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**Presence of selected organic compounds and their intermediates  
in municipal landfill leachates**

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The University of Arizona, 1987

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PRESENCE OF SELECTED ORGANIC COMPOUNDS  
AND THEIR INTERMEDIATES  
IN MUNICIPAL LANDFILL LEACHATES

by

Jill Marie Thompson,

---

A Thesis Submitted to the Faculty of the  
DEPARTMENT OF CIVIL ENGINEERING  
AND ENGINEERING MECHANICS  
In Partial Fulfillment of the Requirements  
For the Degree of  
MASTER OF SCIENCE  
WITH A MAJOR IN CIVIL ENGINEERING  
In the Graduate College  
THE UNIVERSITY OF ARIZONA

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## ABSTRACT

This research involves the evaluation of municipal landfill leachates for specific hazardous compounds in an effort to qualitatively determine the potential for groundwater contamination. Leachate samples from five landfills were evaluated for thirteen EPA priority pollutants using gas chromatography. In addition, samples were analyzed for total organic carbon (TOC) and total organic halide (TOX). A solids analysis was performed on refuse excavated from one landfill. This analysis included organic halide determination of interstitial liquids, and a total halide determination for each solid sample. A solids/liquid partition coefficient was calculated from the results.

The literature review includes a detailed section outlining the biological degradation of hazardous organic compounds in anaerobic environments similar to conditions found in landfills.

## CHAPTER 1

### INTRODUCTION

There is growing concern regarding the entrance of hazardous compounds, originating from industrial, commercial, and residential wastes, into the environment. Of particular interest is the potential threat these compounds pose to our groundwater supplies and, thus, human health. Presently, almost five of six public water supply systems rely primarily on groundwater. As a result, at least 73 million people in the United States drink groundwater (Theme Introduction, 1986). A few large cities, such as Tucson, Arizona, depend solely on groundwater to satisfy drinking water requirements.

Unfortunately, incidences of groundwater contamination and pollution are becoming increasingly common. Much of the degradation of these valuable water supplies may be attributed to man's activities, yielding water which is unsafe for human consumption.

Man's past waste disposal practices can be implicated as a major cause of today's groundwater pollution. Land disposal (open dumps and landfills) of both

solid and liquid wastes has historically been the most common method of waste disposal and is the most prevalent source of groundwater contaminants.

Sanitary landfills, used primarily for the disposal of residential and commercial wastes, are responsible for the contamination of groundwater in a number of areas across the United States. The term "sanitary landfill" means an operation in which the wastes to be disposed are compacted and covered with a layer of soil at the end of each day's operation (Tchobanoglous, 1976). Groundwater contamination occurs when leachate, carrying hazardous chemicals, is allowed to exit through the bottom of the landfill and percolate through the soil to an underlying aquifer.

Until recently, household hazardous wastes have been largely ignored by persons studying the hazardous waste problem. In fact, the Environmental Protection Agency (EPA) has excluded household refuse from the definition of hazardous wastes (Federal Register, 1983). As a result, there are no specific requirements regarding the disposal of household hazardous wastes (HHW). Presently, HHW may be discarded with all other household refuse. However, recent evidence suggests that household hazardous wastes may pose a significant threat to groundwater supplies (Brown, 1987 and Rathje, 1985).

These findings indicate the need to study household hazardous wastes and determine the potential for groundwater contamination. To gain knowledge in this area, the Departments of Civil Engineering and Engineering Mechanics and Anthropology of the University of Arizona became involved in an interdisciplinary research effort called the Garbage Project, or Le Projet Du Garbage.

Dr. Bill Rathje, of the University of Arizona, founded the Garbage Project in 1973 to conduct a detailed analysis of residential wastes (Rathje, 1986). Since the study's inception, data have been collected from more than 10,000 sample pickups of household refuse in Tucson, Arizona; Milwaukee, Wisconsin; Marin County, California; and Mexico City.

Data from the project have been used to answer questions concerning nutrition, interview-survey bias, resource conservation and recycling, consumer behavior, market research, solid waste management, and most recently, household hazardous wastes. The portion of the project centered on the quantification of household hazardous wastes is funded by the National Science Foundation (NSF). From the information gathered in this study, Rathje and his colleagues hope to build a model that will support the estimation of hazardous waste discard patterns for any

community desired; controlling for variable income, ethnicity, family size, geographic location, seasonality, and other behavioral and environmental factors (Rathje, 1985 and Wilson, 1985).

In order to qualitatively determine the potential for groundwater contamination, the Department of Civil Engineering's Environmental Laboratory is analyzing landfill leachates obtained from leachate collection systems for various hazardous compounds.

The objective of this research was to relate compounds identified in leachate with those deposited in landfills, as recorded by Anthropology. In addition, an effort was made to determine whether the biodegradative pathways of the compounds of interest within landfills are similar to those found by other researchers in other anaerobic environments, such as soils or groundwater aquifers.

## CHAPTER 2

### LITERATURE REVIEW

Groundwater represents approximately 95% of the world's available freshwater supply (Wanielista et al., 1984). As a result, nearly 50% of the United States' population relies on groundwater aquifers to provide the water necessary to meet their demands. Unfortunately, this valuable resource is being threatened by man's past and present activities.

Over the past two decades, a large number of anthropogenic hazardous chemicals have been discovered in groundwater supplies across the country (Dunlap et al., 1976). Trichloroethylene (TCE) and tetrachloroethylene (PCE) are the most frequently identified groundwater contaminants. The presence of these two compounds is due to their large production volumes and widespread usage as dry cleaning solvents and metal degreasing agents (Barrio-Lage et al., 1986 and Bull, 1984). Other compounds occurring at lower frequencies and/or concentrations are dichloromethane (DCM), carbon tetrachloride (CT), vinyl chloride or chloroethylene (VC), dichloroethylenes (DCE), dichloroethanes

(DCA), and benzene (Bull,1984). The major concern regarding the presence of these chemicals in drinking water supplies is their known or suspected health effects. Vinyl chloride and benzene, for example, are proven human carcinogens (Bull,1984). The groundwater concentration which produces an incremental cancer risk of 1 in  $10^6$  is estimated at 0.67 ug/L for benzene, 2.8 ug/L for TCE, and 1.0 ug/L for VC (Wilson, Smith, and Rees,1986). Table 2.1 lists common groundwater contaminants and related health effects.

Unlike the pollution of surface water, groundwater contamination is almost invisible. Contamination can rarely be detected by random monitoring methods, and contaminant presence only becomes evident when the groundwater reaches a water-supply well (Geraghty and Miller,1978). In addition, groundwater does not have the natural cleansing mechanisms common in surface water (McCarty, Reinhard, and Rittman, 1981). Once polluted, groundwater may remain in an unusable or hazardous condition for decades or centuries (Pettyjohn, 1985 and Freeze and Cherry,1979). As a result, man is only beginning to recognize the extent to which his past activities have affected precious groundwater supplies. Groundwater restoration is, unfortunately, both difficult and expensive.

Much of today's groundwater pollution can be attributed to man's past waste disposal practices. Land

Table 2.1. Volatile Organic Compounds Commonly Found in Groundwater and Related Health Effects (Pettyjohn, 1985, Brown n.d., and Bull, 1984)

<u>Compound</u>	<u>Toxicity (1)</u>	
	<u>Acute</u>	<u>Chronic</u>
Vinyl Chloride*	3	M,C
1,1-Dichloroethylene*	2	---
Methylene Chloride <sup>+</sup>	2	M,C
1,2-Dichloroethane <sup>+</sup>	3	---
Cis-1,2-Dichloroethylene*	2	---
Trans-1,2-Dichloroethylene*	3	M,C
1,1,1-Trichloroethane <sup>+</sup>	3	---
Carbon Tetrachloride <sup>+</sup>	3	C,T
Trichloroethylene*	3	C
Tetrachloroethylene*	3	C
Benzene <sup>++</sup>	3	C,T
Chlorobenzene <sup>++</sup>	2	M
DCB(s) <sup>++</sup>	3	M,C

\* Alkene (unsaturated) Compounds

+ Alkane (saturated) Compounds

++ Aromatic Compounds

(1) Toxicity: Acute 1=low, causes reversible changes.  
2=moderate, may cause irreversible changes.  
3=high, capable of causing death and permanent injury.

Chronic M=Mutagenic, C=Carcinogenic  
T=Teratogenic; all others unknown

disposal (open dumps and landfills) of both solid and liquid wastes has been and is the most common method of waste disposal. Land disposal of hazardous and solid wastes is a major source of groundwater contaminants (Wilson et al., 1986). Other sources which contribute to groundwater pollution are leaking underground storage tanks, spills, and septic tanks (Geraghty and Miller, 1978). The remainder of this report will concentrate on the landfilling of solid wastes.

#### Hazardous Wastes

Hazardous wastes are identified by the presence of hazardous materials or by fulfilling specific criteria (Metry, 1980). The Resource Conservation and Recovery Act (RCRA) of 1976 defined hazardous waste as a solid waste, or combination of solid wastes, which because of its quantity, concentration, or physical, chemical, or infectious characteristics may (Dawson and Mercer, 1986):

- (a) cause, or significantly contribute to an increase in mortality or an increase in serious irreversible, or incapacitating reversible illness; or
- (b) pose a substantial present or potential hazard to human health or the environment when improperly treated, stored, transported, or disposed of, or otherwise managed.

Other governmental and scientific organizations have developed more specific criteria. These criteria are generally based upon one or more of the following properties (Dawson and Mercer, 1986):

- Ability to bioconcentrate
- Toxicity (via all routes)
- Flammability
- Explosiveness
- Reactivity
- Irritation or sensitization potential
- Corrosivity
- Genetic-change potential
- Radioactivity

#### Sources of Hazardous Wastes

Hazardous waste generators may be classified as follows (Wilson, 1985):

- (a) large-scale industrial firms
- (b) small-scale commercial enterprises
- (c) agricultural enterprises
- (d) households

Industrial wastes often contain hazardous chemicals and, therefore, have received overwhelming publicity with respect to groundwater pollution. As a result, researchers

and scientists have emphasized industrial waste generators in the study of hazardous wastes and groundwater contamination.

Commercial generators have also received some attention, since many commercially used materials contain hazardous compounds. Examples include photochemicals used in film processing and cleaning solvents used in dry-cleaning.

Agricultural enterprises utilize fertilizers, pesticides, and herbicides which may pollute the environment and water by either direct application to fields and/or by disposal of these materials as wastes.

Household hazardous wastes are just beginning to receive the attention of those studying the hazardous waste problem. Presently, household wastes are exempt from RCRA and are excluded from the Environmental Protection Agency's (EPA) definition of hazardous wastes (Federal Register, 1983). Therefore, homeowners are not required to dispose of household hazardous materials any differently than other household garbage. Recent studies, however, suggest that household hazardous wastes may have a significant impact on groundwater supplies (Brown, 1987; Rathje, 1985; Minnesota, 1985; County Sanitation Districts of Los Angeles County, 1983; and Golden Empire, n.d.).

## Household Hazardous Wastes

Household wastes are defined as "any waste material derived from households" (single and multiple residences, hotels, and motels). Household hazardous wastes (HHW) are household wastes that threaten injury and are dangerous because they are explosive, flammable, corrosive, reactive, or toxic (Laderman et al., 1985). Four classes of household products are known to contain toxic substances: pesticides, paint products, household cleaners, and automotive products. Table 2.2 contains a list of hazardous ingredients often found in common household products. Many of these compounds can be found on the EPA's priority pollutant list, which is presently comprised of 129 compounds including trichloroethylene (TCE) and carbon tetrachloride (CT) (Dawson and Mercer, 1986; Patterson and Kodukala, 1981; and Keith and Telliard, 1979).

### Solid and Hazardous Waste Disposal

In response to the vast amounts of wastes produced annually and the resulting threat these wastes pose to the environment, Congress passed RCRA in 1976 (Dawson and Mercer, 1986). Subtitle C facilities (Class 1 landfills) were created by RCRA to receive hazardous wastes primarily from industry. Subtitle C facilities must be located, designed, constructed, operated, and closed in a manner

Table 2.2. Hazardous Ingredients in Common Household Products (Wilson, 1985, Garbage Project, 1987, and Laderman, 1985).

<u>Product</u>	<u>Possible Hazardous Ingredients</u>
Household Cleaners	
Toilet Bowl Cleaners	p-Dichlorobenzene Sodium Acid Sulfate or Oxalate or Hypochloric Acid Chlorinated Phenols Trichloro-S-triazine trione
Drain Openers	Sodium or Potassium Hydroxide Hydrochloric Acid 1,1,1-Trichloroethane o-Dichlorobenzene p-Dichlorobenzene Trichlorobenzene Petroleum Distillates
Laundry, Dish Detergents	Surfactants Ethanol Methylene Chloride Tetrachloroethylene Tetrachloroethane Sodium Hypochlorite
Ammonia, Glass Cleaner, Disinfectant	Ammonia Ammonium Hydroxide Surfactants Hexachlorobenzene Phenol Cresol Phosphoric Acid Sodium Hypochlorite Ethoxylated Alcohol Xylenols
Floor Cleaner and Wax	Petroleum Distillates Ammonia Diethylene Glycol

Table 2.2. (continued)

<u>Product</u>	<u>Possible Hazardous Ingredients</u>
Furniture and Metal Polish	1,1,1-Trichloroethane Petroleum Distillates Oxalic Acid Mineral Spirits Petroleum Solvents Denatured Ethanol or Isopropanol Phosphoric Acid
Oven Cleaner	1,1,1-Trichloroethane Sodium or Potassium Hydroxide Methylene Chloride
Air Sanitizer/Deodorizer	Napthalene Formaldehyde p-Dichlorobenzene o-Dichlorobenzene Petroleum Distillates Methylene Chloride Ethanol
Automotive Maintenance	
Lubricating Oils	Petroleum Distillates Lead
Oil and Fuel Additives	Mineral Spirits 1,1,2-Trichloroethylene Methylene Chloride Xylenes Toluene
Antifreeze/Coolant	Ethylene Glycol Methanol
Carburetor Cleaners	Toluene Methanol Methylene Chloride Xylenes Acetone

Table 2.2. (continued)

<u>Product</u>	<u>Possible Hazardous Ingredients</u>
Auto Wax, Polish	Petroleum Distillates
Degreaser, Rust Remover	Toluene Chlorinated Aliphatic Hydrocarbons Potassium Dichromate Cresol
Paints and Adhesives	
Paint	Toluene Xylenes Methylene Chloride Halogenated Aromatic Hydrocarbons Mineral Spirits
Paint Thinners	Mineral Spirits Toluene Chlorinated Aliphatic Hydrocarbons Chlorinated Aromatic Hydrocarbons Alcohols Ketones
Stain/Varnish	Methylene Chloride Benzene Lead Pentachlorophenol Alcohols Mineral Spirits
Adhesives	Toluene Xylenes Methylene Chloride Acetone Hexane Petroleum Distillates 1,2-Dichloroethane 1,1-Dichloroethane Mineral Spirits Formaldehyde

Table 2.2. (continued)

<u>Product</u>	<u>Possible Hazardous Ingredients</u>
Paint Strippers and Removers	Methylene Chloride Toluene Trichloroethylene Benzene Ketones Petroleum Distillates
Yard Maintenance	
Pesticides	Aromatic Petroleum Hydrocarbons Petroleum Distillates Naphthalene Xylenes Pentachlorophenol Trichlorophenol Other Chlorinated Hydrocarbons
Fertilizers	Concentrated Potassium, Ammonia, Nitrogen, Phosphorous
Herbicides	Chlorinated Phenoxys Nitrophenols
Other	
Batteries	Mercuric Oxide Sulfuric Acid
Selected Cosmetics	Benzene Toluene Xylenes Alcohols Acetone

that will protect human health and the environment. This includes superior siting, impermeable liners, and leachate collection, monitoring, and treatment systems (Dawson and Mercer, 1986).

Subtitle D facilities (after Subtitle D of RCRA) are more commonly known as sanitary landfills and are defined as the approved, safe, sanitary locations to dispose of most solid wastes (Dawson and Mercer, 1986 and Metry, 1980). Sanitary landfills are used in the disposal of municipal wastes. Municipal wastes often include both residential and commercial wastes. A typical sanitary landfill consists of a series of cells containing solid wastes. The solid wastes are reduced in volume by compaction and covered with earth. The earth cover is placed over the refuse at the end of each day's operation. The landfill, consisting of successive layers of compacted refuse and earth may be constructed on the ground surface or in excavations. Some sanitary landfills include impermeable liners and leachate collection, monitoring, and treatment systems to better manage the solid wastes and protect underlying groundwater. Selection of a particular landfill design is site specific and often based on political and economic considerations as well as the geologic and hydrologic characteristics of the area (Tchobanoglous, Theisen, and Eliassen, 1976). In the United States, a large number of older municipal waste

disposal sites remain open dumps or are poorly operated. Newer sites are generally better situated and better operated (Freeze and Cherry,1979).

According to EPA estimates, there are presently 94,200 subtitle D facilities in the United States, 18,500 of which are municipal landfills (Schuster,1985; Wilson,1985; and Geraghty and Miller,1978). The majority of wastes produced in the U.S. are received by these landfills.

In North America approximately 3 kg of refuse per capita are produced daily (Freeze and Cherry,1979). More than 180,000,000 tons of solid wastes were generated in 1977 (Wanielista et al.,1984) with nearly 197,000,000 tons expected in 1990 (Schomaker,1979). Although materials recovery and incineration may eventually decrease the amount of waste disposed of by landfilling, landfills will continue to be the primary method of disposal of these wastes during the next few decades (Freeze and Cheery,1979).

In order to protect underlying groundwater from leachate contamination, sanitary landfills often employ a liner and leachate collection system. Leachate is produced when rain water, flood water, and/or snow melt is allowed to enter the landfill. As the water migrates through the refuse, it picks up hazardous compounds which are either deposited in the landfill or created within the landfill by chemical, physical, or biological activity. Groundwater

contamination by leachates is more likely to occur in humid areas receiving greater amounts of precipitation. Landfill liners, in theory, act as impervious boundaries that inhibit the escape of leachate. Commonly, liners are composed of clay, PVC plastic, or both. Leachate is collected at the bottom of the landfill and is either pumped to a leachate treatment facility, recirculated and spread over the landfill, or transported to a subtitle C facility. Leachate monitoring systems allow the operator to monitor the water beneath the landfill to be sure the containment system is functioning properly. Wells are the most common monitoring device (Wilson,1985). Unfortunately, some chemicals found in leachate may reduce the effectiveness of liners, allowing leachate to escape into the environment. The life span of landfill liners is presently unknown, and it is generally not feasible to repair a liner after the landfill is in operation (Buranek,1987).

#### Groundwater Contamination Case Studies

Land disposal of industrial hazardous wastes, both legal and illegal, has been implicated in many cases of groundwater contamination. Love Canal is a controversial and classic example of this. The canal area, located near Niagara Falls, was used as a chemical dumpsite from 1920

to 1953. During this time, at least 21,000 tons of chemicals including phenols, toluenes, chlorobenzenes, and pesticides were deposited in the dump (McDougall, Fusco, and O'Brien, 1980 and Wilson, 1985). More than 200 hazardous chemicals were identified in the nearby groundwater. In 1978, health studies were initiated, resulting in a massive relocation of households. More than 500 families were moved at an expense of approximately 20 million dollars in Federal and New York state funds. In addition to intense media publicity, Love Canal created controversy within the scientific community, resulting in increased efforts to identify hazardous wastes and accompanying health effects (McDougall et al., 1980).

Dunlap et al. (1976) were among the first to report the potential hazard of non-industrial solid wastes. The report discovered that the hazardous industrial organic chemicals found in the groundwater beneath a Norman, Oklahoma landfill were not from industrial generators. The landfill had not received significant industrial wastes at any time during its operation. Therefore, the chemicals were believed to originate from commercial and domestic products (Rathje, 1985).

The Minnesota Pollution Control Agency (MPCA) published the results of a study of household hazardous wastes in 1984. Leachate from six municipal landfills were

analyzed. Landfills researched included three urban sites, receiving industrial, commercial, and residential solid wastes, and three rural landfills, receiving only commercial and residential wastes (Minnesota, 1985). Researchers found that the leachates from the two types of landfills contained similar hazardous compounds and that, in many cases, the concentration of hazardous materials did not differ. These results suggest that the disposal of commercial and residential wastes are contributing significant quantities of contaminants to groundwater.

It is argued that available data suggest that (Wilson, 1985):

- (1) Many common household commodities contain hazardous substances.
- (2) These commodities are disposed of as wastes and residues in residential solid wastes.
- (3) In some cases, residential solid wastes have higher concentrations of hazardous substances than commercial wastes.
- (4) Residential and commercial solid wastes together can contribute to groundwater contamination through landfills in the same way as industrial wastes. Therefore, residential wastes may have the same effects alone.

#### The Garbage Project

The Garbage Project was founded in 1973 by Dr. William Rathje, Department of Anthropology at the University of Arizona. The project utilizes residential garbage sorts

to study the American culture. Data from the project have been used, for example, to answer questions regarding nutrition and consumer behavior (Rathje, 1985). Recently, the Departments of Anthropology and Civil Engineering began researching the impact of household hazardous wastes on groundwater. This portion of the Garbage Project was funded by the National Science Foundation (NSF).

