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Description, Properties, and Degradation of Selected Volatile Organic Compounds Detected in Ground Water— A Review of Selected Literature

Open-File Report 2006-1338

U.S. Department of the Interior
U.S. Geological Survey

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Contents

Figures

Tables

Abbreviations and Acronyms

ATSDR	Agency for Toxic Substances and Disease Registry
BTEX	benzene, toluene, ethylbenzene, xylenes
CA	chloroethane
CAA	Clean Air Act
CB	chlorobenzene
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CDC	Centers for Disease Control
CO_2	carbon dioxide
CSIA	compound-specific isotope analysis
CTET	carbon tetrachloride
CVOC	chlorinated volatile organic compounds
DCA	dichloroethane
11-DCA	1,1-dichloroethane
12-DCA	1,2-dichloroethane
12-DCB	1,2-dichlorobenzene
13-DCB	1,3-dichlorobenzene
14-DCB	1,4-dichlorobenzene
DCE	dichloroethene
12-cDCE	*cis*-1,2-dichloroethene
12-tDCE	*trans*-1,2-dichloroethene
DNA	deoxyribonucleic acid
DO	dissolved oxygen
FDA	U.S. Food and Drug Administration
gVOC	volatile gasoline compounds
H	Henry's Law constant
IUC	International Union of Chemistry
IUPAC	International Union of Pure and Applied Chemistry
K_{oc}	soil organic carbon partition coefficient
K_{ow}	octanol-water partition coefficient
MTBE	methyl *tert*-butyl ether
NAPL	non-aqueous phase liquid
ORD	Office of Research and Development
PCA	tetrachloroethane
PCE	tetrachloroethene
PLFA	phospholipid fatty acid
RCRA	Resource Conservation and Recovery Act
RFG	Reformulated Gasoline program
RNA	ribonucleic acid
SMA	signature metabolites analysis
TBA	*tert*-butyl alcohol
TCA	trichloroethane
112-TCA	1,1,2-trichloroethane
TCB	trichlorobenzene
123-TCB	1,2,3-trichlorobenzene
124-TCB	1,2,4-trichlorobenzene
TCE	1,1,2-trichloroethene
TEA	terminal electron acceptor
124-TMB	1,2,4-trimethylbenzene
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VC	vinyl chloride
VOC(s)	volatile organic compound(s)

Conversion Factors

Multiply	By	To obtain
microgram per liter (µg/L)	$6.243 \cdot 10^8$	pound per cubic foot
microgram per liter (µg/L)	1×10^{-3}	milligram per liter (mg/L)
milligram per liter (mg/L)	$6.243 \cdot 10^5$	pound per cubic foot
gram mole per cubic meter (g mol/m^3)	6.243×10^5	pound per cubic foot
kiloPascal (kPa)	$9.8692 \cdot 10^{-3}$	standard atmosphere

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$°F = (1.8 \times °C) + 32$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$°C = (°F - 32)/1.8$$

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (µg/L).

Description, Properties, and Degradation of Selected Volatile Organic Compounds Detected in Ground Water— A Review of Selected Literature

By Stephen J. Lawrence

Abstract

This report provides abridged information describing the most salient properties and biodegradation of 27 chlorinated volatile organic compounds detected during ground-water studies in the United States. This information is condensed from an extensive list of reports, papers, and literature published by the U.S. Government, various State governments, and peer-reviewed journals. The list includes literature reviews, compilations, and summaries describing volatile organic compounds in ground water. This report cross-references common names and synonyms associated with volatile organic compounds with the naming conventions supported by the International Union of Pure and Applied Chemistry. In addition, the report describes basic physical characteristics of those compounds such as Henry's Law constant, water solubility, density, octanol-water partition (log K_{ow}), and organic carbon partition (log K_{oc}) coefficients. Descriptions and illustrations are provided for natural and laboratory biodegradation rates, chemical by-products, and degradation pathways.

Introduction

The presence of volatile organic compounds (VOCs) in ground water is a major concern to all who use ground water as a drinking water source because many of these compounds can adversely affect human health. Likewise, concern about VOCs in ground water is shared by State and Federal regulatory agencies responsible for protecting the ground-water resource from contaminants and for protecting human health. This report is prepared in cooperation with The Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services (ATSDR) and provides under one cover an abridged description of selected properties, and biodegradation information published in academic and government literature. In addition, the report cross references commonly used names with a generally accepted international naming convention for 27 VOCs frequently detected in ground water.

Purpose and Scope

The purpose of this report is to (1) list 27 VOCs frequently detected in ground water, (2) cross-reference common VOC names and synonyms associated with the naming conventions supported by the International Union of Pure and Applied Chemistry (IUPAC), (2) describe the basic chemical properties of selected VOCs by subclass, and (3) describe the various pathways and chemical by-products associated with the degradation of selected VOCs in ground water. The goal of the report is not to supplant previously published literature reviews on VOCs in ground water, but rather to condense that information, and information from other papers, into a "digest" or abridged document that describes only the most salient and generally accepted scientific information regarding nomenclature, properties, and degradation paths for 27 VOCs detected in ground water in the United States.

Available Literature Addressing Volatile Organic Compounds

The information for this report is condensed from selected academic and government literature published within the last 30 years (1975–2006) that describe laboratory and field experiments and ground-water studies of VOC. The 27 VOCs described in this report are among the VOCs commonly detected in aquifers and ground-water sources of drinking water in the United States (Zogorski and others, 2006).

The amount of academic, government, and popular literature addressing volatile organic compounds in ground water is vast and scattered among paper and electronic venues, some published and some unpublished. Reviewing this literature would be a daunting task and certainly beyond the scope for this report. Fortunately, a number of published papers and reports are readily available that reviewed, compiled, or summarized the properties, chemistry, or degradation paths of VOCs in ground water. Citations for several of these compilations and the information summarized are listed in table 1. Unless a report provided newly synthesized information, all facts or interpretations described in summary reports or literature reviews are cited using the primary source reported in the publication.

Table 1.   List of selected publications providing literature reviews and summaries of volatile organic compound degradation and behavior in ground water.

[BTEX, benzene, toluene, ethyl benzene, xylenes; PCE, tetrachloroethylene; VOC, volatile organic compound; MTBE, methyl *tert*-butyl ether]

Publication citation	Subject
Aronson and others, 1999	Aerobic biodegradation rates for BTEX, PCE
Aronson and Howard, 1997	Anaerobic biodegradation rates for BTEX, naphthalene, styrene, chlorinated aliphatic compounds
Azadpour-Keeley and others, 1999	Microbial degradation and natural attenuation of VOCs in ground water
Beek, 2001	Natural degradation processes and rates for VOCs
Christensen and others, 2000	Oxidation-reduction conditions in ground-water contaminant plumes
Howard and others, 1991	Environmental degradation rates of chemical compounds
Vogel and others, 1987	Chemical reactions involved in VOC degradation
Vogel, 1994	Biodegradation of chlorinated solvents
Washington, 1995	Hydrolysis rates of dissolved VOCs
Wiedemeier and others, 1998	Natural attenuation of VOCs in ground water
Wilson and others, 2005	Natural attenuation of MTBE in ground water

Although a large amount of the citations in the academic or government literature or on the Internet are published through reliable agencies or entities, some citations reference obscure sources or sources that are generally inaccessible to the public. Because of this issue, the literature cited in this report is confined to the body of work that is available and easily accessed through mainstream academic journals, State or Federal agencies using various libraries, or online databases on the Internet.

In general, the academic literature focuses on VOCs from two perspectives: (1) analytical and physical chemistry and (2) environmental occurrence, transport, and fate. The analytical and physical chemistry literature provide information on the physico-chemical properties of VOCs—such as experimental and computed Henry's Law constants, fugacity, water solubility, organic carbon solubility, octanol-water partition coefficients, partitioning among various physical phases (that is, gas, liquid, solid), experimentally derived and computer-simulated reaction rates, microbial degradation, and reaction types (that is, hydrolysis, oxidation-reduction, dehalogenation). The literature describing the environmental occurrence, transport, and fate of VOCs in ground water primarily deals with site-specific contamination, and the abiotic and microbial transformation, attenuation, and degradation observed in ground water. Some of those documents attempt to confirm or apply in vitro (laboratory microcosm) results to contaminated areas in situ and many are written from a remediation perspective.

