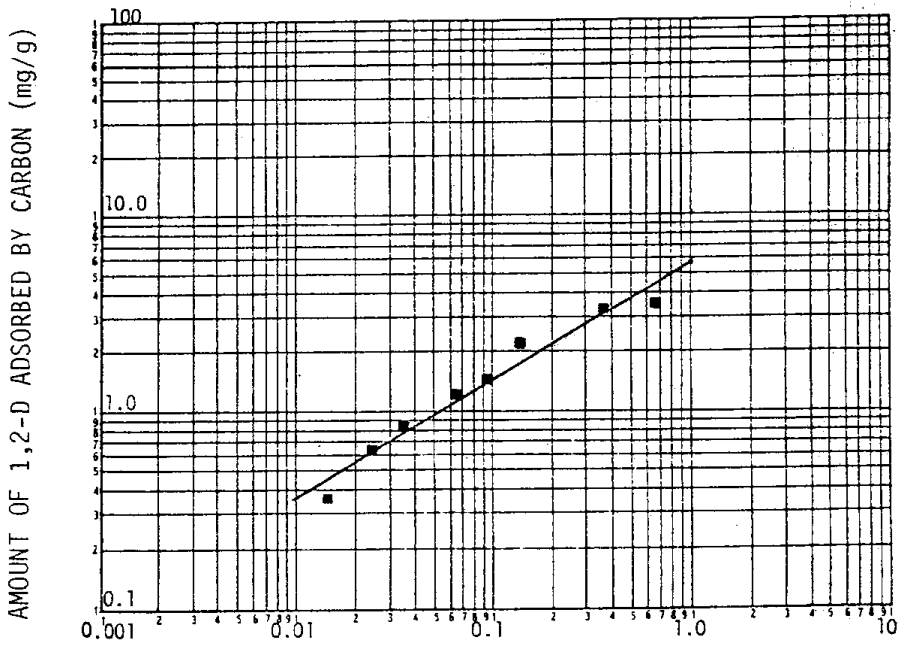
of DBCP-contaminated water at a use level of 500 to 600 gallons per day (Redlin, 1983). DHS has discouraged the use of indoor tap or undersink carbon filtering devices since the necessary carbon contact time and the rate of adsorbent exhaustion have not been determined for these units. It appears, in contrast, that no studies have been conducted to determine optimum methods and conditions for removal of 1,2-D residues from private systems.

Since 1,2-D is highly volatile and shows limited affinity for activated carbon (by a factor of 10 less), air-stripping may prove to be the effective method of cleanup.

There are several current examples of measures being taken to decontaminate ground water in California. Occidental Chemical Company in Lathrop, California, has constructed a treatment facility at the site where ground water was contaminated with DBCP, EDB, and other volatile organics. Ground water here is pumped to the surface, treated with activated carbon and recharged into the aquifer. At the Aerojet General Corporation, Sacramento, water contaminated with TCE is pumped to the surface, air-stripped and then is injected back to the aquifer or placed in surface impoundments. However, air-stripping must be viewed cautiously because of health risks from contamination of the atmosphere around the stripping towers.

Figure VIII-1

ADSORPTION ISOTHERM OF 1,2-DICHLOROPROPANE ON ACTIVATED CARBON POWDER (Filtrasorb-300; pH 5.3; 22±2°C) (Dobbs and Cohen, 1980)



APPENDICES

APPENDIX I

DICHLOROPROPANE, DICHLOROPROPENE PESTICIDE PRODUCTS
REGISTERED FOR USE IN CALIFORNIA

D-D MIXTURE

SEARCH NO. 001
DATE 03/09/83
ACTIVITY

STATUS O
TYPE
USE
WARNING
FORM
CHEMICAL 00185
CLASS
CHEMICAL
CLASS
STATUS
CMDY
NO. PROD 00027

AMVAC CHEMICAL CORP

4100 E WASHINGTON BLV
LOS ANGELES, CA 90023

05481 50179 AA FUM-A-CIDE 15-D

05481 50184 AA FUM-A-CIDE 30-D

BAKERSFIELD AG-CHEM, INC.

RT. 11 BOX 858
BAKERSFIELD, CA 93308

11369 50013 AA BAC-FUME D SOIL FUMIGANT

BRITZ INC.

P.O. BOX 366
FIVE POINTS, CA 93624

10951 50040 AA BRITZ BRAND VIDDEN D SOIL FUMIGANT

BROWN & BRYANT INC

P O BIN T
SHAFTER , CA 93263

11373 50003 AA BEEBEE D-D SOIL FUMIGANT

DOW CHEMICAL COMPANY, THE

P.O. BOX 1706
MIDLAND , MI 48640

00464 00511 AA TELONE II SOIL FUMIGANT

GREAT LAKES CHEMICAL CORP., DR. L. VERNON WHITE

P. O. BOX 2200
WEST LAFAYE,TIN 47906

05785 00027 AA TERR-O-GAS 57/43T

05785 00033 AA TERR-O-CIDE 15-D

05785 00036 AA TERR-O-CIDE 30-D

NOR-AM AGRICULTURAL PRODUCTS, INC

THE ATRIUM-350 W SHUMAN BLVD
NAPERVILLE , IL 60566

02139 00055 AA VORLEX

OCCIDENTAL CHEMICAL COMPANY DIVISION OF OCCIDENTAL
PETROLEUM CORPORATION
P O BOX 198
LATHROP , CA 95330

07001 50379 AA NEMATOCIDE D-D

SHELL CHEMICAL COMPANY A DIVISION OF SHELL OIL COM
PANY AGRICULTURAL CHEMICALS
P.O. BOX 3871
HOUSTON , TX 77001

00201 00119 AA D-D SOIL FUMIGANT

00201 00253 AA D-D SOIL FUMIGANT FOR MANUFACTURING PURPOSES ONLY

SOIL CHEMICALS CORPORATION

P O BOX 531
MORGAN HILL, CA 95037

08536 00008 AA PIC-CLOR-60

08536 00010 AA BROM 70/30

08536 50014 AA PIC-CLOR-30

08536 50017 AA PIC-CLOR-35

SOILSERV INC

PO BOX 3650
SALINAS , CA 93912

06973 50006 AA SOILSERV D-D SOIL FUMIGANT

TAYLOR JOHN FERTILIZERS CO

P O BOX 15289
SACRAMENTO , CA 95813

07729 50018 AA JOHN TAYLOR CHEMICALS FUMIGANT D

TRI-CAL INC

P O BOX 2
MORGAN HILL, CA 95037

11220 00001 AA TRI-CAL TELONE II SOIL FUMIGANT

11220 50008 AA TRI-FORM 40/60

11220 50011 AA TRI-CON D

UNION CHEMICALS DIVISION, UNION OIL COMPANY OF CAL
IFORNIA
PO BOX 60235
LOS ANGELES, CA 90060

09018 00004 AA UNION TELONE II

WESTERN FARM SERVICE INC

3075 CITRUS CIRCLE, SUITE 195
WALNUT CREE, CA 94598

11656 00027 AA D-D SOIL FUMIGANT

WESTERN FARM SERVICE INC. MONTEREY BAY DIV.

P. O. BOX 148
WATSONVILLE, CA 95076

11079 50021 AA LESCO D-C FUMIGANT 70-30

11079 50022 AA LESCO D-C FUMIGANT 85-15

WILBUR-ELLIS COMPANY

191 W SHAW AVE SUITE 107
FRESNO , CA 93704

02935 50090 AA RED-TOP D-C SOIL FUMIGANT

DICHLOROPROPENE

SEARCH NO. 002
DATE 03/09/83
ACTIVITY

STATUS O
TYPE
USE
WARNING
FORM
CHEMICAL 00206
CLASS
CHEMICAL
CLASS
STATUS
CMDY
NO. PROD 00011

AID LABORATORIES, INC.

P.O. BOX DRAWER 1607
OKEECHOBEE , FL 33472

13330 50001 AA AID WORM-X

ANCHOR LABORATORIES, INC. A DIVISION OF PHILIPS
ROXANE, INC.
2621 N BELT HWY
ST JOSEPH , MO 64502

04691 00003 AA MANGE LOTION

BIO-CEUTIC LABORATORIES,INC. A DIVISION OF PHILIPS
ROXANE, INC.
2621 NORTH BELT HIGHWAY
ST. JOSEPH , MO 64502

04691 00003 AA 11770 BIO-CEUTIC DEMODECTIC AND SARCOPTIC MANGE LOTION

GEERPRES

P O BOX 658
MUSKEGON , MI 49443

06081 00005 ZA BOL-TABS

PET CHEMICALS INC

P.O. BOX 660656
MIAMI SPRIN,SFL 33166

04758 00011 AA HOLIDAY OINTMENT

04758 00011 ZA VIP OINTMENT REPELS BITING FLIES

04758 00032 AA HOLIDAY FLEA STOP FOR DOGS

STOCKTON VETERINARY SUPPLY COMPANY

338 E. LAFAYETTE STREET
STOCKTON , CA 95203

02382 00013 AA 33191 DR. SAUNDERS ANIMAL HOSPITAL PET SPRAY

TENNECO CHEMICALS INC. ATTN J. P. VOELKER

P.O. BOX 365
PISCATAWAY , NJ 08854

01100 00048 ZA NUOPHENE

THIOKOL/VENTRON DIVISION

150 ANDOVER STREET
DANVERS , MA 01923

02829 00030 AA CUNIPHEN 2721

WESTERN FARM SERVICE INC

3075 CITRUS CIRCLE, SUITE 195
WALNUT CREE, CA 94598

11656 00064 AA TELONE II SOIL FUMIGANT

SEARCH NO. 001
DATE 07/28/82
ACTIVITY

STATUS 0
TYPE
USE
WARNING
FORM
CHEMICAL 00573
CLASS
CHEMICAL
CLASS
STATUS
CMDY
NO. PROD 00009

BRITZ INC.

P.O. BOX 9050
FRESNO , CA 93790

10951 50039 AA TELONE

CHEMICAL DISTRIBUTORS DBA ARIZONA AGROCHEMICAL CO.

P O BOX 21537
PHOENIX , AZ 85036

01526 00503 AA AGRO-CHEM BRAND TELONE II

DOW CHEMICAL COMPANY, THE

P.O. BOX 1706
MIDLAND , MI 48640

00464 00379 ZB TELONE C-17 SOIL FUNGICIDE AND NEMATICIDE (REVISED FORMULA)

OCCIDENTAL CHEMICAL COMPANY DIVISION OF OCCIDENTAL PETROLEUM CORPORATION
P O BOX 198
LATHROP , CA 95330

07001 00117 AA TELONE

PUREGRO COMPANY

1276 HALYARD DRIVE
WEST SACRAM,NCA 95691

01202 00308 AA PUREGRO TELONE II SOIL FUMIGANT

ROCKWOOD CHEMICAL CO

P O BOX 34
BRAWLEY , CA 92227

10226 00054 AA TELONE II--SOIL FUMIGANT

SOIL CHEMICALS CORPORATION

P O BOX 531
MORGAN HILL, CA 95037

08536 50016 AA PIC-CLOR-15

TAYLOR JOHN FERTILIZERS CO

P O BOX 15289
SACRAMENTO , CA 95813

07729 00006 AA JOHN TAYLOR CHEMICALS TELONE 11

TOXO SPRAY DUST, INC.

12651 EAST LOS NIETOS ROAD
SANTA FE SP,ICAS90670

35296 00001 AA TOXO TELONE II SOIL FUMIGANT

DOW*

TELONE* II

SOIL FUMIGANT

A Clean, Clear, Non-Clogging Liquid for Preplant Treatment of Crop Lands to Control Plant Parasitic Nematodes and Certain Other Soil Pests

204.4 L / 54 GAL

THE DOW CHEMICAL COMPANY
AND SUBSIDIARIES
MIDLAND, MICHIGAN 48640, USA HORGEN, SWITZERLAND HONG KONG
CORAL GABLES, FLORIDA 33134, USA SARNIA, ONTARIO, CANADA

SL1940

ACTIVE INGREDIENT:	
1,3-Dichloropropene	92%
INERT INGREDIENTS:	8%

E.P.A. Registration No. 464-511

E.P.A. Est. No. 464-TX-1(TB); 464-CA-1(WP); 05770-CO-1(V); 33780-SC-1(J); 33776-WA-1(W); 14775-FL-1(B).
Superscript used corresponds to letter in Lot No.

PRECAUCION AL USUARIO: Si usted no lee inglés, no use este producto hasta que la etiqueta le haya sido explicada ampliamente.

TRANSLATION: (TO THE USER: If you cannot read English, do not use this product until the label has been fully explained to you.)

86-1350 PRINTED IN U.S.A. IN FEBRUARY, 1983.
REPLACES SPECIMEN LABEL 86-1350 PRINTED IN MAY, 1980.
DISCARD PREVIOUS SPECIMEN LABELS.
REVISIONS INCLUDE: Revised DOT shipping name and added UN#.

KEEP OUT OF REACH OF CHILDREN

DANGER

PRECAUTIONARY STATEMENTS
HAZARDS TO HUMANS AND DOMESTIC ANIMALS

HAZARDOUS LIQUID AND VAPOR • MAY BE FATAL IF INHALED, ABSORBED THROUGH SKIN, OR SWALLOWED • CAUSES BURNS OF SKIN OR EYES • MAY PRODUCE KIDNEY AND LIVER DAMAGE UPON PROLONGED EXPOSURE

Do Not Breathe Vapor • Do Not Get in Eyes, on Skin, on Clothing
Do Not Take Internally • Use Only With Adequate Ventilation
Wear Eye and Skin Protection Necessary to Prevent Contact
When Handling TELONE II • Wash Thoroughly After Handling and Before Eating or Smoking

If protective gear, such as boots or gloves, becomes contaminated, immediately wash with soap and water. Never wear protective gear having the odor of 1,3-dichloropropene. Aerate and wash all protective gear thoroughly after use until all odor is gone.
Render unusable and dispose of contaminated leather goods, including shoes.

SEE FURTHER INSTRUCTIONS UNDER HANDLING PRECAUTIONS SECTION ON SIDE PANEL

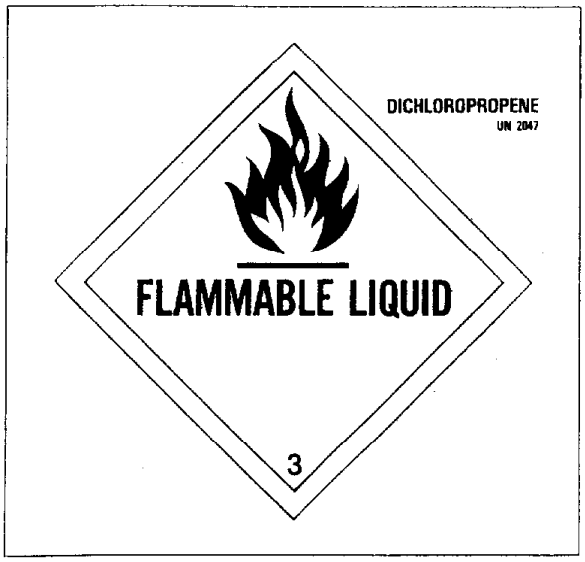
IF INHALED, remove to fresh air. If not breathing, give artificial respiration, preferably mouth-to-mouth. If breathing is difficult, give oxygen. Call a physician.
IF ON SKIN, *immediately* flush skin with plenty of water for at least 15 minutes while removing contaminated clothing and shoes. Call a physician. If water not immediately available, remove excess chemical from skin with sorbent material such as towel or dry soil, then proceed at once to location where water is available and thoroughly wash contaminated skin with plenty of water. Call a physician.
IF IN EYES, *immediately* flush eyes with plenty of water for at least 15 minutes. Call a physician.
IF SWALLOWED, *immediately* induce vomiting by giving two glasses of water and sticking finger down throat. Call a physician. Never give anything by mouth to an unconscious person.

PHYSICAL OR CHEMICAL HAZARDS
COMBUSTIBLE
Do Not Use, Pour, Spill, or Store Near Heat or Open Flame
Do Not Cut or Weld Container

ENVIRONMENTAL HAZARDS
To avoid injury to fish and other wildlife, do not spill or empty into streams, ponds, or any other bodies of water. Do not contaminate water by cleaning of equipment or disposal of wastes.

In case of an emergency endangering life or property involving this product, call collect
517-636-4400

AGRICULTURAL CHEMICAL
Do Not Ship or Store with Food, Feeds, Drugs, or Clothing



TELONE* II
SOIL FUMIGANT

DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

HANDLING PRECAUTIONS

DO NOT INHALE VAPORS: NIOSH- or MSHA-approved respiratory protection should be worn when TELONE II liquid soil fumigant is exposed to the atmosphere or when conducting operations which vent to the atmosphere. A NIOSH- or MSHA-approved half-face respirator with chemical worker's goggles or full-face respirators shall be used during small spills, repairs, calibrations, transfers, sampling and when working in poorly ventilated areas. When in use cannisters or cartridges shall be replaced daily or sooner if specified by manufacturer or at first sign of odor breakthrough, whichever comes first. NIOSH-approved cartridges, such as a Welsh 7400-IL, will be adequate for short-term situations such as listed above.

Where very high concentrations of vapors might be expected (such as large spills in poorly ventilated areas) a self-contained or air-supplied respirator should be used.

DO NOT GET ON SKIN: When handling or working with TELONE II, wear clean body covering including gloves and heavy footwear. Immediately remove contaminated coverings. Aerate and wash all protective clothing and gear thoroughly after use.

There are no protective clothing materials that are *completely* impervious. Rubber, vinyl protective gear, thin layers of polyethylene (minimum 1 mil), give short-term protection and shall be immediately discarded upon contamination. Heavy (3+ mil) polyethylene, rubber, neoprene provide longer term protection. Leather gives no protection. If gear becomes contaminated, immediately wash with soap and water. Never wear protective gear having odor of TELONE II. Wash and aerate all protective gear thoroughly after use until all odor is gone.

DO NOT GET IN EYES: Wear eye protection such as chemical worker's goggles or full-face respirator when handling TELONE II.

DO NOT SWALLOW: Do not use the mouth to siphon TELONE II from containers or to blow out clogged lines, nozzles, etc.

STORAGE, SHIPMENT AND DISPOSAL

STORAGE: Store in tightly-closed original container in a cool place away from dwellings. Do not allow contamination of seeds, plants, fertilizers, or other pesticide chemicals. Do not contaminate food, feedstuffs, drugs, or domestic water supplies. In outside storage, store drums on sides to avoid accumulation of rain water in top or bottom recessed areas.

SHIPMENT: Do not ship or store with food, feeds, drugs, or clothing.

DISPOSAL: Rinse equipment and containers and dispose of wastes, including spills or rinsates, in a landfill approved for pesticides or by burying in non-crop lands away from domestic water supplies. Punch holes in containers before disposal. Dispose of empty containers in approved landfill or bury in a safe place. Consult Federal, State or local disposal authorities for approved alternative procedures.

DO NOT REUSE ORIGINAL CONTAINERS SUCH AS DRUMS

GENERAL INFORMATION

Use TELONE II soil fumigant only as a **preplanting soil treatment** to control plant parasitic nematodes [root-knot, meadow (lesion), citrus, cyst formers (golden, sugar beet, soybean), burrowing, ring, spiral, sting, pin, stubby root, stylet, dagger]; also to control wireworms and garden centipedes (symphylans). Fumigate land to be planted to the crops listed below by applying TELONE II under the conditions, and at the rates recommended under DIRECTIONS FOR USE, DOSAGE AND USE RECOMMENDATIONS, and USE PRECAUTIONS. Read the entire label before using TELONE II.