The presence of commodities containing hazardous chemicals in residential solid wastes has been recorded by Anthropology student sorters. Household products include paints, oils, and pesticides (See Tables 2.3 and 2.4). Preliminary waste discard estimates have been obtained for Marin County, California; Tucson, Arizona; and New Orleans, Louisiana. Households in Marin County discard an average of 55.9 g of household hazardous wastes per week. New Orleans' households dispose of approximately 59.6 g weekly. The results from Marin County and New Orleans include household maintenance items (paints and sealants), automotive maintenance products (motor oil), household cleaning products, and batteries. Tucson households were found to discard 8.5 g of household maintenance commodities and 3.5 g of household cleaning items per week (Wilson and Rathje, 1987a). See Table 2.5 for more complete results. Table 2.6 compares data obtained from Puente Hills (L.A. County), Marin County, and Tucson. In contrast with wastes



Table 2.4 HAZARDOUS WASTE PULL CODES

<u>Hazardous Waste Code</u>	<u>Types and Notes</u>
	<u>Household Cleaners</u>
01 Toilet Bowl Cleaner ....	BOWLCLEA.
02 Drain Opener .....	DRAINOPE.
03 Laundry Soap .....	POWDER (powdered laundry soap). LIQUID (liquid laundry soap). FABSOF (fabric softener). SPOTREM (spot remover).
04 Bleach .....	BLEACH. SUBBLEACH (bleach substitute).
05 Dish Detergent .....	DISH (liquid dish soap). AUTODISH (automatic detergent).
06 Cleaner .....	CLEANSER (all purpose cleanser). FLOORCL (floor cleaners). TUBTILE (bathroom cleaners). UPOLSTER (upholstery cleaners).
07 Ammonia Based Cleaners .	AMMONIA GLASSCLE (glass cleaner). DISINFEC (disinfectant).
08 Polish .....	FURNITURE (polish and wax). WOOD (polish and wax). METAL. VINYL (preservatives / polish).
09 Floor Finish .....	WAX (floor wax). RUGSHAM (rug shampoo).
10 Air Freshener .....	AIRFRESH.
11 Other Household .....	OVENCLE (oven cleaner). REFRIGER (refrigerants for air conditioners and refrigerators).
	<u>Automotive Maintenance</u>
20 Oil .....	MOTOROIL GREASE. SEWING (sewing machine oil). HYDRAUL (hydraulic fluid). ALLPURPOSE (all purpose oil).
21 Transmission Fluid .....	TRANIFLU (transmission fluid).
22 Engine Treatment .....	FUELADD (fuel additives). OILADD (motor oil additives). TRANIADD (transmission add'ves). RADIADD (radiator additives). STOPLEAK (radiator stopleaks). CARBLEAN (carbureator cleaner). STARTFLU (starter fluid).

Table 2.4 (continued)

<u>Hazardous Waste Code</u>	<u>Types and Notes</u>
	<u>Automotive Maintenance (cont.)</u>
23 Antifreeze/Coolant .....	FREEZE (antifreeze). COOLANT.
24 Auto Wax .....	WAX. POLISH.
25 Other Auto .....	GREASESOLV (grease solvent). RUSTSOLV (rust solvent). PUTTY (body putty, bondo). REFRIGER (auto air cond refrig).
	<u>Household Maintenance</u>
30 Paint .....	LATEX (latex paint). SPRAY (spray paint). OILBASE (oil base paint). ART (artist and model paints).
31 Paint Thinner .....	THINNER. STRIPPER (paint remover).
32 Stain/Varnish .....	STAIN. VARNISH. SEALANT (wood sealant).
33 Glue .....	MODEL. ALLPURPO (general purpose). SUPER (fast drying). EPOXY.
34 Painting Tool .....	BRUSH. TRAY (painting tray). ROLLER.
35 Other Maintenance .....	ASPHALT. CAULKING. GROUT.
	<u>Pesticides and Yard Maintenance</u>
40 Fertilizer .....	use manufacturer's type if present or plant used for.
41 Pesticides .....	See code 40 Fertilizer.
42 Herbicides .....	See code 40 Fertilizer, includes FUNGICIDE. WOODPRES (eg. creosote).
43 Pet Maintenance .....	COLLAR (flea, tick collar). POWDER (flea, tick powder). DIP (flea, tick dip).

Table 2.4 (continued)

<u>Hazardous Waste Code</u>	<u>Types and Notes</u>
	<u>Household/Personal Equipment</u>
50 Batteries/ Electrical ..	AUTO. for flashlight batteries, indicate size (eg. AAA). SOLDER. SWITCH (electrical switches). FLOODLIG (floodlights).
60 Prescription Drugs .....	indicate name of drug as type.
62 Selected Cosmetics .....	NAILPOLI (nail polish). NAILREMO (nail polish remover). PERFUME (perfume and cologne). HAIRSPRA. SHAMPOO. ANTIPERS (antiperspirants). DEODORANT. BASE (make-up base). BLUSH. MASCARA. EYE (eye make-up, not mascara). REMOVER (make-up remover). HAIRCOLOR (hair coloring).
70 Hobby Related .....	DYE (fabric dyes). INK (writing ink, copier ink). FOTOCHEM (photographic chemicals if known use type, eg. FIXER).
80 Other .....	POOLACID (pool acid). POOLCHLO (pool chlorine). POOLTREA (other pool treatment).

Table 2.5 Hazardous Household Waste in Three Cities  
(Wilson and Rathje, 1987a)

Waste Type	Mean Weight (grams) of Hazardous Materials (per household per week)		
	New Orleans	Marin County	Tucson
Household Cleaners	7.91	8.46	3.50
Automotive Maintenance	12.58	6.52	
Household Maintenance	25.85	15.52	8.48
Pesticides and Yard Maintenance	0.58	4.85	
Batteries	7.08	14.90	
Prescription Drugs	0.63	1.80	
Selected Cosmetics	2.96	2.13	
Other	2.03	1.75	
Total	59.63	55.92	
Sample Size (pickups)	1,061	1,022	692

Table 2.6 Comparison of Three Cities (Rathje, 1986)

## Puente Hills (Los Angeles County)

249 hazardous waste items

4.14 tons of refuse (not including yard waste)

60.14 items per ton of refuse

## Marin County

160 hazardous waste items

2.21 tons of refuse (not including yard waste)

75.54 items per ton of refuse

## Tucson, Arizona

1195 hazardous waste items

13.1 tons of refuse (not including yard waste)

91.20 items per ton of refuse

from Puente Hills and Marin County, Tucson waste contains a considerably higher number of hazardous waste items per ton of refuse. The comparison data indicate that significant variability may exist between cities and suggest that characteristics of hazardous wastes in one area may be quite different than in another (Wilson,1985).

Rathje and his colleagues have found that the type of wastes discarded are a function of income, ethnicity, and other social and economic characteristics of the people responsible for generating the waste (Rathje,1985). Marin County data suggests that higher income households tend to discard more lawn care products such as fertilizers and pesticides, while lower income families discard automotive maintenance commodities such as motor oil and antifreeze. Similar results were obtained from data collected in Tucson, Arizona (Rathje,1985 and Wilson,1985).

Data obtained by the Garbage Project and similar studies imply that residential wastes contain greater concentrations of certain hazardous materials than commercial wastes and are more heterogeneous in composition. The study further indicated that concentrations of hazardous materials can and do leach into groundwater from landfilled residential wastes (Rathje,1985 and Dunlap et al.,1976).

Anthropology hopes to use the information gathered from this portion of the Garbage Project to build a model

for predicting hazardous waste discard patterns for any community desired (Rathje,1985).

#### Mechanisms Of Degradation Within A Landfill

Degradation of chemicals within a landfill can occur both chemically and microbiologically. The resulting degradation rate is affected by chemical structure and solubility, soil properties, and temperature (Bridle,1982 and 1981). The remainder of this review will focus on the biological degradation of chemicals that are often found in sanitary landfills.

Waste degradation and stabilization within a landfill proceeds at a slow rate. Although the minimization of leachate production is desirable, decreasing moisture to a landfill will also decrease the rate and predictability of biological stabilization. Reduction of bioactivity in a landfill extends the period required for waste stabilization. As a result, the organic content in leachate remains high for long periods of time, exposing surface water and groundwater to highly contaminated leachate (Tittlebaum,1982).

Bacterial decomposition of the biodegradable organics begins immediately after the wastes are placed in a landfill. Aerobic degradation occurs initially since a certain amount of air is trapped with freshly buried refuse.

When the oxygen in the trapped air is exhausted, long-term anaerobic degradation begins. The soil used in daily cover is the primary source of both the aerobic and anaerobic microorganisms. The overall rate at which organic materials decompose depends on their characteristics and, to a large extent, moisture content (Tchobanoglous et al., 1976).

Bookter and Ham (1982) utilized cellulose/lignin ratios to determine the rate and level of decomposition within a landfill. Cellulose was chosen since it is the major chemically identifiable constituent in refuse. Because cellulose degrades at a much greater rate than lignin, the ratio of the two substances changes with time, as waste decomposition occurs. The cellulose/lignin ratio was found to be approximately 4.0 for fresh refuse, 0.9-1.2 for partially stabilized landfills, and 0.2 for a relatively well-stabilized landfill. The rate and extent of stabilization in a landfill can be used in predicting future leachate generation, gas production, and differential settlement (Bookter and Ham, 1982).

Collins and Spillman (1982) used lysimeters for simulating leachate production in sanitary landfills. The researchers found that leachate formation occurs before the material is saturated and the rate of outfall may increase considerably after the operation of the landfill ceases.

Landfilling in Switzerland involves spreading and

compacting thin layers of refuse. While compaction prevents blowing, fires, and reduces leachate production, decomposition can occur under anaerobic conditions only (Leumann,1986). Compaction of the wastes thin layers expels any trapped air, creating an anaerobic environment.

Four phases of waste biodegradation have been found to exist within a landfill (Leumann,1986 and Eicher and Pauli,1986). Each phase of biological decomposition forms characteristic products. Some of these products escape from the landfill in gaseous form or dissolve in leachate, while others are further decomposed to  $\text{CH}_4$ ,  $\text{CO}_2$ , and water in subsequent phases (Leumann,1986). These phases include:

- Phase I. Aerobic elution and hydrolysis
- II. Anaerobic without methane production (acid fermentation)
- III. Anaerobic with unstable methane production
- IV. Anaerobic with stable methane production

Figure 2.1 illustrates a chronological sequence of the waste conversion process and resulting products. Figure 2.2 is a schematic representation of the anaerobic decomposition processes. Gas concentrations within landfills vary with depth and the previously described phases (See Figure 2.3).

Figure 2.1 Chronological Sequence of Waste Material Conversion (Leumann, 1986)

Phase I (weeks)	Phase II (months)	Phase III (years)	Phase IV (decades)
Elution, hydrolysis	Acid fermentation	Initial stage of alkaline fermentation (unstable methane fermentation)	Alkaline fermentation (stable methane fermentation)
Aerobic	Optional anaerobic		Obligatory anaerobic
Initial products: dissolved inorganic substances (salts) dissolved organic monomers	Intermediate products: amino acids, mono-saccharides, alcohols fatty acids  End products: hydrogen, carbon dioxide		Final products: methane, carbon dioxide, water

Figure 2.2 Schematic Representation of Anaerobic Decomposition Processes (Eicher and Pauli, 1986)

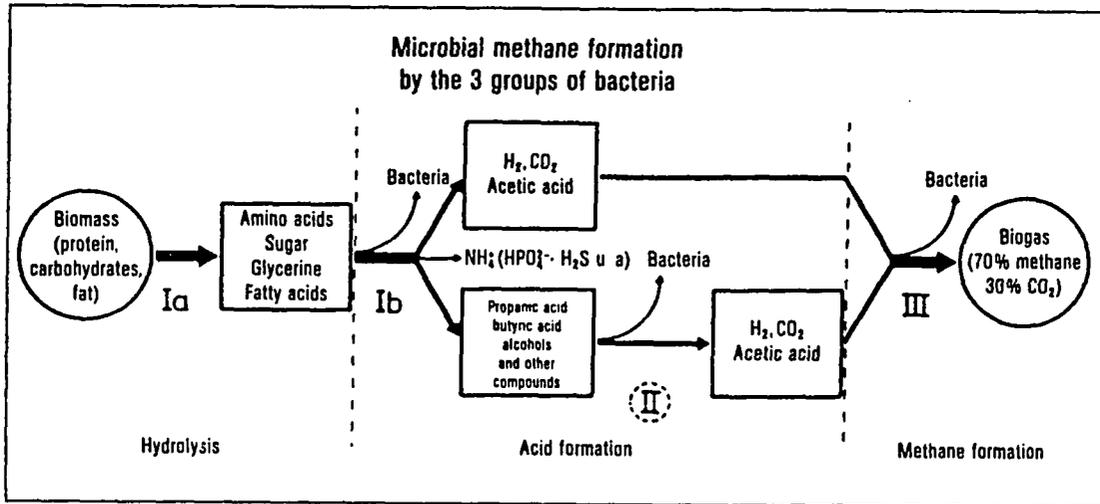
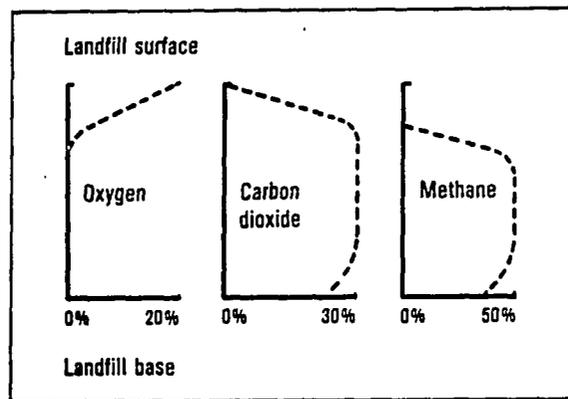


Figure 2.3 Concentration Gradients of Gas in Landfill as a Function of Depth (Leumann, 1986)



Refuse is usually not processed prior to deposition in landfills. However, a number of studies have examined the disposal of shredded and baled wastes in an effort to limit leachate production and other problems associated with land disposal. Kemper and Smith (n.d.) found that baled wastes resulted in larger quantities of dilute leachate and shredded wastes yielded smaller quantities of more concentrated leachate. Ham and Bookter (1982) utilized test lysimeters to study shredded solid waste decomposition, leaving some of the test cells uncovered. At first, cells left uncovered produced highly contaminated leachates. This phase was followed by rapid stabilization to consistently low levels of contaminants. Shredding was also found to increase rates of decomposition resulting in quicker methane production. Major concerns regarding landfill disposal of shredded refuse without daily cover include leachate quantity and quality, gas generation, and decomposition within the landfill (Ham and Brookter, 1982).

Bridle (1981) reported that the solubility of many non-polar toxic organic compounds are significantly increased by the presence of low-molecular-weight organics generated in municipal landfill leachates. In addition, most toxic organics are more mobile in soils with high organic content (Bridle, 1981).

### Biodegradation Of Organic Chemicals

Although little information exists with respect to the biological degradation and transformation of organic chemicals within landfills, many researchers have extensively studied these mechanisms in other environments such as sewage sludges, groundwater aquifers, and soils. The information obtained in these studies can be useful in the examination of landfills.

Many man-made chemicals are relatively refractory to biodegradation. Often, the organisms present cannot produce the enzymes necessary to bring about transformation of the original compound to intermediates that can enter common metabolic pathways and be completely mineralized (Kobayashi and Rittman, 1982). In addition, many environmentally important man-made chemicals are halogenated and halogenation is often cited as the reason for persistence. Some of the characteristics that affect the persistence of halogenated compounds are the location of the halogen atom, the halide involved, and the extent of halogenation (Kobayashi and Rittman, 1982). Also, organic chemicals may persist in some environments as a result of low prevailing concentration or low solubility in water. Little or no biodegradation may occur at low chemical concentrations and there may exist a threshold below which no mineralization will occur. Trace concentrations may be insufficient to

induce the necessary enzymes, and if enzymes are present, the energy obtained from the oxidation of the compounds may be too low to meet energy demands (Boethling and Alexander, 1979a,b; Alexander, 1985; and Kobayashi and Rittman, 1982).

The occurrence and feasibility of biodegradation is controlled by DO, oxidation-reduction potential, temperature, pH, salinity, particulate matter, concentration of compounds, and presence of adapted or adaptable organisms. A compound's physical or chemical characteristics such as solubility, volatility, hydrophobicity, and octanol-water partition coefficient contribute to its solvation potential. Compounds not soluble in water are not readily available for biodegradation (Parsons and Lage, 1985 and Kobayashi and Rittman, 1982). Microbial transformations of a compound may lead to more soluble and, consequently, more mobile products (Reinhard, Goodman, and Barker, 1984).

Most of the organic chemicals that have been identified in groundwaters can be classified as either aliphatic or aromatic hydrocarbons. Aliphatic hydrocarbons are further divided into families: alkanes, alkenes, alkynes, and their cyclic analogs (Morrison and Boyd, 1966). The families of primary concern, with respect to groundwater contamination, are the alkanes and alkenes. Aromatic

compounds are benzene or compounds related to benzene.

### Aliphatic Compounds

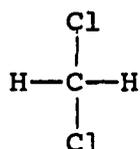
Aliphatic compounds of interest are open-chained with 1- or 2-carbon atoms. The alkane family includes both 1- and 2-carbon compounds with a single bond between the two carbons. Alkanes are considered saturated since they contain the maximum number of hydrogen atoms with respect to carbon atoms. Chlorinated ethanes and methanes are among the alkanes of interest.

The alkene family contain a pair of double-bonded carbons and are considered unsaturated. Chlorinated ethylenes or ethenes are examples of alkenes (Morrison and Boyd, 1966). Figure 2.4 illustrates the chemical structures of aliphatic compounds commonly found in groundwater.

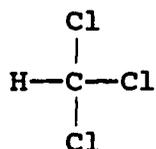
A study by Bouwer and McCarty (1983) suggests that 1- and 2-carbon halogenated aliphatic compounds are persistent in the environment and are easily transported through soils by groundwater movement. Parsons and Lage (1985) concluded that chlorinated alkenes were more resistant to biotransformation than chlorinated alkanes and, thus, may be more dangerous pollutants. Wilson et al. (1983) found that low-molecular-weight, chlorinated, aliphatic compounds are resistant to biodegradation in aerobic subsurface environments. The biodegradative

Figure 2.4 Chemical Structures of Chlorinated Aliphatic Compounds of Interest.

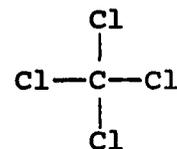
Chloromethanes



Dichloromethane

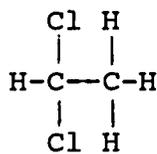


Chloroform

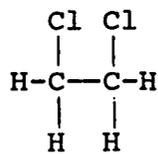


Carbon Tetrachloride

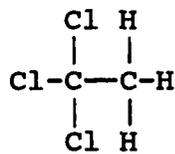
Chloroethanes



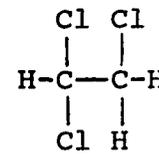
1,1-DCA



1,2-DCA

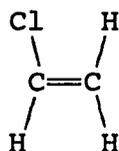


1,1,1-TCA

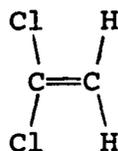


1,1,2-TCA

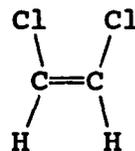
Chloroethylenes



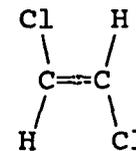
VC



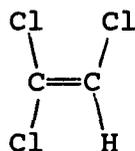
1,1-DCE



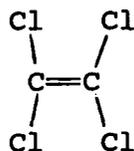
cis-1,2-DCE



trans-1,2-DCE



TCE



PCE

resistance of these compounds contributes to their presence in polluted groundwater. In addition, Parsons, Woods, and DeMarco (1984) determined that anaerobic transformation in subsurface materials is often incomplete and occasionally results in accumulations of products that are considered more toxic or carcinogenic than the original.

The first step in biodegradation of these compounds is sometimes dehalogenation. Dehalogenation can occur by any of several mechanisms (Gossett, 1985):

- (1) Reductive Dehalogenation  

$$\begin{array}{l} \text{CH}_3\text{-CCl}_3 + \text{H}_2 == \text{CH}_3\text{-CHCl}_2 + \text{HCl} \\ \text{1,1,1-TCA} \qquad \qquad \qquad \text{1,1-DCA} \end{array}$$
- (2) Dehydrohalogenation (Acid halide is removed abiotically)  

$$\begin{array}{l} \text{CH}_3\text{-CCl}_3 == \text{CH}_2\text{=CCl}_2 + \text{HCl} \\ \text{1,1,1-TCA} \quad \text{1,1-DCE} \end{array}$$
- (3) Replacement reaction with hydroxide as mediated by halohydrases  

$$\text{CH}_2\text{Cl}_2 + \text{H}_2\text{O} == \text{CH}_2\text{OHCl} + \text{HCl}$$
- (4) Reaction with oxygen as mediated by oxygenases

Presently, anaerobic dehalogenation, either biological or non-biological, is recognized as the critical factor in the transformation of 1- and 2-carbon aliphatic compounds. As illustrated above, reductive dehalogenation involves the removal of a halogen atom by oxidation-reduction and replacement with a hydrogen atom (Parsons and Lage, 1985; Bouwer and McCarty, 1983; and Kobayashi and

Rittman,1982). The mechanisms for biological transformation for each class of compounds will be described in more detail later in this chapter. Compounds of interest include chlorinated aliphatics (ethenes, ethanes, and methanes).

### A. Chlorinated Ethenes

Much of the recent research examining groundwater contaminants has focused on the chlorinated ethenes. Tetrachloroethylene (PCE) and trichloroethylene (TCE), in particular, have become increasingly common in contaminated aquifers. Both compounds have been widely used since World War II as metal-cleaning solvents and in dry-cleaning fluids. Leaking underground storage tanks and improper disposal are the primary sources contributing to PCE and TCE contamination of groundwater. However, sanitary landfills have also been implicated in PCE and TCE groundwater contamination (Khare and Dondero, 1977 and Dunlap et al., 1976).