The local, State, territorial, and U.S. Government literature on VOCs in ground water typically encompass issues important to its citizenry in an environmental or regulatory context. This literature commonly involves larger geographical areas than those of a typical academic paper. With some exceptions, publications of the U.S. Geological Survey (USGS) are less attentive to site-specific contamination in ground water and more attentive to contamination issues of areal, regional, or national importance (Grady, 2003; Hamlin and others, 2002, 2005; Moran, 2006; Zogorski and others,

2006). One exception is the USGS Toxic Substances Hydrology Program (*http://toxics.usgs.gov/*), which routinely publishes USGS reports and scientific articles in refereed journals. The primary focus of that program is site-specific fate and transport studies involving trace metal and organic (including VOCs) contamination in ground water.

In contrast to USGS reports, the literature produced by the U.S. Environmental Protection Agency (USEPA) primarily focuses on applying scientific results to regulatory and remediation issues in compliance with the Clean Air and Clean Water Acts and their amendments, and those statutes underwriting the Resource Conservation and Recovery Act (RCRA) and the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA). The Office of Research and Development (ORD) is the scientific research arm of the USEPA that routinely publishes reports addressing the fate and transport of VOCs in ground water within a regulatory context. Moreover, each State and territory within the United States publishes scientific and regulatory literature regarding the occurrence of VOCs in ground water and its transport, fate, and impact on human and ecological health that are specific to those States. Other government agencies such as the Centers for Disease Control (CDC) and the ATSDR publish printed and electronic literature relating the potential human-health effects of VOCs in drinking water.

Paper and electronic literature published by the popular press, such as sports and outdoor magazines, and publications of environmental groups such as the Sierra Club and the Nature Conservancy typically use academic and government publications as sources for their articles. These articles are intended to educate their readers and members on environmental contamination and regulatory issues. With the exception of literature published by the popular press, the literature selected and used in this report spans the venues described in preceding paragraphs. Most of this literature, particularly the environmental fate and transport literature, focuses on fewer than 30 VOCs in ground water.

Naming Conventions and Descriptions of Volatile Organic Compounds in Ground Water

The compounds addressed in this report belong to the class of organic chemicals called volatile organic compounds (VOCs). Depending on the source, a VOC has two definitions—one within a physico-chemical context and the other within a regulatory context. The physico-chemical definition of a VOC as stated by Australia's National Pollutant Inventory is: *Any chemical compound based on carbon chains or rings (and also containing hydrogen) with a vapor pressure greater than 2 mm of mercury (mm Hg) at 25 degrees Celsius (°C). These compounds may contain oxygen, nitrogen and other elements. Substances that are specifically excluded are: carbon dioxide, carbon monoxide, carbonic acid, carbonate salts, metallic carbides and methane* (Australian Department of Environment and Heritage, 2003). A physico-chemical definition of VOC as explicit as that from Australia and originating in the United States was not found during extensive Internet searches. In the United States, the regulatory definition of VOC is provided by the USEPA under the Clean Air Act and published in the Code of Federal Regulations—*Volatile organic compound (VOC) means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions* (U.S. Environmental Protection Agency, 2000a).

Among the academic, government, and popular literature, it is common to find a confusing variety of names used to identify VOCs. For example, tetrachloroethene (IUPAC name) is also known as perchloroethylene, PCE, and tetrachloroethylene (table 2). Furthermore, some compounds are identified using the various brand names under which they are sold. The name used to identify any particular compound may depend on a number of variables. These variables include the area or region where the compound is used (for example, Europe, United States, Northeastern United States, and so forth), the type of publication referring to the compound (journal article, administrative report, government report, or popular magazine), the popularity of that name in recently published literature, and the profession of the person using the name (that is, analytical chemist, environmental scientist, environmental toxicologist, biologist or ecologist, organic chemist, journalist, farmer, and so forth). Because of the numerous name variations for VOCs, attempts to merge information from a variety of venues "on-the-fly" for a particular compound are tedious, confusing, and fraught with error. As early as the late 1800s, chemists and others recognized the need for a consistent naming convention for all chemical compounds.

In 1889, an international consortium of chemists, encouraged by the need for a consistent naming convention for all chemical compounds, formed the International Union of Chemistry (IUC). During 1892 at a meeting in Geneva, Switzerland, the IUC was formalized with a goal to create a system of rules for naming chemical compounds (Geneva Rules). The Geneva Rules established the foundation, the framework, and the initial rules for a consistent, international naming convention for all chemical compounds, including the complex organic compounds. Since this first meeting, the IUC has evolved into the International Union of Pure and Applied Chemistry (IUPAC), an organization responsible for creating new rules and keeping established rules current (Brown and LeMay, 1977, p. 723). The history of the IUPAC organization and the Geneva Rules establish provenance for the formal names given to the VOCs described in this report.

Under the IUPAC naming convention, VOCs are commonly assigned to two general groups: (1) aliphatic hydrocarbons (alkanes, alkenes), and (2) aromatic hydrocarbons (Brown and LeMay, 1977). An alkane is a straight chain or cyclic (ring-like; such as cycloalkane) structure that consists of carbon-carbon and carbon-hydrogen single bonds. A chlorinated alkane also contains at least one chlorine-carbon single bond. A chemical bond is the electrical attraction between two atoms, one that has a negative charge and the other a positive charge. In organic compounds, these chemical bonds are covalent, meaning that two bonded atoms share electrons (Brown and LeMay, 1977). An alkene is typically a straight-chain structure that contains at least one carbon-carbon double bond. A chlorinated alkene also contains at least one chlorine-carbon single bond. These double bonds indicate stronger covalent bonds between two carbon atoms and impart more stability to the compound than the single bond in an alkane compound.

In contrast to the aliphatic compounds, aromatic compounds are those with alternating carbon-carbon single and double bonds arranged in a ring structure. Benzene is the most commonly recognized aromatic compound (Brown and LeMay, 1977). Chlorinated aromatic compounds also contain one chlorine-carbon single bond (for example, chlorobenzene). Aromatic compounds are typically more resistant to degradation (more stable) than the alkane and alkene compounds.

The aliphatic and the aromatic hydrocarbons are commonly subgrouped even further based on the presence of attached halogen atoms (chlorine as chloro, bromine as bromo, or fluorine as fluoro) or functional groups including, but not limited to, alkyl radicals. The VOC subgroups include the alkyl benzenes (such as methylbenzene), chlorinated alkanes (such as 1,2-dichloroethane), chlorinated alkenes (such as 1,1-dichloroethene), and the chlorinated aromatics (such as 1,2-dichlorobenzene; table 2). The alkyl radicals are the lower molecular weight alkanes minus one hydrogen atom (table 3) and are highly reactive compounds that can easily displace a hydrogen atom on another molecule. Halogenated or alkylated aromatics such as chlorobenzene or toluene are more easily degraded than benzene in aerobic and anaerobic ground water because the stability of the benzene ring is reduced and the ring is weakened (Borden and others, 1997). Adding halides or alkyl groups to the ring structure disperses the electrical charges from the carbon-carbon bonds on the ring and weakens that bond.

Table 2.   Names and synonyms of volatile organic compounds commonly detected in ground water.