Vegetable Crops:

asparagus	cauliflower	horseradish	parsnips	shallots
beans	celery	kale	peas	spinach
beets	collards	kohlrabi	peppers	squash (summer)
blackeyed peas	corn	leeks	pimentoes	squash (winter)
broccoli	cowpeas	lettuce	potatoes	sweet potatoes
brussels sprouts	cucumbers	melons	pumpkins	swiss chard
cabbage	egg plant	mustard greens	radishes	tomatoes
cantaloupe	endive	okra	rutabaga	turnips
carrots	garlic	onions	salsify	watermelons

Field Crops:

alfalfa	flax	oats	sorghum
barley	grasses	pasture grass	soybeans
birdsfoot trefoil	hops	peanuts	sugar beets
buckwheat	lespedeza	popcorn	sugarcane
clover	millet	rice	tobacco
corn	milo	rye	vetch
cotton	mint	safflower	wheat

Citrus Fruit Tree Planting Sites:

grapefruit kumquats lemons limes oranges tangerines tangelos

Deciduous Fruit and Nut Tree Planting Sites:

almonds	dates	olives	plums
apples	figs	peaches	pomegranates
apricots	filberts	pears	prunes
cashews nuts	hazelnuts	pecans	quince
cherries	hickory nuts	persimmons	walnuts
chestnuts	nectarines	pineapple	

Bush and Vine Planting Sites:

blackberries	currants	huckleberries	youngberries
blueberries	dewberries	loganberries	
boysenberries	gooseberries	raspberries	
cranberries	grapes	strawberries	

Nursery Crops including floral plants, ornamentals, shrubs, and bushes; forest, shade, fruit and nut trees and vine and bramble fruits of all types.

APPLICATION DIRECTIONS

WHEN TO TREAT: Apply TELONE II either in the spring or fall, whenever soil type and conditions permit. For best results with annual crops, treat the soil each year. In northern states, late summer, or early fall treatment (before October 15) is best for land to be planted to early spring crops, especially transplanted crops such as celery, tomatoes, and nursery and orchard stock. Early fall treatment permits planting a fall cover crop. **Note:** Treat muck soils only in the early fall and plant as late as possible in the spring; treat fine textured (clay) soils only when they are near or at the wilting point. Do not use TELONE II to treat any type of soil when it is cold and/or wet.

SOIL PREPARATIONS: TELONE II gives best results when conditions permit rapid diffusion of the fumigant through the soil and the soil surface can be sealed to prevent excessive fumigant loss during the exposure period. The soil should be in good seed bed condition, free of clods and undecomposed plant material, moisture at about one-half of field capacity, and temperature between 40° and 80°F at the depth of injection. If undecomposed plant debris is present, it should be plowed down and allowed to decompose before applying TELONE II. Tillage deeper than 12 inches is necessary for good fumigant penetration in soils where a hard or "plow" pan occurs at plow depth. Where deep tillage is used, the tillage equipment may often be modified to simultaneously apply the fumigant and thus avoid going over the field twice.

APPLICATION: TELONE II may be applied either as an **overall (broadcast)** or **row treatment,** using suitable application equipment that will ensure placement of the fumigant at least 6 to 8 inches below the final soil surface. **For overall application** use either plowsole or chisel equipment with the chisels spaced 12 inches apart. When the fumigant is injected at a depth of 12 inches or more (deep tillage), the chisel spacing may be up to twice the application depth but should not exceed 30 inches. Application may be made in the same direction or at an angle to the direction of the planting row, whichever is most convenient. **For row application,** use chisel equipment with one chisel per row or two chisels spaced 12 inches apart to treat only the soil where the crop is to be planted. When one chisel per row is used, adjust the fumigant flow rate to distribute about 1⅓ times more fumigant per chisel than is recommended for overall application. When two chisels are used per row, apply at the same flow rate per chisel as for overall. In both cases, the amount of fumigant required per acre will decrease as the distance between rows is increased and vice versa. At time of planting, avoid placing the seed row directly over the furrow left by the applicator chisel. When a single chisel is used per row, place the seed 3 to 4 inches to one side of the chisel furrow; when two chisels are used, plant in the center of the area between the chisel furrows.

SEALING: Immediately after application, compact the soil surface to prevent excessive fumigant loss. After chisel application, use a roller, cultipacker, or similar sealing device. After plow-sole application, disk the land, then compact it by floating or rolling. Sealing after row application can be accomplished by the tractor wheel, by listing, or by bedding so that the fumigant will be 12 to 14 inches below the top of the bed. When fumigating listed rows, seal in the fumigant with ring rollers, press sealers, or by re-listing.

EXPOSURE PERIOD: After application and sealing, leave the soil undisturbed for 7 to 14 days. A longer exposure period will be required if the soil becomes excessively cold or wet during the exposure period.

AERATION AND PREPARATION OF SOIL BEFORE PLANTING: At the end of the exposure period allow the soil to aerate completely before planting the crop. Aeration is usually complete when the odor of TELONE II is no longer evident. Under optimum soil and weather conditions, allow one week of aeration time for each 10 gallons of TELONE II applied per acre. When TELONE II is used for treating deep-rooted tree and shrub planting sites, a 3 to 6 months aeration period should be allowed. To hasten aeration, **especially if heavy rains or low temperatures occur during the exposure period,** work the soil to the depth of the treatment zone. After row treatment use a knife-like chisel in the bed without turning the soil, thus reducing possible recontamination of the treated soil. To hasten aeration after overall treatment, plow or deep cultivate to the depth of the treatment zone. This is especially desirable in northern states after fall fumigation of muck soils.

DOSAGE AND USE RECOMMENDATIONS
to Control Nematodes, Symphylans[†], and Wireworms[†]

Crops (consult list of individual crops under General Information)	Type of Treatment	Soil Type	Dosage: Gallons Per Acre[1]	Dosage: Fl. Oz./1000 Ft. Row Per Chisel
Shallow Rooted Plants: Field Crops, Floral Crops, Grasses and Turf, Small Fruits, Vegetables, Ornamentals	Row (42")[6]	Mineral	4.5 to 6	46 to 62
		Muck or Peat	9 to 12	93 to 123
	Overall (Broadcast)	Mineral	9 to 15[2]	26 to 44
		Muck or Peat	24[3] to 36	71 to 106
Strawberries	Overall	Mineral	24 to 36	71 to 106
Sugar Beets Root-Knot Nematode	Row (42")	Mineral	6	62
	Overall		12 to 15	35 to 44
Sugar Beet Nematode	Row (42")		9	93
	Overall		12 to 18	35 to 53
Pineapple[4]	Row	Mineral	24 to 36	—
Citrus — Florida[5]	Overall	Mineral	36	106

Nursery and Field:[7] Citrus Fruit Trees, Deciduous Fruit Trees[8], Forest Trees, Grapes, Nut Trees, Ornamentals (deep rooted)	Overall: Gallons Per Acre to Penetrate Various Depths				
	Mineral Soils	3 ft.	4 ft.	5 ft.	6 ft.
	Sand	15	21	27	33
	Sandy Loam	27	30	36	48
	Silt Loam	42	51	63	75
	Clay Loam	54	69	84	102

[1]Use the higher rates in heavier soil

[2]For cyst-forming nematodes increase dosage to 18 gallons per acre (53 fl. oz./1000 ft. row per chisel)

[3]For muck soils containing less than 30% organic matter use 18 gallons per acre

[4]For Hawaiian pineapple, application may be made at time of or just before planting

[5]For burrowing nematode in citrus inject on 18-inch centers, 12 inches deep. Keep free of plants susceptible to burrowing nematodes for 2 years before replanting to citrus

[6]Row treatment is not recommended for potatoes in irrigated areas of western and northwestern states.

[7]Tree planting sites prepared by backhoeing may be treated by pouring 27 fl. oz. of TELONE II into the hole during backfilling. For best results prepare and treat sites in the fall and plant in the spring

[8]Use TELONE II as an aid in the control of bacterial canker and decline of peach trees by application as a preplant, overall treatment of light (sandy) soils at the rate of 24 to 36 gallons per acre (71 to 106 fl. oz./1000 ft. row per chisel) preferably in the fall when the soil is warm (50-85° F at 6-inch depth) and moist. Inject the fumigant at a depth of 10 to 12 inches with chisels mounted on 12 inch centers. Follow directions for soil preparation, sealing, exposure, and aeration as specified elsewhere on this label

[†]**NOTE:** To control symphylans (garden centipedes) use only overall at 18 or more gallons per acre, and apply during late summer or early fall when the soil is warm. To control wireworms use the higher dosages recommended for nematodes in overall or broadcast treatments

White Potatoes in Northwestern States: Use TELONE II as a spring or preferably a fall treatment to control quackgrass and for suppression of the damaging effects of Verticillium wilt in fields to be planted to white potatoes. Apply as an overall treatment according to the following directions:

Time of Treatment	Gallons per Acre	Fl. Oz./1000 Ft. Row per Chisel
Spring	17 to 25	50 to 73
Fall	25 to 34	73 to 100

Mint in Northwestern States: Use 59 gallons of TELONE II per acre (173 fl. oz./1000 ft. row per chisel) as an overall treatment in the spring, or preferably in the fall, to aid in the reduction of the damaging effects of Verticillium wilt in disease infested land to be used for mint production. After treatment allow at least 7 to 8 weeks or until the odor of the fumigant has left the soil before planting. Consult State Agricultural Experiment Station or State Extension Service Specialists for the use of other practices such as flaming the stubble, weed control, and cultural practices when using TELONE II as an aid to reducing damage caused by Verticillium wilt.

USE PRECAUTIONS

Important — Note Carefully. Fumigation may temporarily raise the level of ammonia nitrogen and soluble salts in the soil. This is most likely to occur when heavy rates of fertilizer and fumigant are applied to soils that are either cold, wet, acid, or high in organic matter. To avoid injury to plant roots, fertilize as indicated by soil tests made after fumigation. To avoid ammonia injury or nitrate starvation, or both, to crops on high organic soils do not use fertilizers containing ammonium salts and use only fertilizers containing nitrates, until after the crop is well established and the soil temperature is above 65°F.

Certain crops including cotton, sugarcane, and pineapple are tolerant to ammonia and the above rule does not apply to them. When using high rates of TELONE II as required by certain state nursery regulations, liming of highly acid soils before fumigation may stimulate nitrification and reduce the possibility of ammonia toxicity. Certain nursery crops such as citrus seedlings, *Cornus sp.*, *Crataegus sp.*, spruce, and vegetable crops such as cauliflower have shown evidence of phosphorus deficiency following fumigation. To avoid this possible effect, it is suggested that additional phosphate fertilizer be used on soils where experience indicates a deficiency may occur.

Attention: To avoid reinfestation of treated soil do not use irrigation water, transplants, tools, seed pieces, or crop remains that could carry soilborne pests from infested land. Clean equipment carefully before using.

Since TELONE II soil fumigant is corrosive under certain conditions, flush all applicators with fuel oil or kerosene immediately after use. DO NOT USE WATER. **Do not use containers, pumps, or other transfer equipment made of aluminum, magnesium or their alloys, as under certain conditions TELONE II may be severely corrosive to such metals.**

Use this product only as specified on this label.

NOTICE: Seller warrants that the product conforms to its chemical description and is reasonably fit for the purposes stated on the label when used in accordance with directions under normal conditions of use, but neither this warranty nor any other warranty of MERCHANTABILITY or FITNESS FOR A PARTICULAR PURPOSE, express or implied, extends to the use of this product contrary to label instructions, or under abnormal conditions, or under conditions not reasonably foreseeable to seller, and buyer assumes the risk of any such use.

Shell

D-D®

SOIL FUMIGANT

KEEP CONTAINER AND CONTENTS AWAY FROM HEAT OR OPEN FLAME

ACTIVE INGREDIENTS	**BY WEIGHT**
Chlorinated C_3 Hydrocarbons, including 1,3-Dichloropropene, 1,2-Dichloropropane, 3,3-Dichloropropene, 2,3-Dichloropropene, and Other Related Chlorinated Hydrocarbons	100%

EPA Reg. No. 201-119

This product contains 10 pounds active ingredient per gallon.

KEEP OUT OF REACH OF CHILDREN

DANGER

HAZARDOUS LIQUID AND VAPOR. MAY BE FATAL IF INHALED, ABSORBED THROUGH SKIN, OR SWALLOWED. CAUSES BURNS OF SKIN OR EYES. MAY PRODUCE KIDNEY AND LIVER DAMAGE UPON PROLONGED EXPOSURE.

STATEMENT OF PRACTICAL TREATMENT

IF SWALLOWED, call a physician, poison control center, or hospital emergency room immediately and follow the directions given. If medical advice is not available, induce vomiting. NEVER INDUCE VOMITING OR GIVE ANYTHING BY MOUTH TO AN UNCONSCIOUS OR DROWSY PERSON. To induce vomiting, give one or two glasses of water followed by two tablespoons (30 cc or one ounce) Syrup of Ipecac. For a child, give one glass of water followed by one tablespoon (15 cc or one-half ounce) Syrup of Ipecac. If Ipecac is not available, give two glasses of water (one glass for a child) and induce vomiting by touching finger to back of victim's throat. Keep victim's head below hips while vomiting. After vomiting has occurred, get medical attention. If you are not successful at inducing vomiting, get medical attention immediately. Do not waste time with further attempts.

IF INHALED, remove to fresh air. If not breathing, give artificial respiration, preferably mouth to mouth. If breathing is labored, give oxygen. *Get medical attention.*

IF ON SKIN, immediately flush skin with plenty of water for 15 minutes while removing contaminated clothing and shoes or boots. If water is not immediately available, remove excess chemical from skin with sorbent material such as a towel or dry soil, then proceed at once to a location where water is available. *Get medical attention.*

IF IN EYES, immediately flush eyes with water for 15 minutes. *Get medical attention immediately.*

See Side Panel For Additional Precautionary Statements

ACL 2144C 11-82

SHELL CHEMICAL COMPANY, A Division of Shell Oil Company,
AGRICULTURAL CHEMICALS, HOUSTON, TEXAS 77001

PRECAUTIONARY STATEMENTS

HAZARDS TO HUMANS AND DOMESTIC ANIMALS

DANGER!

HAZARDOUS LIQUID AND VAPOR. MAY BE FATAL IF INHALED, ABSORBED THROUGH SKIN OR SWALLOWED. CAUSES BURNS OF SKIN OR EYES. MAY PRODUCE KIDNEY AND LIVER DAMAGE UPON PROLONGED EXPOSURE.

DO NOT INHALE
NIOSH-approved respiratory equipment should be worn when liquid D-D is exposed to the atmosphere. A NIOSH-approved half mask organic vapor respirator (such as MSA 460968 with a 464031 cartridge or Wilson 1721) should be worn during loading and maintenance operations where only small amounts of liquid or vapor are released. For loading and maintenance operations where sizeable amounts of liquid or vapor are released in unconfined spaces, a NIOSH-approved full facepiece (such as MSA 460560 with 464031 cartridge or a Wilson 1621) organic vapor cartridge respirator is recommended. When liquid D-D is exposed to the atmosphere in confined spaces where high concentrations may occur, where oxygen deficiency may occur, when handling large spills, and during fire fighting, a self-contained breathing apparatus is required. Cartridges should be replaced per manufacturer's instructions but should in no case be used if the odor of the product is present. Used cartridges should be destroyed immediately.

DO NOT GET ON SKIN
When handling or working with D-D, wear clean body covering including polyethylene or neoprene gloves and heavy (greater than 3 mil thickness) polyethylene, neoprene, or rubber footwear. Leather goods offer no protection. Wash and aerate all clothing and gear thoroughly after use or immediately following significant contamination. Never wear clothing, footwear or gear having an odor of D-D. Dispose of thin rubber and leather items that are accidentally contaminated; do not reuse.

DO NOT GET IN EYES
Wear eye protection such as chemical workers' goggles when handling D-D.

DO NOT SWALLOW
Do not use the mouth to siphon D-D from containers or to blow out clogged lines, nozzles, etc. Wash thoroughly after handling and before eating or smoking.

FOR 24-HOUR EMERGENCY MEDICAL ASSISTANCE, CALL (713) 473-9461.

ENVIRONMENTAL HAZARDS
To avoid injury to fish and other wildlife, do not spill or empty containers into streams, ponds, or any other body of water. Do not contaminate water by cleaning of equipment or disposal of wastes.

PHYSICAL OR CHEMICAL HAZARDS
FLAMMABLE. Do not use, pour, or store near heat or open flame. Do not cut or weld container. Do not store in or use containers or equipment made of aluminum, magnesium, or their alloys.

IN CASE OF A SIGNIFICANT SPILL, CALL (713) 473-9461 or CHEMTREC (800) 424-9300.

DIRECTIONS FOR USE

It is a violation of Federal law to use this product in a manner inconsistent with its labeling.

STORAGE AND DISPOSAL

PROHIBITIONS: Do not contaminate water, food, or feed by storage or disposal. Open dumping is prohibited. Do not reuse empty container.

PESTICIDE DISPOSAL: Pesticide or rinsate that cannot be used according to label instructions must be disposed of according to Federal or approved State procedures under Subtitle C of the Resource Conservation and Recovery Act.

CONTAINER DISPOSAL: Triple rinse (or equivalent). Dispose of in a sanitary landfill or by other approved State and local procedures.

DO NOT REUSE CONTAINER
DO NOT CUT OR WELD CONTAINER

APPLICATION PRECAUTIONS

IMPORTANT: NOTE CAREFULLY. Fumigation may temporarily raise the level of ammonia nitrogen and soluble salts in the soil. This is most likely to occur when heavy rates of fertilizer and fumigant are applied to soils that are either cold, wet, acid, or high in organic matter. To avoid injury to plant roots, fertilize as indicated by soil test following fumigation. To avoid ammonia injury, nitrate starvation, or both to crops, avoid using fertilizers containing ammonium salts and use only fertilizers containing nitrates until after the crop is well established and the soil temperature is above 65°F. Certain crops,

including cotton, sugarcane, and pineapple, are tolerant to ammonia, and the above rule does not apply to them. Liming highly acid soils before fumigation stimulates nitrification and reduces the possibility of ammonia toxicity.

Do not store in or use containers or equipment made of aluminum, magnesium, or their alloys. Store in cool place away from dwellings. After use, always empty and clean applicator thoroughly with kerosene or fuel oil. Avoid using water in equipment.

Avoid reinfesting treated soil. Do not use irrigation water, transplants, tools, seed pieces, or crop remains that could carry soilborne pests from infested land. Clean equipment carefully before using.

GENERAL DIRECTIONS

Use D-D Soil Fumigant at full strength as a preplanting treatment by injection in the soil only, for control of cyst (soybean, golden, tobacco, sugar beet) root knot, root lesion or meadow, burrowing, citrus, stem and bulb, sting, ring, awl, spiral, lance, pin, stubby root, stylet, dagger and other plant parasitic nematodes, symphylids, and wireworms. Nematodes, wireworms, and symphylids appear on many field, forage, vegetable, nursery crops, grasses, ornamentals, small fruits, citrus, avocados, nut and deciduous fruits, mint, hops, sugar beets, and vineyards. For best results, treat prior to each crop planting. Do not use on heavy clay soils. Avoid reinfestation of treated soil from transplants, tools, equipment, or crop remains from infested areas.