Initially, the chlorinated ethenes were thought to be completely resistant to microbial degradation under both aerobic and anaerobic conditions (Bouwer, Rittman, and McCarty, 1981). More recent studies, however, indicate that these compounds are subject to biological attack under both aerobic and anaerobic conditions.

Tabak et al. (1981) conducted research under normal waste-treatment conditions using wastewater microbiota. The study found that chlorinated ethenes were susceptible to biodegradation under aerobic conditions. Both PCE and TCE were shown to be biodegradable. After the first of three subcultures, 1,1-dichloroethylene (1,1-DCE) was also

significantly degraded. In contrast, the two isomers of 1,2-dichloroethylene (1,2-DCE), cis- and trans-, were degraded more slowly.

Recently, Wilson and Wilson (1985) found that TCE could be degraded aerobically to carbon dioxide (CO<sub>2</sub>) in an unsaturated soil column exposed to a mixture of natural gas in air (0.6%). The biodegradation was attributed to the metabolic activities of methane-utilizing bacteria. Nelson et al. (1986) isolated a gram-negative, rod-shaped bacterium (strain G4) that was capable of aerobically degrading TCE to CO<sub>2</sub> as well as some unidentified, nonvolatile products. Nelson et al. (1987) recently discovered that the previously isolated bacterial strain G4 requires aromatic compounds (such as phenol, toluene, and cresols) in order to transform TCE.

The aerobic biodegradation of chlorinated ethenes was also investigated by Fogel, Taddeo, and Fogel (1986). Again, methanotrophs, methane-utilizing bacteria, were linked to the degradation of five chlorinated ethenes. Methanotrophs, often found at aerobic/anaerobic interfaces, oxidize methane to methanol in order to obtain carbon for growth and energy. These organisms oxidize methane by using the enzyme methane monooxygenase and obtain the oxygen directly from molecular oxygen. The products of vinyl chloride (VC), 1,1-DCE, and TCE degradations did not include

volatile chlorinated organics. TCE did not degrade to any of the DCEs or VC. Also, VC was not a product of 1,1-DCE transformation. These results differ from those obtained under anaerobic conditions and are significant since the anaerobic products of PCE and TCE biodegradation, VC and 1,1-DCE, are the most toxic of the chlorinated ethenes. Although cis- and trans-1,2-DCE were transformed to chlorinated products, VC was not among them. In addition, an aerobic, methane-utilizing culture isolated from primary sewage was able to degrade VC (Fogel et al., 1986).

Degradation of chlorinated aliphatic compounds carried out by methanotrophs occurred very rapidly (days) and did not require acclimation of cultures. Also, methanotrophs are much easier to grow than methanogens and, therefore, appear to be good candidate microorganisms for bioremediation of aquifers and wastewaters contaminated with chloroethenes (Fogel et al., 1986).

Because groundwaters tend to be anaerobic, a large number of researchers have concentrated on the anaerobic biodegradation of chlorinated ethenes. Early studies found no or only slight degradation of PCE and TCE under anaerobic conditions utilizing methanogenic bacteria (Bouwer, Rittman, and McCarty, 1981). Wilson et al. (1981) also found that these compounds were not anaerobically degraded in sandy soils with low organic content (0.087% organic carbon).

Bouwer and McCarty (1983) later utilized a mixed methanogenic culture with a primary substrate of acetate. All of the compounds, with the exception of 1,2-DCE, were almost completely transformed under these conditions. As a result, Bouwer and McCarty suggested that a possible mechanism for some of the observed transformations was reductive dehalogenation or the replacement of a halogen with a hydrogen atom.

Parsons, Wood, and DeMarco (1984) injected PCE into static microcosms containing muck from the bed of a recharge basin in Florida. Resulting data indicated that PCE was biotransformed to TCE and that both PCE and TCE were biotransformed to VC, cis- and trans-1,2-DCE, and dichloromethane (DC).

Gossett (1985) also found that PCE was completely converted to TCE by methanogenic cultures derived from anaerobic digester sludge. However, TCE was not further degraded to any significant degree.

In contrast, Kleopfer et al. (1985) determined, using an isotopically labeled TCE, that TCE is definitely dechlorinated to 1,2-DCE in soil. No 1,1-DCE was detected. Kleopfer et al. (1985) also hypothesized that since it has been shown that microbes capable of degrading one member of a homologous series of compounds can also simultaneously adapt to degrade other members of the same series, the

possibility exists that DCE can be further transformed to VC in soils.

In a study utilizing microcosms composed of aquifer material, Parson and Lage (1985) observed that the first step in biotransformation of the chlorinated ethenes was reductive dechlorination. Further, Parsons and Lage (1985) found that the reductive dehalogenation of PCE and TCE resulted in both isomers of 1,2-DCE, although the cis-isomer was always produced in greater concentrations.

Under methanogenic conditions, another study found that the biodegradation of PCE resulted in the formation of the chlorinated metabolites TCE, DCE, and VC (Vogel and McCarty, 1985). Vogel and McCarty determined that TCE is the major intermediate in the biotransformation of PCE and suggested at least two different pathways (See Figure 2.5). Either the pathway resulting in TCE, DCE, and VC formation is different from that which produces carbon dioxide (CO<sub>2</sub>) or CO<sub>2</sub> is the result of VC mineralization.

Wilson, Smith, and Rees (1986) studied the biotransformation of selected halogenated aliphatic compounds in methanogenic aquifers. Vinyl chloride appeared as a daughter product of 1,1-DCE, TCE, and trans-1,2-DCE, but not of cis-1,2-DCE.

Barrio-Lage et al. (1986) also looked at the sequential dehalogenation of chlorinated ethenes. The study

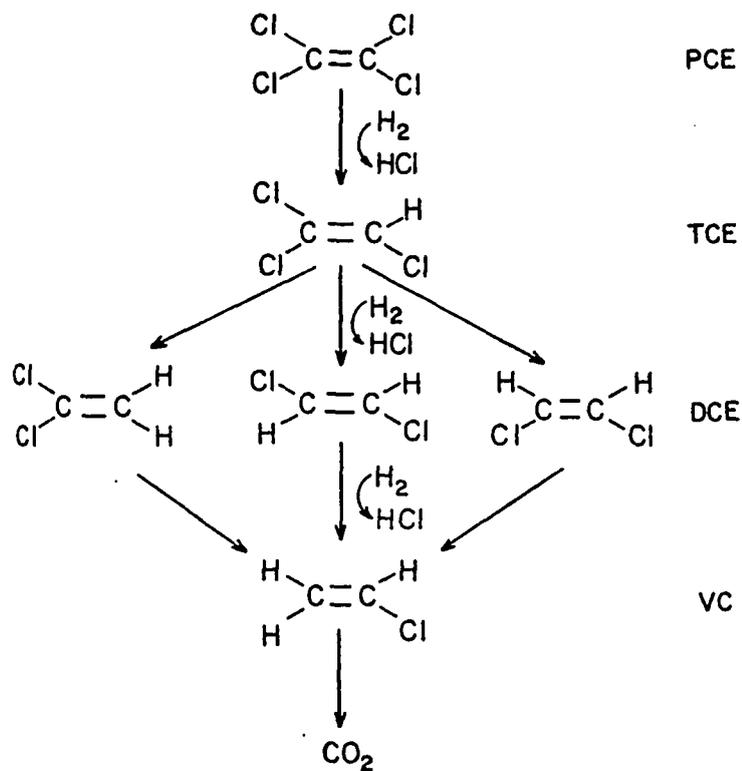


Figure 2.5 Schematic for Possible Pathway for Conversion of PCE to CO<sub>2</sub> Through Reductive Dehalogenation (Vogel and McCarty, 1985)

again found that PCE and TCE undergo reductive dehalogenation to form cis- and trans-1,2-DCE. In addition, 1,1-DCE and both isomers of 1,2-DCE were reductively dechlorinated to VC. However, the isomers of DCE undergo different transformations. In this study, the cis-isomer led to the formation of chloroethane (CE) and only traces of VC, while the trans-isomer produced CE only. 1,1-DCE yielded a greater concentration of VC and no CE. The fate of VC was not examined. Figure 2.6 illustrates possible dechlorination pathways in anaerobic environments (Barrio-Lage et al., 1986).

A recent study looked at the transformability of PCE under conditions of denitrification, sulfate respiration, and methanogenesis (Bower and Wright, 1987). PCE was continuously administered to anoxic biofilms with acetate as the primary substrate. In agreement with previous research, PCE was significantly transformed (>86%) under methanogenic conditions and reductive dehalogenation appeared to be the predominant mechanism for removal. However, only slight transformation of PCE was achieved under sulfate-reducing and denitrifying conditions: Efforts were not made to identify transformation products.

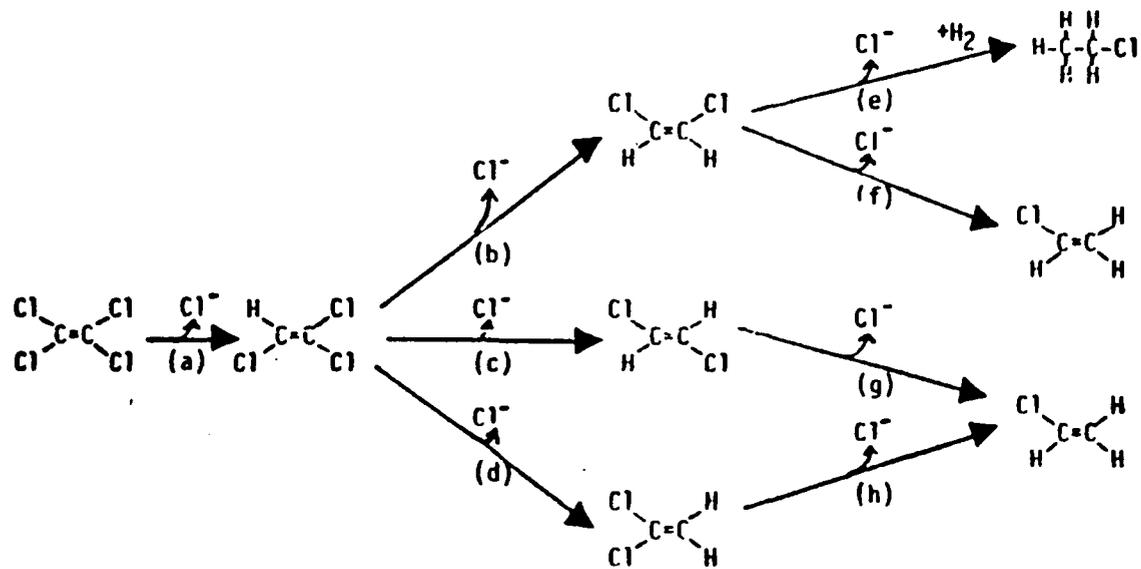


Figure 2.6 Summary Pathways for Dechlorination of Tetra- and Tri-chloroethene in Anaerobic Environments (Barrio-Lage et.al., 1986)

## B. Chlorinated Alkanes

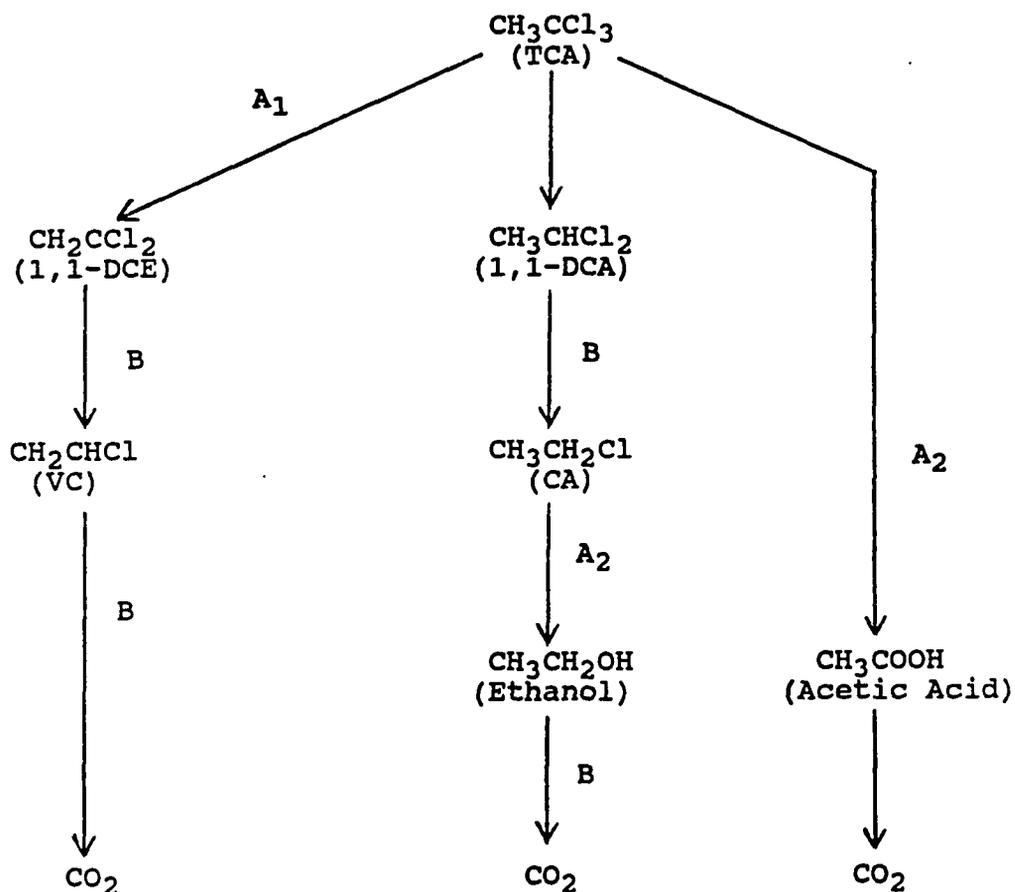
Ethanes and methanes are the most prevalent alkanes found in contaminated groundwater and landfills. These compounds include solvents such as trichloroethane and carbon tetrachloride.

Wilson et al. (1981) found that 1,2-dichloroethane (1,2-DCA) and 1,1,1-trichloroethane (1,1,1-TCA) were not degraded in sandy soil with low organic content. These compounds percolated rapidly through the soil. A subsequent study indicated that there was no evidence of 1,1-dichloroethane (1,1-DCA) and 1,1,1-TCA degradation by subsurface microorganisms (Wilson et al., 1983).

A study conducted by Parsons and Lage (1985) determined that 1,1-DCA is a product of more chlorinated analogs such as 1,1,1-TCA. Gossett (1985) found that at least 40% of 1,1,1-TCA was reductively dechlorinated to 1,1-DCA by an unacclimated anaerobic culture over a period of 6 days.

Vogel, Criddle, and McCarty (1987) also found that 1,1,1-TCA is reductively dehalogenated to 1,1-DCA under methanogenic conditions. In addition, 1,1,1-TCA is abiotically transformed to 1,1-DCE via dehydrohalogenation in dilute aqueous solutions at neutral pH and 20°C, conditions commonly found in aquifers (Vogel et al., 1987). Figures 2.7 and 2.8 illustrate pathways for the

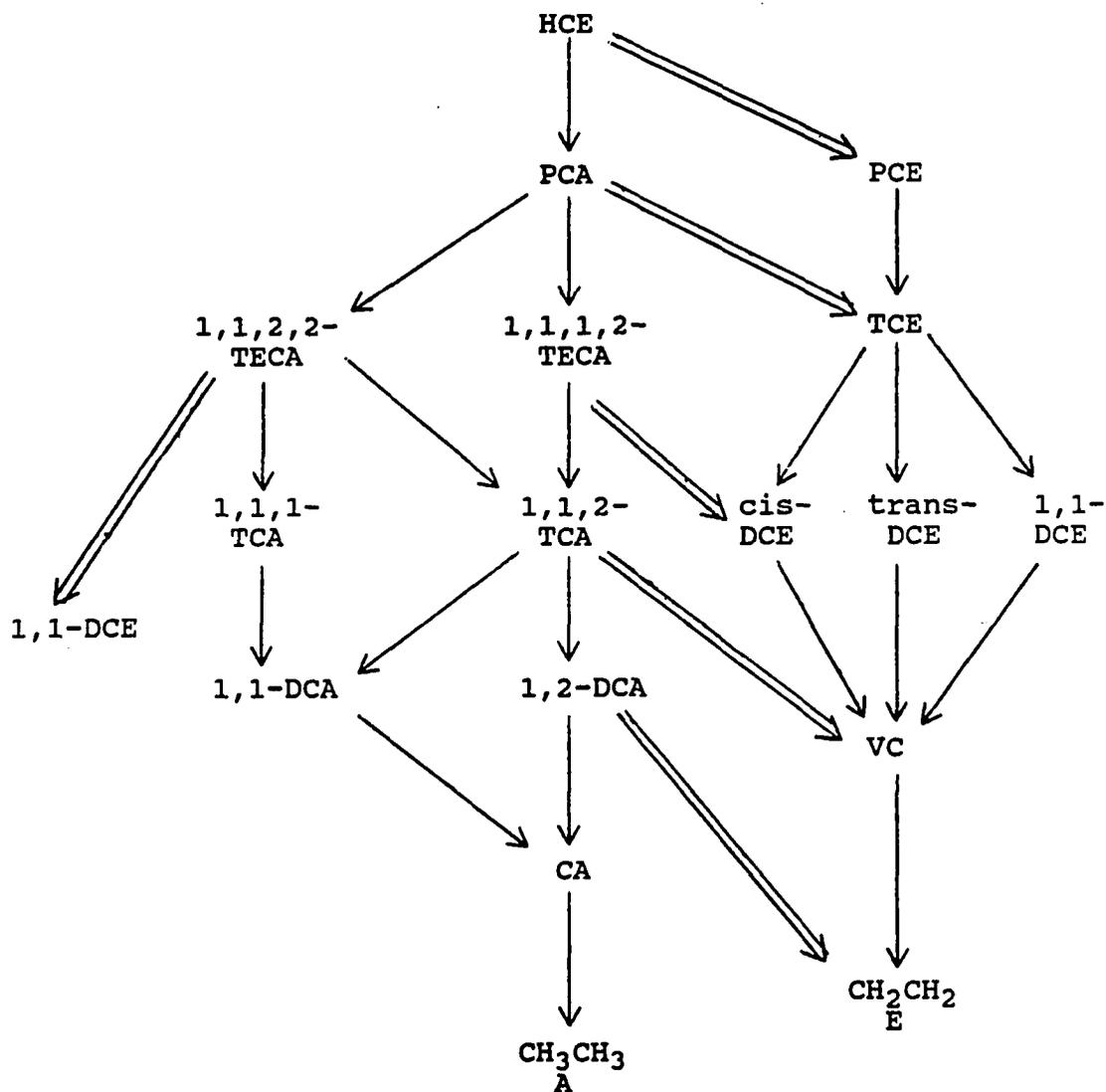
Figure 2.7 Pathways for the transformation of TCA under Methanogenic conditions (Vogel, Criddle, and McCarty, 1987)



A indicates abiotic reactions.  $A_1$  = dehydrohalogenation.

B indicates biotic reactions.  $A_2$  = hydrolysis.

Figure 2.8 Possible Pathways of Biological Transformation for Chlorinated Ethanes and Ethenes.  
(Vogel, Criddle, and McCarty, 1987)



==> Dihaloeelimination (aerobic) - elimination of two halogens to form an alkene.

-> Hydrogenolysis (anaerobic only) - replace halogen with hydrogen.

transformation of chlorinated ethanes.

Chlorinated methanes, specifically trihalomethanes (THMs), are formed when waters with high humic content are chlorinated. Chloroform is the most common THM. However, chloroform, as well as dichloromethane and chloromethane, have also been identified as transformation products of carbon tetrachloride (CT) degradation. A study conducted by Brunner, Staub, Leisinger (1980) reported that the most likely mechanism for the dehalogenation of dichloromethane (DCM) is a halohydrase substitution of a hydroxyl group for a chlorine atom. Wilson et al. (1981) found that chloroform or trichloromethane (CF) was not degraded in sandy soils with low organic content and, therefore, migrated rapidly through the soil. In 1983, Wilson et al. reported no evidence of CF degradation by subsurface microbes.

Bouwer and McCarty (1983) proposed that carbon tetrachloride (CT) is reductively dechlorinated to CF which is almost completely oxidized to  $\text{CO}_2$ , confirming removal by biooxidation. Parsons and Lage (1985) also showed that CF is a product of biotransformation of more chlorinated analogs such as CT. Gossett (1985) found that approximately 31% of the CF was anaerobically converted in less than 9 days to DCM by microflora obtained from municipal waste treatment plants. Chloromethane (CM) was also detected in

the samples. About 32-44% of the CF and 86-91% of the DCM carbon was converted to carbon dioxide. Figures 2.9 and 2.10 illustrate possible pathways for metabolism of CF and DCM.

Finally, a more recent study (Strand and Shippert, 1986) determined that the biooxidation of CF to carbon dioxide was stimulated by the acclimation of sandy soil to an air-natural gas mixture.