[IUPAC, International Union of Pure and Applied Chemistry; CAS, Chemical Abstract Services; —, not applicable]

IUPAC name[1]	Common or alternative name (synonyms)[2]	Other possible names[2]	Predominant source	CAS number[1]
Alkyl benzenes				
1,2-dimethylbenzene	*o*-xylene	The X in BTEX, dimethyltoluene, Xylol	gasoline	95-47-6
1,3-dimethylbenzene	*m*-xylene			108-38-3
1,4-dimethylbenzene	*p*-xylene			106-42-3
ethylbenzene	—	The E in BTEX, Ethylbenzol, phenyl-ethane	gasoline	100-41-4
methylbenzene	toluene	The T in BTEX, phenylmethane, Methacide, Toluol, Antisal 1A	gasoline	108-88-3
1,2,4-trimethylbenzene	pseudocumene	pseudocumol, asymmetrical trimethyl-benzene	gasoline	95-63-6
Aromatic hydrocarbons				
benzene	—	The B in BTEX, coal naphtha, 1,3,5-cyclohexatriene, mineral naphtha	gasoline	71-43-2
naphthalene	naphthene	—	gasoline, organic synthesis	91-20-3
stryrene	vinyl benzene	phenethylene	gasoline, organic synthesis	100-42-5
Ethers				
2-methoxy-2-methylpropane	methyl *tert*-butyl ether, MTBE	*tert*-butyl methyl ether	fuel oxygenate	1634-04-4
Chlorinated alkanes				
chloroethane	ethyl chloride, monochloroethane	hydrochloric ether, muriatic ether	solvent	75-00-3
chloromethane	methyl chloride	—	solvent	74-87-3
1,1-dichloroethane	ethylidene dichloride	—	solvent, degreaser	75-34-3
1,2-dichloroethane	ethylidene dichloride	glycol dichloride, Dutch oil	solvent, degreaser	107-06-2
tetrachloromethane	carbon tetrachloride	perchloromethane, methane tetrachloride	solvent	56-23-5
1,1,1-trichloroethane	methyl chloroform	—	solvent, degreaser	71-55-6
Chlorinated alkenes				
chloroethene	vinyl chloride	chloroethylene, monochloroethene, monovinyl chloride (MVC)	organic synthesis, degradation product	75-01-4
1,1-dichloroethene	1,1-dichloroethylene, DCE	vinylidene chloride	organic synthesis, degradation product	75-35-4
cis-1,2-dichloroethene	*cis*-1,2-dichloroethylene	1,2 DCE, Z-1,2-dichloroethene	solvent, degradation product	156-59-2
trans-1,2-dichloroethene	*trans*-1,2-dichloroethylene	1,2 DCE, E-1,2-dichloroethene	solvent, degradation product	156-60-2
dichloromethane	methylene chloride	—	solvent	74-09-2
Chlorinated alkenes				
tetrachloroethene	perchloroethylene, PCE, 1,1,2,2-tetrachloroethylene	ethylene tetrachloride, carbon dichloride, PERC®, PERK®	solvents, degreasers	127-18-4
1,1,2-trichloroethene	1,1,2-trichloroethylene, TCE	acetylene trichloroethylene	solvents, degreasers organic synthesis	79-01-6
Chlorinated aromatics				
chlorobenzene	monochlorobenzene	benzene chloride, phenyl chloride	solvent, degreaser	108-90-7
1,2-dichlorobenzene	o-dichlorobenzene	ortho dichlorobenzol	organic synthesis	95-50-1
1,2,3-trichlorobenzene	1,2,6-trichlorobenzene	—	organic synthesis	87-61-6
1,2,4-trichlorobenzene	1,2,4-trichlorobenzol	—	organic synthesis	102-82-1

[1]International Union of Pure and Applied Chemistry, 2006
[2]U.S. Environmental Protection Agency, 1995

The simplest IUPAC rules for naming organic chemicals are those for the alkane compounds. First, the compound is named for the longest carbon-carbon (C-C) chain in the compound. If the compound contains a halogen or a branching alkyl group, then each carbon in the compound is numbered starting at the end that is closest to the halogen or alkyl group. The longest carbon chain may include the original branching alkyl group and result in a branching alkyl group with a different carbon position and name. After identifying the longest C-C chain in the compound, the numerical position of the alkyl group or halogen, if any, on a particular carbon is determined. The alkyl group is named based on the number of carbon atoms it contains corresponding to a name in the alkane series (table 3). To illustrate the IUPAC naming process, consider the following example: before the IUPAC rules, a seven-carbon alkane (septane) with an ethyl functional group (table 3) on the second carbon would be named 2-ethyl septane (fig. 1). Under IUPAC rules, however, the longest carbon chain in this example begins at the first carbon in the ethyl group. This new carbon chain contains eight carbon atoms rather than the original seven and is now called octane. Moreover, the octane compound now has a methyl group branching from its third carbon. Therefore, the new IUPAC name is 3-methyl octane (fig. 1).

Figure 1. Generic and International Union of Pure and Applied Chemistry (IUPAC) naming conventions for the same aliphatic compound.

Table 3. The first four members of the straight-chain alkane series and associated alkyl radical.[1]

[IUPAC, International Union of Physical and Applied Chemistry; C, carbon atom; H, hydrogen atom; n, normal; t, tertiary; °C, degrees Celsius]

Alkane series condensed formula (IUPAC name)[2]	Number of carbon atoms in chain	Alkyl group, condensed formula (IUPAC name)[2]	Boiling point (°C)
CH_4 (*methane*)	1	CH_3-- [methyl]	−161
CH_3CH_3 (*ethane*)	2	CH_3CH_2-- [ethyl]	−89
$CH_3CH_2CH_3$ (*propane*)	3	$CH_3CH_2CH_2$-- [n-propyl]	−44
		--$CHCH_3CH_3$ [isopropyl]	
$CH_3CH_2CH_2CH_3$ (*butane*)	4	$CH_3CH_2CH_2CH_2$-- [n-butyl] CH_3 CH_3C-- [t-butyl] CH_3	−0.5

Under IUPAC naming conventions, higher molecular weight alkanes are not typically present as alkyl radicals in volatile organic compounds

[1]Brown and LeMay, 1977, tables 24.1, 24.2
[2]International Union of Pure and Applied Chemistry, 2006

Sources of Volatile Organic Compounds Detected in Ground Water

A relatively large amount of literature exists that describes VOCs in ground water at specific, known areas of contamination. Few documents, however, describe VOC contamination in a regional or national context. One report by Arneth and others (1989) lists the top 15 VOCs detected in ground water near landfills in the United States and in Germany (table 4). This list shows that the VOCs contaminating ground water near landfills are similar in both countries. Most of these VOCs are chlorinated solvents (CVOCs) and gasoline compounds (gVOCs). Furthermore, the frequency of VOCs detected in representative studies completed on national, regional, and site-specific scales in the United States show a remarkable similarity to those in table 4 (table 5; Delzer and Ivahnenko, 2003; Moran, 2006; Zogorski and others, 2006). Although the number of VOCs analyzed in ground-water samples is large for national and regional studies, the most commonly detected compounds, primarily CVOCs and gVOCs, are similar to those at site-specific studies completed at U.S. Department of Defense installations (table 6). The 10 most commonly detected VOCs in the studies summarized in tables 5 and 6 are methyl *tert*-butyl ether (MTBE), tetrachloroethene (PCE), 1,1,2-trichloroethene (TCE), methylbenzene (toluene), 1,1,1-trichloroethane (111-TCA), benzene, *cis*-1,2-dichloroethene (12-cDCE), 1,1-dichloroethane (11-DCA), *trans*-1,2-dichloroethene (12-tDCE), the dimethylbenzenes (*m*-, *o*-, *p*-xylenes)

Sources of Chlorinated Alkanes

The chlorinated solvents within the alkane group are listed in table 2. The CVOCs are typically used in the manufacturing of industrial, chemical, electronic, and consumer goods (Smith and others, 1988; U.S. Environmental Protection Agency, 2005b). In addition, these compounds are heavily used as solvents in cleaning and degreasing products. For example, 111-TCA is used as a solvent for adhesives and in metal degreasing, pesticides, textile processing, cutting fluids, aerosols, lubricants, cutting oil formulations, drain cleaners, shoe polishes, spot cleaners, printing inks, and stain repellents.

Carbon tetrachloride (CTET) was used as feedstock for the production of chlorofluorocarbon gases, such as dichlorodifluoromethane (F-12) and trichlorofluoromethane (F-11), which were used as aerosol propellants in the 1950s and 1960s (Holbrook, 1992). During 1974, the U.S. Food and Drug Administration (FDA) banned the sale of CTET in any product used in the home and the USEPA regulated the use of chlorofluorocarbon gases as aerosols or propellants. By 2000, CTET production for nonfeedstock purposes was phased-out completely.