WHEN TO TREAT

Treat in spring or fall, whenever soil conditions are suitable. Soil temperature 6 inches deep should be between 40 and 80°F. (Cold or wet soils retain fumigant longer. Dry or hot soils release fumigant too rapidly.) Fall treatment is suggested for land to be planted to early planted crops such as celery, tomatoes, and nursery stock. Early fall treatment allows planting a fall cover crop. A three-month period should be allowed before planting treated muck and heavy soils to allow complete aeration. For symphylid control, time application in accordance with local, state, and federal recommendations.

SOIL PREPARATION

Plow to a depth of 16 to 12 inches. Disc soil thoroughly to break up clods and cut up trash. Cover trash or allow to rot before fumigation. Soil should be smooth and free of debris with adequate moisture for good germination. Deep tillage, 12 to 18 inches, often improves results, especially in heavy and muck soils.

APPLICATION

OVER-ALL (BROADCAST) APPLICATION: Apply with chisel or plow-sole equipment. Apply in uniform streams 10 to 12 inches apart and at least 6 to 12 inches deep in the soil. With chisel application, seal chisel channels with a drag, ring roller, or press wheel behind the applicator. With plow-sole applications, disc IMMEDIATELY to break clods and then seal with roller or drag.

ROW (BAND) TREATMENT: Adjust injection chisels to same spacing as planter. Inject at least 6 to 12 inches below the final soil surface. Seal with roller or drag. Plant directly in treated strips.

SPLIT APPLICATION: (Use only for dosages in excess of 80 gallons per acre.) Apply only half the suggested dosage, wait one to two weeks and plow, turning the treated soil completely over. (Discing is not satisfactory.) Then apply the remainder and seal with drag or roller.

CITRUS REPLANTING SITES: Space chisels 18 to 20 inches apart and inject 12 to 14 inches deep over-all.

FOR DECIDUOUS ORCHARDS, FOREST AND NURSERY CROP PLANTING SITES:
Treat large areas over-all or in strips 10 feet wide. Individual tree sites can be treated by injecting with a handgun in a 10 foot square area. Inject 10 to 12 inches deep with injections spaced 12 inches apart. When using a handgun, seal the injection hole with the foot.

WHEN TO PLANT

Under normal conditions, a waiting period of one week for each 10 gallons of D-D Soil Fumigant used on a broadcast basis should be allowed. (Pineapple land can be treated at time of planting.) Allow additional time before planting if temperatures are below 60°F or if there have been heavy rains.

Soil treated with massive doses of fumigant before planting, such as for deep-rooted trees and shrub planting sites, requires a 3 to 6 months waiting period. Before planting, plow or open planting hole to thoroughly aerate soil.

MISCELLANEOUS USES

BACTERIAL CANKER AND DECLINE OF PEACH TREES
Use as a preplant treatment of light (sandy) soils using 40-60 gallons of D-D Soil Fumigant per acre. Apply by chisel injections at 10-12 inch depth on 12-inch spacings. Seal soil soon after treatment with ring roller or drag. Soil should be warm (50-85°F at 6 in. depth), moist and cultivated thoroughly before application. Remove roots and other plant debris prior to treatment. Fall application usually is best because of warm soil. Pre-irrigation may be necessary to provide sufficient moisture. A waiting period of one week should be allowed for each 10 gallons of D-D Soil Fumigant used on a broadcast basis.

WHITE POTATOES IN NORTHWESTERN STATES: To control quackgrass in fields to be planted to white potatoes, apply D-D Soil Fumigant as a spring or preferably a fall broadcast (over-all) treatment using 20 to 28 gallons per acre. For suppression of the damaging effects of verticillium wilt in fields to be planted to white potatoes, apply D-D Soil Fumigant as a spring or preferably a fall broadcast (over-all) treatment using 40 to 48 gallons per acre.

FIELD BINDWEED (PERENNIAL MORNINGGLORY) SUPPRESSION: Use 30-50 gallons of D-D Soil Fumigant per acre over-all as a spring or preferably fall treat ment to aid in the control of field bindweed (perennial morningglory) on bare ground. Prior to planting, see section on "When to Plant."

MINT IN NORTHWESTERN STATES: Use 40 gallons of D-D Soil Fumigant per acre as a spring or preferably a fall treatment to aid in the reduction of the damaging effects of verticillium wilt in disease-infested land to be used for mint production. After treatment, allow at least 7 to 8 weeks or until the odor of the fumigant has left the soil before planting. Consult local Agricultural Experiment Station authorities for the use of other practices such as flaming the stubble, weed control, and cultural practices when using D-D Fumigant as an aid in reducing damage caused by verticillium wilt.

DOSAGE AND USE REQUIREMENTS

CROP		TYPE OF TREATMENT	SOIL TYPE	DOSAGE (GALLONS) PER ACRE[1,2]
Field Crop (Tobacco,[3] Cotton, Etc.) Floral Crops Grasses and Turf Ornamentals Small Fruits Vegetables		Row (42")	Mineral	7½ to 10
			Muck or Peat	15 to 20
		Over-all (or broadcast)	Mineral	18 to 25[4]
			Muck or Peat	40[5] to 60
Carrots		Over-all (or broadcast)	Mineral	18 to 25[4]
			Muck or Peat	40[5] to 60
Sugar Beets	Root Knot Nematodes	Row (42")	Mineral	9
		Over-all	Mineral	20
	Sugar Beet Nematodes	Row (42")	Mineral	15 to 20
		Over-all	Mineral	25 to 30
Deciduous Orchards Forest Nurseries Nut Trees Ornamental Nurseries[6] Strawberries Vineyards		Strip-treatment	Mineral	Treat a 10 ft wide strip in which new trees are to be planted at 40 gal/acre.[7]
		Over-all	Mineral	40 to 60
Pineapples		Row	Mineral	40 to 60
Citrus, Avocados	Florida	Over-all	Sandy	60
	California	Over-All	Sandy	60 to 100
			Loam	80 to 150
			Clay Loam	120 to 200

[1]One gallon of D-D Soil Fumigant weighs 10 pounds.
[2]For symphylid control, apply 30 to 40 gallons of D-D Soil Fumigant per acre in accordance with local, state, and federal recommendations. To control wireworms, use dosage recommended for nematodes in broadcast treatment.
[3]To calibrate equipment for tobacco — The following steps will help calibrate your gravity flow applicator for row treatment of tobacco to insure 10 gallons of D-D per acre. Measure 156 feet of row (52 steps). Lower injector 8-10 inches in soil. Place tube into pint or quart jar. Start tractor and open valve on gravity flow. After 156 feet, applicator must deliver 1 pint. This is 10 gallons per acre. If less, decrease tractor speed. If more, increase speed. Once set, maintain the same tractor speed. Calibrate each outlet separately.
[4]For cyst-forming nematodes, increase dosage to 25 to 30 gallons per acre.
[5]For muck soils containing less than 30% organic matter, reduce dosage to 30 gallons per acre.
[6]In California, consult local recommendations for specific rates on individual nursery crops.
[7]Example: If trees are to be planted in rows 20 feet apart, only half of the area is treated (alternate 10 ft. strips), thus, only 20 gallons are applied — the part treated is at the over-all rate of 40 gallons per acre.

Formula for calculating dosage rate on strips:

$$\frac{\text{Width of strip to be treated}}{\text{Row Spacing}} \times \text{Over-all Rate} = \text{Actual gallons to be applied}$$

NOTICE OF WARRANTY

SHELL CHEMICAL COMPANY MAKES NO WARRANTY OF MERCHANTABILITY, FITNESS FOR ANY PURPOSE, OR OTHERWISE, EXPRESS OR IMPLIED, concerning this product or its use, which extend beyond the statements on this label.

DICHLOROPROPENE AND PROPYLENE DICHLORIDE MIXTURE, Flammable Liquid (Corrosive) NA 2047

APPENDIX III

Soil Properties

(McKerry and Thomason, 1974)

Soil Type	Sand	Silt	Clay	pH
		%		
Moreno Silty Clay Loam	13	62	25	7.3
Hanford Sandy Loam	63	22	15	7.1

APPENDIX IV

ESTIMATION OF 1,3-DICHLOROPROPENE VOLATILIZATION (1981)

Total use of 1,2-D and 1,3-D type fumigants in 1981 in California:

D-D mixture	16,426,393 pounds
1,2-Dichloropropane, 1,3-Dichloropropene and related Chlorinated C_3 hydrocarbons	357,088 pounds
Total Use	16,783,481 pounds

Assuming that 50 percent of the total pounds applied were D-D (approximately 60 percent 1,3-D) and 50 percent Telone II (approximately 90 % 1,3-D), the total 1,3-D application is 12,587,610 pounds.

Under the best soil fumigation conditions, volatilization losses can range from 5 to 10 percent (McKenry and Thomason, 1974). Assuming a 10 percent loss, the annual release of 1,3-D to atmosphere will be 1,258, 761 pounds, equivalent to 629.4 tons.

APPENDIX V

SOIL CORES - METHODS AND ANALYTICAL PROCEDURES

PART A - SRI INTERNATIONAL

III. Soil Characterization

A. Moisture

The percent moisture in each core tube* was determined by drying a weighed sample (weighed in field) at 95°C for 48 hrs. and subtracting the dried weight from the wet weight. The percent moisture data appear in Table 1 and plot of percent moisture versus depth appears in Figure 1.

B. Percent Carbon

The percent organic carbon was determined titrimetrically using the Walkley and Black method. Briefly, a dried soil sample (letter-2 sample) was ground in a mortar and pestle. A 1.0 gm sample was placed in a flask with 10.0 ml of 0.167M potassium dichromate and digested with 20 ml of concentrated sulfuric acid. Upon cooling, 200 ml of water was added along with 10 ml of phosphoric acid. An indicator solution was added (barium diphenylamine sulfate) and the solution was titrated with 0.500 M ammonium ferrous sulfate. The results appear in Table 2 and show a fairly consistent distribution of carbon except for the top samples which are closer to the area of vegetation.

C. Soil Morphology

The frozen core samples were slightly warmed and plunged from the steel container. The frozen soil was cut lengthwise with a bandsaw. Half of the core was wrapped (still frozen) in foil and stored at -20°C. The other half of sample was evaluated for color, texture character, etc. by Dr. Ruldolph Urlich, a consulting soil scientist. His evaluations appear in Appendix 1.

IV. Chemical Analysis

A. Soil Samples

Our initial investigations centered around an analytical method developed by Shell Development Company in which water and a small amount

*The labeling of the tubes was as follows: The first core sample contained three tubes that were labeled A-3, A-2, A-1 from top to bottom; the second core sample was labeled B-3, B-2, B-1, etc. Thus, sample A-1 was on top of sample B-3. All the letter-3 samples were given to Dr. Bruce Herman of Shell Development Company, Modesto, Ca.

(10 ml) of an organic solvent is added to the soil and the suspension is refluxed. The condensate passes through a crankcase dilution receiver where the organics are concentrated in the organic solvent by liquid-liquid extraction and the water is returned to the soil. The organic layer is then analyzed for the compounds of interest by gas chromatography using the halogen selective Hall detector. In the absence of a Hall detector, the method was applied as developed by Shell only an electron capture (^{63}Ni) detector was used in place of the Hall detector.

Ethyl acetate was used as the extracting solvent, however, this solvent was incompatible with the electron capture detector for low level analysis. The solvent was switched to hexane and better results were obtained. Therefore, the following procedure was used:

To a 500 ml round-bottomed flask was added 20 to 50 gm of soil followed by 200 ml of water and 10 ml of hexane (Burdick and Jackson). The crankcase dilution receiver was added coupled to a condenser. The suspension was heated to reflux and the heating continued for 1 hour. The hexane was removed from the crankcase dilution receiver and 2 µl was chromatographed under the following conditions:

Instrument:	Hewlett-Packard 5840 Gas Chromatograph
Column:	30 meter DB 1701 fused silica capillary column (J + W Scientific)
Temperature:	75°C (0.5 min hold) → 100°C @ 20°/min
Carrier Gas:	Argon/Methane (95/5)
Mode:	Splitless
Injection Volume:	2.0 µl
Detector:	Electron Capture - ^{63}Ni

A soil sample was spiked with 209 ppb of 1,2-D and carried through the above extraction and analysis procedure along with an unspiked blank soil. The recovery of 1,2-D was 100.9% suggesting that the extraction procedure was quite efficient. However, the minimum detection level was estimated to be 33 ppb. Assuming a 100% recovery for the remaining compounds, we estimated their lower detection limits (based on a spiked soil blank extract) to be 16 ppb for 1,3-dichloropropene; 59 ppb for cis - 3-chloroallyl alcohol; and 70 ppb for trans - 3-chloroallyl alcohol.

A number of the core samples were extracted by the developed procedure and none of the studied compounds were observed. Representative chromatograms of samples E-1 and F-1 an shown in Figure 2.

B. Water Samples

The two water samples (L-3 and P-1) collected during the field study were analyzed by the purge and trap methodology using a Coulson electrolytic conductivity detector and a photoionization detector. 1,2-D was identified in both samples by comparative chromatography with authentic standards. Several aromatics along with large amounts of acetone were found using the photoionization detector. The chromatographic profiles for these samples appear in Figure 3-6 and the quantitative determinations appear in Table 3. Sensitivity limits of 0.1 ppb and 1.0 ppb were determined for 1,2-D and 1,3-dichloropropane, however, the chloroallyl alcohols could not be observed under 100 ppb by this methodology.

Table 3

COMPOUNDS FOUND IN WATER SAMPLES L-3 AND P-1

	P-1			L-3	
Compounds	PPB	Detector	Compounds	PPB	Detector
1,2-Dichloro-propane	4.6	CED	1,2-Dichloropane	0.4	CED
M-xylene	0.5	PID	Acetone	saturated	PID
O,P-Xylenes	0.5	PID	Benzene	0.2	PID
Acetone	saturated	PID			

C. Soil Reanalysis by Aqueous Extraction

The concentration of 1,2-D observed in the water samples suggested that possibly much lower levels were present in the soil than that which would be detected by the previously developed method. Since the solubility of 1,2-D is quite high in water (2700 ppm), we investigated an aqueous extraction method to which we could apply the purge and trap methodology for sample analysis.

A 20 to 25 gm soil sample was placed in a 40 ml screw cap centrifuge tube and 20 to 30 ml of high purity water was added. The tube was capped (nearly zero headspace) and the slurry was mixed thoroughly by inversion for 15 min. The slurry was then centrifuged at 3000 rpm for 10 minutes. A 10 ml aliquot was removed and analyzed under the following conditions:

Instrument:	Hewlett-Packard 5730A Gas Chromatograph equipped with a HP 7675A purge and trap sampler
Trap:	10 cm × 0.4 cm glass column packed with 60/80 mesh Tenax-GC
Column:	1.2 m × 2 mm glass column packed with 1% SP1000 on 80/100 mesh Carbopak B
Temperature:	75°C (4 min hold) → 180°C (HOLD) @ 4°/min
Flow Rate:	30 ml/min N_2
Detector:	Electron Capture (^{63}Ni)
Integrator:	Hewlett-Packard 3380A
Retention Times:	Bromochloromethane (I.S.) 15.77 minutes 1,2-Dichloropropane 24.20 minutes 1,3-Dichloropropane 24.78 minutes (trans) 27.05 minutes (cis)

Since a large portion of the sample extract is analyzed by the above method (10 ml versus, 2 µl by the previous method), sensitivities less than 1 ppb were readily attained.

A spiked soil sample (10 ppb) was carried through the procedure and a 62% recovery was obtained. The sample was reextracted and analyzed yielding 24% of the initial spike and a third extract yielded 15% of the initial spiked amount. A chromatographic profile appears in Figure 7. The spiked sample was quantified by the internal standard method, however, the linearity of the response nor the recovery was evaluated over a concentration range.

Based on the spike study, the soil samples were analyzed by the purge and trap methodology and the preliminary results appear in Table 4. The chromatographic profile appear in Appendix 2.

APPENDIX V - PART B

SHELL DEVELOPMENT COMPANY
Biological Sciences Research Center
Modesto, California

TECHNICAL INFORMATION RECORD

TIR-24-665-82

Title	: SOIL RESIDUE LEVELS OF 1,2-DICHLOROPROPANE, THE E AND Z ISOMERS OF 1,3-DICHLOROPROPENE, AND THE E AND Z ISOMERS OF 3-CHLORO ALLYL ALCOHOL FOUND IN A CORE SAMPLE TAKEN NEAR DOMESTIC WELLS CONTAMINATED WITH 1,2-DICHLOROPROPANE.
Cooperator	: Mr. Charles Fisher California State Water Resources Control Board
Shell Representative	: B. W. Hermann
Date Written	: January 31, 1983
Date Issued	: March 18, 1983
Author	: B. W. Hermann
Analysts	: B. W. Hermann and H. Matsuyama
Reviewed by	: R. D. Collins
Approved by	: R. A. Newman
Research Project No.	: 81080.00
References	: MOLR 2841-87-88 MMS-R-505-2 MMS-R-506-2
Keywords	: SD 3876, SD 949, SD 950, WL 42311, WL 42312, residue, soil, analysis, California.

Title: SOIL RESIDUE LEVELS OF 1,2-DICHLOROPROPANE, THE E AND Z ISOMERS OF 1,3-DICHLOROPROPENE, AND THE E AND Z ISOMERS OF 3-CHLORO ALLYL ALCOHOL FOUND IN A CORE SAMPLE TAKEN NEAR DOMESTIC WELLS CONTAMINATED WITH 1,2-DICHLOROPROPANE.

B. W. Hermann

Abstract: A 24' deep soil core sample was taken by the environmental monitoring unit of the California Department of Food and Agriculture under direction of the California State Water Resources Control Board from a field between two domestic wells known to be contaminated with levels of >10 ppb 1,2-dichloropropane. Samples were taken every six inches, with eleven of the samples taken to BSRC for analysis. Residues of 1,2-dichloropropane of 3, 11, 7, and 3 ppb were found at depths of 1.5, 6, 7.5 and 9 feet, respectively. Traces of 1,3-dichloropropene (<1 ppb) were found at 1.5 feet. Z and E 3-chloro allyl alcohol residue levels of 45 and 42 ppb were found at a depth of 1.5 feet.

Introduction

The California State Water Resources Control Board had found significant levels (>10 ppb) of 1,2-dichloropropane (1,2-D) in two domestic wells near Lathrop, CA. These wells were adjacent to a tomato field with a history of the possible use of a 1,3-dichloropropene (1,3-D) type soil fumigant. As part of an effort to determine if agricultural applications were responsible for levels of 1,2-D found in the well water, a hole was drilled in the tomato field, with soil core residue samples taken every six inches. Samples were split for residue analysis between BSRC and SRI, International. In addition to residue levels, the core samples taken to SRI were to be checked for moisture content and morphology. This report describes the sample handling, analytical methodology, and results of the samples analyzed at BSRC.

Sampling Procedure

On December 7, 1982, a soil core was taken from the middle of a tomato field with a history of probable application of a 1,3-D type soil fumigant. This field was located between two wells containing significant (11 and 15 ppb) residues of 1,2-dichloropropane (Figure 1).