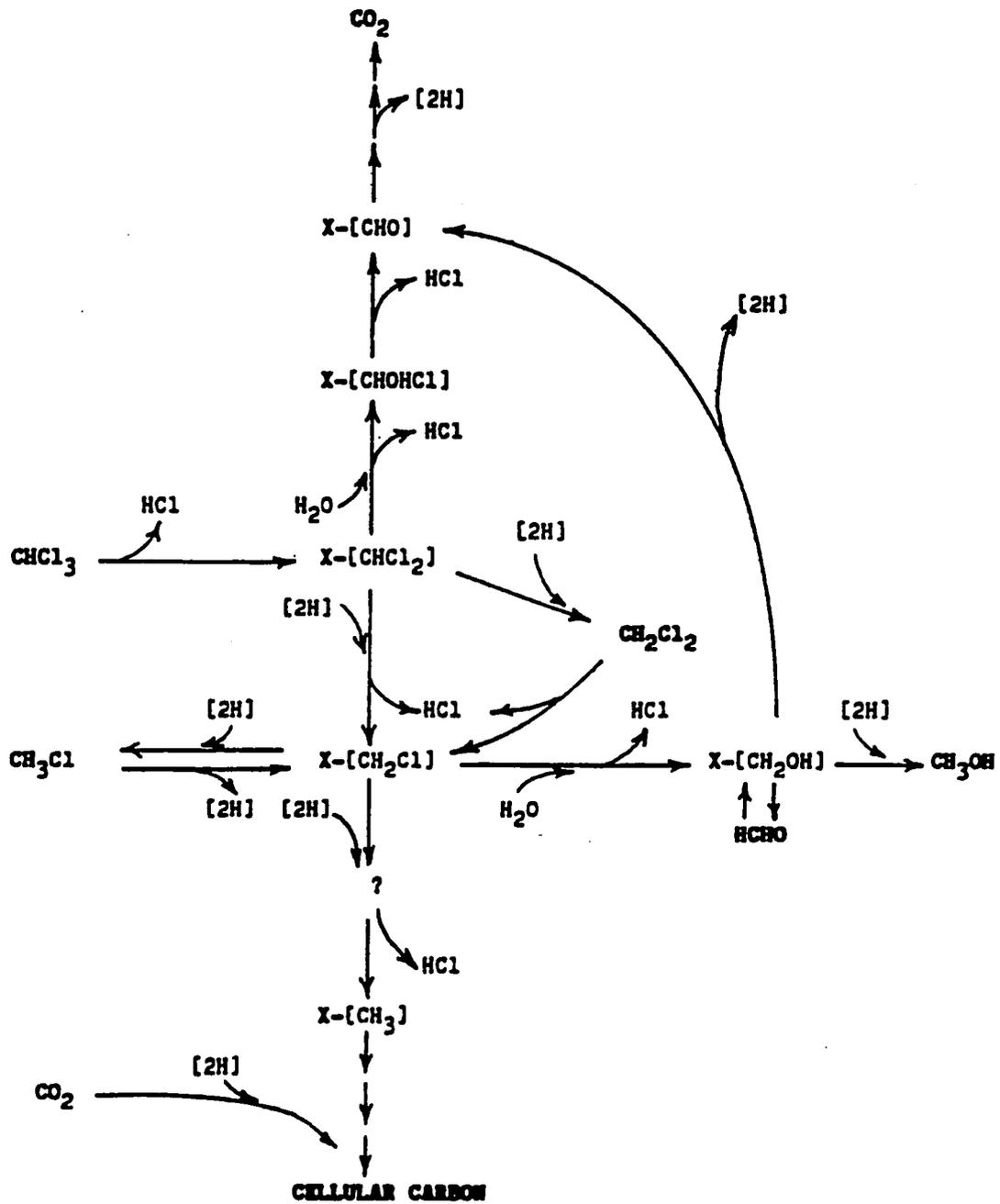


Figure 2.9 Hypothetical Pathways for Metabolism of Chloroform by Methanogenic Systems (Gossett, 1985)

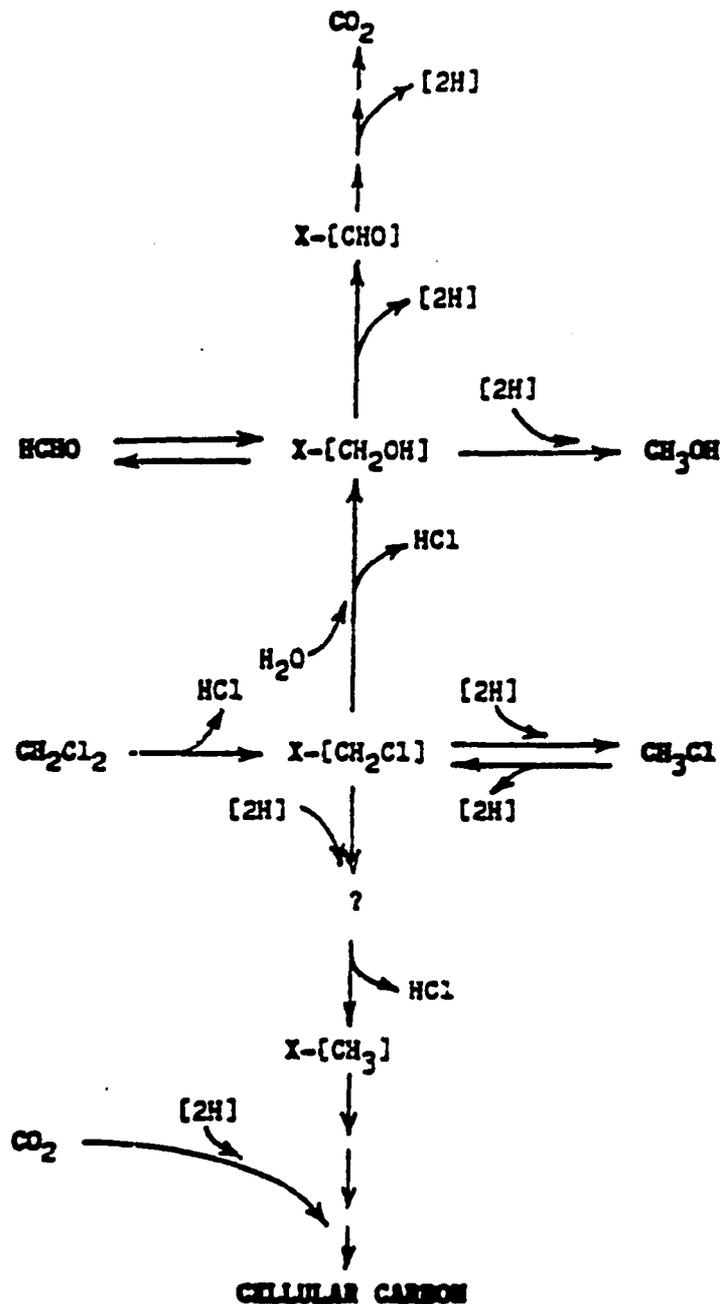


Figure 2.10 Hypothetical Pathways for Metabolism of Dichloromethane by Methanogenic Systems (Gossett, 1985)

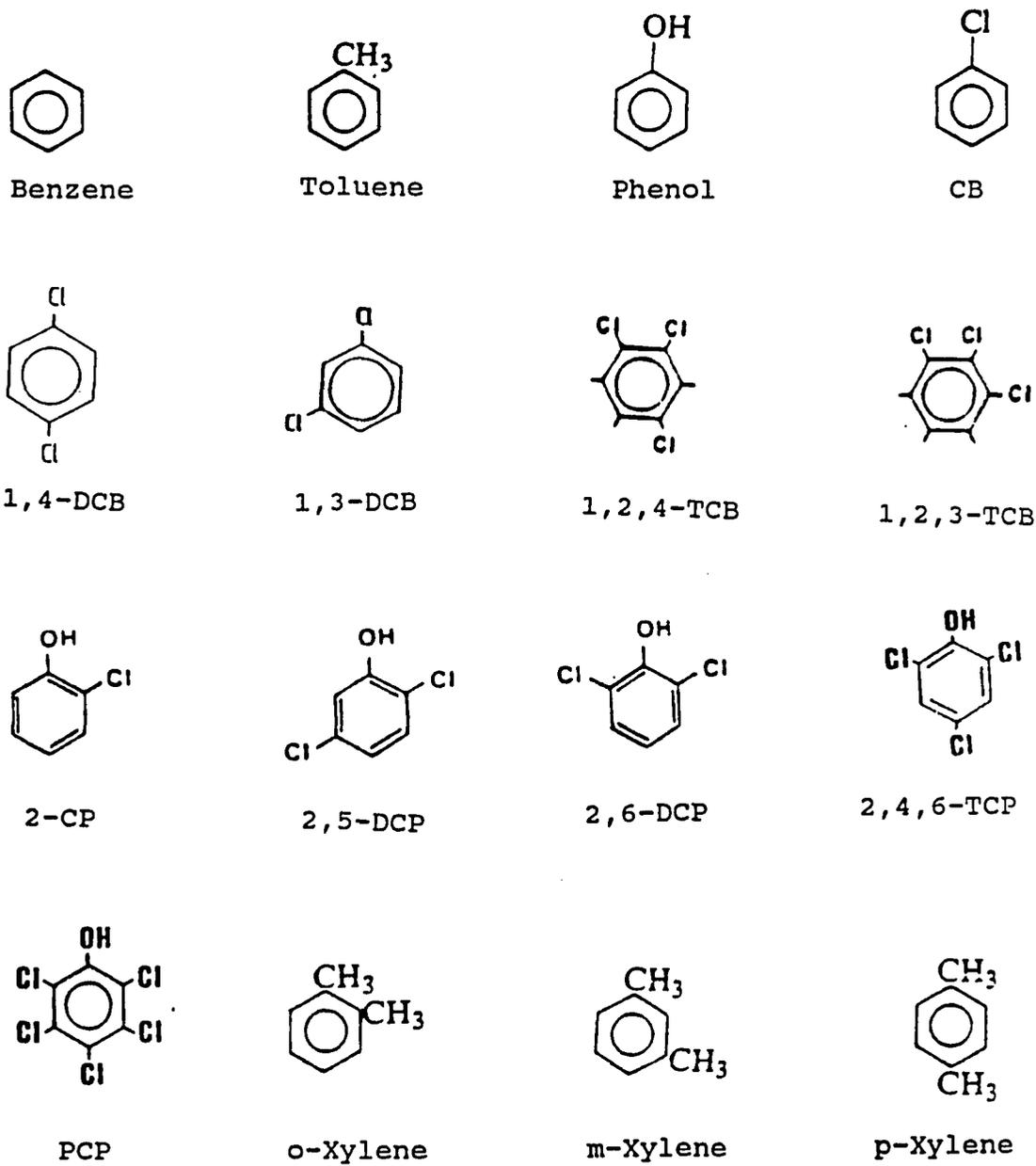
## Aromatic Compounds

Aromatic compounds are benzene and compounds that resemble benzene in chemical behavior (Morrison and Boyd, 1966). Figure 2.11 illustrates the chemical structure of the aromatic compounds of interest. Halogen substituents on the aromatic rings tend to confer increased resistance to biodegradation (Thom and Agg, 1975 and Kim and Maier, 1980). Jones et al. (1977) maintain that halogenated aromatics are likely to pose more of a problem than halogenated aliphatics due to their lower volatility and relatively slow biodegradation rates. The requirement of molecular oxygen to prepare the benzene ring for cleavage was reported by Taylor, Campbell, and Chinoy (1970). Oxygen is incorporated directly into degradative products and is essential for the catabolism or enzymatic degradation of aromatic compounds. Aromatic compounds of interest include benzene, chlorobenzenes, xylenes, phenol, and chlorophenols.

### A. Benzenes

Benzene, toluene, and xylenes were found to be rapidly degraded under anaerobic conditions (Zeyer, Kuhn, and Schwarzenbach, 1986). Results reported by Grbic-Galic and Vogel (1987) indicate that methanogenic cultures derived from ferulic acid-degrading sewage sludge can partially mineralize benzene and toluene to carbon dioxide (CO<sub>2</sub>) and

Figure 2.11 Structures of Aromatic Compounds of Interest



methane ( $\text{CH}_4$ ). The oxygen for ring hydroxylation is apparently derived from water. Vogel and Grbic-Galic (1987) also found that both benzene and toluene were transformed and eventually mineralized by mixed methanogenic cultures (See Figure 2.12 and 2.13). Zeyer et al. (1986) reported that m-xylene or 1,3-dimethylbenzene is totally degraded in the absence of molecular oxygen with nitrate as the electron acceptor. Wilson, Smith, and Reese (1986) found that alkyl benzenes such as toluene and xylenes are readily degraded in aerobic subsurface environments. In addition, benzene, toluene, and ortho-xylene were reduced to less than 1% of their original concentrations in methanogenic aquifer material after 120 weeks of incubation.

Reineke and Knackmuss (1984) isolated a chlorobenzene-degrading bacterium from a mixture of soil and sewage samples through continuous enrichment. The organism, strain WR1306, was able to degrade chlorobenzene aerobically. Figure 2.14 is a proposed catabolic pathway of chlorobenzene by strain WR1306. Chlorophenols have been identified as bacterial degradation products of chlorobenzenes. However, these products were probably derived from cis-1,2-dihydroxycyclohexa-3,5-diene as initial metabolites from arene double hydroxylation. It is well known that cis-dihydrodiols readily rearomatize with formation of phenols under mildly acidic conditions (Reinke

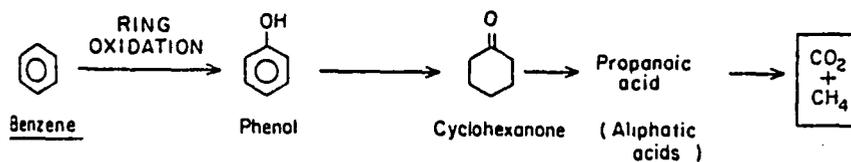


Figure 2.12 Tentative Sequences of Anaerobic Benzene Degradation in Mixed Methanogenic Cultures (Grbic-Galic and Vogel, 1987)

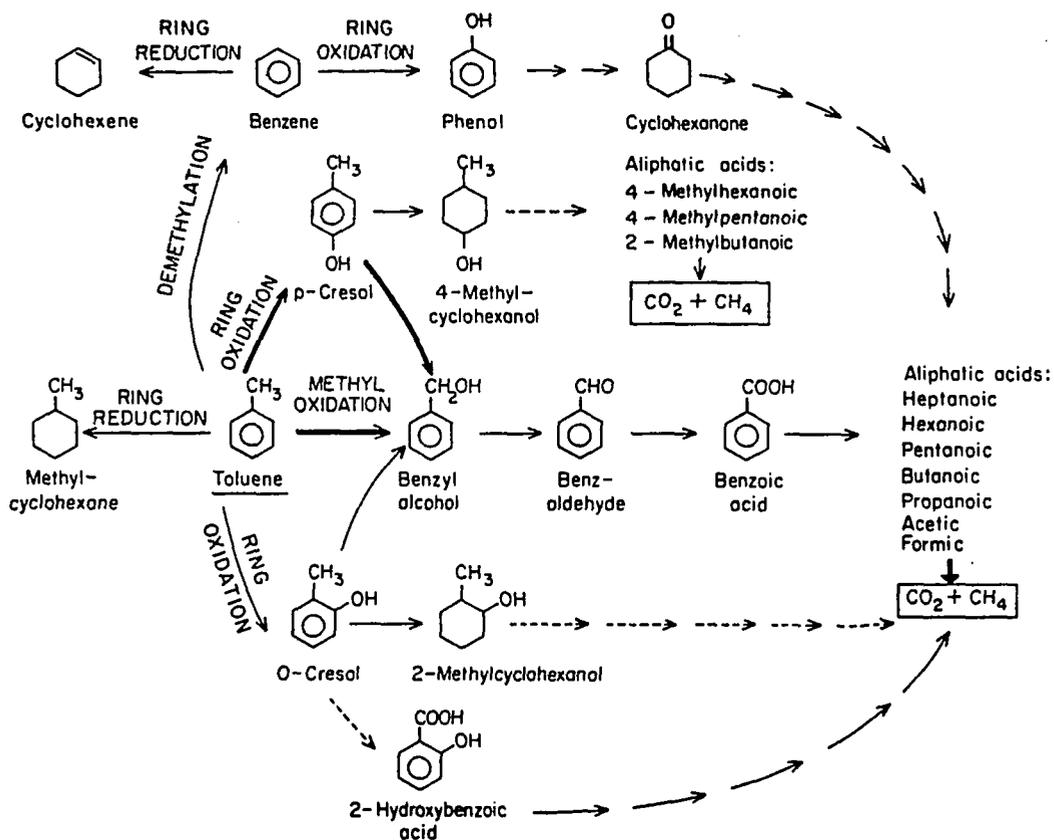


Figure 2.13 Tentative Sequences of Anaerobic Toluene Degradation by Mixed Methanogenic Cultures (Grbic-Galic and Vogel, 1987)

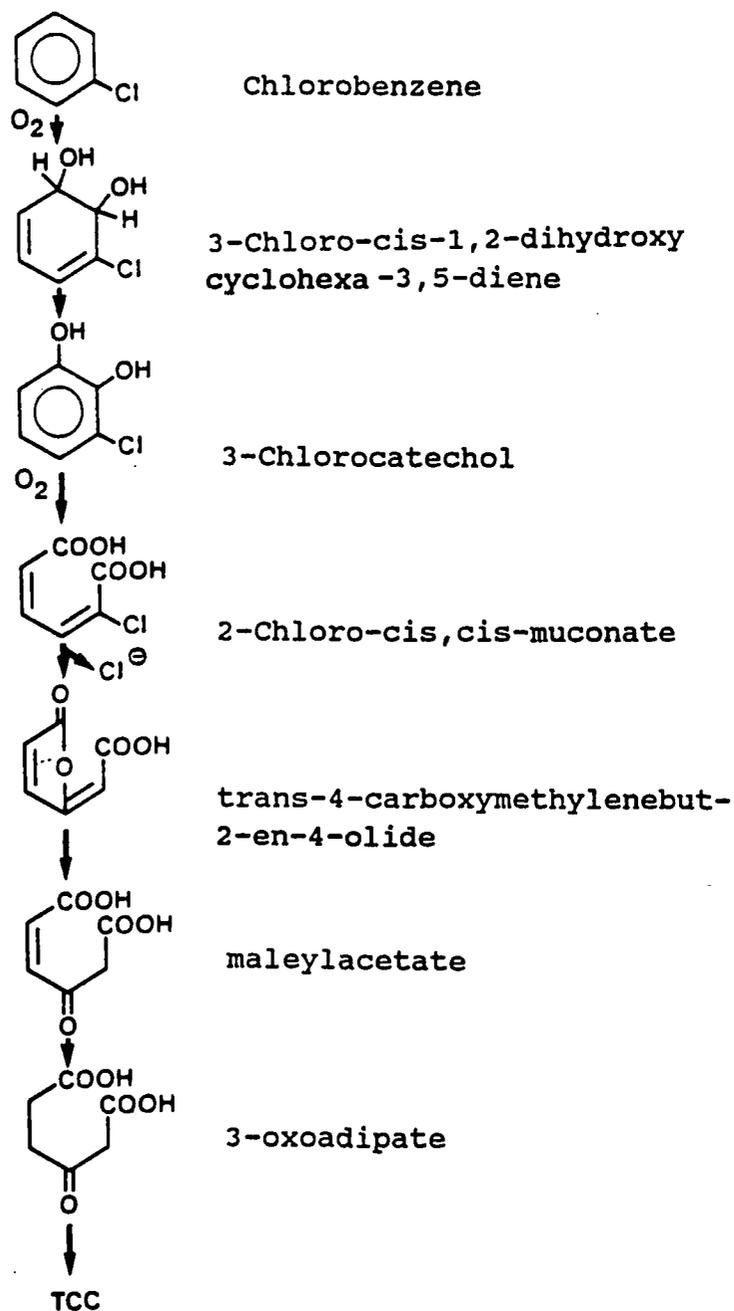


Figure 2.14 Proposed Catabolic Pathway of Chlorobenzene by Strain WR1306 (Reineke and Knackmuss, 1984)

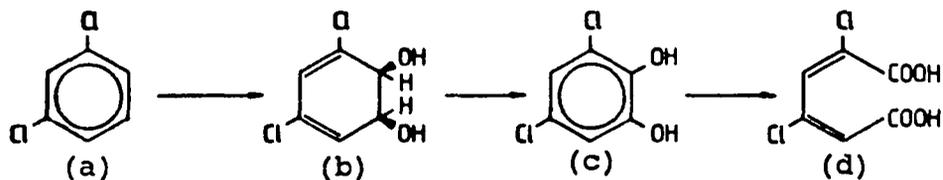
and Knackmuss, 1984).

While toluene was degraded in some soils, chlorobenzene (CB), 1,4-dichlorobenzene (1,4-DCB), 1,2,4-trichlorobenzene (1,2,4-TCB) were not degraded and percolated quickly through sandy soils (Wilson et al., 1981). In a subsequent study, however, chlorobenzene was shown to be readily degraded under aerobic conditions (Wilson et al., 1983).

Both 1,3-DCB and 1,4-DCB are degraded aerobically by Alcaligenes sp., which utilize these compounds as sole carbon and energy sources (DeBont et al., 1986 and Schraa et al., 1986). Figure 2.15 and 2.16 illustrate the proposed aerobic degradation pathways for 1,3- and 1,4-DCB.