Table 4. Volatile organic compounds ranked by those frequently detected in ground water near landfills and hazardous waste dumps in the United States and the Federal Republic of Germany.[1]

[IUPAC, International Union of Physical and Applied Chemistry; —, not applicable]

	United States of America		Federal Republic of Germany	
Rank	**IUPAC name[2]**	**Common or alternative name**	**IUPAC name[2]**	**Common or alternative name**
1	1,1,2-trichloroethene	1,1,2-trichloroethylene, TCE	tetrachloroethene	perchloroethylene, tetrachloroethylene, PCE
2	tetrachloroethene	perchloroethylene, tetrachloroethylene, PCE	1,1,2-trichloroethene	1,1,2-trichloroethylene, TCE
3	*cis*-1,2-dichloroethene	*cis*-1,2-DCE	*trans*-1,2-dichloroethene	*trans*-1,2-DCE
4	benzene	benzene	trichloromethane	—
5	chloroethene	vinyl chloride	1,1-dichloroethene	1,1-dichloroethylene, DCE
6	trichloromethane	—	dichloromethane	methylene chloride
7	1,1,1-trichloroethane	methyl chloroform	1,1,1-trichloroethane	methyl chloroform
8	dimethylbenzene	xylene	1,1-dichloroethane	ethylene dichloride
9	*trans*-1,2-dichloroethene	*trans*-1, 2-dichloroethylene	1,2-dichloroethane	ethylene dichloride
10	methylbenzene	toluene	phenol	—
11	ethylbenzene	ethylbenzene	acetone	dimethyl ketone, 2-propanone, and beta-ketopropane
12	dichloromethane	methylene chloride	toluene	methyl benzene
13	dichlorobenzene, total	—	bis-(2-ethylhexyl)-phthalate	—
14	chlorobenzene	chlorobenzene	benzene	benzene
15	tetrachloromethane	carbon tetrachloride	chloroethene	vinyl chloride

[1]Arneth and others, 1989, p. 399
[2]International Union of Pure and Applied Chemistry, 2006

Table 5. Volatile organic compounds detected in regional and national ground-water studies in the United States.

[μg/L, micrograms per liter; [12], percentage of samples above the analytical reporting limit; <, less than; ND, not detected above analytical reporting level]

Rank	Statewide, ground water in Wisconsin[1]	Ground water in the Santa Ana River Basin, California[2]	Ground-water and drinking-water supply wells in the United States (concentrations greater than 0.2 μg/L)[3]		
			Aquifer studies[4]	Domestic water-supply wells[5]	Public water-supply wells[6]
1	dichloromethane [16.3]	1,1,2-trichloroethene (TCE) [12]	tetrachloroethene (PCE) [3.7]	2-methoxy-2-methylpropane (MTBE) [2.9]	2-methoxy-2-methylpropane (MTBE) [5.4]
2	1,1-dichloroethane [13.6]	1,1,1-trichloroethane [10.5]	2-methoxy-2-methylpropane (MTBE) [2.8]	tetrachloroethene (PCE) [2.0]	tetrachloroethene (PCE) [5.3]
3	*cis*-1,2-dichloroethene, 1,1-dichloroethane [13.6]	tetrachloroethene (PCE) [9.1]	1,1,2-trichloroethene (TCE) [2.6]	1,1,1-trichloroethane [1.4]	1,1,2-trichloroethene (TCE) [4.3]
4	1,1,2-trichloroethene (TCE) [13.3]	1,1-dichloroethene [5.7]	methylbenzene [1.9]	methylbenzene [1.0]	1,1,1-trichloroethane [2.2]
5	methylbenzene [11.6]	2-methoxy-2-methylpropane (MTBE) [5.3]	1,1,1-trichloroethane [1.7]	chloromethane [.97]	1,1-dichloroethane [2.0]
6	tetrachloroethene (PCE) [9.8]	*cis*-1,2-dichloroethene [4.3]	chloromethane [1.1]	1,1,2-trichloroethene (TCE) [.92]	*cis*-1,2-dichloroethene [1.5]
7	benzene [8.5]	methylbenzene [3.8]	*trans*-1,2-dichloroethene [0.91]	dichloromethane [.67]	1,1-dichloroethene (DCE) [1.3]
8	chloroethene [8.0]	1,1-dichloroethane [2.9]	dichloromethane [0.89]	1,2,4-trimethylbenzene [.32]	*trans*-1,2-dichloroethene [1.0]
9	1,3- and 1,4-dimethylbenzenes [7.9]	benzene [1.4]	1,1-dichloroethane [0.86]	1,1-dichloroethane [.29]	methylbenzene [1.0]
10	1,1,1-trichloroethane [7.8]	1,2-dimethylbenzene [1.4]	1,1-dichloroethene [0.66]	benzene, 1,2-dichloroethane [.21]	tetrachloromethane [.73]
11	ethylbenzene [7.6]	1,3- and 1,4-dimethylbenzene [1.4]	benzene [.63]	tetrachloromethane [.21]	1,3- and 1,4-dimethylbenzene [0.60]
12	1,2,4-trimethylbenzene [7.1]	*trans*-1,2-dichloroethene [<1]	1,2,4-trimethylbenzene [.63]	1,1-dichloroethene [.21]	1,2-dichloroethane [.56]
13	1,2-dimethylbenzene [6.8]	dichloromethane [<1]	1,2-dichloroethane [.47]	total xylenes [0.21]	1,2-dimethylbenzene [.48]
14	chloromethane [6.7]	ethylbenzene [<1]	*cis*-1,2-dichloroethene [.42]	*cis*-1,2-dichloroethene [.18]	benzene, dichloromethane, ethylbenzene [.46]
15	naphthalene [6.5]	naphthalene [<1]	total xylenes [.38]	naphthalene [.15]	chloromethane [.38]
16	chloroethane [6.3]	tetrachloromethane [<1]	tetrachloromethane [.31]	ethylbenzene [.12]	1,2,4-trimethylbenzene [0.32]
17	chlorobenzene [4.3]	1,2,4-trimethylbenzene [<1]	chloroethane [.29]	chloroethane [.093]	chloroethane [.28]
18	1,2-dichloroethane [3.7]	chlorobenzene [ND]	chloroethene [.26]	chloroethene [.083]	vinyl benzene [.19]
19	*trans*-1,2-dichloroethene [3.3]	chloroethane [ND]	ethylbenzene [.26]	*trans*-1,2-dichloroethene [.045]	chlorobenzene, 1,2-dichlorobenzene [.18]
20	1,1-dichloroethene (DCE) [2.6]	chloromethane [ND]	chlorobenzene [.17]	chlorobenzene [.042]	chloroethene [.18]
21	1,2-dichlorobenzene [2.4]	chloroethene [ND]	naphthalene [.16]	1,2-dichlorobenzene [.042]	naphthalene [.10]
22	2-methoxy-2-methylpropane (MTBE) [2.3]	1,2-dichlorobenzene [ND]	1,2-dichlorobenzene [.12]	vinyl benzene [ND]	1,2,4-trichlorobenzene [ND]
23	tetrachloromethane [1.8]	1,2-dichloroethane [ND]	vinyl benzene [ND]	1,2,4-trichlorobenzene [ND]	1,3-dichlorobenzene [ND]
24	vinyl benzene [1.2]	1,2,3-trichlorobenzene [ND]	1,2,3-trichlorobenzene [ND]	1,1,2-trichloroethane [ND]	1,1,2-trichloroethane [ND]
25	1,2,4-trichlorobenzene, 1,1,2-trichloroethane [<1.0]	vinyl benzene [ND]		1,2,3-trichlorobenzene [ND]	1,2,3-trichlorobenzene [ND]

[1] 1,305–4,086 samples (Wisconsin Department of Natural Resources, 2000)
[2] 9–112 samples (Hamlin and others, 2002)
[3] Zogorski and others, 2006
[4] 1,710–3,498 samples
[5] 1,190–1,208 samples
[6] 828–1,096 samples

Table 6.   Volatile organic compounds detected in ground-water case studies at selected U.S. Department of Defense installations.