The soil core was taken with a mobile drilling rig supplied and operated by the Environmental Monitoring Unit of the California Dept. of Food and Agriculture. The hollow auger type drill was designed to accommodate a sampling probe containing three 6" soil sampling tubes to allow sequential sampling of the soil core. The sampling drill was kept in place while the probe was brought to the surface and the samples removed. The probe was then cleaned and fitted with new sampling tubes before being lowered back inside the drill.

After removal from the sampling probe, the soil samples were subsampled for moisture analysis, then sealed and frozen in dry ice for shipment to the laboratory. The samples taken to BSRC are indicated in Figure 2.

Sample Handling

The soil cores were contained in metal cylinders sealed with plastic caps and stored frozen at -120°F. The foil-lined plastic caps were removed and the metal tube heated with hot air gun until the cores could be slipped out of the cylinder. About an inch of each end of the soil core was removed. The remainder (still frozen) was placed in a plastic bag and broken with a hammer. 2-100 gram aliquots were immediately weighed into separate 1 liter round bottom flasks and covered with either 200 ml water (1,2-D; 1,3-D) or 200 ml 1 N H_2SO_4(3-chloro allyl alcohol [3-CAA]).

Extraction

1,2-D and 1,3-D. 100 gms of frozen sample, 200 ml of water and 10 ml of ethyl acetate were co-refluxed for 30-90 min. The ethyl acetate was collected in the sidearm of a crankcase dilution receiver (MMS-R-505-2).

3-CAA. 100 gms of frozen sample plus 200 ml 1 N H_2SO_4 and one spray of silicone antifoam were distilled in a round bottom flask until 100-125 ml were overheaded (MMS-R-506-2).

Clean Up

1,2-D and 1,3-D. None required.

3-CAA. The distillate was washed 2 times with 40 ml hexane. The analytes were then partitioned 2 times with 60 ml ethyl ether. The ether was concentrated for analysis with in a centrifuge tube fitted with a 2-ball mini-Snyder column and heated with a 45°C water bath.

GLC-HECD Analysis

Operating Attn	: 1 x 5
Pyrolysis Temp.	: 950°C
Detector Base Temp.	: 200°C
Column	: 30m x 0.25 mm ID WCOT fused silica Durawax DX-4.
Column Temperature	: 60°C - 1,2-D, 1,3-D 103°C - 3-CAA
Gas Flows	
Reaction/Make-up Gas	: H_2 @ 130 ml/min
Carrier Gas	: He @ 30 psi
Injection	
Mode	: Split ~ 1:5
Volume	: 5 µl
Temp.	: 150°C

Results

SAMPLE II	NET WT (GMS)	RESIDUES FOUND (PPB) 1,2-D SD 3876	1,3-D CIS(Z) SD 949	1,3-D TRANS(E) SD 950	3-CAA CIS(Z) SD 42311	3-CAA TRANS(E) SD 42312
B-3	443	3	<1A)	<1	45	42
E-3	623	11	N.D.B)	N.D.	N.D.	N.D.
F-3	686	7	N.D.	N.D.	N.D.	N.D.
G-3	687	3	N.D.	N.D.	N.D.	N.D.
H-3	703	N.D.	N.D.	N.D.	N.D.	N.D.
J-3	782	N.D.	N.D.	N.D.	N.D.	N.D.
K-3	790	N.D.	N.D.	N.D.	N.D.	N.D.
L-3	761	N.D.	N.D.	N.D.	N.D.	N.D.
M-3	754	N.D.	N.D.	N.D.	N.D.	N.D.
N-3	719	N.D.	N.D.	N.D.	N.D.	N.D.
O-3	806	N.D.	N.D.	N.D.	N.D.	N.D.

A) N.D. = Not Detected. Limit of Detection = 0.5 ppb.
B) <1 ppb but greater than the limit of detection of 0.5 ppb.

RECOVERY DATA[a)]

FORTIFICATION LEVEL (PPM)	1,2-3	E-1,3-D	E-3-CAA
10	91	110	110
10	100	77	100
5	84		

a) Samples were fortified prior to extraction to monitor recovery through the method.

B. W. Hermann

BWH/sia
March 17, 1983

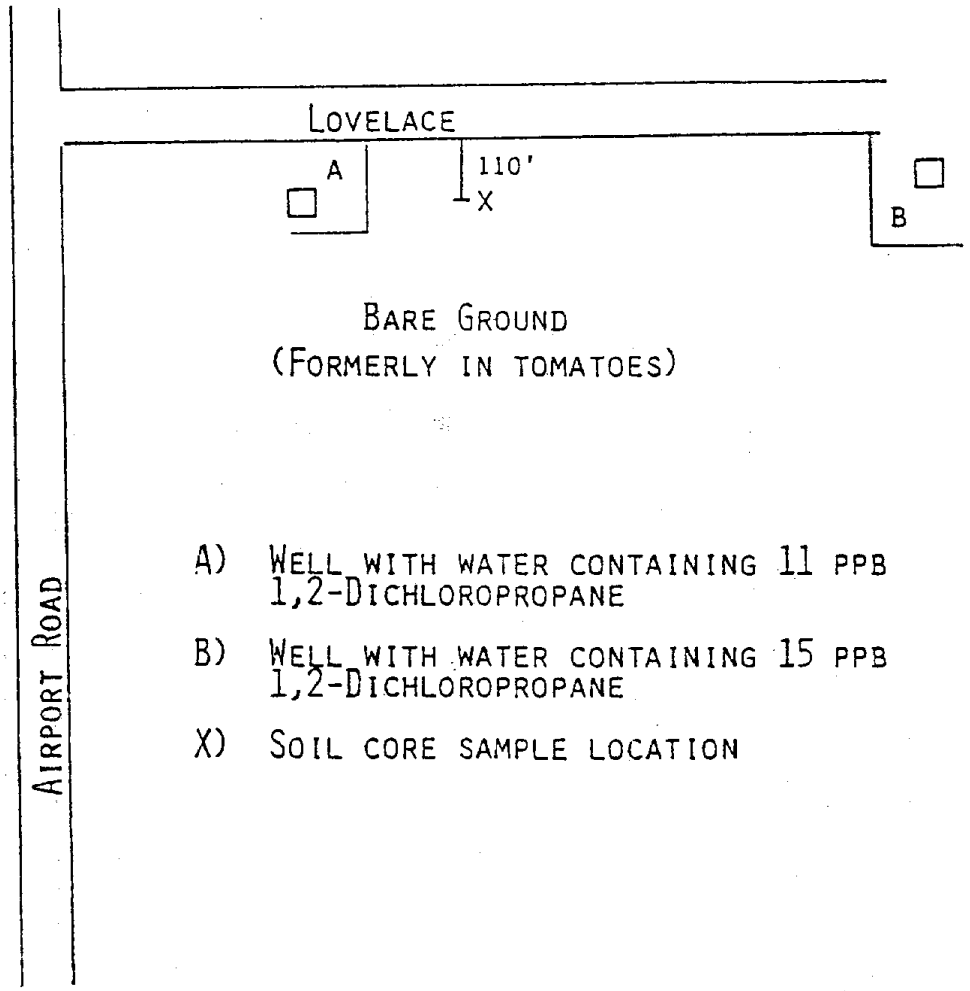


FIGURE 1. SITE DESCRIPTION

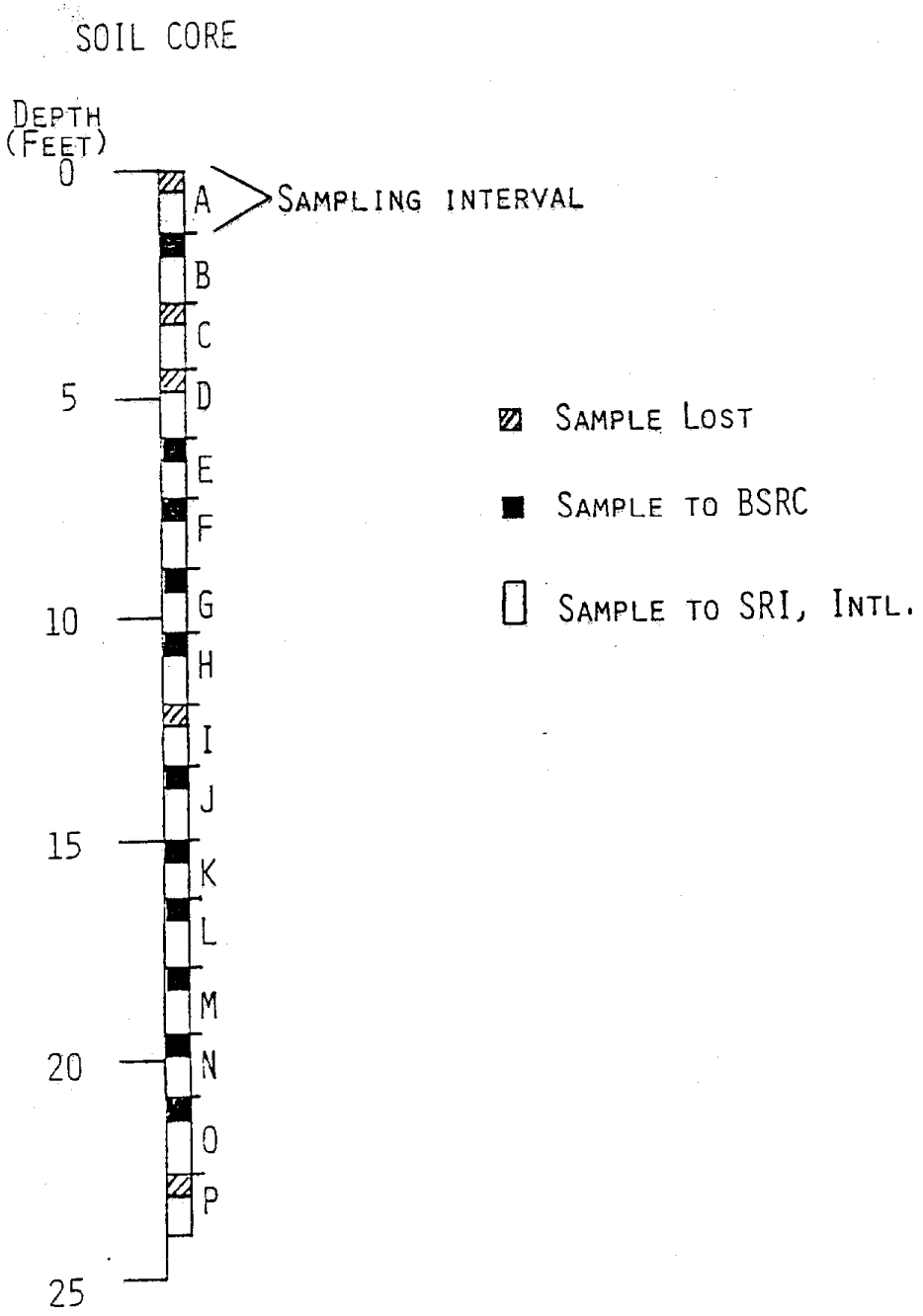


FIGURE 2. SOIL CORE SAMPLING.

APPENDIX VI

MODESTO METHOD SERIES

MMS-R-505-2
July, 1981

SHELL DEVELOPMENT COMPANY
BIOLOGICAL SCIENCES RESEARCH CENTER
MODESTO, CALIFORNIA

RESIDUE DETERMINATION OF 1,2-DICHLOROPROPANE AND THE Z AND E ISOMERS OF 1,3-DICHLOROPROPENE IN AGRICULTURAL COMMODITIES, SOIL, AND WATER

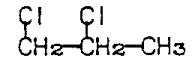
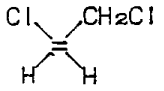
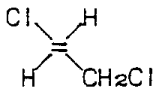
Capillary GLC/Hall Electrolytic Conductivity Detector Method

Hazardous materials used in this method are designated "(*CAUTION*)" in the REAGENTS section. A Material Safety Data Sheet for each material so designated may be found in the PRECAUTIONARY INFORMATION section at the end of the method.

SCOPE

1. An analytical method is described for the determination of the residues of 1,2-dichloropropane (SD 3876) and the Z and E isomers of 1,3-dichloropropene (SD 949 and SD 950, respectively) in agricultural commodities, soils, and water. 1,2-dichloropropane and the isomers of 1,3-dichloropropene are the major components of D-D ® Soil Fumigant. The minimum detectable concentration for the three compounds in agricultural commodities and soils is about 0.01 mg/kg and in water is about 0.001 mg/kg.

ANALYTES

SD 3876	1,2 dichloropropane	
SD 949	cis (Z) 1,3 dichloropropene	
SD 950	trans (E) 1,3 dichloropropene	

METHOD SUMMARY

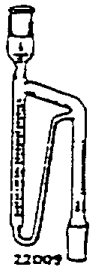
2. (a) Agricultural Commodities and Soils

A representative sample is macerated while frozen at dry ice temperature (-78°C). A subsample of 20 gm is weighed into a round-bottom flask to which water and ethyl acetate are added. A crankcase dilution distilling receiver and a chilled water condenser are attached to the flask, and the sample distilled for 15-20 min after the first reflux. An aliquot of the ethyl acetate distillate is diluted with hexane and analyzed by capillary GLC (CGLC) with a Hall Electrolytic Conductivity Detector (HECD).

(b) Water A 200 gm aliquot is added to a 250 ml volumetric flask and NaCl added to excess. The solution is partitioned with a 50/50 mixture of ethyl acetate/hexane, with an aliquot taken for analysis by CGLC/HECD.

SPECIAL APPARATUS

3. (a) Distilling receiver, crankcase dilution; 12.5 ml capacity with 24/40 joints, Cal-Glass, #22009, Costa Mesa, California.



(b) Heating mantle to accommodate a 1000 ml round-bottom boiling flask and a variable transformer.

(c) Condenser, Allihn - 250 to 300 mm jacket with 24/40 lower joint with drip tip, Cal-Glass, #4680.

(d) Food chopper, a Hobart food cutter, Model #8142 manufactured by the Hobart Manufacturing Company, Troy, Ohio, or equivalent.

(e) Gas chromatograph, Tracor 560 equiped with a Model 700A Hall Electrolytic Conductivity Detector.

(f) Glass capillary column, 30 meter Carbowax 20M wall coated column (WCOT) 0.25 mm I.D. (J & W #10173) or equivalent.

(g) Bath and circulator, Model 2160 Masterline by Forma Scientific, or equivalent to cool Allihn condensers (+10°C).

All of the other apparatus and glassware needed for this method would typically be available in a well-equipped residue laboratory.

REAGENTS

4. (a) SD 3876 (1,2 dichloropropane) from Phaltz and Bauer or Eastman Organic Chemicals. SD 14647 (about 43.5% SD 949 and about 48.35% SD 950) available from Shell Chemical Company, One Shell Plaza, Houston, Texas 77001.

Weigh 100 mg of SD 3876 and 200 mg of SD 14647 into a 100 ml volumetric flask and dilute to volume with acetone to obtain a stock

solution of ca. 1000 µg/ml of SD 3876, SD 949 and SD 950. This stock solution is further diluted with acetone to obtain a fortification standard or is diluted with 50/50 ethyl acetate/hexane to make standards for GLC calibration. (*CAUTION*)

(b) Acetone, ethyl acetate, hexane; distilled-in glass solvents from Burdick and Jackson laboratories, Muskegon, Michigan, or equivalent. (*CAUTION*)

(c) Dow Corning stopcock or vacuum grease (silicone grease).

(d) Deionized water.

SAMPLE PREPARATION

5. (a) Agricultural Commodities and Soil

Chill the sample to dry ice temperature (-78°C) then macerate or otherwise reduce a representative sample and put into a tightly sealed container with a minimum head space (for freezer storage).

NOTE 1: Care should be taken to keep sample frozen during preparation to prevent loss of compound.

(b) Water

No sample preparation is necessary.

EXTRACTION

6. (a) Agricultural commodities and Soils

Weigh a 20 gm aliquot of the frozen macerate or soil into a 1-liter RB flask and immediately add 200 ml of water. Pipet 10 ml of the ethyl acetate containing 0.125 % w/v silicone grease [Section 4 (c)] into the flask containing the macerated crop or soil and 200 ml of water.

NOTE 2: The silicone grease acts as an antifoam agent. Weigh and dissolve 0.5 gm of silicone lubricant in 400 ml of ethyl acetate. Sonication facilitates the dissolving.

Place flask in the heating mantle, attach the crankcase dilution receiver, and fit with the Allihn condenser cooled with refrigerated water (<10°C). The two 24/40 joints can be lubricated with silicone grease.

When the mixture begins to boil and the reflux starts, continue the distillation for 15-20 minutes. Verify that 10 ml of ethyl acetate have been collected in the receiver. Remove the condenser to obtain a portion of the ethyl acetate for analysis by GLC/HECD. A portion of the ethyl acetate should be diluted to the desired concentration at a 50/50 ratio of ethyl acetate and hexane.

NOTE 3: The solvent composition of the standard and the sample should be the same to minimize matrix effects.

(b) Water

Weigh out 200 gm of the refrigerated water into a 250 ml volumetric flask. Add 6.7 ml of 50/50 mixture of ethyl acetate and hexane and saturate with sodium chloride. Shake the flask for 2 minutes and allow the two phases to separate (upper phase should be 5 ml). Add additional sodium chloride to move the hexane into the neck of the volumetric flask, take an aliquot and dry with sodium sulfate.

GLC ANALYSIS

7. GLC Operating Conditions - GLC columns and operating parameters are chosen which achieve optimum balance between sensitivity and column efficiency with a symmetrical peak emerging at a reasonable retention time. The retention time is relative due to differences in capillary columns, and the operating conditions listed below should serve only as a guide.

Detector	:	Hall Electrolytic Conductivity
Reaction Tube Temperature	:	950°C
Reaction Gas	:	Hydrogen; 70 ml/min
Conductivity Solution	:	1-Propanol; 0.3 ml/min
Injector		
Temperature	:	200°C
Inlet Gas	:	Helium; 20 ml/min
Injection Mode	:	Split; ca. 1:5
Column	:	30M x 0.25mm WCOT borosilicate glass capillary
Liquid Phase	:	Carbowax 20M
Temperature	:	60°C
Pressure	:	30 psi
Linear Flow Velocity	:	500 cm/sec
Attenuation	:	10 x 10^{-12} ma
Recorder chart speed	:	40 cm/hr
Vent	:	1.25 min.

Using the above conditions, an injection of 0.15 ng of 1,2-dichloropropane (SD 3876) and the two 1,3-dichloropropenes (SD 949 and SD 950) has resulted in 30-40% full scale deflection peaks at 1.7, 2,5, and 3.6 min for the compounds, respectively, with <1.0% noise.

PREPARATION OF CALIBRATION CURVE

8. (a) From the stock solutions of the three D-D standards under 4 (a), prepare three standard solutions in 50/50 mixture of ethyl acetate and hexane to effect concentrations of 0.01, 0.03, and 0.05 µgm/ml. Five µl of the dilute standard solutions will contain 0.05, 0.15, 0.25 ng of all three compounds.

NOTE 4: The conditions of analysis makes it imperative that the solvents be screened on the GLC for possible interference prior to use as a diluting solvent.

(b) Inject 5 µl of the standard solutions and measure the peak heights resulting from the elution of the compounds. Strict observance of the peak shape and elution time is essential. A change of more than 5% in response or in the emergence time will cause the injection to be suspect, and usually can be traced to changes in the operating parameters, i.e. temperature, flow rates, inlet conditions, etc.

(c) Plot calibration curves using all the standard injections. The abscissa is amount injected in nanograms, and the ordinate is GLC response in percent of full scale or area.