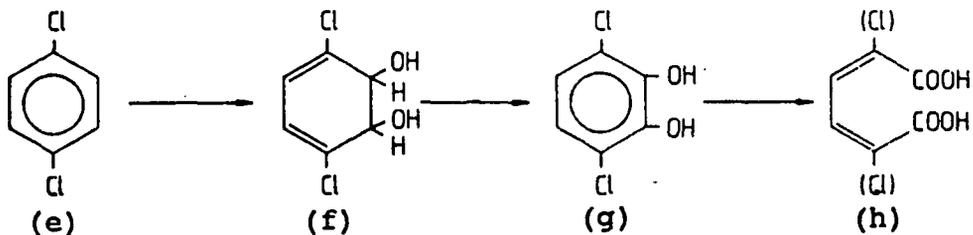
Marinucci and Bartha (1979) studied the anaerobic degradation of two isomers of trichlorobenzene (TCB). Results indicate that TCBS are degraded slowly in soil with a release of CO<sub>2</sub>. The degradation of the two TCB isomers was believed to be mediated by monooxygenase, halohydrolyase, or dioxygenase. The first isomer, 1,2,3-TCB, was anaerobically transformed to 2,3- and 2,6-dichlorophenol (DCP). Dichlorophenol is formed via cleavage of a chlorine atom, followed by hydroxylation or the addition of a hydroxyl group. Degradation products for 1,2,4-TCB were 2,4-, 3,4-, and 2,5-DCP with 2,4-DCP as the most frequent intermediate (See Figure 2.17). Pathways for

Figure 2.15 Proposed Pathway for Catabolism of 1,3-DCB by *Alcaligenes* sp. (DeBont et.al., 1986)



- (a) 1,3-Dichlorobenzene  
 (b) 3,5-Dichloro-cis-1,2-dihydroxycyclohexa-3,5-diene  
 (c) 3,5-Dichlorocatechol  
 (d) 2,4-Dichloromuconate

Figure 2.16 Proposed Initial Steps of 1,4-DCB Degradation by *Alcaligenes* sp. Strain A175 (Schraa et.al., 1986)



- (e) 1,4-Dichlorobenzene  
 (f) 3,6-Dichloro-cis-1,2-dihydroxycyclohexa-3,5-diene  
 (g) 3,6-Dichlorocatechol  
 (h) (2,5-Dichloro)muconic acid

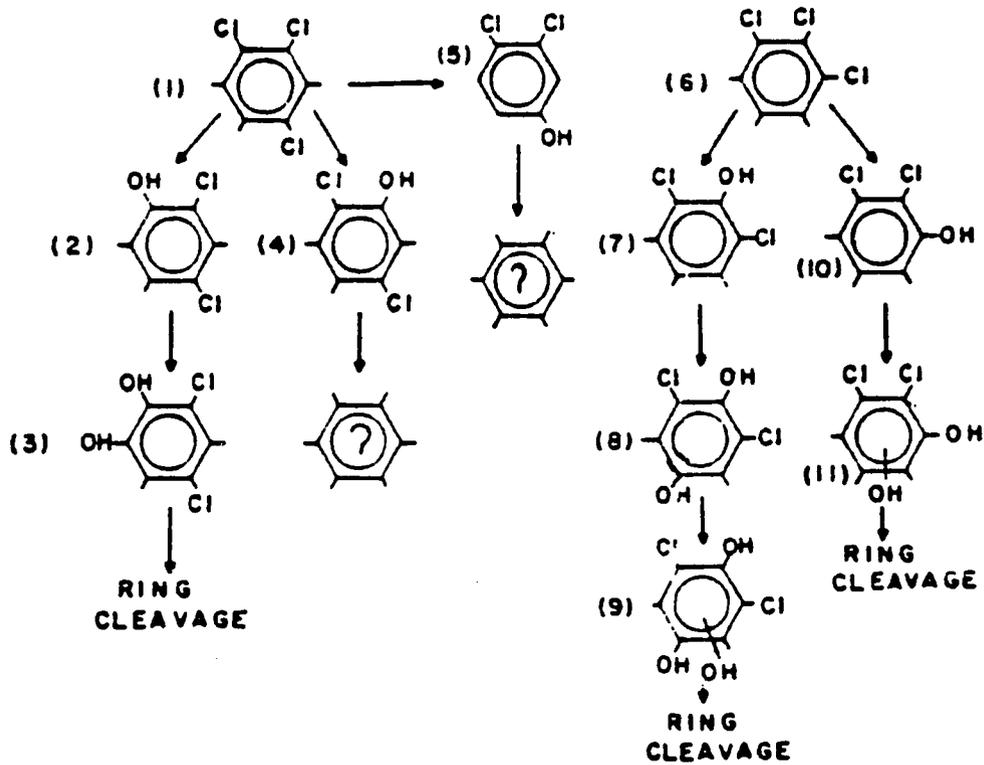


Figure 2.17 Products of TCB Dechlorination Arranged in Probable Degradation Sequence (Marinucci and Bartha, 1979)

complete metabolism are not known. Marinucci and Bartha also hypothesized that although anaerobic conditions promote some dechlorination reactions, they also tend to suppress the mineralization of the aromatic ring carbon.

#### B. Phenolic Compounds

The aerobic and anaerobic degradation of phenolic compounds, pentachlorophenol in particular, has been studied extensively by a number of researchers. Phenolic compounds are widely used in synthetic chemical processes and are common products of pesticide decomposition. Approximately 2.6 billion pounds of phenol were produced in 1983 (Young and Rivera, 1985). Pentachlorophenol (PCP) is a frequently used wood preservative, insecticide, and herbicide (Klecka and Maier, 1986). PCP kills a wide variety of organisms by inhibiting oxidative phosphorylation (Saber and Crawford, 1985).

In 1972, Chu and Kirsch isolated a microbial species (Anthrobacter sp.) capable of aerobically metabolizing 2,4-dichlorophenol (2,4-DCP) to form TCA intermediates and finally CO<sub>2</sub> and chloride. Pentachlorophenol (PCP) was utilized as a carbon and energy source by another bacteria (KC3). Chu and Kirsch also stated that susceptibility of halophenols to biodegradation is related to molecular composition and structure. Multiple halogenation,

particularly with meta substitution, has been believed to cause increased resistance to microbial attack (Chu and Kirsch, 1972 and Alexander and Lustigman, 1966).

Watanabe (1973) studied the aerobic fate of PCP in Japan's rice paddies. During the research period, he noted a disappearance of PCP with a liberation of chloride ions. Within 22 days, 90% of the chloride ions were liberated. Watanabe isolated a genus of bacteria believed responsible for the PCP degradation and tentatively identified it as Pseudomonas or a closely related species. Kuwatsuka and Igarashi (1975) conducted a similar but more detailed experiment. In this study, PCP was biodegraded in soil to: 2,3,4,5-, 2,3,4,6-, and 2,3,5,6,-tetrachlorophenol (TeCP) and 2,3,5-, 2,3,6-, 2,3,4-and/or 2,4,5- and 2,4,6-trichlorophenol (TCP). Two isomers of 2,3,4- and 2,4,5-TCP co-eluted during the gas chromatographic analysis and could not be separated. Unfortunately, the researchers were not clear with respect to the oxidation-reduction potential (ORP) conditions of the experiment.

Petrasek et al. (1983) utilized sewage sludge to degrade phenolic compounds yielding 95% removal of phenol and 19% removal of PCP. Saber and Crawford (1985) isolated another species, Flavobacterium sp., which can utilize PCP as its sole source of energy and carbon. Baker and Mayfield (1980) found that phenol, o-chlorophenol (o-CP), p-CP,

2,4-DCP, 2,6-CP, and 2,4,6-TCP were rapidly degraded by aerobic soil organisms. It was also noted that chlorophenols containing chlorine in the meta-position are not readily degraded by aerobic soil organisms (ie. PCP, 3,4-DCP, m-CP, and 2,4,5-TCP).

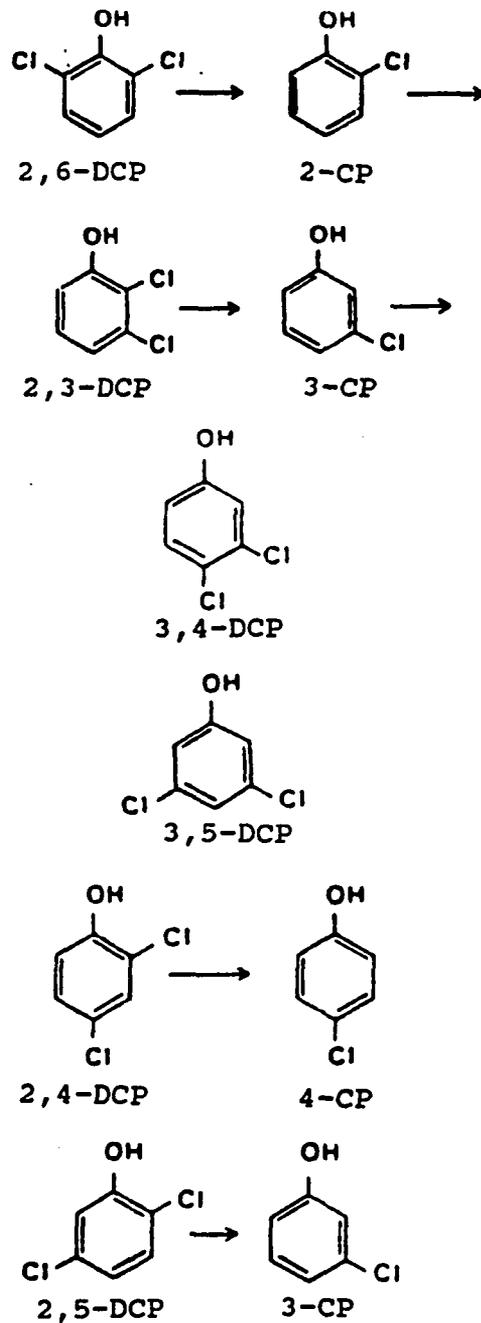
Healy and Young (1979 and 1978) found that both phenol and catechol are stoichiometrically converted to  $\text{CO}_2$  and  $\text{CH}_4$  by methanogenic populations of bacteria, indicating that anaerobic ring fission and complete mineralization occur. Anaerobic bacteria in groundwater environments were also found to convert phenolic compounds to  $\text{CO}_2$  and  $\text{CH}_4$ . In fact, Erhlich et al. (1982) determined that more than 95% of the phenolic compounds were removed within 1000 m of the contamination source.

Boyd et al. (1983) conducted studies using digester sewage sludge. Results indicated that there is no obvious relationship between substituent position and susceptibility to anaerobic biodegradation. The dechlorination of o-CP yielded phenol as an initial breakdown product, supporting dechlorination as the initial step in the reductive dehalogenation of chlorinated aromatic compounds. All monosubstituted phenols, with the exception of p-CP and o-cresol, were significantly degraded during the 8-week incubation period. Using unacclimated digester sludge, Boyd and Shelton (1984) observed the removal of chlorine groups

ortho to the phenolic hydroxyl group for each of the DCP isomers (See Figure 2.18). Two isomers, 3,5- and 3,4-DCP were found to be persistent since neither compound contains the ortho chlorine. Rates of degradation were found to depend upon which chlorophenolic isomer the sludges were acclimated to.

Deely, Skierkowski, and Robertson (1985) observed that organisms indigenous to both sewage and landfill leachates can degrade phenol. Degradation in landfill leachates is slower due to lack of nutrients and acclimation. Young and Rivera (1985) examined the fate of substituted phenols and found that during anaerobic metabolism, ring substituents are removed to yield phenol. Ring saturation then takes place followed by ring fission, yielding organic acid intermediates serving as  $\text{CH}_4$  precursors. During ring saturation, the double bonds between the carbons are replaced with single bonds and an additional hydrogen atom bonds to each carbon atom within the ring. The ring is now saturated because it contains a maximum number hydrogen atoms (2) for each carbon atom. Metabolism of aromatic nuclei under aerobic conditions relies on mono- and di-oxygenase enzymes responsible for incorporation of oxygen into the compound. Aerobic metabolism is both rapid and efficient. Figure 2.19 represents the metabolic fate of some substituted phenols.

Figure 2.18 Degradation of Chlorinated Phenols in Unacclimated Anaerobic Digester Sludge (Boyd and Shelton, 1984)



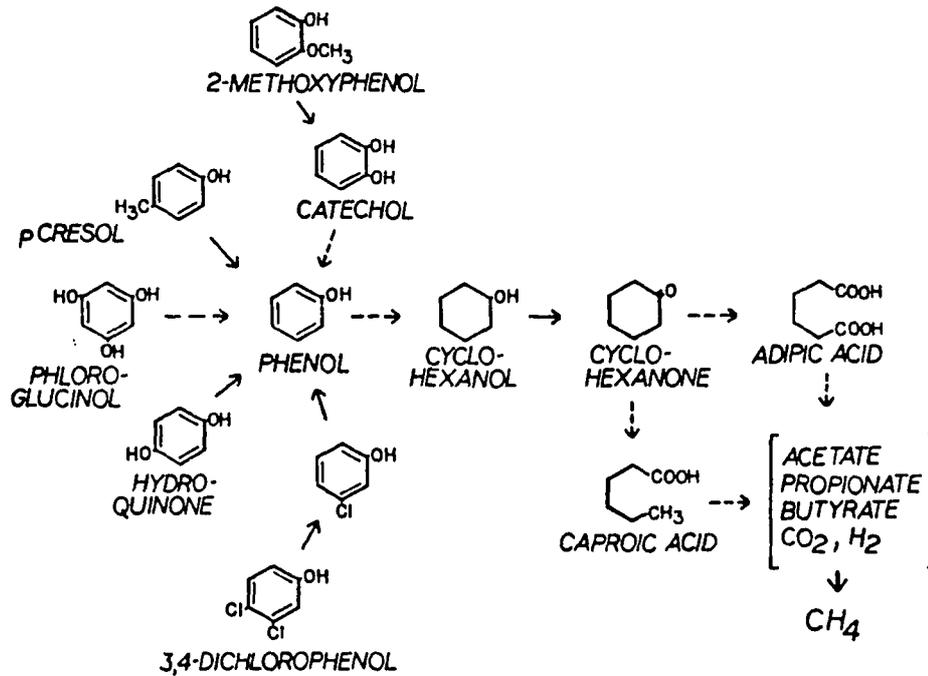


Figure 2.19 The Metabolic Fate of a Range of Substituted Phenols Under Anaerobic, Methanogenic Conditions (Young and Rivera, 1985)

Gibson and Sulfito (1986) determined that the microflora of leachate-contaminated groundwater and anaerobic sewage sludge can transform a variety of chlorophenols. Organisms isolated from sulfate-reducing aquifers were also found to be capable of transforming a number of chlorophenols, although to a lesser degree. Figure 2.20 illustrates a proposed pathway for the methanogenic degradation for chlorinated phenols.

Mikesell and Boyd (1986) utilized anaerobically digested municipal sewage sludge in their study. Results indicate that chlorine substituents ortho to the phenolic OH group are removed more readily than those in the meta or para positions. Proposed pathways for the degradation of PCP in a mixture of CP-acclimated sludges can be found in Figure 2.21. Reductive dechlorination, or removal of Cl atoms directly from a ring of aromatic compounds in a single step does not appear to occur under aerobic conditions. This is a significant process since dechlorinated products are usually less toxic and more readily degraded either aerobically or anaerobically. Figure 2.22 illustrates a pathway of PCP degradation in a mixture of CP-acclimated sludges.

Figure 2.20 Proposed Pathway for Methanogenic Degradation of Chlorinated Phenols (Gibson and Sulfito, 1986)

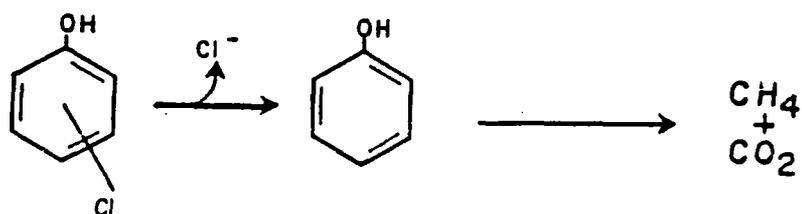


Figure 2.21 Products Resulting from the Dechlorination of PCP in Sludges Acclimated to 2-, 3-, or 4-CP (Mikesell and Boyd, 1986)

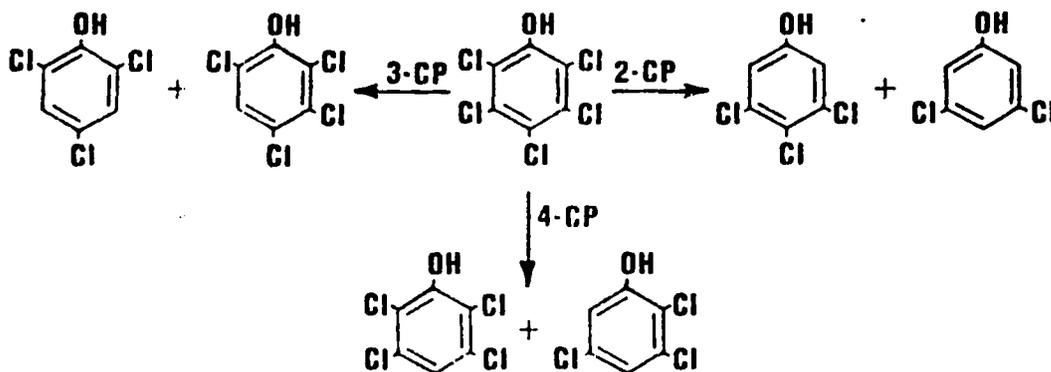
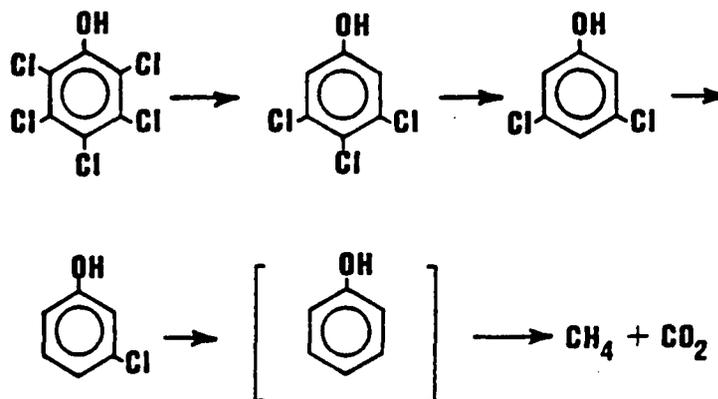


Figure 2.22 Pathway of PCP Degradation in the Mixture of CP-acclimated Sludges (Mikesell and Boyd, 1986)



## Summary

A large number of researchers have investigated the biological fate of organic chemicals in environments such as sewage sludges, groundwater aquifers, and soils. This section will provide a short summary of the biodegradative pathways previously described.

Anaerobic dehalogenation, either biologically or abiotically, is widely recognized as the critical factor in the transformation of both 1- and 2-carbon aliphatic compounds. While early results were contradictory, the biological fate of these compounds is now generally agreed upon.

The chlorinated ethenes, specifically TCE and PCE, can be attacked under both aerobic and anaerobic conditions. A number of researchers identified methanotrophs capable of degrading 5 chlorinated ethenes aerobically. In addition, several investigators agree on the reductive dechlorination of chlorinated ethenes under anaerobic conditions. The degradation products are very different for the two ORP conditions.

Chlorinated ethanes were found to be biologically reductively dechlorinated to other ethanes and abiotically transformed to chlorinated ethenes via dehydrohalogenation. Information was not available for the aerobic fate of the chlorinated ethanes.

Chlorinated methanes such as carbon tetrachloride were also reductively transformed to chloroform and dichloromethane. Methanotrophs were found to oxidize chloroform under aerobic conditions.

The aerobic fate of aromatic compounds including benzene and toluene is well documented. However recent studies have found that these compounds can be rapidly degraded and partially mineralized to CO<sub>2</sub> under methanogenic conditions. The oxygen required to prepare the benzene ring for cleavage is apparently derived from water.

Researchers recently isolated bacterium capable of degrading chlorinated benzenes aerobically, producing chlorocatechols and chloro-cis-1,2-dihydroxycyclohexa-3,5-dienes. The anaerobic transformation of trichlorobenzenes resulted in the production of chlorinated phenols.

The aerobic and anaerobic fate of phenolic compounds, specifically pentachlorophenol, has been studied extensively. Many researchers have found that significant degradation occurs under both conditions. In addition, the extent and rate of degradation were found to depend upon the chlorophenolic isomer to which the organisms were acclimated.

## CHAPTER 3

### EXPERIMENTAL METHODS

#### Sample Collection

Landfill leachate samples were collected from within the leachate collection system by landfill personnel. The leachate collection systems were specific to the landfills of interest, ranging from sewers to ponds.

Samples from Landfill A were collected in amber 4 liter acid washed, glass sample bottles and sealed with teflon lined caps. Samples from the remaining landfills were collected in amber 250 ml glass sample bottles sealed with teflon septa and screw caps. All bottles were filled so as to minimize head space and, thus, reduce the loss of volatile organic compounds. However, it was impossible to obtain samples completely void of headspace. Labels containing the location and sampling date were attached to all bottles. Immediately following sampling, bottles were placed in styrofoam coolers with commercial blue ice and shipped via air freight to the University of Arizona's Environmental Engineering Laboratory for analysis.

### Sample Preservation and Storage

All sample bottles were immediately placed in a 4°C refrigerator for storage until sample preparation and analysis was possible. Once a portion of the sample was removed for a total organic halide (TOX) analysis, the samples from Landfill A were transferred to either 120 or 160 ml acid washed serum vials under negative pressure (using nitrogen gas) to minimize volatile losses. The serum vials were promptly sealed with teflon septa and crimped aluminum tear-off caps. Storage at 4°C was necessary until sample analysis was practical. Samples from all other landfills were poured from the 250 ml sample bottles to 120 ml serum vials, capped, and stored in the manner described above. The size of the 250 ml bottles did not allow for sample transfer under pressure, thus, permitting some loss of compounds due to volatilization.