[[43.3], percentage of samples with a detected concentration; ND, not detected above analytical reporting level]

Rank	Dover Air Force Base, Maryland[1]	U.S. Army Armament Research and Development Center, Picatinny, New Jersey, 1958–85[2]	U.S. Naval Undersea Warfare Center, Washington, D.C.[3]	Wright-Patterson Air Force Base, Ohio, 1993–94[4]
1	2-methoxy-2-methylpropane (MTBE) [25.5]	1,1,2-trichloroethene (TCE) [58.5]	chloroethene [64]	1,1,2-trichloroethene (TCE) [12.5]
2	*cis*-1,2-dichloroethene [21.7]	tetrachloroethene (PCE) [24.9]	*cis*-1,2-dichloroethene [59]	tetrachloroethene (PCE) [5.8]
3	1,1,2-trichloroethene (TCE) [20.3]	*trans*-1,2-dichloroethene (DCE) [18.6]	*trans*-1,2-dichloroethene [44.8]	1,1,1-trichloroethane [2.3]
4	tetrachloroethene (PCE) [13.7]	1,1,1-trichloroethane [16.8]	1,1,2-trichloroethene (TCE) [40.4]	chloromethane [2.3]
5	benzene [10.4]	1,1-dichloroethane [9.6]	total BTEX compounds [40.1]	*cis*- and *trans*-1,2-dichloroethene [1.2]
6	methylbenzene [6.6]	*cis*-1,2-dichloroethene (DCE) [9.6]	1,1-dichloroethane [37.2]	chloroethene [.9]
7	dimethylbenzenes (*m*-, *p*-xylene) [3.7]	methylbenzene (toluene) [4.4]	chloroethane [33.9]	dichloromethane [.9]
8	ethylbenzene [2.3]	benzene [2.6]	1,1-dichloroethane [31.3]	methylbenzene [.6]
9	chloroethene [ND]	—	tetrachloroethene (PCE) [9.6]	benzene [.3]
10	—	—	1,1,1-trichloroethane [6.9]	chloroethane [.3]
11	—	—	—	tetrachloromethane [.3]

[1] 212 samples (Barbaro and Neupane, 2001; Guertal and others, 2004)

[2] 607 samples (Sargent and others, 1986)

[3] 121–179 samples (Dinicola and others, 2002)

[4] 343 samples (Schalk and others, 1996)

Chemical manufacturing is the largest use of 11-DCA and 1,2-dichloroethane (12-DCA). Both compounds serve as an intermediate during the manufacture of chloroethene (vinyl chloride, VC), 111-TCA, and to a lesser extent high-vacuum rubber. Both DCA isomers also are used as a solvent for plastics, oils, and fats, and in cleaning agents and degreasers (Agency for Toxic Substances and Disease Registry, 1990c, p. 51; 2001, p. 160). About 98 percent of the 12-DCA produced in the United States is used to manufacture VC. Smaller amounts of 12-DCA are used in the synthesis of vinylidene chloride, TCE, PCE, aziridines, and ethylene diamines, and in other chlorinated solvents (U.S. Environmental Protection Agency, 1995).

The compound 111-TCA was initially developed as a safer solvent to replace other chlorinated and flammable solvents. The compound is used as a solvent for adhesives (including food packaging adhesives) and in metal degreasing, pesticides, textile processing, cutting fluids, aerosols, lubricants, cutting oil formulations, drain cleaners, shoe polishes, spot cleaners, print-ing inks, and stain repellents, among other uses (Agency for Toxic Substances and Disease Registry, 2004, p. 181). The other TCA isomer, 1,1,2-trichloroethane (112-TCA), has limited use as a common, general-use solvent but is used in the production of chlorinated rubbers (Archer, 1979). In some cases, 112-TCA may be sold for use in consumer products (Agency for Toxic Substances and Disease Registry, 1989, p. 59).

Before 1979, the single largest use of chloroethane was in the production of tetraethyl lead. As recently as 1984, the domestic production of tetraethyl lead accounted for about 80 percent of the chloroethane consumed in the United States; whereas about 20 percent was used to produce ethyl cellulose, and used in solvents, refrigerants, topical anesthetics, and in the manufacture of dyes, chemicals, and pharmaceuticals. Since the 1979 ban on tetraethyl lead in gasoline and its subsequent phase out in the mid-1980, the production of chloroethane in recent years has declined substantially in the United States (Agency for Toxic Substances and Disease Registry, 1998, p. 95).

Sources of Chlorinated Alkenes and Benzenes

The chlorinated alkenes listed in table 2 include two of the most widely used and distributed solvents in the United States and Europe. These solvents, PCE and TCE, also are among the most common contaminants in ground water (tables 5 and 6). The textile industry uses the largest amount of PCE during the processing, finishing of raw and finished textiles, and for industrial and consumer dry cleaning (U.S. Environmental Protection Agency, 2005b, Web page: *http://www.epa.gov/opptintr/chemfact/f_perchl.txt*, accessed May 23, 2006). Most of the TCE used in the United States is for vapor degreasing of metal parts and some textiles (U.S. Environmental Protection Agency, 2005b, Web page: *http://www.epa.gov/OGWDW/dwh/t-voc/trichlor.html*, accessed May 23, 2006). Other uses of PCE and TCE include manufacturing of pharmaceuticals, other organic compounds, and electronic components, and in paint and ink formulations (Smith and others, 1988).

Four chlorinated benzenes commonly detected in ground-water contamination studies include chlorobenzene (CB), 1,2-dichlorobenzene (12-DCB), and two isomers of trichlorobenzene, 1,2,3-trichlorobenzene (123-TCB) and 1,2,4-trichlorobenzene (124-TCB; tables 5 and 6). Chlorobenzene is commonly used as a solvent for pesticide formulations, in the manufacturing of di-isocyanate, as a degreaser for automobile parts, and in the production of nitrochlorobenzene. Solvent uses accounted for about 37 percent of chlorobenzene consumption in the United States during 1981 (Agency for Toxic Substances and Disease Registry, 1990a, p. 45). The compound 12-DCB is used primarily to produce 3,4-dichloroaniline herbicides (Agency for Toxic Substances and Disease Registry, 1990b, p. 263). The two trichlorobenzene isomers are primarily used as dye carriers in the textile industry. Other uses include septic tank and drain cleaners, the production of herbicides and higher chlorinated benzenes, as wood preservatives, and in heat-transfer liquids (U.S. Environmental Protection Agency, 2005b, Web page: *http://www.epa.gov/OGWDW/dwh/t-voc/t-124-tric.html*, accessed May 23, 2006).

Sources of Gasoline Compounds

At a basic level, gasoline production is simply a process of sequential distillations that separate, by vaporization, volatile hydrocarbons from crude oil. Typically, these hydrocarbons are the lower molecular weight compounds that commonly are the most volatile compounds in crude oil. More advanced methods such as heat "cracking" are used to breakdown the complex aromatic hydrocarbons in crude oil into smaller, more volatile compounds that are easily distilled. Once the hydrocarbons are in a vapor form, a condensation process cools the vapor and the resulting liquid is collected for further refining. The hydrocarbon composition of gasoline depends on the source of the crude oil used, the refining process, the refiner, the consumer demand, the geographic location of the refinery, and the distributional area of the gasoline (Harper and Liccione, 1995).

Gasoline is typically a mixture of various hydrocarbons that include alkanes, cycloalkanes, cycloalkenes, akylbenzenes, and aromatic compounds, and some oxygenated alcohol additives (table 7). Many of the hydrocarbons in gasoline are additives and blending agents intended to improve the performance and stability of gasoline. These additives typically consist of oxygenates such as methyl *tert*-butyl ether (MTBE), ethanol, or methanol, antiknock agents, antioxidants, metal deactivators, lead scavengers, antirust agents, anti-icing agents, upper-cylinder lubricants, detergents, and dyes. At the end of the refining process, finished gasoline commonly contains more than 150 separate compounds; however, some blends may contain as many as 1,000 compounds (Harper and Liccione, 1995).