SAMPLE ANALYSIS

9. Inject 5 µl of the D-D samples extracts from Section 6 (a) and (b) into the GLC.

Carefully check the retention time of any peak eluting with a retention time close to that of the standard. If the retention times agree, i.e. the peak is identified as the compound of interest, measure the peak height and compare with the standard curve established in Section 8.

NOTE 5: During routine analyses, it is a good practice to inject a standard after every two or three samples injections to ensure the integrity of the sample analysis.

Calculate the concentrations of the analytes in the sample by means of the following equation:

$$C=\frac{W}{S}$$

Where: C = Concentration of the compound in mg/kg of sample (ppm)

W = Weight of compound, in ng, found in the aliquot of the sample injected.

S = Amount of sample, in mg, represented by the aliquot injected.

SHELL DEVELOPMENT COMPANY
BIOLOGICAL SCIENCES RESEARCH CENTER
MODESTO, CALIFORNIA

RESIDUE DETERMINATION OF THE Z AND E ISOMERS OF 3-CHLOROALLYL ALCOHOL (CAA) IN AGRICULTURAL COMMODITIES, SOILS, AND WATER

Capillary GLC/Hall Electrolytic Conductivity Detector Method

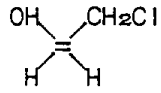
Hazardous materials used in the method are designated "(*CAUTION*)" in the REAGENTS section. A Material Safety Data Sheet for each material so designated may be found in the PRECAUTIONARY INFORMATION Section at the end of the method.

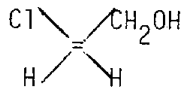
SCOPE

1. An analytical method is described for the determination of the residues of the Z and E isomers of CAA (SD 42311 and SD 42312, respectively), possible soil metabolites of D-D® Soil Fumigant. The minimum detectable concentration for these compounds is about 0.01 mg/kg in agricultural commodities and about 0.001 mg/kg in water.

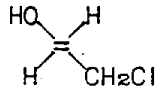
ANALYTES

SD 42311 cis (Z) 3-chloro-2-propen-1-ol or
cis (Z) 3-chloroallylalcohol (CAA)

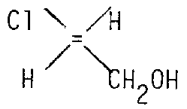




SD42312 trans (E) 3-chloro-2-propen-1-ol or
trans (E) 3-chloroallylalcohol (CAA).



(Incorrect structures)



(Corrected structures)

SUMMARY

2. (a) Agricultural commodities and soils

A representative sample is macerated while frozen at dry ice temperature. A 20 gm subsample is weighed into a round-bottom flask to which 1N H_2SO_4 is added. A Kjeldahl trap, an adaptor, a condenser, and a receiver are attached to the round-bottom flask, and the mixture is distilled until about 125 ml are collected. The distillate is washed with hexane, saturated with NaCl and the compounds partitioned into ether. The ether extract is concentrated, then brought to volume with 50/50 ethyl acetate/hexane for analysis by capillary GLC (CGLC) with Hall Electrolytic Conductivity detection.

(b) Water

A 200 gm sample is saturated with NaCl and extracted with ether. The ether extract is concentrated, then brought to the desired concentration with 50/50 ethyl acetate/hexane for quantitation by CGLC/HECD.

SPECIAL APPARATUS

3. (a) Adapter, 105 bend, full length standard taper, vacuum delivery tube with 24/40 joint, Cal-Glass, #LG-2030.

(b) Adapter, three-way, full length with 24/40 joint, Cal-Glass, #LG-1470.

(c) Condenser, Liebig with 24/40 joint and drip tip, Cal-Glass, #LG-5150.

(d) Adapter, straight with 24/40 joint, Kjeldahl trap, Cal-Glass, #ML-300.

(e) Heating mantle to accommodate a 1000 ml round-bottom boiling flask and variable transformer.

(f) Food chopper, Hobart food cutter, Model #8142, manufactured by the Hobart Manufacturing Company, Troy, Ohio.

(g) Gas chromatograph, Tracor 560 equipped with a Model 700A Hall Electrolytic Conductivity Detector.

(h) Bath and circulator, Model 2160 Masterline by Forma Scientific.

(i) Glass capillary column, 30 meter Carbowax 20M wall coated column with 0.25 mm I.D. (J & W #10173).

(j) Mini Snyder column, Cal-Glass, #LG-6860.

(k) Snyder distilling column, 3 sections, Cal-Glass, #LG-5850-100.

All other apparatus and glassware needed for this method would typically be available in a well-equipped Residue laboratory.

REAGENTS

4. (a) Analytical standards of SD 42311 and SD 42312 (~97% pure) are available from Shell Chemical Company, Houston, Texas. Weigh 100 mg each of SD 42311 and SD 42312 into a 100 ml volumetric flask and dilute to volume with acetone to obtain a stock solution containing 1000 ug/ml of each compound. This stock solution is further diluted with acetone to obtain fortification standards or with ethyl acetate for preparing GLC calibration standards for (*CAUTION*)

(b) Acetone, ethyl acetate, hexane; distilled-in-glass solvents from Burdick and Jackson Labs., Muskegon, Michigan, or equivalent. (*CAUTION*)

(c) Diethyl ether, Mallinckrodt Nanograde or equivalent. (*CAUTION*)

(d) Dow Corning stopcock or vacuum grease (silicone grease).

(e) Sodium chloride, granular.

(f) Antifoam A spray (Dow Corning).

(g) Deionized water.

(h) 1N H_2SO_4

SAMPLE PREPARATION

5. (a) Agricultural Commodities and Soil.

Chill the sample to dry ice temperature (-78.5°C) before processing. Macerate or otherwise reduce a representative sample while frozen. Store in a tightly sealed container with a minimum headspace (for freezer storage).

NOTE 1: Care should be taken to keep sample frozen during preparation to prevent loss of compound.

(b) Water

No sample preparation is necessary. Samples are stored in glass containers with teflon or foil lined lids with no headspace at 4°C. Proceed to Section 8.

SAMPLE DISTILLATION

6. Weigh out a 20 gm aliquot of the frozen macerate or soil into a 1-liter RB flask, and immediately add 200 ml of 1N H_2SO_4. For samples other than water, spray the contents once with Antifoam A. Connect the following glassware in series (in the order of mention) to the boiling flask using stopcock grease at each joint; the Kjeldahl trap straight adapter, the three-way adapter (with glass stopper on top), the Liebig condenser, the adapter with 105° bend, and 250 Erlenmeyer flask. Provide circulating water at <10°C to the condenser. Distill 100-125 ml of water into the Erlenmeyer flask and proceed to Section 7.

CLEANUP

7. (a) Agricultural Commodities and Soil

Transfer the distillate to a 250 ml separatory funnel (See Note 1). Wash the aqueous solution with 40 ml hexane by shaking for about 0.5 min. Drain the aqueous phase containing the analytes into the original 250 ml Erlenmeyer flask. Drain the hexane into a 125 ml Erlenmeyer flask. Transfer the distillate back into the 250 ml separatory funnel and repeat the hexane wash with another 40 ml hexane. Combine the two hexane washes in a 250 ml separatory funnel and partition with 20 ml water. Add this water to the washed distillate.

NOTE 2: Because of the specific nature of HECD, step 6 (a) may be omitted for some samples (i.e. water).

SAMPLE PARTITION

8. (a) Agricultural Commodities, Soil, and Water

Transfer the cleaned distillate (200 ml water) into a 250 ml separatory funnel and saturate with NaCl. Partition the saturated aqueous solution with two 60 ml portions of diethyl ether by shaking vigorously for two min. Collect and save the diethyl ether phase in a 250 ml Erlenmeyer flask. Attach a three-balled Snyder column to the flask and concentrate gently on a steam table until the volume is reduced to about 20 ml (see Note 2). Quantitatively transfer the ether into a centrifuge tube and attach a small Snyder column to the tube. Place the tube in a 44°C water bath to further reduce the volume to 1-2 ml. Bring to 10 ml with a 50/50 mixture of ethyl acetate and hexane for analysis. This will result in a concentration of 2.0 gm/ml for agricultural commodities and soil, and 20 gm/ml for water.

NOTE 3: Solvents should be screened on the CGLC for possible interferences prior to use for dilution purposes.

CGLC ANALYSIS

9. CGLC Operating Conditions - CGLC columns and operating parameters are chosen which achieve optimum balance between sensitivity and column efficiency with a symmetrical peak emerging at a reasonable retention time. The retention time is relative due to differences in capillary columns, and the operating conditiions listed below should serve only as a guide.

Detector	:	Hall Electrolytic Conductivity
Reaction Tube Temperature	:	950°C
Reaction Gas	:	Hydrogen; 70 ml/min
Conductivity Solution	:	1-Propanol; 0.3 ml/min
Base Temperature	:	320°C
Injector		
Temperature	:	200°C
Gas	:	Helium; 10 ml/min

Injection Mode	:	Split, ca. 1.5
Column	:	30M x 0.25mm WCOT borosilicate glass capillary
Liquid Phase	:	Carbowax 20M
Temperature	:	150°C
Pressure	:	30 psi
Linear Flow Velocity	:	500 cm/sec
Attenuation	:	5×10^{-12} ma
Recorder Chart Speed	:	40 cm/hr
Vent	:	1.75 min

Using the above conditions, an injection of 1.5 ng of the Z and E isomers of CAA (SD 42311 and SD 42312, respectively) results in about 40% full scale deflection for peaks at 2.7 and 2.1 min for the compounds, respectively. The noise is typically <1.0%.

PREPARATION OF CALIBRATION CURVE

10. (a) From the stock solutions of the CAA standards under 4 (a), prepare three standard solutions in 50/50 mixture of ethyl acetate and hexane to effect concentrations of 0.1, 0.2, and 0.3 µgm/ml (See Note 3), so that

Five µl of the dilute standard solutions will contain 0.5, 1.0, and 1.5 ng of each compound.

(b) Inject 5 µl of the standard solutions and measure the peak heights resulting from the elution of the compounds. Strict observance of the peak shape and elution time is essential. A change of more than 5% in response or in the emergence time will cause the injection to be suspect, and usually can be traced to changes in the operating parameters, i.e. temperature, flow rates, inlet conditions, etc.

(c) Plot calibration curves using all the standard injections. The abscissa is amount injected in ng, and the ordinate is CGLC response in percent of full scale or area.

SAMPLE ANALYSIS

11. Inject 5 µl of the CAA sample extracts from Section 8 into the GLC.

Carefully check the retention time of any peak eluting with a retention time close to that of the standard. If the retention times agree, i.e. the peak is identified as the compound of interest, measure the peak height and compare with the standard curve established in Section 10.

Note 4: During routine analyses, it is a good practice to inject a standard after every two or three samples injections to ensure the integrity of the sample analysis.

Calculate the concentrations of the analytes in the sample by means of the following equation:

$$C = \frac{W}{S}$$

Where: C = Concentration of the compound in mg/kg of sample (ppm).

W = Weight of compound, in ng, found in the aliquot of the sample injected.

S = Amount of sample, in mg, represented by the aliquot injected.

ASSESSMENT OF THE METHOD

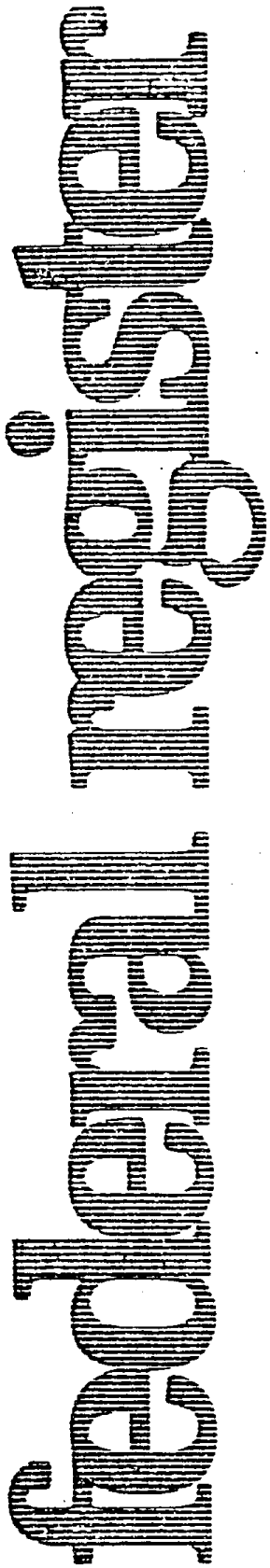
12. To evaluate the efficiency of the procedure, 0.05 ppm of SD 42311 and SD 42312 were added to non-treated check samples; and the samples were analyzed using the procedure described, with water sustituted for 1N H_2SO_4 (MMS-R-506-1). Soybeans have been carried through both methods, with increased recoveries using 1N H_2SO_4.

RECOVERIES (0.05 ppm) THROUGH MMS-506-1

COMMODITIES (Replicates)	SD 42311	SD 42312
Peanuts, crude oil	87	79
plants	84	78
shell	87	88
Tomatoes	70	72
Corn	88	88
Brussel sprouts (3)	80	87
Potatoes, peels	77	75
whole	82	71
Peaches	86	95
Sweet potatoes, peeled (2)	89	87
Pineapples, whole	93	88
bran	91	90
leaves	94	87
cannery waste	85	94
Cotton, seed	88	78
lint	96	94
Grapes	88	87
Chili peppers (3)	75	77
Bell peppers (4)	88	82
Average (± 1 SD)	86±7%	84±7%

RECOVERIES THROUGH MMS-R-506-2

Soybeans - MMS-R-506-1	50	34
MMS-R-506-2 (2)	96±2	108±1



Monday
December 3, 1979

Part III

Environmental Protection Agency

Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations

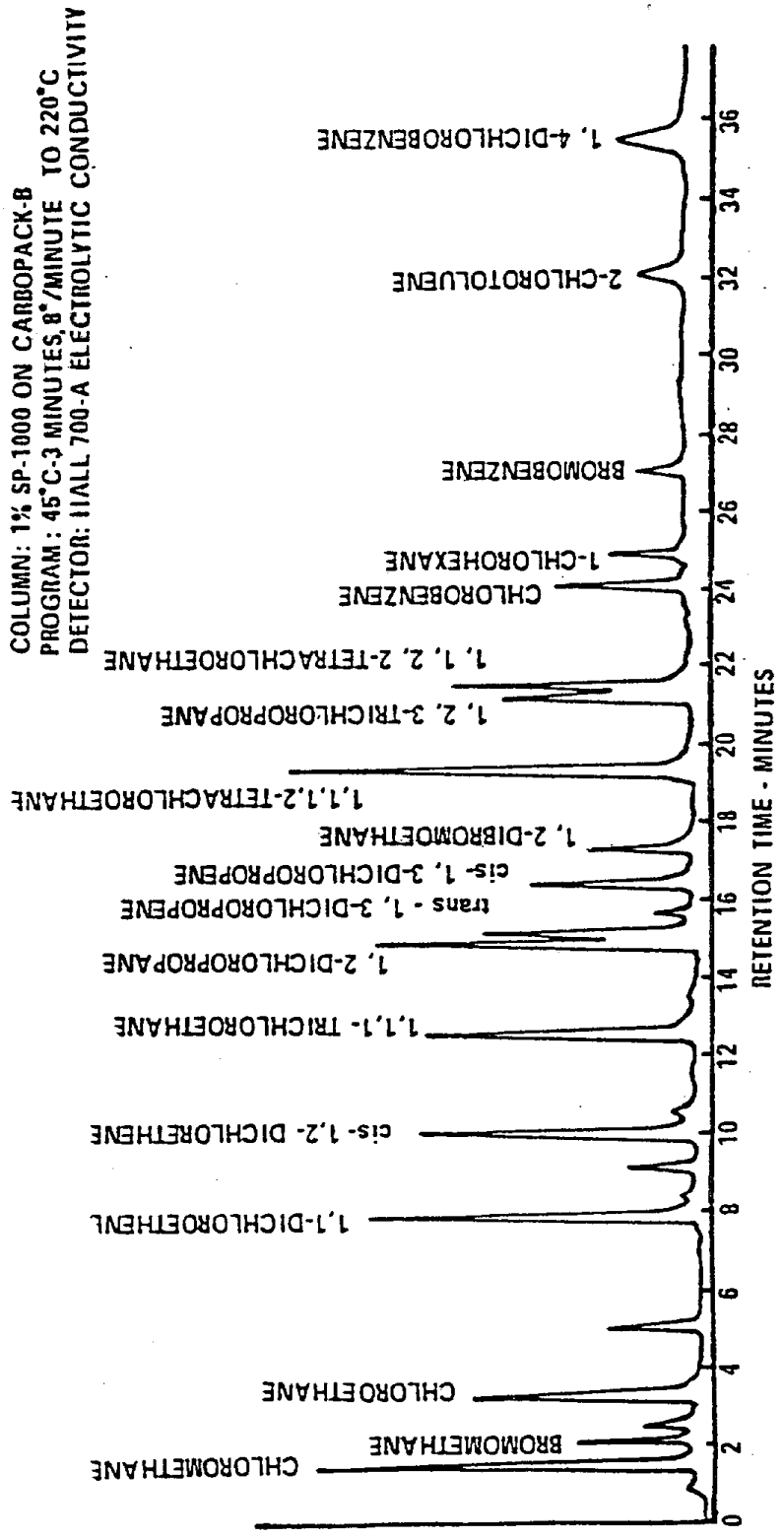


Figure 6. Gas chromatogram of purgeable halocarbons

BILLING CODE 6560-01-C

Purgeables—Method 624

1. *Scope and Application.*

1.1 This method is designed to determine volatile organic materials that are amenable to the purge and trap method. The parameters listed in Table 1 may be determined by this method.

1.2 This method is applicable to the determination of these compounds in municipal and industrial discharges. It is designed to be used to meet the monitoring requirements of the National Pollutants Discharge Elimination System (NPDES).

1.3 The detection limit of this method is usually dependent upon the level of interferences rather than instrumental limitations. The limits listed in Table 2 represent sensitivities that can be achieved in wastewaters.

1.4 The GC/MS parts of this method are recommended for use only by persons experienced in GC/MS analysis or under the close supervision of such qualified persons.

1.5 The trapping and chromatographic procedures described do not apply to the very volatile pollutant, dichlorodifluoromethane. An alternative three stage trap containing charcoal is to be used if this compound is to be analyzed. See EPA Method 601 and Reference 1. Primary ion for quantitative analysis of this compound is 101. The secondary ions are 85, 87, and 103.

1.6 Although this method can be used for measuring acrolein and acrylonitrile, the purging efficiencies are low and erratic. For a more reliable quantitative analysis of these compounds, use direct aqueous injection (Ref. 4–6) or EPA Method 603, Acrolein and Acrylonitrile, EMSL, Cincinnati, Ohio.

2. *Summary of Method.*

21. A sample of wastewater is purged with a stream of inert gas. The gas is bubbled through a 5 ml water sample contained in a specially designed purging chamber. The volatile organics are efficiently transferred from the aqueous phase into the gaseous phase where they are passed through a sorbent bed designed to trap out the organic volatiles. After purging is complete, the trap is backflushed while being rapidly heated in order to thermally desorb the components into the inlet of a gas chromatograph. The components are separated via the gas chromatograph and detected using a mass spectrometer which is used to provide both qualitative and quantitative information. The chromatographic conditions as well as typical mass spectrometer operating parameters are given.