### Ultra-filtration Procedure

Following filtration through a Whatman GF/C filter, attempts were made to fractionate the sample from Landfill A on the basis of molecular weight. Amicon membranes (YM and YC series) and stirred cells were employed to obtain six sample fractions with apparent molecular weights of less than 30,000, 10,000, 5,000, 1,000, and 500.

First, 45 ml of sample was poured into the Amicon stirred cells holding the membranes. Nitrogen gas, at an operating pressure of 35 psig, was utilized to drive the sample through the membranes.

The first 5 ml of the filtrate was discarded. Past studies have concluded that this aliquot contains distilled water which was trapped in the membrane and is, therefore, dilute. In addition, the wasting of 5 ml flushes the teflon tube that carries the filtrate from the stirred cell to the collection test tubes. The next 20 ml of the permeate was collected in test tubes washed in chromic acid and thoroughly rinsed with distilled water. Following filtration, the test tubes were sealed with parafilm and stored at 4°C until non-purgeable organic halide (NPOX) and total organic carbon (TOC) analyses could be performed.

Flux times were recorded for each filtration run and compared to expected flux times. Any significant change in flux times indicates membrane-related problems. Membrane problems were noted during the ultrafiltration of the sample from Landfill A. Although the membranes were used only twice, large increases in flux times were noticed. The time increase may have been due in part to a brownish film which formed at the filter surface. Soaking in the 2 molar NaCl membrane wash did not remove the film. According to Amicon

representatives, certain compounds commonly found in landfill leachates, such as phenol, may be incompatible with the membranes resulting in an alteration of the surface composition. The Landfill A leachate seemed to clog and degrade the surface of the membrane, rendering the membrane useless. As a result, the use of ultrafiltration in the processing of landfill leachates was discontinued. Tables 3.1 and 3.2 contain TOX and TOC data which indicate inconsistencies in the apparent molecular weight fractions and support the cessation of ultrafiltration as a part of the sample processing procedure. Contrary to the data obtained, TOX and TOC values are expected to decrease with decreasing molecular weight. In addition, the fractionation and TOX analysis was repeated. As presented in Table 3.1, TOX values changed significantly between the first and second runs. Again, the degradation of the membranes is suspected.

#### Total Organic Carbon Procedure

Total organic carbon (TOC) analysis was performed using a Dohrmann DC-80 Total Organic Carbon Analyzer. In order to ensure accuracy, the analyzer was calibrated daily with a potassium acid phthalate (KHP) standard. Samples evaluated for TOC were also evaluated for TOX.

Table 3.1. NPOX Data for Landfill A Leachate based on AMW for Two Dates.

<u>AMW</u>	<u>NPOX (ug/l)</u>	
	<u>1/28/87</u>	<u>2/18/87</u>
Total	496	343
<30,000	624	404
<10,000	498	301
< 5,000	566	358
< 1,000	441	274
< 500	---	182

Table 3.2. TOC Data for Landfill A Leachate based on AMW.

<u>AMW</u>	<u>Ave. TOC (ppm)</u>
Total	2065
<30,000	2085
<10,000	2024
< 5,000	1980
< 1,000	2418
< 500	1795

Three-milliliter aliquots were prepared for TOC analysis using a two step procedure. In the first step, the pH of the sample was adjusted to approximately two with two drops of phosphoric acid. Next, carbon dioxide was stripped from the sample via sparging with nitrogen gas. Stripping of the CO<sub>2</sub> is necessary to prevent false high TOC readings. Acidification of the sample prior to sparging increases the stripping efficiency of CO<sub>2</sub> as well as converting any alkalinity within the sample to CO<sub>2</sub>. The addition of two drops of acid prevents any significant increases in pH as the CO<sub>2</sub> is stripped, allowing for complete removal. With sample preparation accomplished, the sample was ready for injection.

All three of the DC-80's concentration channels were utilized in the analysis of the leachate samples, depending on sample strengths. Volumes of 40 microliters (ul), 200 ul, or 1 ml were injected into the analyzer, corresponding to the desired channel. The resulting direct readouts had units of parts per million (ppm). Samples were run in triplicate and the results were recorded.

### Solids Processing Procedure

All solids samples received from the Department of Anthropology were stored at 4°C in glass canning jars until processing was possible. Due to liquid/solid separation during storage, the samples were stirred to achieve a homogeneous mixture. Next, the mixed samples were transferred to 50 ml plastic centrifuge tubes and centrifuged for at least 20 minutes at approximately 7500 rpm.

Prior to centrifuging, the level of each mixed sample was marked on the side of the centrifuge tube and the corresponding volume was measured. The volume of the interstitial water separated by centrifugation was also measured. Centrifugation was repeated until at least 10 ml of interstitial water was collected. After GF/C filtering, the water was stored at 4°C in acid washed test tubes sealed with parafilm until NPOX and NPOC analyses could be completed. The remaining solids portion was mixed and placed in 10 ml vials. The vials were sealed with parafilm and stored at 4°C until the solids could be evaluated for solid halides (SX).

In addition to SX, total residues (TR) and volatile residues (VR) were performed on the solids following the procedures outlined in Standard Methods. First, approximately six grams were placed in aluminum evaporation

pans and dried at 103°C overnight to determine the percentage of water remaining in the solid material. After reweighing, the sample was then placed in the 550°C oven for 60 minutes to quantify the volatile fraction. The following equations were then used to calculate the desired parameters.

$$\begin{aligned} \%TR &= A/B*100 && \text{Where: A = weight of dry solids (g)} \\ \%VR &= (A-C)/A*100 && \text{B = weight of wet solids (g)} \\ & && \text{C = weight of ash (g)} \end{aligned}$$

#### Purgeable Organic Halides

A purgeable organic halide (POX) analysis was used to determine the purgeable or volatile fraction of organically-bound halides. However, the POX method was found to be inappropriate in the analysis of the landfill leachates of interest due to nature of the samples.

The POX method calls for the injection of a 10 ml aliquot of sample into the sparging unit of the Dohrmann DX-20 TOX analyzer. Following the injection of the leachate, foaming caused a portion of the sample to enter the pyrolysis and inlet tubes of the instrument. Once contamination occurred, the analyzer had to be taken out of service for cleaning and reconditioning, wasting valuable research time. Attempts to halt foaming through sample

dilution failed. As a result, POX analysis of leachate samples was discontinued. Subsequently, calculations were used to determine the purgeable fraction. The purgeable organic halide (POX) is the difference between the total organic halide (TOX) and the non-purgeable organic halide (NPOX). Procedures for determining the TOX and NPOX are explained later in this chapter.

#### Total Organic Halide Procedure

A Dohrmann DX-20 Total Organic Halide (TOX) analyzer was utilized to measure the totality of organically-bound halides, specifically chlorine. The method is similar to the EPA method 506 with the modifications described below.

The first of two steps in TOX analysis involves the adsorption of chlorinated organic compounds onto Calgon Filtrasorb 400 granular activate carbon (GAC) 100/200 mesh. Dohrmann selected this GAC due to its affinity to halogenated organic compounds and its high purity (halogen-free). The second step is combustion of the carbon containing the adsorbed organo-chlorine compounds. An adsorption module accompanying the DX-20 analyzer was used in the adsorption step.

Glass mini-columns, provided by Dohrmann, were packed with the GAC in accordance to EPA method 506. Consistency in column packing is of particular importance in

order to ensure uniformity in blank values and adsorption times. At least two columns, containing only carbon, were burned to obtain blank values. The resulting values were then applied to up to 12 other columns. Low readings due to low mass loadings of compounds to the carbon columns are significantly affected by deviations in blank values and, thus, column packing.

Prior to the introduction of sample, the sample channels of the adsorption module were cleaned with a few milliliters of methanol and rinsed twice with distilled water. This procedure was found to be adequate to prevent cross-contamination, as supported by consistent blank values.

A pair of GAC columns were installed, in-series, on the sample channels. Preceding sample addition, 5 ml of distilled water was passed through the columns. Pre-moistening of the carbon minimized "channeling" during initial sample contact and low recoveries.

Because the DX-20 analyzer performs more accurately when the readout is between 3.00 and 50.00 micrograms, up to 25 ml of leachate samples was adsorbed in an attempt to achieve these levels. Distilled water was used to bring the total volume up to 50 ml. Next, 0.25 ml of 0.5 M sodium sulfite and 0.25 ml of concentrated nitric acid were added to the diluted sample. The addition of nitric acid

decreases the pH, improving adsorption. Sodium sulfite binds to free chlorine to prevent false high readings.

All of the sample mixture was then allowed to pass, under pressure, through the columns. High purity carbon dioxide (99.995%) at an operating pressure of 20 psig was utilized to force the sample through the carbon columns. Following adsorption, the columns were attached to a second channel containing a 5000 ppm nitrate solution wash. Two milliliters of the solution were passed through the columns at a pressure of 5 psig to remove the free chlorine bound by the sodium sulfite. Finally, the carbon with the adsorbed halogenated compounds was pyrolyzed within the TOX analyzer.

Following warm-up of the TOX analyzer, several steps were carried out to verify the instrument's stability. First, at least one dry run was performed in which the analyzer was run through a cycle without the addition of carbon. A reading of -0.04 to 0.00 was expected after the ten minute cycle was completed. This verified that the analyzer was stable and ready for operation.

Second, a standard containing a known mass of 2,4,6-trichlorophenol (TCP) was placed on a previously combusted piece of cerafelt, the fiberglass packing used in the GAC mini-columns, in a cool, clean boat (used for standards only). The standard was prepared by dissolving 114 mg of TCP in 100 ml of methanol. A 20 microliter volume

of the standard was used for the recovery check. A 100% recovery would have resulted in a readout of 12.2 ug. Typical recoveries ranged from 95% to 97%. Lower recoveries indicated a need for instrument maintenance.

Finally, prior to sample analysis, two blank GAC columns were burned. The blank columns were created by passing 5 ml of distilled water through a pair of carbon columns followed by the 2 ml nitrate wash. This step aided in the stabilization of the analyzer and provided an operational check. With all verification steps complete, the instrument was ready for normal operation.

Carbon columns were burned individually, bottom column first. The readouts, in micrograms (ug), were recorded and the resulting mass concentrations of organic halides were calculated using the following equation:

$$\text{TOX} = ((T+B) - 2BL) * DF * (1000/VOL)$$

Where: TOX = total organic halide (ug/l)  
T = readout for top column (ug)  
B = readout for bottom column (ug)  
BL = average value for blank column (ug)  
DF = dilution factor  
VOL = volume of sample passed through GAC columns (ml)

A number of the TOX analyses were replicated to ensure the accuracy of the measurements. Coefficients of variation (cv) were calculated to determine the dispersion of the values obtained. The cv is the ratio of the standard

deviation to the mean. A cv of less than 10% was considered acceptable.

#### Non-purgeable Organic Halide Procedure

The procedure is similar to that for TOX with the exception that the sample is exposed to either atmosphere or purged with nitrogen prior to the adsorption step.

#### Solid Halide Procedure

Solids obtained from the centrifugation step were placed in the TOX analyzer's quartz boat and weighed. Burning the solid sample resulted in a total solid halide (TSX) value in micrograms. The actual solid halide (SX) was calculated using the equation given below, allowing for the deduction of the organically-bound halides contributed by the water found within the solid sample.

$$SX \text{ (ug/mg)} = \frac{TSX - (Wt * WC * (1 \text{ ml}/1000\text{mg}) * TOX)}{Wt \text{ (mg)}}$$

Where: SX = actual solid halide (ug/mg)  
TSX = total solid halide (ug)  
Wt = solid sample weight (mg)  
TOX = liquid TOX (ug/l)  
WC = water content (decimal)

### Gas Chromatographic Procedure

Gas chromatography was employed to identify and quantify the presence of selected organic compounds in landfill leachate. Data used in this report was obtained through the use of two Hewlett Packard Gas Chromatographs (GC).

First, a number of chlorinated organic compounds (Table 3.3) were identified using a Hewlett Packard 5790A GC. The 5790A GC was equipped with an electron capture detector (ECD) and a DB-1 Megabore column. Electron capture detectors measure the ability of a compound to absorb or capture beta particles (electrons) emitted by a radioactive source ( $\text{Ni}^{63}$ ). Therefore, ECDs are highly sensitive to halogenated organic compounds (TCE, pesticides, etc.) and virtually insensitive to aromatic hydrocarbons. The electrons produce a current, which decreases when the organics "capture" the electrons. A HP 3390A integrator receives an indication of this reduction and converts the signal to a peak corresponding to the compound of interest. Due to its sensitivity to water, the ECD will accept non-aqueous injections only. The 30 meter-long DB-1 Megabore column has a 1.5  $\mu\text{m}$  methylsilicone stationary phase which is chemically bonded to the support and is, thus, compatible with compounds of low polarity. Next, a Hewlett Packard 5890A GC was utilized in the identification of a few

Table 3.3. Halogenated Compounds of Interest.

Chloroform  
1,1,1-Trichloroethane  
Carbon Tetrachloride  
Trichloroethylene  
Perchloroethylene  
Chlorobenzene  
m-Dichlorobenzene  
p-Dichlorobenzene  
o-Dichlorobenzene

Table 3.4. Aromatic Hydrocarbons of Interest.

Benzene  
Toluene  
m-Xylene  
p-Xylene  
o-Xylene

aromatic hydrocarbons listed in Table 3.4. A flame-ionization detector (FID) and a DB-WAX Megabore column were installed in the 5890A GC for this application. The FID, with the widest linear range for any detector, is the most sensitive to hydrocarbons. When passed through the detector's burning hydrogen flame, the organic compounds of interest are combusted forming ion fragments and electrons. The resulting electrical current is monitored and sent to a HP 3392A integrator. The concentration of charged particles is proportional to the electrical conductivity of a gas. Unlike the ECD, the FID is insensitive to water and, therefore, can accept direct aqueous injections. The 30 meter DB-WAX column is the most polar Megabore column available and is, thus, the best column for the analysis of polar hydrocarbons. A 1.0  $\mu\text{m}$  polyethyleneglycol stationary phase is present in the DB-Wax column.

#### Stock and Standard Preparation

Stocks of each compound were prepared volumetrically, using  $\mu\text{l}$  syringes, in 160 ml acid-washed serum vials filled with methanol. The vials were sealed with teflon-lined septa and crimped aluminum tear-off caps. Chemical cross-contamination necessitated the preparation of individual stocks and standards. Standards, used in the calibration of the GC, were made through the injection of a

volume of stock into a 120 ml serum vial containing distilled water. The vials were sealed in the same manner described previously. Compound concentration within the stocks were such that a volume of 10 to 100 ul would yield a standard with levels similar to those expected in the leachate samples. Stocks were stored at 10°C for no more than two weeks while the standards were prepared the day of use. All of the pure chemicals and the stocks were allowed to warm-up for at least an hour prior to stock and standard preparations.

#### ECD and Chlorinated Organic Compounds

Because the ECD cannot accept direct aqueous injections, liquid/liquid extractions were necessary. Five ml of pentane was injected into the 120 ml standard (or sample) via the double syringe technique illustrated in Figure 3.1. Following the addition of pentane, the vial was shaken for two minutes, allowing the chemicals to leave the water and concentrate in the pentane layer. Past studies have found that recoveries of approximately 95% may be expected.

Calibration of the GC involved the injection of 2 ul of the pentane layer. A split flow mode was utilized (except for the sample from Landfill A) so that only a portion of the sample actually passed through the column.

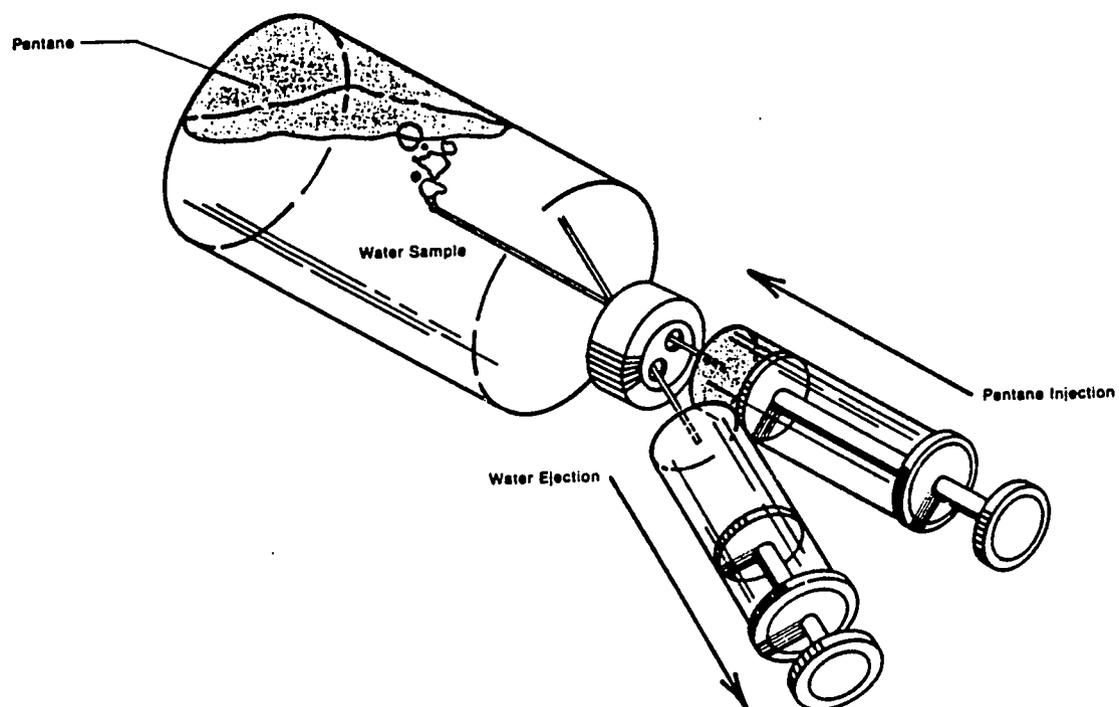


Figure 3.1 Addition of Pentane to Water Sample (Trussell et. al., 1979)

Flow splitting was found to be necessary to remain within the detector's linear range. The compounds adsorb to the stationary phase of the column and are retained for varying lengths of time based on boiling points and polarities. Each compound produces a peak with an area count in  $\mu\text{m}^2$  based on its concentration. A response factor (RF) may be calculated by dividing the known concentration or amount by the corresponding area count. The calibration was then used to evaluate unknown samples. Extraction and injection techniques were similar to that for the standards. Concentrations of compounds in unknown samples were determined by multiplying the resulting area counts by the response factors obtained for the standards. Tables 3.5 and 3.6 contain GC operating and flow conditions for the ECD/GC analysis. Figure 3.2 represents a sample chromatogram of the halogenated compounds of interest.

#### FID and Aromatic Hydrocarbons

The steps for calibration are similar to that described in the previous section with a few exceptions. As mentioned earlier, the FID can accept direct aqueous injections. Injections were made using the more accurate sandwich technique. The sandwich technique involves the sandwiching a 1  $\mu\text{l}$  aqueous volume of sample between air.

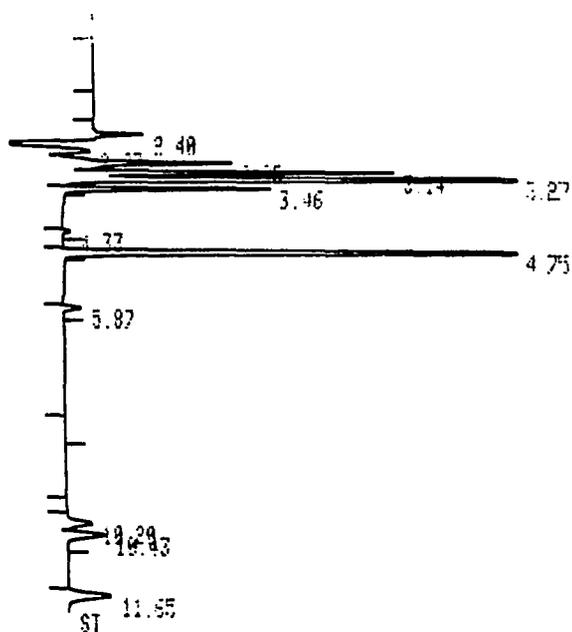
Table 3.5. GC/ECD Operating Conditions.

Inlet Temperature.....	250°C
Detector Temperature.....	280°C
Oven Temperature.....	100°C
Temperature Program.....	Isothermal
Column Type.....	DB-1 Megabore
Carrier Gas.....	Helium
Auxiliary.....	Nitrogen

Table 3.6. GC/ECD Split-Flow Conditions

Column Flow.....	2.36 ml/min
Split Exhaust Flow.....	27.44 ml/min
Aux + Column Flow. ....	46.08 ml/min
Split Ratio.....	215

Figure 3.2. GC/ECD Chromatogram.



RT (min)	Compound
2.95	CHCl <sub>3</sub>
3.14	1,1,1-TCA
3.27	CT
3.46	TCE
4.75	PCE
10.20	m-DCB
10.43	p-DCB
11.65	o-DCB

RUN # 43

RT	AREA	TYPE	AR/HT	AREA
2.40	775260	↓ BP	0.217	12.68
2.73	278860	↓ PV	0.151	4.56
2.95	401020	VB	0.083	6.56
3.14	485670	PV	0.054	7.94
3.27	1972700	VB	0.055	32.28
3.46	348970	BB	0.057	5.71
4.33	13349	PB	0.062	0.21
4.75	1387200	PB	0.068	22.70
5.87	41692	BB	0.080	0.68
10.20	89206	BV	0.122	1.46
10.43	137200	VB	0.124	2.24
11.65	178580	BB	0.141	2.92

Flow splitting was not necessary for the FID analysis. GC operation and flow conditions are listed in Tables 3.7 and 3.8. The FID chromatogram can be found in Figure 3.3.