Table 7.   Major organic compounds in a typical gasoline blend.[1]

[n, C_5-C_{13} carbon chain; MTBE, methyl *tert*-butyl ether; TBA, *tert*-butyl alcohol]

Major compounds	Percent composition by weight
n-alkanes	17.3
Branched alkanes	32.0
Cycloalkanes	5.0
Olefins	1.8
Aromatic hydrocarbons	30.5
Benzene	3.2
Toluene	4.8
Ethylbenzene	1.4
Xylenes	6.6
Other benzenes	11.8
Other aromatics	2.7
Other possible additives	

Octane enhancers: MTBE, TBA, ethanol
Antioxidants: N, N'-dialkylphenylenediamines, di- and tri-alkylphenols, butylated methyl, ethyl and dimethyl phenols
Metal deactivators: various N, N'-disalicylidene compounds
Ignition controllers: tri-o-cresylphosphate (TOCP)
Detergents/dispersants: alkylamine phosphates, poly-isobutene amines, long-chain alkyl phenols, alcohols, carboxylic acids, and amines
Corrosion inhibitors: phosphoric acids, sulfonic acids, carboxylic acids

[1]Harper and Liccione, 1995

BTEX Compounds (Benzene, Toluene, Ethylbenzene, and Xylene)

About 16 percent of a typical gasoline blend consists of BTEX compounds (collectively, benzene, toluene, ethylbenzene, and three xylene compounds; table 7). Of the different components contained in gasoline, BTEX compounds are the largest group associated with human-health effects. Because of the adverse impact on human health, BTEX compounds are typically the fuel components analyzed in ground-water samples collected from fuel-contaminated aquifers. Furthermore, three minor components of gasoline: naphthalene, vinyl benzene (styrene), and 1,2,4-trimethylbenzene (124-TMB) are commonly detected along with BTEX compounds and MTBE in contaminated ground water (tables 5 and 6). Although the individual BTEX compounds are widely used as solvents and in manufacturing (Swoboda-Colberg, 1995), gasoline leaks from underground storage tanks and distribution pipelines is the primary contributor of BTEX contamination in ground water (U.S. Environmental Protection Agency, 2000b; U.S. Environmental Protection Agency, 2005a).

Methyl *Tert*-butyl Ether

Methyl *tert*-butyl ether (MTBE; IUPAC 2-methoxy-2-methylpropane) is a gasoline additive within the class of fuel oxygenates. Oxygenates are organic compounds that enrich gasoline with oxygen to improve the combustion efficiency of gasoline and reduce carbon monoxide emissions in vehicle exhaust. Since the late 1980s, gasoline shipped to areas of the United States that fall under the Reformulated Gasoline (RFG) and Oxygenated Fuel (Oxyfuel) Programs of the Clean Air Act (CAA) and its amendments has contained oxygenates (Moran and others, 2004). Moreover, 30 percent of the gasoline used in the United States since 1998 contained oxygenates in compliance with RFG requirements while 4 percent of the gasoline used complied with the Oxyfuel requirements (U.S. Environmental Protection Agency, 1998). Reformulated gasoline contains about 11 percent MTBE by volume (Delzer and Ivahnenko, 2003).

Basic Properties of Selected Volatile Organic Compounds

Volatile organic compounds have a number of unique properties that both inhibit and facilitate ground-water contamination. Tables 8 through 12 list basic physical properties of 27 VOCs detected in ground water. Physical properties unique to each compound typically are governed by the number of carbons and the covalent bonding in the compound, the number and location of chlorine atoms, and the number, location and type of alkyl groups. The physical properties addressed in this report include the Henry's Law constant (H), water solubility, density, octanol-water partitioning (Log K_{ow}), and organic carbon partitioning (Log K_{oc}) of the non-aqueous phase liquid (NAPL). Models that estimate the fate and transport of VOCs in ground water depend on the accuracy and reliability of physical property measurements. Some models, such as the fugacity models, also use these properties to predict a compound's rate of movement into and out of environmental compartments (soil, water, air, or biota; Mackay, 2004). Predicting the environmental fate of a compound in ground water depends on data that quantifies: (1) the compound's tendency to volatilize (gaseous phase), (2) to dissolve in water (aqueous phase), (3) to float on or sink beneath the water surface, (4) to dissolve in or sorb to other organic compounds (including natural organic matter), and (5) the compound's affinity for ionically charged surfaces such as clay or soil particles. Fugacity models of varying complexity are in common use and rely on the physical properties of these compounds to estimate plume migration and persistence, and to guide the remediation of contaminated ground water (Mackay and others, 1996; Institute for Environmental Health, 2004; Saichek and Reddy, 2005).

Degradation of Selected Volatile Organic Compounds in Ground Water

Under specific conditions, most organic compounds degrade at a particular rate during a given length of time. The speed of the degradation depends on the presence and activity of microbial consortia (bacteria and fungi species), environmental conditions (temperature, aquifer materials, organic matter content), and the availability and concentration of carbon sources (primary substrate) available to the microbial consortia. The primary substrate can be a VOC or organic carbon found dissolved in water or sorbed to aquifer sediments. When primary substrate concentrations are small, the microbial population is small and biodegradation rates are relatively slow. As the substrate concentrations increase, the microbial population grows and the degradation rate increases concomitantly (Bradley and Chapelle, 1998). The microbial population will grow until they reach a maximum growth rate (Aronson and others, 1999).

The degradation of VOCs in ground water is a transformation of a parent compound to different compounds commonly called daughter products, degradates, or degradation by-products. These transformations can be grouped into two general classes: (1) those that require an external transfer of electrons, called oxidation-reduction reactions; and (2) those that do not involve a transfer of electrons, called substitutions and dehydrohalogenations (Vogel and others, 1987). Table 13 summarizes these reactions. Oxidation-reduction reactions are the dominant mechanisms driving VOC degradation and most of these reactions are catalyzed by microorganisms (Wiedemeier and others, 1998; Azadpour-Keeley and others, 1999). Substitution reactions that can remove chlorine atoms, such as hydrolysis, can degrade some chlorinated alkanes (trichloroethane) to nonchlorinated alkanes (ethane) with or without a microbial population catalyzing the reaction (Vogel

and others, 1987; Olaniran and others, 2004). Typically, the polychlorinated compounds (for example, PCE and TCE) easily degrade under anaerobic conditions and are less mobile in soil and aquifer materials than the di- and mono-chlorinated compounds (fig. 2). Degradation pathways are illustrated in figures 3 through 19 for a subset of the compounds listed in table 2. These figures are modifications of pathways described in the University of Minnesota's biodegradation/biocatalysis database (Ellis and others, 2006) accessible via the Internet at *http://umbbd.msi.umn.edu*, accessed May 23, 2006.

Table 8.   Henry's Law constants for selected volatile organic compounds detected in ground water.