3. *Interferences.*

3.1 Interferences coextracted from the samples will vary considerably from source to source, depending upon the diversity of the industrial complex or municipality being sampled. Impurities in the purge gas and organic compounds out-gassing from the plumbing ahead of the trap account for the majority of contamination problems. The analytical system must be demonstrated to be free from interferences under the conditions of the analysis by running method blanks. Method blanks are run by charging the purging device with organic-free water and analyzing it in a normal manner. The use of non-TFE plastic tubing, non-TFE thread sealants, or flow controllers with rubber components in the purging device should be avoided.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride) through the septum seal into the sample during shipment and storage. A field blank prepared from organic-free water and carried through the sampling and handling protocol can serve as a check on such contamination.

3.3 Cross contamination can occur whenever high level and low level samples are sequentially analyzed. To reduce cross contamination, it is recommended that the purging device and sample syringe be rinsed out twice, between samples, with organic-free water. Whenever an unusually concentrated sample is encountered, it should be followed by an analysis of organic-free water to check for cross-contamination. For samples containing large amounts of water soluble materials, suspended solids, high boiling compounds, or high organohalide levels, it may be necessary to wash out the purging device with a soap solution, rinse with distilled water, and then dry in a 105°C oven between analyses.

4. *Apparatus and Materials.*

4.1. Sampling equipment, for discrete sampling.

4.1.1 Vial, with cap—40 ml capacity screw cap (Pierce #13075 or equivalent). Detergent wash and dry vial at 105°C for one hour before use.

4.1.2 Septum—Teflon-faced silicone (Pierce #12722 or equivalent). Detergent wash and dry at 105°C for one hour before use.

4.2 Purge and trap device—The purge and trap equipment consists of three separate pieces of apparatus: a purging device, a trap, and a desorber. The complete device is available commercially from several vendors or can be constructed in the laboratory according to the specifications of Bellar and Lichtenberg (Ref. 2,3). The sorbent trap consists of ⅛ in. O.D. (0.105 in. I.D.) x 25 cm long stainless steel tubing packed with 15 cm of Tenax-GC (60–80 mesh) and 8 cm of Davison Type-15 silica gel (35–60 mesh). See figures 1 through 4. Ten centimeter traps may be used providing that the recoveries are comparable to the 25 cm traps.

4.3 Gas chromatograph—Analytical system complete with a temperature programmable gas chromatograph suitable for on-column injection and all required accessories including an analytical column.

4.3.1 Column 1—An 8 ft. stainless steel column (⅛ in. OD x 0.90 to 0.105 in. ID) packed with 1% SP–1000 coated on 60/80 mesh Carbopack B preceded by a 5-cm precolumn packed with 1% SP–1000 coated on 60/80 mesh Chromosorb W. A glass column (¼ in OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.3.2 Column 2—An 8 ft. stainless steel column (⅛ in OD x 0.09 to 0.105 in. ID) packed with 0.2% Carbowax 1500 coated on 60/80 mesh Carbopack C preceded by a 1 ft. stainless steel column (⅛ in. OD x 0.09 to 0.105 in. ID) packed with 3% Carbowax 1500 coated on 60/80 mesh Chromosorb W. A glass column (¼ in. OD x 2 mm ID) may be substituted. The precolumn is necessary only during conditioning.

4.4 Syringes—glass, 5-ml hypodermic with Luer-Lok tip (3 each).

4.5 Micro syringes—10, 25, 100 µl.

4.6 2-way syringe valve with Luer ends (3 each, Teflon or Kel-F).

4.7 Syringe—5 ml gas-tight with shut-off valve.

4.8 8-inch, 20-gauge syringe needle—One per each 5-ml syringe.

4.9 Mass Spectrometer—capable of scanning from 20–260 in six seconds or less at 70 volts (nominal), and producing a recognizable mass spectrum at unit resolution from 50 ng of DFTPP when injected through the GC inlet. The mass spectrometer must be interfaced with a gas chromatograph equipped with an all-glass, on-column injector system designed for packed column analysis. All sections of the transfer lines must be glass or glass-lined and deactivated. Use Sylon-CT, Supelco, (or equivalent) to deactivate. The GC/MS interface can utilize any separator that gives recognizable mass spectra (background corrected) and acceptable calibration points at the limit of detection specified for each compound in Table 2.

4.10 A computer system should be interfaced to the mass spectrometer to allow acquisition of continuous mass scans for the duration of the chromatographic program. The computer system should also be equipped with mass storage devices for saving all data from GC–MS runs. There must be

computer software available to allow searching any GC/MS run for specific ions and plotting the intensity of the ions with respect to time or scan number. The ability to integrate the area under a specific ion plot peak is essential for quantification.

5. *Reagents.*

5.1 Sodium thiosulfate—(ACS) Granular.

5.2 Trap Materials

5.2.1 Porous polymer packing 60/80 mesh chromatographic grade Tenax GC (2,6-diphenylene oxide).

5.2.3 Silica gel-(35–60 mesh)—

5.2.2 Three percent OV–1 on Chromosorb-W 60/80 mesh. Davison, grade-15 or equivalent.

5.3 Activated carbon—Filtrasorb-200 (Calgon Corp.) or equivalent.

5.4 Organic-free water

5.4.1 Organic-free water is defined as water free of interference when employed in the purge and trap procedure described herein. It is generated by passing tap water or well water through a carbon filter bed containing about 1 lb. of activated carbon.

5.4.2 A water system (Millipore Super-Q or equivalent) may be used to generate organic-free deionized water.

5.4.3 Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for one hour. While still hot, transfer the water to a narrow mouth screw cap bottle equipped with a Teflon seal.

5.5 Stock standards (2 mg/ml)—Prepare stock standard solutions in methanol using assayed liquids or gases as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials should be prepared in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of such materials.

5.5.1 Place about 9.8 ml of methanol into a 10 ml ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes or until all alcohol wetted surfaces have dried. Tare the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material:

5.5.2.1 Liquids—using a 100 μl syringe, immediately add 2 to 3 drops of assayed reference material to the flask, then reweigh. Be sure that the drops fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases—To prepare standards of bromomethane, chloroethane, chloromethane, and vinyl chloride, fill a 5-ml valved gas-tight syringe with the reference standard to the 5.0-ml mark. Lower the needle to 5 mm above the methyl alcohol menicus. Slowly inject the reference standard into the neck of the flask (the heavy gas will rapidly dissolve into the methyl alcohol).

5.5.3 Reweigh the flask, dilute to volume, stopper, then mix by inverting the flask several times. Transfer the standard solution to a 15-ml screw-cap bottle equipped with a Teflon cap liner.

5.5.4 Calculate the concentration in mg per ml (equivalent to μg per μl) from the net gain in weight.

5.5.5 Store stock standards at 4° C. Prepare fresh standards every second day for the four gases and 2-chloroethylvinyl ether. All other standards must be replaced with fresh standards each week.

5.6 Surrogate Standard Dosing Solution—From stock standard solutions prepared as above, add a volume to give 1000 μg each of bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane to 40 ml of organic-free water contained in a 50-ml volumetric flask, mix and dilute to volume. Prepare a fresh surrogate standard dosing solution weekly. Dose the surrogate standard mixture into every 5-ml sample and reference standard analyzed.

6. *Calibration.*

6.1 Using the stock standards, prepare secondary dilution standards of the compounds of interest, either singly or mixed together in methanol. The standards should be at concentrations such that the aqueous standards prepared in 6.2 will bracket the working range of the chromatographic system. If the limit of detection listed in Table 2 is 10 μg/l, for example, prepare secondary methanolic standards at 100 μg/l, and 500 μg/l, so that aqueous standards prepared from thee secondary calibration standards, and the primary standards, will define the linearity of the detector in the working range.

6.2 Using both the primary and secondary dilution standards, prepare calibration standards by carefully adding 20.0 μl of the standard in methanol to 100, 500, or 1000 ml of organic-free water. A 25 μl syringe (Hamilton 702N or equivalent) should be used for this operation. These aqueous standards must be prepared fresh daily.

6.3 Assemble the necessary gas chromatographic and mass spectrometer apparatus and establish operating parameters equivalent to those indicated in Table 2. By injecting secondary dilution standards, establish the linear range of the analytical system for each compound and demonstrate that the analytical system meets the limit of detection requirements in Table 2.

6.4 Assemble the necessary purge and trap device. Pack the trap as shown in Figure 2 and condition overnight at a nominal 180° C by backflushing with an inert gas flow of at least 20 ml/min. Daily, prior to use, condition the traps for 10 minutes by backflushing at 180° C. Analyze aqueous calibration standards (6.2) according to the purge and trap procedure in Section 9. Compare the responses to those obtained by injection of standards (6.3), to determine the analytical precision. The analytical precision of the analysis of aqueous standards must be comparable to data presented by Bellar and Lichtenberg (1978, Ref. 1) before reliable sample analysis may begin.

6.5 Internal Standard Method—The internal standard approach is acceptable for the purgeable organics. The utilization of the internal standard method requires the periodic determination of response factors (RF) which are defined in equation 1.

Eq. (1) $RF = (A_s C_{is})/(A_{is} C_s)$

Where:

A_s is the integrated area or peak height of the characteristic ion for the priority pollutant standard.

A_{is} is the integrated area or peak height of the characteristic ion for the internal standard.

C_{is} is the amount of the internal standard in μg.

C_s is the amount of the pollutant standard in μg.

The relative response ratio for each pollutant should be known for at least two concentration values—50 ng injected to approximate 10 μg/l and 500 ng to approximate the 100 μg/l level. Those compounds that do not respond at either of these levels may be run at concentrations appropriate to their response. The response factor (RF) must be determined over all concentration ranges of standard (C_s) which are being determined. (Generally, the amount of internal standard added to each extract is the same so that C_{is} remains constant.) This should be done by preparing a calibration curve where the response factor (RF) is plotted against the standard concentration (C_s). Use a minimum of three concentrations over the range of interest. Once this calibration curve has been determined, it should be verified daily by injecting at least one standard solution containing internal standard. If significant drift has occurred, a new calibration curve must be constructed.

Note.—EPA, through its contractors and certain of its Regional Laboratories, is currently evaluating selected compounds for

use as internal standards in the analysis of organics by purge and trap.

6.6 The external standard method can also be used at the discretion of the analyst. Prepare a master calibration curve using a minimum of three standard solutions of each of the compounds that are to be measured. Plot concentrations versus integrated areas or peak heights (selected characteristic ion for GC/MS). One point on each curve should approach the method detection limit. After the master set of instrument calibration curves have been established, they should be verified daily by injecting at least one standard solution. If significant drift has occurred, a new calibration curve must be constructed.

7. *Quality Control.*

7.1 Before processing any samples, the analyst should daily demonstrate, through the analysis of an organic-free water method blank, that the entire analytical system is interference-free.

7.2 Standard quality assurance practices should be used with this method. Field replicates should be collected to validate the precision of the sampling technique. Laboratory replicates should be analyzed to validate the precision of the analysis. Fortified samples should be analyzed to validate the accuracy of the analysis.

7.3 The analyst should maintain constant surveillance of both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by determining the precision of the method in blank water and spiking each 5-ml sample, standard, and blank with surrogate halocarbons.

7.3.1 Determine the precision of the method by dosing blank water with the compounds selected as surrogate standards—bromochloromethane, 2-bromo-1-chloropropane, and 1,4-dichlorobutane—and running replicate analyses. Calculate the recovery and its standard deviation. These compounds represent early, middle, and late eluters over the range of the pollutant compounds.

7.3.2 The sample matrix can affect the purging efficiencies of individual compounds; therefore, each sample must be dosed with the surrogate standards and analyzed in a manner identical to the internal standards in blank water. If the recovery of the surrogate standard shows a deviation greater than two standard deviations (7.3.1), repeat the dosed sample analyses. If the deviation is again greater than two standard deviations, dose another aliquot of the same sample with the compounds of interest at approximately two times the measured values and analyze. Calculate the recovery for the individual compounds using these data.

8. *Sample Collection, Preservation, and Handling.*

8.1 Grab samples must be collected in glass containers having a total volume greater than 20 ml. Fill the sample bottles in such a manner that no air bubbles pass through the sample as the bottle is being filled. Seal the bottles so that no air bubbles are entrapped in it. Maintain the hermetic seal on the sample bottle until time of analysis.

8.2 The sample must be iced or refrigerated from the time of collection until extraction. If the sample contains residual chlorine, add sodium thiosulfate preservative (10 μg/40 ml) to the empty sample bottles just prior to shipping to the sample site, fill with sample just to overflowing, seal the bottle, and shake vigorously for 1 minute.

8.3 All samples must be analyzed within 7 days of collection.

9. *Sample Extraction and Gas Chromatography.*

9.1 Remove standards and samples from cold storage (approximately an hour prior to an analysis) and bring to room temperature by placing in a warm water bath at 20–25°C.

9.2 Adjust the purge gas (nitrogen or helium) flow rate to 40 ml/min. Attach the trap inlet to the purging device, and set the device to the purge mode. Open the syringe valve located on the purging device sample introduction needle.

9.3 Remove the plunger from a 5 ml syringe and attach a closed syringe valve. Open the sample bottle (or standard) and carefully pour the sample into the syringe barrel until it overflows. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 ml. Since this process of taking an aliquot destroys the validity of the sample for future analysis, the analyst should fill a second syringe at this time to protect against possible loss of data. Add 5.0 μl of the surrogate spiking solution (7.3) through the valve bore, then close the valve.

9.4 Attach the syringe-valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the sample into the purging chamber.

9.5 Close both valves and purge the sample for 12.0 ±.05 minutes.

9.6 After the 12-minute purge time, attach the trap to the chromatograph, and adjust the device to the desorb mode. Introduce the trapped materials to the GC column by rapidly heating the trap to 180°C while backflushing the trap, with an inert gas, at 20 to 60 ml/min for 4 minutes. If rapid heating cannot be achieved, the gas chromatographic column must be used as a secondary trap by cooling it to 30°C (or subambient, if problems persist) instead of the initial program temperature of 45°C.

9.7 While the trap is being desorbed into the gas chromatograph, empty the purging chamber using the sample introduction syringe. Wash the chamber with two 5-ml flushes of organic-free water. After the purging device has been emptied, continue to allow the purge gas to vent through the chamber until the frit is dry, and ready for the next sample.

9.8 After desorbing the sample for four minutes, recondition the trap by returning the purge and trap device to the purge mode. Wait 15 seconds then close the syringe valve on the purging device to begin gas flow through the trap. Maintain the trap temperature at 180°C. After approximately seven minutes, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample. (Note: If this bake out step is omitted, the amount of water entering the GC/MS system will progressively increase causing deterioration of and potential shut down of the system.)

9.9 The analysis of blanks is most important in the purge and trap technique since the purging device and the trap can be contaminated by residues from very concentrated samples or by vapors in the laboratory. Prepare blanks by filling a sample bottle with organic-free water that has been prepared by passing distilled water through a pretested activated carbon column. Blanks should be sealed, stored at 4°C, and analyzed with each group of samples.

10. *Gas Chromatography—Mass Spectrometry.*

10.1 Table 2 summarizes the recommended gas chromatographic column materials and operting conditions for the instrument. Included in this table are estimated retention times and sensitivities that should be achieved by this method. An example of the separation achieved by Column 1 is shown in Figure 5.

10.2 GC–MS Determination—Suggested analytical conditions for determination of the pollutants amenable to purge and trap, using the Tekmar LCS–1 and GC/MS are given below. Operating conditions vary from one system to another; therefore, each analyst must optimize the conditions for each purge and trap and GC/MS system.

10.3 Purge Parameters.

federal register

Tuesday
December 18, 1979

Part IV

Environmental Protection Agency

Guidelines Establishing Test Procedures for the Analysis of Pollutants; Proposed Regulations; Correction

TABLE I. LIST OF APPROVED TEST PROCEDURES (Cont.)

Parameter and units	Method	Reference (Page Nos.) 1974 EPA Methods	14th Ed. Standard Methods	Part 31 1975 ASTM	USGS Methods[1]	Other Approved Methods
137. 1,3-Dichlorobenzene micrograms per liter	GC methods (601)[29] (602)[30] (612)[40]	-	-	-	-	-
	GC/MS method (625)[26]	-	-	-	-	-
138. 1,4-Dichlorobenzene, micrograms per liter	GC methods (601)[29] (602)[30] (612)[40]	-	-	-	-	-
	GC/MS method (625)[26]	-	-	-	-	-
139. 3,3'-Dichlorobenzidine, micrograms per liter	HPLC method (605)[33]	-	-	-	-	-
	GC/MS method (625)[26]	-	-	-	-	-
140. Dichlorodifluoromethane micrograms per liter	GC method (601)[29]	-	-	-	-	-
141. 1,1- Dichloroethane micrograms per liter	GC method (601)[29]	-	-	-	-	-
	GC/MS method (624)[26]	-	-	-	-	-
142. 1,2-Dichloroethane, micrograms per liter	GC method (601)[29]	-	-	-	-	-
	GC/MS method (624)[26]	-	-	-	-	-
143. 1,1-Dichloroethene micrograms per liter	GC method (601)[29]	-	-	-	-	-
	GC/MS method (624)[26]	-	-	-	-	-
144. trans-1,2-Dichloroethene, micrograms per liter	GC method (601)[29]	-	-	-	-	-
	GC/MS method (624)[26]	-	-	-	-	-
145. 2,4-Dichlorophenol, micrograms per liter	GC method (604)[32]	-	-	-	-	-
	GC/MS method (625)[26]	-	-	-	-	-
146. 1,2-Dichloropropane, micrograms per liter	GC method (601)[29]	-	-	-	-	-
	GC/MS method (624)[26]	-	-	-	-	-
147. cis-1,3-Dichloropropene micrograms per liter	GC method (601)[29]	-	-	-	-	-
	GC/MS method (624)[26]	-	-	-	-	-
148. trans-1,3-Dichloropropene micrograms per liter	GC method (601)[29]	-	-	-	-	-
	GC/MS method (624)[26]	-	-	-	-	-
149. Dieldrin, micrograms per liter	GC method (608)[36]	-	-	-	-	-
	GC/MS method (625)[26]	-	-	-	-	-
150. Diethyl phthalate, micrograms per liter	GC method (606)[34]	-	-	-	-	-
	GC/MS method (625)[26]	-	-	-	-	-
151. 2,4-Dimethylphenol, micrograms per liter	GC method (604)[32]	-	-	-	-	-
	GC/MS method (625)[26]	-	-	-	-	-
152. Dimethyl phthalate, micrograms per liter	GC method (606)[34]	-	-	-	-	-
	GC/MS method (625)[26]	-	-	-	-	-

TABLE II. CONTAINERS, PRESERVATION, AND HOLDING TIMES (cont.)