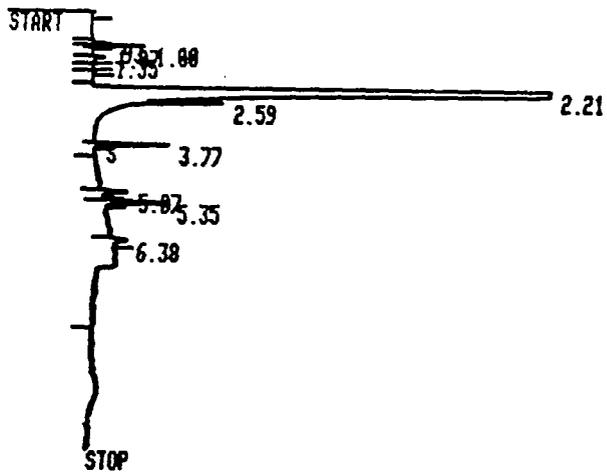
Table 3.7. GC/FID Operating Conditions.

Inlet Temperature.....	200°C
Detector Temperature.....	200°C
Oven Temperature.....	70°C
Column Type.....	DBWAX Megabore
Carrier Gas.....	Helium

Table 3.8. GC/FID Flow Conditions.

Column Flow.....	4.92 ml/min
Air Flow.....	250 ml/min
Hydrogen Flow.....	30 ml/min

Figure 3.3. GC/FID Chromatogram.



RT (min)	Compound
2.59	Benzene
3.77	Toluene
5.07	m-Xylene
5.35	p-Xylene
6.38	o-Xylene

RUN # 20  
 WORKFILE ID: B  
 WORKFILE NAME:

AREA%	RT	AREA	TYPE	AR/HT	AREA%
	0.93	3006	D PB	0.018	0.014
	1.00	15568	D PP	0.020	0.070
	1.07	5620	D PB	0.021	0.025
	1.35	9916	PB	0.053	0.045
	2.21	2.1943E+07	SPB	0.047	98.888
	2.59	45213	TBB	0.040	0.204
	3.77	60844	BB	0.054	0.274
	5.07	24085	PB	0.064	0.109
	5.35	64545	BB	0.071	0.291
	6.38	19007	BB	0.091	0.089

TOTAL AREA= 2.2191E+07  
 MUL FACTOR= 1.0000E+00

## CHAPTER 4

### RESULTS AND DISCUSSION

The original objective of this project was the analysis of municipal landfill leachate samples for more than 30 organic chemicals as well as the non-specific parameters of TOX and TOC. Resulting data were to be compared with the landfill input data obtained by the Department of Anthropology. The purpose was to determine the extent to which the landfilling of household hazardous wastes threatens underlying groundwater. In addition, samples from a number of landfills were expected to be delivered at three month intervals. A time-sequenced study of landfill leachates was anticipated to result in the elucidation of the biodegradation pathways within the landfills for the compounds of interest. Unfortunately, a series of problems arose, resulting in a limited data base. Although the data base is small, it does provide useful information regarding the effects of various landfill operating procedures on the organic carbon and organic halide concentrations in leachate.

Table 4.1 contains TOX and TOC results for Landfills A through E. GC results for Landfills A through E can be found in Table 4.2. Due to sample procurement difficulties, only one sample was analyzed for each landfill. Also, the number of compounds of interest were reduced from 30 to 12.

#### Landfill A versus E

Landfills A and E are both urban sanitary landfills. Landfill A serves a population base of 300,000 people, has been in operation for 10 years, and accepts commercial and residential wastes (ratio is approximately 50/50). Landfill E serves a population base of 557,000, has been in operation for 12 years, and accepts only residential wastes. Table 4.3 contains a more detailed comparison of the two landfills. The annual waste loads are about the same for each landfill.

Both the TOX and TOC values for Landfill A are very high, 1870 ug/l and 2065 mg/l, respectively. The TOX and TOC values for Landfill E are 472 ug/l and 181 mg/l, respectively.

The large variation between the landfills is due mainly to the differences in operation. Wastes deposited in Landfill A are covered with soil daily. In contrast, wastes discarded in Landfill E are shredded and left uncovered. As

Table 4.1. TOX and TOC Results for Landfills A - E.

<u>Landfill</u>	Parameters			
	<u>TOX</u> <u>(ug/l)</u>	<u>NPOX</u> <u>(ug/l)</u>	<u>POX</u> <u>(ug/l)</u>	<u>TOC</u> <u>(mg/l)</u>
A	1870	496	1374	2065
B	655	51	604	7.53
C	266	156	110	189.9
D	305	290	15	125.4
E	472	462	10	180.9

Table 4.2. GC Results for Landfills A - E.

<u>Compounds</u>	<u>Concentration (ug/l)</u>				
	<u>A</u>	<u>B</u>	<u>C</u>	<u>D</u>	<u>E</u>
<u>Aliphatic</u>					
Chloroform	8.52	--	--	--	ND
1,1,1-Trichloroethane	2.52	--	--	--	2.56
Carbon Tetrachloride	0.10	--	--	--	0.37
Trichloroethylene	1.65	--	--	--	ND
Tetrachloroethylene	17.7	--	--	--	ND
Chlorobenzene	ND	--	--	--	ND
m-Dichlorobenzene	ND	--	--	--	ND
p-Dichlorobenzene	130.7	--	--	--	ND
o-Dichlorobenzene	65.8	--	--	--	ND
<u>Aromatic</u>					
Benzene	--	ND	ND	ND	ND
Toluene	—	ND	--	--	ND
m-Xylene	--	ND	ND	ND	ND
p-Xylene	--	ND	ND	ND	ND
o-Xylene	--	ND	ND	ND	ND

ND = Not Detectable

-- = Not Available

Table 4.3. Comparison of Landfills A and E

<u>Characteristics</u>	Landfill	
	<u>A</u>	<u>E</u>
Annual Waste Volume (tons)	276,230	249,600
Type of Landfill	Municipal	Municipal
Population Base	300,000	557,000
Type of Wastes	Res/Comm (50/50)	Residential
Leachate Collection System	8" PVC	Open Ditch
Leachate Volume	1.25 L/sec	3 Million Gallons
Leachate Treatment	Anaerobic	ClO <sub>2</sub>
Sampling Point	Trtmt Plant	Ditch
Years in Operation	10	12
Annual Precipitation	53.6"	65"
Landfill Liner	3' of Clay	None
HHW Collection Programs	June, 1988	None
Recycling Programs	None	None
Landfill Operation	Daily Cover	Shredded w/o Cover

discussed in Chapter 2, Ham and Bookter (1982) studied the decomposition of refuse in all modes of landfill operation. Their results for the decomposition of shredded, uncovered refuse indicate that a highly contaminated leachate is initially produced. This phase is followed by rapid stabilization to consistently low concentrations of contaminants. Although the inputs to the landfills differ, the data are in agreement with Ham and Bookter's (1982) findings.

Annual precipitation levels are comparable for the two landfills. The area in which Landfill A is located receives approximately 53.6 inches of rain and snow each year. Landfill E covers about 65 acres and is situated in an area that receives about 65 inches of rainfall annually. Because the wastes in Landfill E are left uncovered, all of the rain water enters the landfill and is considered leachate. The leachate is collected through a series of open ditches and is pumped to an oxidation pond for treatment with chlorine dioxide. Presently, Landfill E does not have the necessary discharge permits and all leachate remains on-site. An estimation of the flow through the landfill is possible by multiplying the annual rainfall by the landfill area. As a result, approximately 115 million gallons of leachate are produced each year.

Landfill A is an engineered landfill and is operated

in a more typical fashion than Landfill E. It is designed to minimize water infiltration and is lined with 3 feet of clay. Leachate is collected at the bottom of the landfill via 8 inch, perforated PVC pipes buried in gravel-filled trenches. Following collection, the leachate is pumped at a rate of 1.25 l/sec to an up-flow, anaerobic biological reactor for treatment. Assuming that the flow is constant, approximately 10.4 million gallons of leachate are produced and exit the landfill annually.

The TOX values, TOC values, and flowrates stated above are supported by the nature of the leachates. Landfill A leachate was very foul-smelling and highly colored (orange). In contrast, the Landfill E leachate had almost no odor and was only slightly colored.

A rough mass flowrate can be calculated for the TOX and TOC of each landfill and allows for a direct comparison. These values are determined by multiplying the TOX and TOC by the volumetric liquid flowrates. The resulting mass flowrates of TOX and TOC for Landfill A are 162 lb/yr and 89.5 tons/yr, respectively. Values for Landfill E are 452 lb/yr and 86.6 tons/yr, TOX and TOC, respectively. The TOC mass flowrate for the two landfills are quite similar, while the mass flowrate of TOX for Landfill E is about 2.8 times greater than the value for Landfill A. Since the landfills receive approximately the same amount of waste annually, the

TOC data is reasonable. The TOX results were somewhat unexpected since Landfill E receives only residential wastes and Landfill A receives 50% residential and 50% commercial wastes. However, Wilson (1985) argues that available data suggest that, in some cases, residential solid wastes have higher concentrations of hazardous substances than commercial wastes. In addition, there may be some wide variation in the discard patterns for the two areas. Unfortunately, input data is available for Landfill E only.

An effort was made to identify specific compounds in the leachates. Seven of the nine volatile, chlorinated compounds of interest were identified in Landfill A leachate using the GC/ECD method described in Chapter 3. However, only 1,1,1-trichloroethane (1,1,1-TCA) and carbon tetrachloride were found at detectable levels in Landfill E leachate. Also, the POX value is 73.5% of the TOX for Landfill A and 2% of the TOX for Landfill E. The low POX level and the absence of most of the volatile compounds in Landfill E is probably due to volatilization in the open ditches of the leachate collection system. Other possible explanations include dilution due to large amounts of rainwater entering the system and/or more rapid biodegradation due to the increased moisture content.

Only about 12% of TOX is in the form of identifiable compounds for the Landfill A leachate and 0.6% for Landfill

E. These percentages may be higher since the leachates were not analyzed for the chlorophenols or pesticides. Kringstad and Lindstrom (1984) found that only 4% of the TOX for paper mill wastes were identifiable compounds.

Landfill A leachate was not analyzed for aromatic compounds (GC/FID). Benzene, toluene, and the xylenes were not detected in Landfill E leachate.

#### Rural Landfills

In addition to the analysis of two municipal landfills, three rural landfills (B, C, and D) were sampled. Each of these landfills serves population bases of about 10,000. The majority of the wastes deposited in these landfills is residential, although the landfills do accept some agricultural wastes. There was no odor or color associated with any of the leachates. As evidenced by the TOC data (Table 4.1), the wastes in Landfill B are more stabilized than those in the other landfills. However, a large portion of these wastes are associated with organically-bound halides, suggesting the deposition of products containing hazardous ingredients. The larger fractions of NPOX for Landfills C and D are probably due to the leachate collection system and the point of sampling, allowing for compound volatilization. Due to equipment failures, GC data was not collected for any of the

landfills. Detailed information with respect to landfill operation and leachate collection systems are not available for Landfills B, C, and D.

#### Landfill F

Solid samples were collected from Landfill F by personnel from the Anthropology Department. The samples were obtained at different depths by drilling three test wells. The locations of the wells are marked on the landfill map (Figure 4.1). Depth and approximate deposition dates were recorded for each sample. The dates were obtained from newspapers and receipts found in the landfill. Additional information was gathered from the methane wells found throughout the landfill (Wells W-1 to W-21). With the exception of solid sample 33-9, solids from the test wells were sieved to obtain fine particles and washed. Although any volatile organic compounds originally present were lost in the washing process, the samples provide information for non-volatile organics. The solid samples were processed and analyzed as described in Chapter 3. Table 4.4 contains the results of the solids analysis. The chemistries of both the interstitial water and the solids were evaluated.

As expected, information from the methane wells indicates that the extent of decomposition is higher in areas of increased moisture content, usually near the bottom

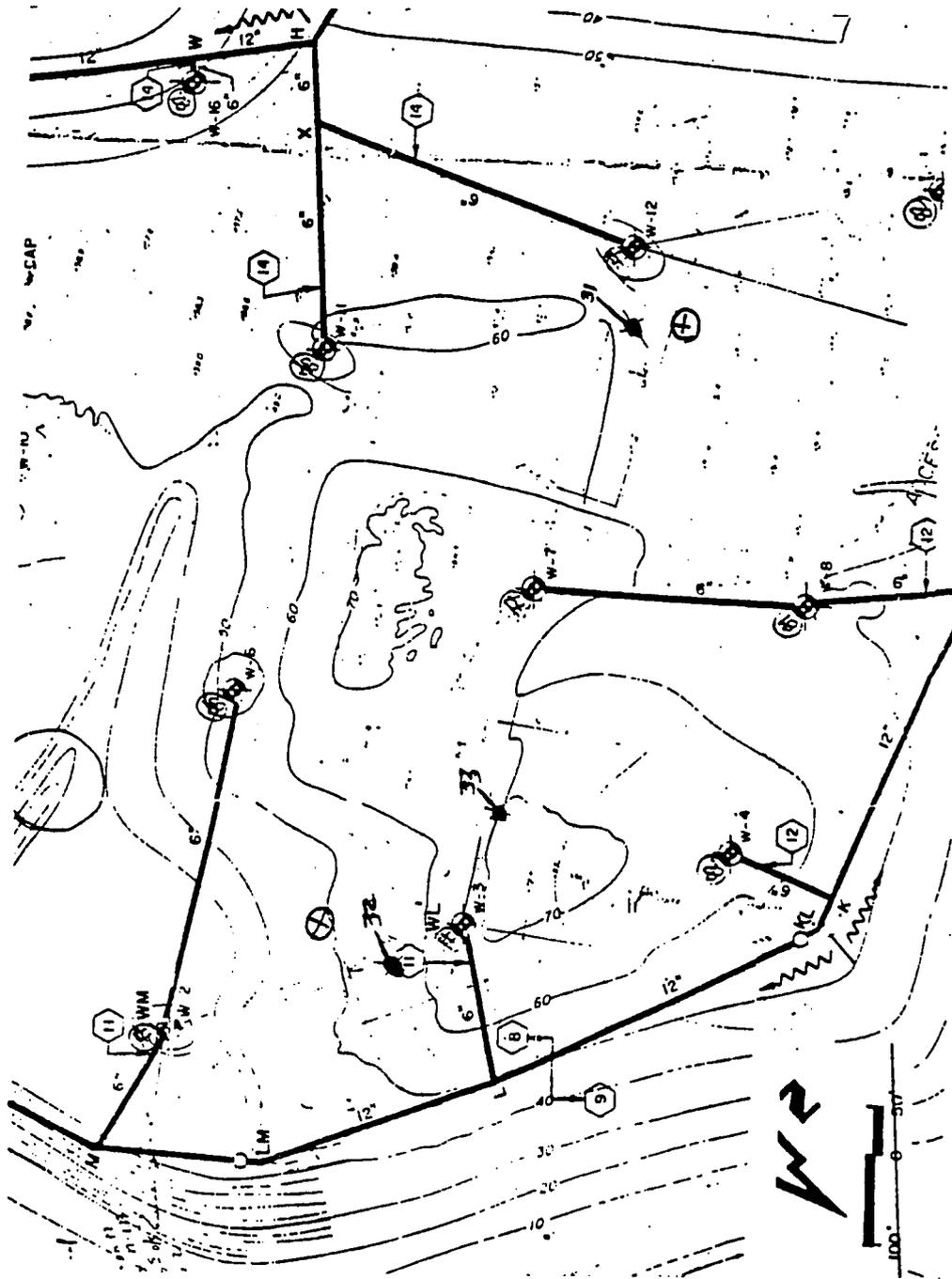


Figure 4.1 Map of Landfill F

Table 4.4 Summary of Solids Analyses for Landfill F

Sample	Location (Feet)	Approx Date of Deposition	Liquid		Solid Fraction						
			TOC (ppm)	NPOX (ug/l)	% VR	% TR	% Water	Sample Wt (mg)	TSX (ug/mg)	SX (ug/g)	K
31-1	9	1982	398	400	5.69	80.9	19.1	70.1	.0297	29.6	74.0
31-5	47	1979	2203	562	11.70	74.2	25.8	156.0	.1800	179.5	319.4
31-7	54	1979	282	604	11.60	71.8	28.2	16.1	2.3360	2,336.0	3,867.0
32-1	5	1986	2266	742	12.70	69.4	30.6	136.6	.1540	154.0	207.6
32-3	21	1981	315	418	4.49	81.3	18.7	200.8	.0140	14.2	34.0
33-2	21.5	1981	242	684	4.96	79.4	20.6	165.0	.1290	128.5	187.9
33-5	46	1980	3115	2416	11.80	72.7	27.3	62.0	.3370	337.4	139.7
33-8	61.5	1978	556	276	16.50	65.0	35.0	47.4	.1220	121.4	439.9
33-9*	63.6	1977	2726	1396	—	—	—	23.6	2.4400	2,439.0	1,747.0

\* unwashed solids

K = Solids/Liquid Partition Coefficient

— Not Available

(and oldest section) of the landfill (See Appendix). Also, temperatures were much higher at these depths due to microbial activity. Moisture contents were also higher near the bottom of test wells 31 and 33.

There are no consistent trends with respect to the liquid TOC and NPOX or the solids halide concentration (SX). Halogenated and non-halogenated organic compounds may have been deposited in pockets within the landfill, resulting in locally high concentrations in different areas of the landfill.

The University of Arizona's Analytical Chemistry Laboratory extracted solid a portion of sample 33-9 with methylene chloride and analyzed it with a GC/MS system. Of the semi-volatile organic contaminants listed in EPA Method 625 (priority pollutants) only bis(2-ethylhexyl)phthalate was detected (approximately 100 ug/l). Other organic compounds detected in the sample were aliphatic hydrocarbons commonly found in motor oil. None of the compounds identified were chlorinated, suggesting that most of the NPOX and SX concentrations are non-identifiable, halogenated organic compounds.

Solid/liquid partition coefficients (K) were calculated for each of the samples by dividing the SX (ug/g) by the liquid NPOX (ug/g), assuming that the solid halides are organically-bound. The K values range from 40 to 3877.

With the exception of well 32, the partition coefficients increase with depth, indicating that all of the readily leachable materials have already been leached and there is a significant amount of organochlorine compounds remaining on the solids. The large SX values suggest that there may be a timed-release of chlorinated chemicals into the leachate for years or decades following the deposition of the wastes. Waste leaching tests such as the RCRA Extraction Procedure (EP) are often used to characterize the leaching of compounds, primarily toxic metals (Francis and White, 1987). However, the use of leaching tests to predict the leaching of organochlorine compounds may yield low estimates of organic halide due to the high fraction of adsorbed compounds.

#### Analytical Problems

The first, and greatest, problem was the procurement of leachate samples. At the start of the project, only one landfill had agreed to send samples. Eventually, four additional landfills, three of which are rural, contributed leachate samples. The fifth landfill (Landfill E), however, was contacted only three months prior to the writing of this report. Difficulties with sampling at the landfills and the subsequent analyses prevented the investigation of more than one sample set from each landfill. Therefore, the

time-sequenced study was not possible. In addition, with the exception of Landfill E, leachate samples were not received for the landfills for which Anthropology obtained input data.

Analytical difficulties were also experienced. Initially, the 5790A GC/ECD was calibrated without flow splitting. However, subsequent studies found that the concentrations found in the samples were beyond the detector's linear range. As a result, the GC had to be re-plumbed in order to achieve a flow-split mode. The GC then had to be recalibrated for all of the compounds of interest. Unfortunately, the resulting response factors began to drift with time, necessitating more frequent calibrations. Presently, the GC must be calibrated daily to obtain accurate response factors. In addition, the repeatability of the instrument has deteriorated. The values obtained are not entirely accurate and should only be considered quantitative indicators of the presence of specific compounds.

In order to positively identify a chemical, the sample should be analyzed using either a GC/MS system, another type of column, or another detector. Since this was not possible, compound identification is only tentative. Pentane extraction and flow-splitting resulted in the presence of some negative peaks which interfered with the

identification of the most volatile compounds such as vinyl chloride. A purge and trap separation system would have eliminated this problem. The complex nature of the landfill leachates also created problems with analysis because of the presence of many interfering compounds.

## CHAPTER 5

### CONCLUSIONS

The following major conclusions can be supported by the data:

1. The comparison of two urban landfills (residential and residential/commercial) yielded differences due in large part to the operation of the landfills. As reported in the literature and supported by data obtained for the urban, residential landfill (E), shredded refuse deposited in an uncovered landfill result in a leachate with much lower contaminant concentrations than leachates from normally operated landfills. In addition, the urban, residential/commercial landfill (A) contained more identifiable volatile organic compounds and POX than the urban/residential landfill. The differences were probably operational, due to volatile losses from the open ditch leachate collection system of the urban, residential landfill.

2. The estimated mass flowrate of TOX was much larger for the urban, residential landfill, supporting the hypothesis that residential wastes may contain higher

concentrations of hazardous materials than commercial wastes.

3. The rural landfills, in which most of the refuse is residential, contain significant concentrations of chlorinated organic compounds (TOX). Again, these results indicate that residential wastes may contain large concentrations of hazardous compounds.