[IUPAC, International Union of Physical and Applied Chemistry; kPa, kilopascals; m^3, cubic meter; mol, mole; $°$C, degrees Celsius; —, not applicable]

IUPAC name[1]	Common or alternative name[2]	Henry's Law[3] constant (H) (kPa m^3 mol^{-1} at 25$°$C)
tetrachloromethane	carbon tetrachloride	2.99
chloroethene	vinyl chloride, chloroethylene	2.68
1,1-dichloroethene	1,1-dichloroethylene, DCE	2.62
1,1,1-trichloroethane	methyl chloroform	1.76
tetrachloroethene	perchloroethylene, tetrachloroethylene, PCE	1.73
chloroethane	ethyl chloride, monochloroethane	[4]1.11
1,1,2-trichloroethene	1,1,2-trichloroethylene, TCE	1.03
trans-1,2-dichloroethene	*trans*-1,2-DCE, *trans*-1,2-dichloroethylene	.960
chloromethane	methyl chloride	[5].920
ethylbenzene	—	.843
1,3-dimethylbenzene	*m*-xylene	.730
1,4-dimethylbenzene	*p*-xylene	.690
methylbenzene	toluene	.660
1,1-dichloroethane	1,1-ethylidene dichloride	.630
benzene	—	.557
1,2-dimethylbenzene	*o*-xylene	.551
1,2,4-trimethylbenzene	pseudocumene	.524
cis-1,2-dichloroethene	*cis*-1, 2-dichloroethylene, *cis*-1,2-DCE	.460
chlorobenzene	monochlorobenzene	.320
stryrene	vinyl benzene	.286
1,2,4-trichlorobenzene	1,2,4-trichlorobenzol	.277
1,2,3-trichlorobenzene	1,2,6-trichlorobenzene	.242
1,2-dichlorobenzene	o-dichlorobenzene	.195
1,2-dichloroethane	1,2-ethylidene dichloride, glycol dichloride	.140
1,1,2-trichloroethane	methyl chloroform	.092
2-methoxy-2-methylpropane	methyl *tert*-butyl ether, MTBE	.070
naphthalene	naphthene	.043

Increasing tendency for a compound to move from the water phase to the vapor phase when in equilibrium with pure water

[1]International Union of Pure and Applied Chemistry, 2006

[2]U.S. Environmental Protection Agency, 1995

[3]Lide, 2003

[4]Gossett, 1987

[5]National Center for Manufacturing Sciences, 2006

Table 9. Water-solubility data for selected volatile organic compounds detected in ground water.

[IUPAC, International Union of Pure and Applied Chemistry; mg/L, milligrams per liter; °C, degrees Celsius; —, not applicable]

IUPAC name[1]	Common or alternative name[2]	Water solubility[3] (mg/L at 25°C)
2-methoxy-2-methylpropane	methyl *tert*-butyl ether, MTBE	36,200
1,2-dichloroethane	1,2-ethylidene dichloride, glycol dichloride	8,600
chloromethane	methyl chloride	[4]5,320
chloroethane	ethyl chloride, monochloroethane	[5]6,710
cis-1,2-dichloroethene	*cis*-1,2-dichloroethylene	6,400
1,1-dichloroethane	1,1-ethylidene dichloride	5,000
1,1,2-trichloroethane	methyl chloroform	4,590
trans-1,2-dichloroethene	*trans*-1,2-dichloroethylene	4,500
chloroethene	vinyl chloride, chloroethylene	2,700
1,1-dichloroethene	1,1-dichloroethylene, DCE	2,420
benzene	—	1,780
1,1,1-trichloroethane	methyl chloroform	1,290
1,1,2-trichloroethene	1, 1, 2-trichloroethylene, TCE	1,280
tetrachloromethane	carbon tetrachloride	1,200
methylbenzene	toluene	531
chlorobenzene	—	495
stryrene	vinyl benzene	321
tetrachloroethene	perchloroethylene, tetrachloroethylene, PCE	210
1,2-dimethylbenzene	*o*-xylene	207
1,4-dimethylbenzene	*p*-xylene	181
1,3-dimethylbenzene	*m*-xylene	161
ethylbenzene	—	161
1,2-dichlorobenzene	o-dichlorobenzene	147
1,2,4-trimethylbenzene	pseudocumene	57
1,2,4-trichlorobenzene	1,2,4-trichlorobenzol	37.9
naphthalene	naphthene	[6]31.0
1,2,3-trichlorobenzene	1,2,6-trichlorobenzene	30.9

Increasing amount of non-aqueous phase liquid that can dissolve in water

[1]International Union of Pure and Applied Chemistry, 2006

[2]U.S. Environmental Protection Agency, 1995

[3]Lide, 2003

[4]National Center for Manufacturing Sciences, 2006

[5]Horvath, 1982

[6]Lyman, 1982

Table 10. Density of selected volatile organic compounds detected in ground water compared to the density of water at 20 degrees Celsius.

[IUPAC, International Union of Pure and Applied Chemistry; g/cm, grams per centimeter; °C, degrees Celsius; —, not applicable]

IUPAC name[1]	Common or alternative name[2]	Density[3] (g/cm^3, 20°C)
1,2,3-trichlorobenzene	1,2,6-trichlorobenzene	[4]1.690
tetrachloroethene	perchloroethylene, tetrachloroethylene, PCE	1.623
tetrachloromethane	carbon tetrachloride	1.594
1,1,2-trichloroethene	1,1,2-trichloroethylene, TCE	1.464
1,2,4-trichlorobenzene	1,2,4-trichlorobenzol	[4]1.45
1,1,2-trichloroethane	methyl chloroform	1.44
1,1,1-trichloroethane	methyl chloroform	1.339
1,2-dichlorobenzene	o-dichlorobenzene	1.306
cis-1,2-dichloroethene	*cis*-1,2-dichloroethylene	1.284
trans-1,2-dichloroethene	*trans*-1,2-dichloroethylene	1.256
1,2-dichloroethane	1,2-ethylidene dichloride, glycol dichloride	1.235
1,1-dichloroethene	1,1-dichloroethylene, DCE	1.213
1,1-dichloroethane	1,1-ethylidene dichloride	1.176
chlorobenzene	monochlorobenzene	1.106
pure water at 20°C		1.000
naphthalene	naphthene	.997
chloromethane	methyl chloride	.991
chloroethane	ethyl chloride	.920
chloroethene	vinyl chloride, chloroethylene	[4].910
stryrene	vinyl benzene	.906
1,2-dimethylbenzene	o-xylene	.880
benzene	—	.876
ethylbenzene	—	.867
1,2,4-trimethylbenzene	pseudocumene	.876
methylbenzene	toluene	.867
1,3-dimethylbenzene	m-xylene	.864
1,4-dimethylbenzene	p-xylene	.861
2-methoxy-2-methylpropane	methyl *tert*-butyl ether, MTBE	.740

Increasing density (heavier than water)

Decreasing density (lighter than water)

[1]International Union of Pure and Applied Chemistry, 2006

[2]U.S. Environmental Protection Agency, 1995

[3]Lide, 2003

[4]Chiou and others, 1983

Table 11.   Octanol-water partition coefficients for selected volatile organic compounds detected in ground water.

[IUPAC, International Union of Pure and Applied Chemistry; K_{ow}, octanol-water partition coefficient; —, not applicable]

IUPAC name[1]	Common or alternative name[2]	Octanol/ water partition coefficient[3] (Log K_{ow})
1,2,3-trichlorobenzene	1,2,6-trichlorobenzene	[4]4.07
1,2,4-trichlorobenzene	1,2,4-trichlorobenzol	[4]4.04
1,2,4-trimethylbenzene	pseudocumene	3.65
1,2-dichlorobenzene	o-dichlorobenzene	3.46
naphthalene	naphthene	3.36
1,3-dimethylbenzene	*m*-xylene	3.20
ethylbenzene	ethylbenzene	3.15
1,4-dimethylbenzene	*p*-xylene	3.15
1,2-dimethylbenzene	*o*-xylene	3.12
stryrene	vinyl benzene	3.05
tetrachloroethene	perchloroethylene, tetrachloroethylene, PCE	2.88
chlorobenzene	monochlorobenzene	[4]2.84
methylbenzene	toluene	2.73
tetrachloromethane	carbon tetrachloride	[4]2.64
1,1,2-trichloroethene	1,1,2-trichloroethylene, TCE	[3]2.53
1,1,1-trichloroethane	methyl chloroform	[4]2.49
1,1,2-trichloroethane	methyl chloroform	2.38
1,1-dichloroethene	1,1-dichloroethylene, DCE	2.13
benzene	—	2.13
trans-1,2-dichloroethene	*trans*-1,2-dichloroethylene	1.93
cis-1,2-dichloroethene	*cis*-1,2-dichloroethylene	1.86
1,1-dichloroethane	1,1-ethylidene dichloride	[4]1.79
1,2-dichloroethane	1,2-ethylidene dichloride, glycol dichloride	[4]1.48
chloroethane	ethyl chloride	1.43
chloroethene	vinyl chloride, chloroethylene	1.38
2-methoxy-2-methylpropane	methyl *tert*-butyl ether, MTBE	.94
chloromethane	methyl chloride	.91

Increasing affinity for organic matter and lipids →

[1]International Union of Pure and Applied Chemistry, 2006

[2]U.S. Environmental Protection Agency, 1995

[3]Sangster, 1989

[4]Mackay and others, 1992a

Table 12. Soil-sorption partition coefficients for selected volatile organic compounds detected in ground water.