Measurement[a]		Container[b]	Preservative[c]	Maximum Holding Time[d]
58-59	Mercury	P,G	HNO_3 to pH<2 0.05% $K_2Cr_2O_7$	28 days
24-87	Metals except above	P,G	HNO_3 to pH<2	6 months
88	Nitrate	P,G	Cool, 4°C	48 hours
88(a)[i]	Nitrate-nitrite	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
89	Nitrite	P,G	Cool, 4°C	48 hours
90	Oil and Grease	G	Cool, 4°C H_2SO_4 to pH<2	28 days
91	Organic Carbon	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
93-206	ORGANIC COMPOUNDS[f]			
	Extractables (including phthalates, nitrosamines organochlorine pesticides, PCB's, nitroaromatics, isophorone, polynuclear aromatic hydrocarbons, haloethers, chlorinated hydrocarbons and TCDD)	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[h]	7 days (until extraction) 30 days (after extraction)
	Extractables (phenols)	G, teflon-lined cap	Cool, 4°C H_2SO_4 to pH<2 0.008% $Na_2S_2O_3$[h]	7 days (until extraction) 30 days (after extraction)
	Purgeables (Halocarbons and Aromatics)	G, teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$[h]	14 days
	Purgeables (Acrolein and Acrylonitrite)	G, teflon-lined septum	Cool, 4°C 0.008% $Na_2S_2O_3$[h]	3 days
207	Orthophosphate	P,G	Filter on site Cool, 4°C	48 hours
208	Pesticides	G, teflon-lined cap	Cool, 4°C 0.008% $Na_2S_2O_3$[h]	7 days (until extraction) 30 days (after extraction)
209	Phenols	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days
210	Phosphorus (elemental)	G	Cool, 4°C	48 hours
211	Phosphorus, total	P,G	Cool, 4°C H_2SO_4 to pH<2	28 days

DOW CHEMICAL U.S.A.

MIDLAND, MICHIGAN 48640

March 4, 1981

Dr. S. A. Peoples
Pesticide Management
Department of Food & Ag.
1220 N. Street
Sacremento, CA 95814

Dear Dr. Peoples:

In response to our phone conversation of 3/2/81 I will outline my method for determination of chloroallyl alcohols in water. The method is as follows:

1) Place a 100 ml aliquot of the water sample in a separatory funnel and saturate with sodium chloride. Extract with 40 ml diethyl ether and place the ether in a 125 ml Erlenmeyer with 24/40 ground glass joint. Repeat the extraction with an additional 20 ml ether, combining the ether extracts.

2) Add 2 ml hexane and several small boiling chips to the flask, attach a 3 ball Snyder column and boil off the ether in a hood on a sealed hot plate.

3) Rinse the Snyder column with 1 ml hexane as soon as the ether is gone and transfer the residual liquids to a 5 ml volumetric flask with hexane rinses.

4) Inject a 10 µl aliquot into a gas chromatograph equipped with a Hall 700A electrolytic conductivity detector.

5) Typical operating conditions.

Column: 6' x 2 mm glass column
Packing: 10% SP-1000 on 100/120 mesh Chromosorb WAS
Flow rates: 25 cc/min on column + 35 cc/min reaction gas both ultrapure H_2 (99.999%)
Temperatures: injector - 150°C
column - 135°C
detector - 250°C
reactor - 810°C
Solvent flow rate: 0.3-0.5 ml/min
Output attenuation: 10x5

Dr. S. A. Peoples

March 4, 1981

I have used this method in the analysis of well water from numerous sources. The lowest recovery level run was 1.0 ppb with recoveries typically ranging from 90 to 100% for fortification levels ranging from 1 to 10 ppb.

We are sending the standards of cis- and trans- chloroallyl alcohol separately. When you receive them please handle with caution as they are very effective vesicants and the blisters they raise are slow to heal.

If you have any questions about the method please feel free to call me at 517-636-2396.

Sincerely,

R. D. Glas
Residue/Environmental/Metabolism Research
Agricultural Products Department
9001 Bldg.

cc: H. J. Dishburger
F. C. O'Melia

cr

APPENDIX IX

SOIL CORE PROFILE CHARACTERISTICS
(Lovelace Road, Lathrop, CA, December 7, 1982)*

PERCENT MOISTURE AND CORE DEPTH IN FEET

Sample	Depth	%Moist	Sample	Depth	%Moist
A-3	0.5	Empty core	I-3	12.5	Empty core
2	1.0	11.0	2	13.0	8.0
1	1.5	11.0	1	13.5	6.0
B-3	2.0	10.0	J-3	14.0	19.0
2	2.5	11.0	2	14.5	20.0
1	3.0	12.0	1	15.0	18.0
C-3	3.5	Empty core	K-3	15.5	23.0
2	4.0	Empty core	2	16.0	21.0
1	4.5	16.0	1	16.5	23.0
D-3	5.0	Empty core	L-3	17.0	28.0
2	5.5	19.0	2	17.5	24.0
1	6.0	19.0	1	18.0	21.0
E-3	6.5	9.0	M-3	18.5	18.0
2	7.0	14.0	2	19.0	16.0
1	7.5	21.0	1	19.5	19.0
F-3	8.0	20.0	N-3	20.0	19.0
2	8.5	18.0	2	20.5	21.0
1	9.0	20.0	1	21.0	28.0
G-3	9.5	23.0	O-3	21.5	21.0
2	10.0	24.0	2	22.0	24.0
1	10.5	18.0	1	22.5	25.0
H-3	11.0	11.0	P-3	23.0	Empty core
2	11.5	13.0	2	23.5	33.0
1	12.0	13.0	1	24.0	23.0

* All material in Appendix IX has been extracted from the following report to the Board:

Combs, D. L. and R. J. Spanggord. 1983. Investigation of nematocide products in soils. SRI International, Menlo Park, California.

PERCENT ORGANIC CARBON IN SOIL CORE SAMPLES

Sample No.	Percent Organic Carbon
A-2	0.450
B-2	0.670
C-2	No sample (core empty)
D-2	0.043
E-2	0.020
F-2	0.028
G-2	0.012
H-2	0.036
I-2	0.020
J-2	0.025
K-2	0.028
L-2	0.023
M-2	0.052
N-2	0.025
O-2	0.028
P-2	0.048

Soil: Dinuba fine sandy loam, 0-3% slopes (map symbol Df) or Dinuba fine sandy loam, deep phase 0-3% slopes (Dfp) slightly saline (.2-.5%) or moderately saline (.5-1.0%)

Source of soil classification: Soil Survey of Stockton Area, California U.S. Dept. Agriculture and University of California, issued May, 1951.

Location of soil: 100 feet south of Lovelace Road, north of Manteca, San Joaquin County, California.

Soil sampled November 19, 1982, described January 6, 1983.

Core Number	Depth Inches	Description
A-3	0-6	Not available
A-2	6-12	Brown (10YR 5/3 dry, 10YR 4/3 dark brown moist) fine sandy loam; massive; soft dry, very friable moist, nonsticky and nonplastic wet; non-effervescent (10% HCl)
A-1	12-18	Brown (10YR 5/3, 10YR 4/3 darkbrown moist) fine sandy loam; massive; soft dry, very friable moist, nonsticky and nonplastic wet; non-effervescent.
	18-20	Not sampled
B-3	20-26	Not available
B-2	26-32	Brown (10YR 5/3 dry, 10YR 4/3 dark brown moist) fine sandy loam; massive; soft dry, very friable moist, nonsticky and nonplastic wet; non-effervescent
B-1	32-38	Pale brown (10YR 6/3 dry, 10YR 5/3 brown moist) fine sandy loam; massive; soft dry, very friable moist, nonsticky and nonplastic wet; non-effervescent
	38-40	Not sampled
C-3	40-46	Not available
C-2	46-52	Not available
C-1	52-58	Pale brown (10YR 6/3 dry, 10YR 5/3 brown moist) fine sandy loam; massive; soft dry, very friable moist, nonsticky and nonplastic wet; non-effervescent
	58-60	Not sampled

Core Number	Depth Inches	Description
D-3	60-66	Not available. (Note: This is a very important horizon. It should have a thin (less than 1 inch) lime-silica hardpan on top of horizon for this soil to be classified in the Dinuba soil series. See description of Dinuba series, pages 48-52, Soil Survey of Stockton Area, California).
D-2	66-72	White (10YR 8/2 dry, 10YR 6/2 light brownish gray moist) silt loam; massive; hard dry, firm moist, nonsticky and slightly plastic wet; slightly effervescent, lime disseminated.
D-1	72-78	White (10YR 8/2 dry, 10YR 6/2 light brownish gray moist) with few, medium 2.5Y 6/4 light yellowish brown mottles moist; silt loam; massive; hard dry, friable moist, nonsticky and slightly plastic wet; slightly effervescent, lime disseminated (Note: less effervescence than D-2)
	78-80	Not sampled
E-3	80-86	Not available
E-2	86-92	White (10YR 8/2 dry, 2.5Y 6/2 light brownish gray with few fine 5YR 4/3 reddish brown mottles moist) loamy fine sand; weak thin platy structure; soft dry, very friable moist, nonsticky and nonplastic wet; non-effervescent
E-1	92-98	White (2.5Y 8/2 dry, 2.5Y 6/2 light brownish gray with few fine 7.5 YR 4/4 dark brown mottles moist) fine sandy loam; massive; soft dry, very friable moist, nonsticky and nonplastic wet, non-effervescent
	98-100	Not sampled
F-3	100-106	Not available
F-2	106-112	White (2.5Y 8/2 dry, 2/5Y 6/2 light brownish gray moist) silt loam; massive; slightly hard dry, friable moist, nonsticky and slightly plastic wet; non-effervescent.
F-1	112-118	Light gray (2/5Y 7/2 dry, 2.5Y 5/2 grayish brown moist) light silty clay loam; massive; slightly hard dry, friable moist, slightly sticky and slightly plastic wet; non-effervescent
	118-120	Not sampled
G-3	120-126	Not available
G-2	126-132	Light gray (2.5Y 7/2 dry, 2.5Y 5/2 grayish brown moist) light silty clay loam; massive; slightly hard dry, friable moist, slightly sticky and slightly plastic wet; non-effervescent

Core Number	Depth Inches	Description
G-1	132-138	Light gray (2.5Y 7/2 dry, 2.5Y 5/4 light olive brown moist) silty clay; massive; hard dry, firm moist, slightly sticky and plastic wet; non-effervescent
	138-140	Not sampled
H-3	140-146	Not available
H-2	146-152	Light gray (5Y 7/2 dry, 5Y 5/3 olive moist) silty clay loam; massive; hard dry, firm moist, sticky and plastic wet; non-effervescent
H-1	152-158	Light gray (5Y 7/2 dry, 5Y6/3 pale olive moist) loamy coarse sand; massive, soft dry, very friable moist, nonsticky and nonplastic wet; non-effervescent
	158-160	Not sampled
I-3	160-166	Not available
I-2	166-172	Light gray (5Y 7/2 dry, 5Y 6/3 pale olive moist) loamy coarse sand; massive; soft dry, very friable moist, nonsticky and nonplastic wet; non-effervescent (Note: layer has very thin lenses of loam)
I-1	172-178	Light gray (5Y 7/2, 5Y 5/3 olive moist) stratified lenses of loam and silt loam; massive; soft and slightly hard dry, very friable and friable moist, nonsticky and nonplastic to slightly plastic wet; non-effervescent
	178-180	Not sampled
J-3	180-186	Not available
J-2	186-192	Mottled light gray (5Y 7/2 and olive yellow (2.5 Y 6/6) dry, mottled 5Y 5/3 olive and 2.5Y 5/6 light olive brown moist; fine sandy loam; massive; slightly hard dry, very friable moist, nonsticky and nonplastic wet, non-effervescent.
J-1	192-198	Pale yellow (5Y 7/3 dry, 5Y 5/3 olive moist) silty clay; massive, hard dry, firm moist, slightly sticky and plastic wet, non-effervescent
	198-200	Not sampled

Core Number	Depth Inches	Description
K-3	200-206	Not available
K-2	206-212	Pale yellow (5Y 7/3 dry, 5Y 5/3 olive moist) clay; massive; very hard dry, firm moist; sticky and plastic wet; non-effervescent
K-1	212-218	Pale yellow (5Y 7/3 dry, 5Y 5/3 olive moist) sandy clay loam; massive; hard dry, friable moist, nonsticky and slightly plastic wet; non-effervescent
	218-220	Not sampled
L-3	220-226	Not available
L-2	226-232	Mottled light gray (5Y 7/2) and white (5Y 8/2) dry, mottled olive gray (5Y 5/2) and light olive gray (5Y 6/2) moist; silty clay; massive; hard dry, firm moist, slightly sticky and plastic wet; slightly to strongly effervescent; segregated lime, the lighter colored areas are strongly effervescent
L-1	232-238	Pale yellow (5Y 7/3 dry, 5Y 5/3 olive moist) clay; massive; very hard dry , very firm moist, slightly sticky and plastic wet; non-effervescent
	238-240	Not sampled
M-3	240-246	Not available
M-2	246-252	Mottled light gray (5Y 7/2) and white (5Y 8/2) dry, mottled olive gray (5Y 5/2) and light olive gray (5Y 6/2) moist, silty clay; massive, very hard dry, very firm moist, slightly sticky and plastic wet, slightly to strongly effervescent, lime segregated, light colored areas are strongly effervescent
M-1	252-258	Light gray (2/5Y 7/2 dry, 2/5Y 5/4 light olive brown moist) silty clay; massive; very hard dry, very firm moist, slightly sticky and plastic wet; slightly effervescent
	258-260	Not sampled
N-3	260-266	Not available
N-2	266-272	Mottled light gray (2.5Y 7/2) and white (2.5Y 8/2) dry, mottled grayish brown (2.5Y 5/2) and light brownish gray (2.5 6/2) moist; silty clay; massive; very hard dry, firm moist, slightly sticky and plastic wet; slightly effervescent, segregated lime, lighter colored areas have the most effervescence.
N-1	272-278	Mottled gray (5Y 6/1) and white (5Y 8/1) dry,

Core Number	Depth Inches	Description
		(continued) 5Y 5/2 olive gray moist) silty clay loam; massive; hard dry, firm moist, slightly sticky and plastic wet; slightly effervescent, segrated lime, light colored areas have most effervescence
	278-280	Not sampled
O-3	280-286	Not available
O-2	286-292	Pale yellow (5Y 7/3 dry, 5Y 5/3 olive moist) silty clay; massive; very hard dry, firm moist, sticky and plastic wet; non-effervescent
O-1	292-298	Pale yellow (5Y 7/3 dry, 5Y 5/3 olive moist) silty clay; massive; very hard dry, firm moist, slightly sticky and plastic wet, slightly effervescent
	298-300	Not sampled
P-3	300-306	Not available
P-2	306-312	Light gray (5Y7/2 dry, 5Y 5/3 olive moist) heavy sandy clay loam; massive; hard dry, friable moist, nonsticky and slightly plastic wet, non-effervescent with some very slightly effervescent seams. (Note: Lower half of core saturated with water)
P-1	312-318	Light gray (5Y 7/2 dry, 5Y 5/3 olive moist) sandy clay loam; massive; slightly hard dry, firm moist, nonsticky and slightly plastic wet; non-effervescent

January 11, 1983

Rudolph Ulrich
Certified Professional
Soil Scientist, Number 16,
National Registry

Memorandum

APPENDIX X

To : G. A. Redlin
Regional Engineer
Fresno District Office
Sanitary Engineering Branch

Date : June 2, 1983

Subject: Fruitvale Groundwater Quality Study, Kern County - Summary of Results

From : Stephen J. Nelson
Sanitary Engineering Branch
Berkeley

Attached is a brief preliminary assessment of water quality data from the Fruitvale Groundwater Quality Study. I am still working on more detailed evaluations of subsurface geology and additional water quality issues.

The following is a brief summary of the results:

1. Ethylene dibromide (1,2-dibromoethane or EDB) is present in shallow groundwater under Section 15. The levels found (as high as 4 micrograms per liter, µg/L) are of serious public health concern.

2. A broad area of dichloropropane (1,2-dichloropropane or DCP) contamination of groundwater occurs in a SW-NE trending area from the WSW boundary of the study area through the northern boundary. In the northern area DCP has been found in both shallow and deep aquifers. The highest levels found (8µg/L) are below the Department's 10 µg/L Action Level.

3. Sampling conducted in August, 1982 indicated trace (sub-µg/L) trichlorofluoromethane (Freon 11) contamination of the shallow aquifer in the Greenacres area. This contamination was not confirmed in the Winter, 1983 sampling.

4. Phthalate esters appear frequently throughout the study area.

5. Trace levels of phenols occur sporadically in both shallow and deep aquifers throughout all but the southeast corner of the study area.

6. Butylated hydroxytoluene (BHT) was found in scattered samples in August, 1982. No BHT was detected in February and March, 1983 sampling.

7. Traces of hexane were detected in March, 1983 in two wells in the southeast portion of the study area.

Attachments
cc: D. Spath, SEB
T. Andrews, SEB
H. Collins, Ph.D., EHD
Pete Weisser, Press Office
F. Baumann, So. Cal. Lab. Section
B. Tamplin, SRL
SJN:ba

FRUITVALE GROUNDWATER QUALITY STUDY
PRELIMINARY ASSESSMENT OF WATER QUALITY DATA

April 29, 1983

I. INTRODUCTION

Previous studies (Department of Water Resources, 1981; Kern County Water Agency, 1979) have addressed groundwater quality problems in the Fruitvale area and suggested general spreading of contamination to the north and northwest from the Fruitvale oil field area. These studies, however, did not include detailed analyses of groundwater samples for organic constituents. Because groundwater is the major source of drinking water for local residents, the Department of Health Services undertook this study of the organic quality of groundwater in the Fruitvale area. The specific area of study is Township 29S, Range 27E, Sections 8-11, 14-17 and 19-35, or approximately the area bounded by Snow Road on the north, Airport Road and Highway 99 on the east, Stockdale Highway on the south and Jewetta Avenue on the west. (See Figure 1).

Other researchers have described the presence of a clay layer, locally known as the "300' Clay", which apparently underlies much of the study area, (Dale, R. H., et al, 1966; Kern County Water Agency, 1979.) Using this clay layer (where present) or the extension of its bedding plane (where it is not present or its existence is questionable) to define shallow and deep aquifer systems, the study sought to sample one shallow well from each section and one deep well from each of four sections. Municipal water supply wells were used as much as possible to satisfy these criteria. In areas where no municipal wells were available, private wells were located by going door-to-door. In this fashion, suitable wells were found in most sections; however, in some sections "composite" wells (i.e., wells with significant perforations in both shallow and deep aquifers) were sampled and in other areas no suitable wells were located.

II. RESULTS AND DISCUSSION

Sampling was conducted in two phases; an initial set of municipal well samples collected in August, 1982, followed by sampling of private wells in February, 1983 and resampling of municipal wells in March, 1983. Samples were analyzed using EPA methods 624 and 625 (United States Environmental Protection Agency, 1982). Phenols were analyzed according to methods described in American Public Health Association, et al, (1976). Because the deep well in Section 8 that was sampled in August, 1982 was not in operation in March, 1983, a deep well in Section 3 was sampled in its stead. Sample results are summarized in Tables 1 and 2. Specific findings are discussed below.