4. Information from the solids analysis and methane wells provides insight into waste decomposition within the landfill. Large concentrations of organochlorine compounds were found to be associated with the solids. This suggests that chlorinated organic compounds may be released slowly over time, creating highly contaminated leachate for years or decades following the closure of the landfill. Also, as stated in the literature, moisture content plays a major role in waste stabilization.

## CHAPTER 6

### RECOMMENDATIONS FOR FUTURE RESEARCH

Because of the difficulties encountered in obtaining and analyzing leachates, only one sample was evaluated for each landfill. As a result, the data yield no information regarding the biological fate of organic chemicals within landfills. One suggestion for future research is that data should be developed over a period of years via analysis of leachates from a large number of landfills at intervals of approximately three months. This would provide enough information to support partial elucidation of biological degradation pathways for environmentally important chemicals. In addition, a GC/MS system should be employed in order to confirm the presence of identifiable compounds.

Important information could also be obtained by correlating leachate quality with landfill inputs (residential contributions of hazardous compounds). This would involve quantifying hazardous waste discard patterns for a landfill and comparing the results with the presence of similar chemicals in leachate. Also, information regarding the relative contributions of hazardous wastes by

residential and commercial sources would be helpful.

Work by other researchers also suggests that the impact of land disposal of residential hazardous wastes on groundwater may indeed be significant (Dunlap et al., 1976; Rathje, 1985; Wilson and Rathje, 1987; and Brown, 1987). The importance of groundwater contamination to human health warrants further, more detailed study in this area.

**APPENDIX**











































## REFERENCES

- Alexander M., "Biodegradation of Organic Chemicals." Environ. Sci. Technol., 1985, 18, 106-111.
- Alexander M. and Lustigman B.K., "Effect of Chemical Structure on Microbial Degradation of Substituted Benzene." J. Agr. Food Chem., 1966, 14, 410-413.
- Baker M.D. and Mayfield C.I., "Microbial and Non-Biological Decomposition of Chlorophenols and Phenol in Soil." Water, Air, and Soil Pollution, 1980, 13, 411-424.
- Barker J.F., Tessmann J.J., Plotz P.E., and Reinhard M., "The Organic Geochemistry of a Sanitary Landfill Leachate Plume." Jour. Contam. Hydr., 1986, 1, 171-189.
- Barrio-Lage G., Parsons F.Z., Nassar R.S., and Lorenzo P.A., "Sequential Dehalogenation of Chlorinated Ethenes." Environ. Sci. Technol., 1986, 20, 96-99.
- Boethling R.S. and Alexander M., "Effect of Concentration of Organic Chemicals on Their Biodegradation by Natural Microbial Communities." Appl. Environ. Microbiol., 1979a, 37, 1211-1216.
- Boethling R.S. and Alexander M., "Microbial Degradation of Organic Compounds at Trace Levels." Environ. Sci. Technol., 1979b, 13, 989-991.
- Bookter T.J. and Ham R.K., "Stabilization of Solid Waste in Landfills." Jour. E.E., 1982, 108, 1089-1100.
- Bouwer E.J. and Wright J.P., "Transformations of Trace Halogenated Aliphatics in Subsurface Microcosms with Anoxic Biofilms." Submitted to Jour. Contam. Hydr., February, 1987.
- Bouwer E.J., and McCarty P.L., "Transformations of 1- and 2-Carbon Halogenated Aliphatic Organic Compounds Under Methanogenic Conditions." Appl. Environ. Microbiol., 1983, 45, 1286-1294.

- Bouwer E.J., Rittman B.E., and McCarty P.L., "Anaerobic Degradation of Halogenated 1-and 2-Carbon Organic Compounds." Environ. Sci. Technol., 1981, 15, 596-599.
- Boyd S.A. and Shelton D.R., "Anaerobic Biodegradation of Chlorophenols in Fresh and Acclimated Sludge." Appl. Environ. Microbiol., 1984, 47, 272-277.
- Boyd S.A., Shelton D.R., Berry D., and Tiedje J.M., "Anaerobic Biodegradation of Phenolic Compounds in Digested Sludge." Appl. Environ. Microbiol., 1983, 46, 50-54.
- Bridle T.R., "The Impact of Hazardous Organics on Sludge Management and Disposal." Environment Canada, Presented at the PCAO/MOE Seminar on Hazardous Substances in Wastewater Toronto, Ontario, 1982
- Bridle T.R., "The Impact of Toxic Organics on Residue Management." Unpublished report, WTC, Burlington, Ontario, 1981.
- Brown E.J., Pignatello J.J., Martinson M.M., and Crawford R.L., "Pentachlorophenol Degradation: a Pure Bacterial Culture and an Epilithic Microbial Consortium." Appl. Environ. Microbiol., 1986, 52, 92-97.
- Brown K.W. and Donnelly K.C., "An Estimation of the Risk Associated with the Organic Constituents of Hazardous and Municipal Waste Landfill Leachate." Texas A&M University, Soil and Crop Sciences Department, n.d.
- Brown T.S., "Household Hazardous Waste: The Unresolved Water Quality Dilemma." Jour. WPCF, 1987, 59, 120-124.
- Brunner W., Staub D., and Leisinger T., "Bacterial Degradation of Dichloromethane." Appl. Environ. Microbiol., 1980, 40, 950-958.
- Brunner D.R. and Carnes R.A., "Characteristics of Percolate of Solid and Hazardous Waste Deposits." Jour. AWWA, 1977, 453-457.
- Bull R.J., "Toxicological Data on Selected Hazardous Chemicals and Possible Extrapolation to Man." EPA-600/0-84-261, 1984.

- Buraneck D., "Construction Guide-Liners." Civil Engineering, 1987, 62-63.
- Chian E.S.K. and DeWalle F.B., "Characterization of Soluble Organic Matter in Leachate." Environ. Sci. Technol., 1977, 11, 158-163.
- Chu J. and Kirsch E.J., "Utilization of Halophenols by a Pentachlorophenol Metabolizing Bacterium." 1972.
- Collins H. and Spillmann P., "Lysimeters for Simulating Sanitary Landfills." Jour. E.E., 1982, 108, 852-863.
- County Sanitation Districts of Los Angeles County, "Control of Infectious, Hazardous and Radioactive Waste Disposal at the Puente Hills Landfill." County Sanitation Districts of Los Angeles County, Los Angeles, 1983.
- Criddle C.S., McCarty P.L., Elliott M.C., and Barker J.F., "Reduction of Hexachloroethane to Tetrachloroethylene in Groundwater." Jour. Contam. Hydr., 1986, 1, 133-142.
- Dawson G.W. and Mercer B.W., Hazardous Waste Management, John Wiley & Sons, 1986.
- DeBont J.A.M., Vorlage M.J.A.W., Hartmans S., and Van Den Tweel W.J.J., "Microbial Degradation of 1,3-Dichlorobenzene." Appl. Environ. Microbiol., 1986, 52, 677-680.
- Deeley G.M., Skierkowski P., and Robertson J.M., "Biodegradation of Phenol in Secondary Sewage and Landfill Leachate Measured by Double-Vial Radiorespirometry." Appl. Environ. Microbiol., 1985, 49, 867-869.
- DeWalle F.B. and Chian E.S.K., "Detection of Trace Organics in Well Water Near a Solid Waste Landfill." Jour. AWWA, 1981, 206-211.
- Dunlap W.J., Shew D.C., Robertson J.M., and Toussaint C.R., "Organic Pollutants Contributed to Groundwater by a Landfill." In Gas and Leachate from Landfills: Formation, Collection, and Treatment, MERL, ORD, EPA-600/9-76-004, Cincinnati, 1976, 96-100.

- Ehrlich G.G., Goerlitz D.F., Godsy E.M., and Hult M.F.,  
"Degradation of Phenolic Contaminants in Ground Water by  
Anaerobic Bacteria: St. Louis Park, Minnesota." Ground  
Water, 1982, 20, 703-710.
- Eicher H.P. and Pauli H., "Heat and Electricity from  
Refuse." Phoenix International, 1986, 5, 6-11.
- Fogel M.M., Taddeo A.R., and Fogel S., "Biodegradation of  
Chlorinated Ethenes by a Methane-Utilizing Mixed  
Culture." Appl. Environ. Microbiol., 1986, 51, 720-724.
- Francis C.W. and White G.H., "Leaching of Toxic Metals from  
Incinerator Ashes." JWPCF, 1987, 59, 979-986.
- Freeze R.A. and Cherry J.A., Groundwater. Prentice-Hall,  
Inc., 1979.
- Geraghty J.J. and Miller D.W., "Status of Groundwater  
Contamination in the U.S." Jour. AWWA, 1978, 162-167.
- Gibson S.A. and Sulfito J.M., "Extrapolation of  
Biodegradation Results to Groundwater Aquifers:  
Reductive Dehalogenation of Aromatic Compounds." Appl.  
Environ. Microbiol., 1986, 52, 681-688.
- Golden Empire Health Systems Agency, "Dispose of Household  
Hazardous Waste Safely: A Report on Sacramento County's  
Household Poison Project." Golden Empire Health Systems  
Agency, Sacramento, n.d.
- Gossett J.M., "Anaerobic Degradation of C<sub>1</sub> and C<sub>2</sub>  
Chlorinated Hydrocarbons." Final Report for the Air  
Force Office of Scientific Research, Washington, D.C.,  
1985.
- Grbic-Galic D. and Vogel T.M., "Transformation of Toluene  
and Benzene by Mixed Methanogenic Cultures." Appl.  
Environ. Microbiol., 1987, 53, 254-260.
- Ham R.K. and Bookter T.J., "Decomposition of Solid Waste in  
Test Lysimeters." Jour. E.E., 1982, 108, 1147-1170.
- Harmsen J., "Identification of Organic Compounds in  
Leachate from a Waste Tip." Water Res., 1983, 17,  
699-705.

- Healy J.B., Jr. and Young L.Y., "Anaerobic Biodegradation of Eleven Aromatic Compounds to Methane." Appl. Environ. Microbiol., 1979, 38, 84-89.
- Healy J.B., Jr. and Young L.Y., "Catechol and Phenol Degradation by a Methanogenic Population of Bacteria." Appl. Environ. Microbiol., 1978, 35, 216-218.
- Jones C.J., Hudson B.C., McGugan P.J., and Smith A.J., "The Leaching of Some Halogenated Organic Compounds from Domestic Waste." Jour. Hazardous Materials, 1977, 2, 227-233.
- Keith L.H. and Telliard W.A., "Priority Pollutants: I-A Perspective View." Environ. Sci. Technol., 1979, 13, 416-423.
- Kemper J.M. and Smith R.B., "Leachate Production by Landfilled Processed Municipal Wastes." n.d.
- Khare M. and Dondero N.C., "Fractionation and Concentration from Water of Volatiles and Organics on High Vacuum System: Examination of Sanitary Landfill Leachate." Environ. Sci. Technol., 1977, 11, 814-819.
- Kim C.J. and Maier W.J., "Acclimation and Biodegradation of Chlorinated Organic Compounds in the Presence of Alternate Substrates." Jour. WPCF, 1986, 58, 157-164.
- Klecka G.M. and Maier W.J., "Kinetics of Microbial Growth on Pentachlorophenol." Appl. Environ. Microbiol., 1985, 49, 46-53.
- Kleopfer R.D., Easley D.M., Haas B.B., and Deihl T.G., "Anaerobic Degradation of Trichloroethylene in Soil." Environ. Sci. Technol., 1985, 19, 277-280.
- Kobayashi H. and Rittman B.E., "Microbial Removal of Hazardous Organic Compounds." Environ. Sci. Technol., 1982, 16, 170A-183A.
- Kringstad K.P. and Lindstrom K., "Spent Liquors from Pulp Bleaching." Environ. Sci. Technol., 1984, 18, 236A-248A.
- Kuwatsuka S. and Igarashi M., "Degradation of PCP in Soils." Soil Sci. Plant Nutr., 1975, 21, 405-414.

- Laderman R., Sarnat C., Moore G., Stanek E., Tuthill R., and Willis C., Toward a Comprehensive Program for Management of Household Hazardous Wastes in Massachusetts, Massachusetts Department of Environmental Quality Engineering (DEQE), 1985.
- Leumann P., "Seepage Water from Urban Landfills." Phoenix International, 1986, 5, 16-19.
- McCarty P.L., Reinhard M., and Rittman B.E., "Trace Organics in Groundwater." Environ. Sci. Technol., 1981, 15, 40-41.
- McDougall W.J., Fusco R.A., and O'Brien R.P., "Containment and Treatment of the Love Canal Landfill Leachate." JWPCF, 1980, 52, 2914-2924.
- Marinucci A.C. and Bartha R., "Biodegradation of 1,2,3- and 1,2,4-Trichlorobenzene in Soil and in Liquid Enrichment Culture." Appl. Environ. Microbiol., 1979, 38, 811-817.
- Metry A.A., The Handbook of Hazardous Waste Management. Technomic: Westport, CT., 1980.
- Minnesota Household Hazardous Wastes Task Force, "Management of Hazardous Wastes Generated by Households: A Report on the Problem and Recommendations for Action." Minnesota Household Hazardous Wastes Task Force, Minnesota, 1985.
- Mikesell M.D. and Boyd S.A., "Complete Reductive Dechlorination and Mineralization of Pentachlorophenol by Anaerobic Microorganisms." Appl. Environ. Microbiol., 1986, 52, 861-865.
- Morrison R.T. and Boyd R.N., Organic Chemistry 2nd Ed., Allyn and Bacon, Inc., 1966.
- Nelson M.J.K., Montgomery S.O., Mahaffey W.R., and Pritchard P.H., "Biodegradation of Trichloroethylene and Involvement of Aromatic Biodegradative Pathways." Appl. Environ. Microbiol., 1987, 53, 949-954.
- Nelson M.J.K., Montgomery S.O., O'Neill E.J., and Pritchard P.H., "Aerobic Metabolism of Trichloroethylene by a Bacterial Isolate." Appl. Environ. Microbiol., 1986, 52, 383-384.

- Office of the Federal Register, National Archives,  
Identification and Listing of Hazardous Wastes. Code of  
Federal Regulations GS4-108:40/Part 190-399/983, 1983.
- Parsons F. and Lage G.B., "Chlorinated Organics in  
Simulated Groundwater Environments." Jour. AWWA, 1985,  
52-59.
- Parsons F., Wood P.R., and DeMarco J., "Transformations of  
Tetrachloroethene and Trichloroethene in Microcosms and  
Groundwater." Jour. AWWA, 1984, 56-59.
- Patterson J.W. and Kodukala P.S., "Biodegradation of  
Hazardous Organic Pollutants." CEP, 1981, 48-55.
- Petrasek A.C., Kugelman I.J., Austern B.M., Pressley T.A.,  
Winslow L.A., and Wise R.H., "Fate of Toxic Organic  
Compounds in Wastewater Treatment Plants." Jour. WPCF,  
1983, 55, 1286-1296.
- Pettyjohn W.A., "Protection of Public Water Supplies from  
Ground-Water Contamination." Center for Environmental  
Research, EPA/625/4-85/016, 1985.
- Petura J.C., "Trichloroethylene and Methyl Chloroform in  
Groundwater: A Problem Assessment." Jour. AWWA, 1981,  
200-205.
- Rathje W.L., Hughes W.W., Wilson D.C., and Nelson D.E., "A  
Characterization of Household Solid Waste." The Garbage  
Project, University of Arizona, 1986.
- Rathje W.L., "Estimation and Evaluation of Hazardous  
Materials in Residential Solid Waste: The Dangers of  
Groundwater Pollution." A Proposal to Environmental and  
Water Quality Engineering, National Science Foundation,  
1985.
- Reineke W. and Knackmuss H., "Microbial Metabolism of  
Haloaromatics: Isolation and Properties of a  
Chlorobenzene-Degrading Bacterium." Appl. Environ.  
Microbiol., 1984, 47, 395-402.
- Reinhard M., Goodman N.L., and Barker J.F., "Occurrence and  
Distribution of Organic Chemicals in Two Landfill  
Leachate Plumes." Environ. Sci. Technol., 1984, 18,  
953-961.

- Saber D.L. and Crawford R.L., "Isolation and Characterization of Flavobacterium Strains that Degrade Pentachlorophenol." Appl. Environ. Microbiol., 1985, 50, 1512-1518.
- Schmidt E., Hellwig M., and Knackmuss H., "Degradation of Chlorophenols by a Defined Mixed Microbial Community." Appl. Environ. Microbiol., 1983, 46, 1038-1044.
- Schomaker N.B., "Current Research on Hazardous Waste Disposal." Municipal Solid Waste: Land Disposal Proceedings, 5th Annual Research Symposium, EPA-600/9-79-0223a, 1979, 9-21.
- Schraa G., Boone M.L., Jetten M.S.M., Van Neerven A.R.W., Colberg P.J., and Zehnder A.J.B., "Degradation of 1,4-Dichlorobenzene by Alcaligenes sp." Appl. Environ. Microbiol., 1986, 52, 1374-1381.
- Shuster K.A., Comments...in Proceedings of USEPA Working Meeting Concerning Requirements for Monitoring and Management of Hazardous Waste at RCRA Subtitle D Facilities., 1985.
- Standard Methods for the Examination of Water and Waste-water, 15th Ed., American Public Health Association, U.S.A., 1980.
- Strand S.E. and Shippert L., "Oxidation of Chloroform in an Aerobic Soil Exposed to Natural Gas." Appl. Environ. Microbiol., 1986, 52, 203-205.
- Sulfita J.M., Robinson J.A., and Tiedje J.M., "Kinetics of Microbial Degradation of Haloaromatic Substrates in Methanogenic Environments." Appl. Environ. Microbiol., 1983, 45, 1466-1473.
- Tabak H.H., Quave S.A., Mashni C.I., and Barth E.F., "Biodegradability Studies with Organic Priority Pollutant Compounds." Jour. WPCF, 1981, 53, 1503-1518.
- Taylor B.F., Campbell W.L., and Chinoy I., "Anaerobic Degradation of the Benzene Nucleus by a Facultatively Anaerobic Microorganism." Jour. Bacteriol., 1970, 102, 430-437.

- Tchobanoglous G., Theisen H., and Eliassen R., Solid Wastes: Engineering Principles and Management Issues. McGraw-Hill, 1977.
- Theme Introduction - "Safeguarding Groundwater." Jour. AWWA, 1986, 61.
- Thom N.S. and Agg A.R., "The Breakdown of Synthetic Organic Compounds in Biological Processes." Proc. R. Soc. Lond., 1975, 189, 347-357.
- Tittlebaum M.E., "Organic Carbon Content Stabilization through Landfill Leachate Recirculation." Jour. WPCF, 1982, 54, 428-433.
- Trussell A.R., Umphres M.D., Leong L.Y.C., and Trussell R.R., "Precise Analysis of Trihalomethanes." JAWWA, 1979, 385-396.
- Vogel T.M., Criddle C.S., and McCarty P.L., "Transformation of Halogenated Compounds." Environ. Sci. Technol., 1987, 21, 722-736.
- Vogel T.M. and Grbic-Galic D., "Incorporation of Oxygen from Water into Toluene and Benzene during Anaerobic Fermentative Transformation." Appl. Environ. Microbiol., 1986, 52, 200-202.
- Vogel T.M. and McCarty P.L., "Biotransformation of Tetrachloroethylene to Trichloroethylene, Dichloroethylene, Vinyl Chloride, and Carbon Dioxide under Methanogenic Conditions." Appl. Environ. Microbiol., 1985, 49, 1080-1083.
- Wanielista M.P., Yousef Y.A., Taylor J.S., and Cooper C.D., Engineering and the Environment., Wadsworth, Inc., 1984.
- Watanabe I., "Isolation of Pentachlorophenol Decomposing Bacteria from Soil." Soil Sci. Plant Nutr., 1973, 19, 109-116.
- Wilson B.H., Smith G.B., and Rees J.F., "Biotransformations of Selected Alkylbenzenes Halogenated Aliphatic Hydrocarbons in Methanogenic Aquifer Material: A Microcosm Study." Environ. Sci. Technol., 1986, 20, 997-1002.

- Wilson D.C. and Rathje W.L., "Recent Research on Hazardous Materials in Household Solid Wastes in Three Cities." Prepared for the Conference on Solid Waste Management and Materials Policy, New York City, N.Y., 1987a.
- Wilson D.C., Rathje W.L., and Hughes W.W., "Garbage Project Investigates Hazardous Household Wastes." SAWARA, 1987b, 12-13.
- Wilson D.C., "The Implications of Behavioral Aspects on the Production and Discard of Household Hazardous Wastes." Masters Thesis submitted to the Department of Anthropology, University of Arizona, 1985.
- Wilson J.T. and Wilson B.H., "Biotransformation of Trichloroethylene in Soil." Appl. Environ. Microbiol., 1985, 49, 242-243.
- Wilson J.T., McNabb J.F., Wilson B.H., and Noonan M.J., "Biotransformation of Selected Organic Pollutants in Ground Water." Dev. Ind. Microbiol., 1983, 25, 225-233.
- Wilson J.T., Enfield C.G., Dunlap W.J., Cosby R.L., Foster D.A., and Baskin L.B., "Transport and Fate of Selected Organic Pollutants in a Sandy Soil." J. Environ. Qual., 1981, 10, 501-506.
- Young L.Y. and Rivera M.D., "Methanogenic Degradation of Four Phenolic Compounds." Water Res., 1985, 19, 1325-1332.
- Zeyer J., Kuhn E.P., and Schwarzenbach R.P., "Rapid Microbial Mineralization of Toluene and 1,3-Dimethylbenzene in the Absence of Molecular Oxygen." Appl. Environ. Microbiol., 1986, 52, 944-947.