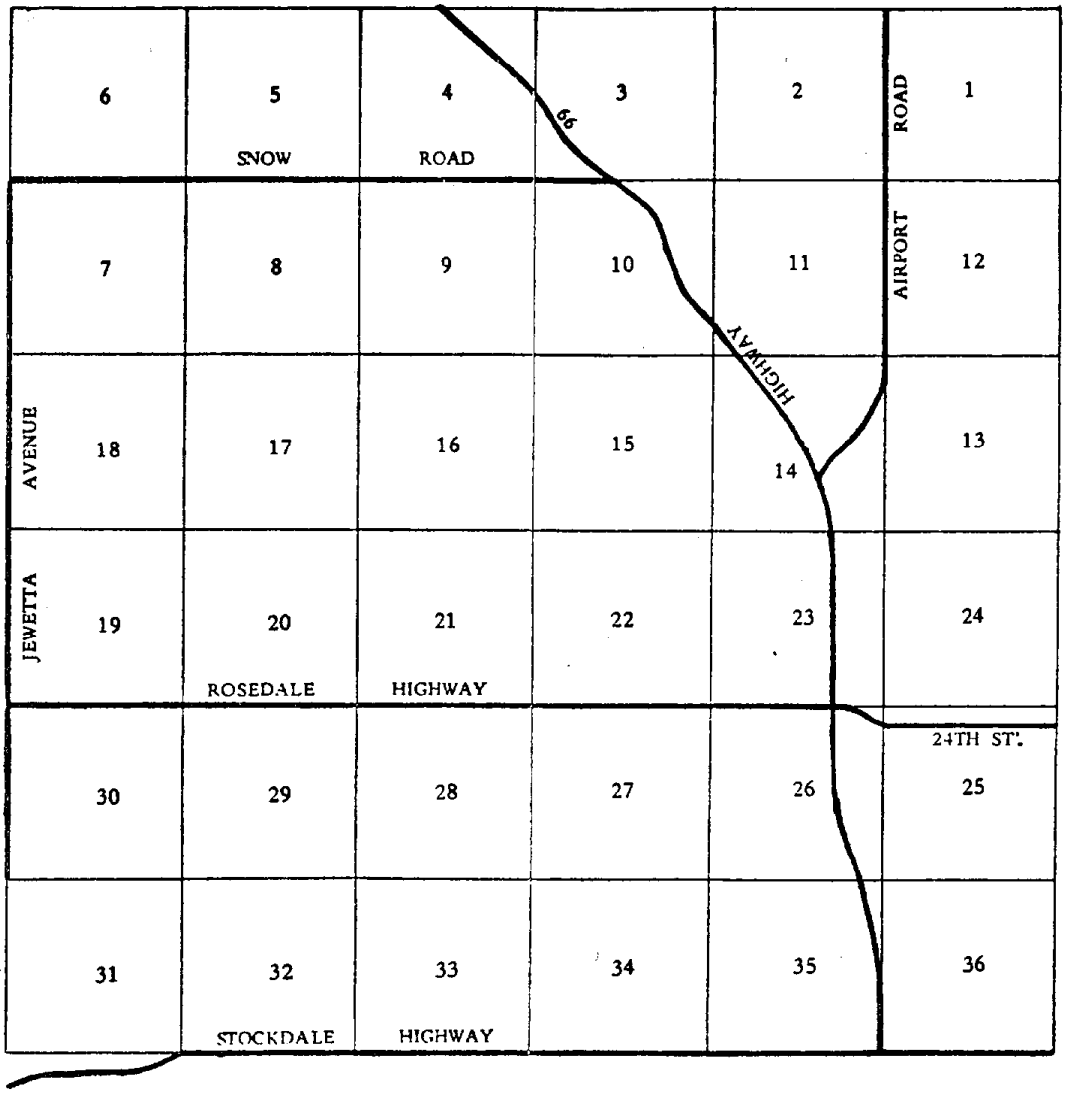


Figure 1. Map of Township 29S. Range 27E.

Sampled: 4 shallow wells in each section
1 deep well in each section

A. Ethylene dibromide

Ethylene dibromide (EDB; 1,2-dibromoethane) at four to five micrograms per liter (µg/L) was found in a shallow well in Section 15. This contamination was confirmed by resampling of the well and testing of additional wells in the area. Eight other wells located within one mile of this well were also sampled. Of these, two contained EDB, although at lower concentrations.

Construction information was readily available for two of the wells in which no EDB was detected; one of these wells is perforated entirely below the 300 foot clay; the other is a composite well. Thus, it appears that the EDB contamination is confined to the shallow aquifer and extends little, if at all, outside of Section 15. This pattern suggests a local point source for the EDB contamination.

EDB is highly toxic material and is an animal carcinogen. Major uses of EDB are the manufacture of leaded gasoline and agricultural fumigation. The Safe Drinking Water Committee of the National Research Council (NRC) has stated that "carcinogenicity data seem to require that water contaminated with ethylene dibromide not be consumed." However, carcinogenicity risk estimates prepared by NRC suggest Action Level of about 0.05 µg/L for EDB to achieve a 10^{-6} risk, assuming lifetime consumption of two liters of water per day. (National Research Council, 1980).

B. Dichloropropane

Dichloropropane (DCP; 1,2-dichloropropane) was found in the north, northwest and west portions of the study area. Although DCP occurred most often in shallow wells in these areas, deep wells in Sections 9 and 16 contained DCP traces. The maximum level found (8µg/L) is below the Department of Health Services' 10 µg/L Action Level. (The Department advises that people avoid consuming water supplies containing more than 10 µg/L of DCP). DCP is used as a solvent for oils, fats and greases, in dry cleaning and in agricultural fumigation.

Additional DCP testing has confirmed the presence of DCP in these wells and in eight other wells in the Greenacres area. DCP testing of additional wells in the northern study area is scheduled.

C. Freon 11

Traces of Freon 11, or trichlorofluoromethane, were found in shallow wells in Sections 21, 28, 29 and 30 in August, 1982. These four sections comprise a single contiguous area, suggestive of movement from a point source.

However, considering that the amounts of Freon 11 detected were very slight and no Freon 11 was detected in the same wells in March 1983, it is possible that the August 1982 findings are spurious. Additional summertime analyses of wells in this area for Freon 11 should be conducted using techniques more sensitive for Freon 11 than those used in this study.

Freon 11 is used in the manufacture of aerosol sprays, refrigerants, blowing agents and cleaning compounds and in fire extinguishers and the analysis of water samples for oil and grease. Available health effects data, though meager, indicate little hazard associated with drinking water containing these trace levels of Freon 11.

D. Phthalate esters

Various phthalate esters appeared frequently in wells throughout the study area. The maximum level found was 11.5 µg/L of diethylhexyl phthalate in Section 8 in February, 1983. Comparison of results from wells sampled both in August, 1982 and March, 1983 indicates that phthalate findings fluctuate in terms of both whether or not phthalates are detected and, if detected, the particular compounds found. Both shallow and deep aquifers are affected, although, on the whole, phthalates seem to occur less often in deep wells. Since all of the deep wells were constructed as municipal wells (and all but one are currently being used for municipal supply), this finding could also reflect generally superior overall construction and operation of deep wells as a group.

Phthalate esters are extensively used as plasticizers, primarily in the production of polyvinyl chloride resins, and the most widely used phthalate is diethylhexyl phthalate. Phthalates have also been used as pesticide carriers; however, this is generally a minor use. Phthalates are frequently isolated from water samples because of their widespread use and dispersal in the environment and their relative ease of detection in water supplies. Thus, the frequency with which phthalates were detected in this study might not be extraordinary. Additional sampling in areas further upgradient and/or south of the Kern River should be conducted to determine if phthalate esters are, in fact, unusually prevalent in the Fruitvale area. Potential health effects associated with ingestion of phthalates are currently being reviewed.

E. Phenols

The previous groundwater quality studies identified phenols as a major groundwater contaminant in the Fruitvale area, presumably as a result of discharge of oil production and oil refinery wastes into unlined sumps. In the 1961 study by the Department of Water Resources, phenol concentrations as high as 11 milligrams per liter (mg/L) in Section 29 were reported.

Phenol analyses from the Winter, 1983 sampling confirmed the presence of phenols in the areas identified in the earlier Department of Water Resources and Kern County Water Agency studies. Although the presence 40 µg/liter of phenols in one well in Section 8 suggests that phenolic contamination might be continuing to spread to the northwest, the lack of any confirming data from other wells in Section 8 or from wells in Sections 7, 17 and 18 equally suggests that this result might be an artifact or a small localized condition.

In any case, the data indicate that phenol concentrations have declined considerably since 1961, to the extent that phenols are now found only sporadically in the study area. This general situation is consistent with observations of phenol movement and degradation in groundwater in a glacial drift aquifer near St. Louis Park, Minnesota, which was contaminated by a highly concentrated waste discharge from a wood treatment plant using creosote as reported by Ehrlich, G. G., et al (1982). In that study, the phenol concentration of groundwater declined rapidly as the water moved down gradient, with strong evidence of microbial degradation of phenols within the aquifer. This evidence included isolation of microbes from the aquifer which was capable of utilizing phenolic substrates. Methane gas was also present in groundwater in the areas where microbial degradation presumably occurred. (Perhaps not coincidentally, during the collection of the Fruitvale samples it was qualitatively observed that many water samples collected in the area of major phenol contamination described in the 1961 study profusely outgassed after sample collection.) To determine whether similar degradation has occurred in the Fruitvale area, it might be feasible to attempt to isolate microbes capable of metabolizing phenols from area wells or to attempt radiocarbon dating of outgas. (If the outgas is the breakdown product of phenols, its radiocarbon characteristics should reflect the age of the related oil field deposits.)

The major problems associated with phenolic compounds in domestic water supplies are disagreeable tastes and odors, which generally make the water unpalatable and objectionable before known toxic levels are reached. The highest levels found in this study are still one order of magnitude

below 0.3 mg/L level above which tastes and odors are likely to be reported. (U. S. Environmental Protection Agency, 1980). Indeed, none of the well owner/users contacted during this study reported any objectionable tastes or odors in their water.

None of the wells tested is routinely chlorinated prior to use. Because chlorination of phenols produces chlorophenols, which are significantly more odorous than simple phenols, chlorination of wells containing phenols can produce objectionable tastes and odors in the water supplies. Chlorophenols themselves can also present some potential health problems. These factors should be considered prior to commencing routine chlorination of wells containing phenolics. However, in case of microbial contamination of a well, the short-term aesthetic problems associated with chlorophenols are vastly outweighed by the benefit of adequate disinfection.

F. Butylated Hydroxytoluene

Butylated hydroxytoluene (BHT) was found in some of the August, 1982 samples. BHT is an antioxidant for a wide variety of products, including petroleum products, and an antiskinning agent in paints and inks. Although BHT always occurred in conjunction with phthalate esters, it was not detected in any of the February or March, 1983 sampling, even when re-samples from wells previously containing BHT still revealed phthalates. Thus, it is possible that the BHT findings are artifacts.

G. Hexane

Traces of Hexane were detected in March, 1983 samples from wells in Sections 34 and 35. Hexane is a low toxicity simple petroleum hydrocarbon. The levels found (1 µg/L, maximum) are not of direct public health concern.

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TABLE I

Results of Organic Analyses of Shallow and Composite Wells
(All Results in Micrograms Per Liter)

Section Number	Shallow (S) or Composite (C)	Date	Volatile Organics (Detection Limit Approx. 0.5)	Acid and Base-Neutral Extractions (Detection Limit Approx. 0.2)	Phenols (Detection Limit = 1)
08	C	2/21/83	1,2-dichloro-propane: 7.8 1,2,3-trichloro-propane: est. <1.0	diethyl phthalate tr. di-n-butyl phthalate tr. diethylhexyl phthalate 11.5	40
14	C	2/21/83	n.d.	di-n-butyl phthalate tr. diethylhexyl phthalate 4.1	4
15	S	2/20/83	ethylene dibromide: 4.3	n.d.	n.d.
19	S	8/25/82	n.d.	diethyl phthalate n.q. diisobutyl phthalate n.q. di-n-butyl phthalate n.q.	n.a.
		3/16/83	1,2-dichloro-propane: 0.54	diethyl phthalate est. 1.0	n.d.
20	S	2/20/83	n.d.	n.d.	3
21	S	8/26/82	trichloro-fluoromethane: tr.	butylated hydroxytoluene n.q. diethyl phthalate n.q. diisooctyl phthalate n.q. di-n-butyl phthalate n.q.	n.a.
		3/16/83	n.d.	diethyl phthalate tr.	n.d.

TABLE I

Results of Organic Analyses of Shallow and Composite Wells
(All Results in Micrograms Per Liter)

Section Number	Shallow (S) or Composite	Date	Volatile Organics (Detection Limit Approx. 0.5)	Acid and Base-Neutral Extractions (Detection Limit Approx. 0.2)	Phenols (Detection Limit = 1)
22	S	2/19/83	n.d.	diethylhexyl phthalate 2.0	4
23	S	2/19/83	n.d.	di-n-butyl phthalate tr. diethylhexyl phthalate tr.	n.d.
25	C	8/25/82	n.d.	n.d.	n.a.
		3/16/83	n.d.	n.d.	n.d.
26	S	8/26/82	n.d.	butylated hydroxytoluene n.q. diethyl phthalate n.q. diisobutyl phthalate n.q. di-n-butyl phthalate n.q.	n.a.
		3/17/83	n.d.	n.d.	n.d.
27	S	2/19/83	n.d.	diethylhexyl phthalate 1.6	2
28	S	8/25/82	trichlorofluoro-methane tr.	butylated hydroxytoluene n.q. diethyl phthalate n.q. diisobutyl phthalate n.q. di-n-butyl phthalate n.q.	n.a.
		3/16/83	n.d.	n.d.	1

TABLE I

Results of Organic Analyses of Shallow and Composite Wells
(All Results in Micrograms Per Liter)

Section Number	Shallow (S) or Composite	Date	Volatile Organics (Detection Limit Approx. 0.5)	Acid and Base-Neutral Extractions (Detection Limit Approx. 0.2)	Phenols (Detection Limit = 1)
28	S	3/16/83	n.d.	n.d.	n.d.
28	S	3/16/83	n.d.	di-n-butyl phthalate tr.	n.d.
29	S	8/25/82	trichlorofluoro-methane tr.	n.d.	n.a.
		3/16/83	n.d.	n.d.	n.d.
30	S	8/25/82	trichlorofluoro-methane tr.	n.d.	n.a.
		3/16/83	1,2-dichloropropane 1.3	diethyl phthalate est. 1.0	n.d.
32	S	2/20/83	n.d.	n.d.	3
35	C	8/26/82	n.d.	butylated hydroxytoluene n.q. diethyl phthalate n.q. diisobutyl phthalate n.q. di-n-butyl phthalate n.q.	n.a.
		3/17/83	hexane 1.0	n.d.	n.d.

Notes: See Appendix A

TABLE 2

Results of Organics Analyses of Deep Wells
(All Results in Micrograms per Liter)

Section Number	Date	Volatile Organics (Detection Limit Approx. 0.5)	Acid and Base-Neutral Extractions (Detection Limit Approx. 0.2)	Phenols (Detection Limit = 1)
03	3/17/83	n.d.	n.d.	n.d.
09	8/25/82	n.d.	butylated hydroxytoluene n.q. diethyl phthalate n.q. diisobutyl phthalate n.q. di-n-butyl phthalate n.q.	n.a.
	3/16/83	methylene chloride tr chloroform tr 1,2-dichloropropane 0.46	diethylhexyl phthalate est. 2.0	n.d.
11	8/25/82	n.d.	butylated hydroxytoluene n.q. diethyl phthalate n.q. diisobutyl phthalate n.q. di-n-butyl phthalate n.q.	n.a.
16	8/26/82	n.d.	n.d.	n.a.
	3/16/83	1,2-dichloropropane 0.31	n.d.	6
20	2/20/83	n.d.	diethylhexyl phthalate 1.8	26

TABLE 2

Results of Organics Analyses of Deep Wells
(All Results in Micrograms per Liter)

Section Number	Date	Volatile Organics (Detection Limit Approx. 0.5)	Acid and Base-Neutral Extractions (Detection Limit Approx. 0.2)	Phenols (Detection Limit = 1)
23	3/16/83	chloroform tr	diethylhexyl phthalate tr.	n.d.
24	8/26/82	n.d.	n.d.	n.a.
26	8/26/82	n.d.	n.d.	n.a.
	3/16/83	n.d.	n.d.	n.d.
34	8/25/82	n.d.	n.d.	n.a.
	3/17/83	hexane 0.35	n.d.	n.d.

Notes: See Appendix A

APPENDIX A

Notes to Tables 1 and 2

1. "est." means estimated concentration; not quantified due to unavailability of standards.

2. "tr" means trace concentration, approximately equal to detection limit but too low to quantify.

3. "n.d." means none detected.

4. "n.q." means chemical present, concentration not quantified.

5. "n.a." means not analyzed.

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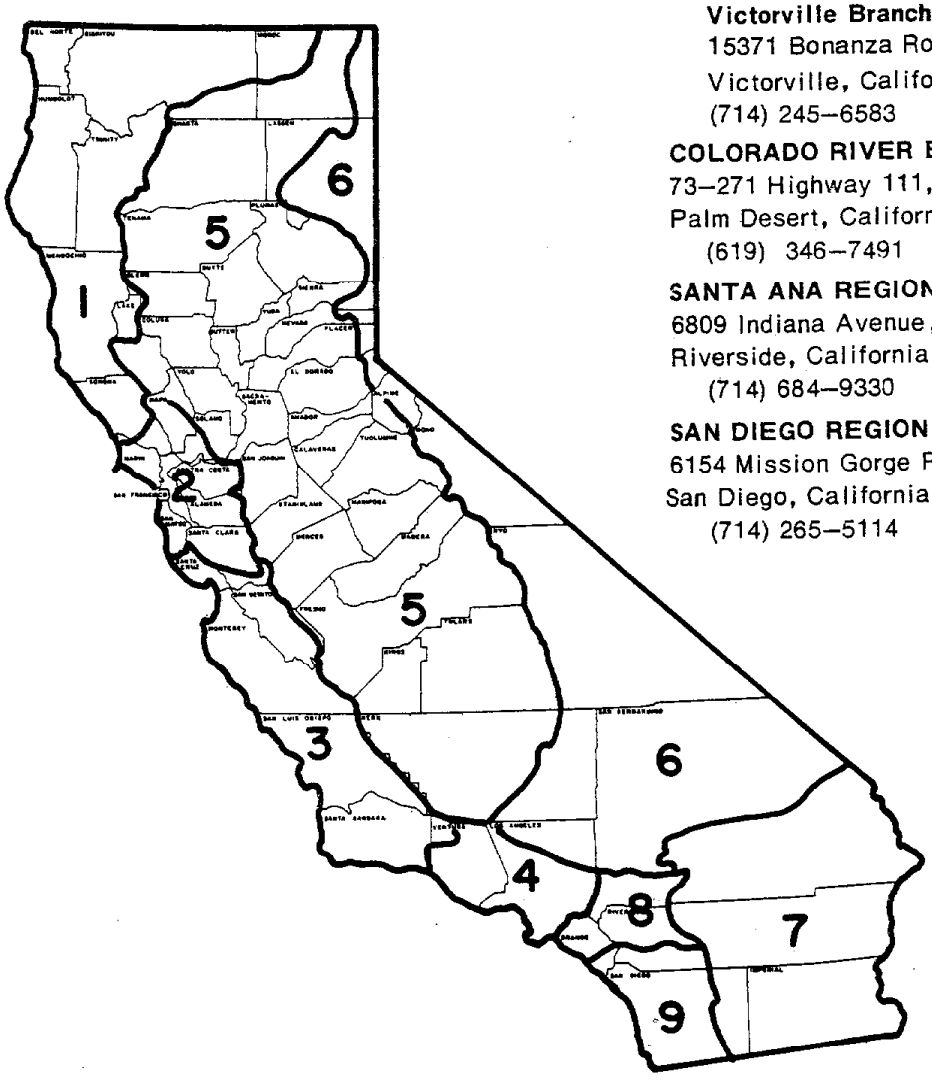

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