[IUPAC, International Union of Pure and Applied Chemistry; K_{oc}, soil organic carbon partition coefficient; —, not applicable]

IUPAC name[1]	Common or alternative name[2]	Soil-sorption coefficient (Log K_{oc} in soil)
1,2,4-trimethylbenzene	pseudocumene	[3]3.34
1,2,3-trichlorobenzene	1,2,6-trichlorobenzene	[4]3.18 – [3]3.42
naphthalene	naphthene	[3]2.98
1,2,4-trichlorobenzene	1,2,4-trichlorobenzol	[5]2.94
vinyl benzene	styrene	[2]2.72–2.74
1,2-dichlorobenzene	o-dichlorobenzene	[6]2.46–[5]2.51
tetrachloroethene	perchloroethylene, tetrachloroethylene, PCE	[7]2.37
ethylbenzene	—	[5]2.22
1,1-dichloroethene	1,1-dichloroethylene, DCE	[2]2.18
1,3-dimethylbenzene	*m*-xylene	[7]2.11–2.46
1,1,1-trichloroethane	methyl chloroform	[8]2.03
1,1,2-trichloroethene	1,1,2-trichloroethylene, TCE	[7]2.00
chlorobenzene	monochlorobenzene	[5]1.91
1,1,2-trichloroethane	methyl chloroform	[7]1.78–2.03
tetrachloromethane	carbon tetrachloride	[9]1.78
methylbenzene	toluene	[7]1.75–[10]2.28
chloroethene	vinyl chloride, chloroethylene	[2]1.75
1,2-, 1,4-dimethylbenzene	*o*-xylene, *p*-xylene	[2]1.68–1.83
chloroethane	ethyl chloride	[4]1.62
cis-1,2-dichloroethene	*cis*-1,2-dichloroethylene	[2]1.56–1.69
1,2-dichloroethane	1,2-ethylidene dichloride, glycol dichloride	[6]1.52
trans-1,2-dichloroethene	*trans*-1,2-dichloroethylene	[2]1.56–1.69
1,1-dichloroethane	1,1-ethylidene dichloride	[12]1.52
benzene	—	[5]1.49–[7]1.73
methyl *tert*-butyl ether	MTBE	[11]1.09
chloromethane	methyl chloride	[3].778

Increasing affinity for soil organic matter

[1] International Union of Pure and Applied Chemistry, 2006

[2] U.S. Environmental Protection Agency, 1995

[3] Boyd and others, 1990

[4] Schwarzenbach and Westall, 1981

[5] Chiou and others, 1983

[6] Chiou and others, 1979

[7] Seip and others, 1986

[8] Friesel and others, 1984

[9] Kile and others, 1996

[10] Garbarini and Lion, 1986

[11] U.S. Environmental Protection Agency, 1994

[12] U.S. Environmental Protection Agency, 2005b

Table 13.   Common abiotic and biotic reactions involving halogenated aliphatic hydrocarbons.[1]

[+, plus; Cl, chloride]

| Reactions	Potential reaction products
Substitution	
abiotic hydrolysis	alcohol then an acid or diol (chloroethanol → chloroacetic acid)
biotic hydrolysis	alcohol then an acid or diol via microbial enzymes (hydrolases or glutathione S-transferases; (chloroethanol → chloroacetic acid)
conjugation or nucleophilic reactions (biotic)	free halide plus a new compound with the nucleophile or conjugate
Dehydrohalogenation	
dehydrohalogenation	halogenated acid (chloroacetic acid), alkane to alkene (dichloroethane → chloroethane)
Oxidation	
α-hydroxylation	monochlorinated alkane to a monochlorinated alcohol (chloroethane → chloroethanol)
halosyl oxidation	monohalogenated alkane to a nonhalogenated alkane (chloroethane → ethane + Cl)
epoxidation	halogenated epoxide compound
biohalogenation	nonhalogenated alkene to a monohalogenated alcohol (ethene + Cl → chloroethanol)
Reduction	
hydrogenolysis	free halide and nonhalogenated compound (chloroethane → Cl + ethane)
dihaloelimination	dihalogenated alkane to a nonhalogenated alkene (dichloroethane → ethene)
coupling	combining of two halogenated compounds into one halogenated compound

[1]Vogel and others, 1987, figure 1
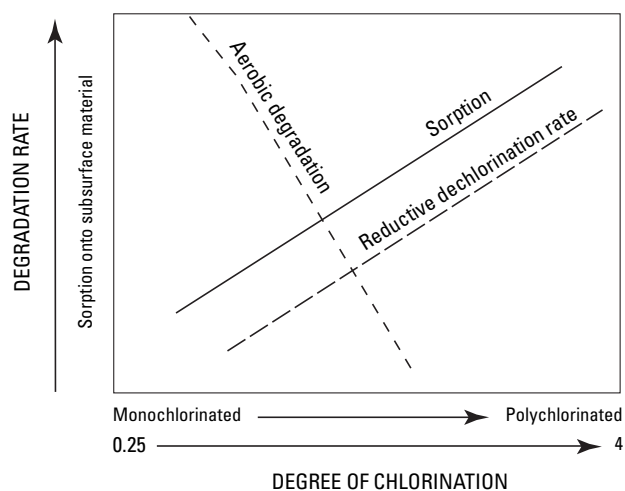
Figure 2.   Relation between degree of chlorination and anaerobic reductive-dechlorination, aerobic degradation and sorption onto subsurface material (modified from Norris and others, 1993, p. 10–19). Degree of chlorination is number of chloride atoms divided by number of carbon atoms.

Aquifer conditions (aerobic and anaerobic) and microbial metabolism (respiration, fermentation, and co-metabolism) control the environmental degradation of VOCs in ground water. In aerobic environments, oxygen serves as the terminal electron acceptor (TEA) and compounds such as MTBE and BTEX are subsequently degraded (oxidized) to other compounds (Azadpour-Keeley and others, 1999). Furthermore, under aerobic conditions CVOCs can be inadvertently degraded (co-metabolized) via nonspecific enzymes (oxygenases) produced by microorganisms during the metabolism of other compounds serving as primary substrates (for example, BTEX, methane, propane, toluene, ammonia, ethene, ethane). Although the aerobic mineralization of most VOCs ultimately yields carbon dioxide and water, co-metabolic biodegradation of CVOCs generally proceeds via an unstable epoxide intermediate that spontaneously decomposes to carbon dioxide, chloride, or other organic by-products such as acetate (Roberts and others, 1986).

Anaerobic degradation is typically a series of decarboxylations and oxidation-reduction (redox) reactions catalyzed either by single microorganisms or by a consortium of microorganisms (Dolfing, 2000). During anaerobic degradation, CVOCs function as terminal electron acceptors in a process called reductive dechlorination (Vogel and others, 1987). Theoretically, reductive dechlorination is the sequential replacement of one chlorine atom on a chlorinated compound with a hydrogen atom. The replacement continues until the compound is fully dechlorinated. For example, PCE can undergo reductive dechlorination to less-chlorinated compounds, such as TCE or 12-DCE, or to nonchlorinated compounds such as ethene, ethane, or methane (methanogenesis). Each successive step in the dechlorination process is theoretically slower than the preceding step. The dechlorination process slows because as chlorines are removed the energy costs to remove another chlorine atom increases (free energy of the reaction decreases; Dolfing, 2000). As a result, biodegradation may not proceed to completion in some aquifers leaving intermediate compounds (for example, dichloroethenes and vinyl chloride) to accumulate in ground water (Azadpour-Keeley and others, 1999). Other constraints on biodegradation such as a reduction in or loss of primary substrate, or microbial suppression also can play a role in the accumulation of intermediate compounds. This is a particular concern with VC because it is a known human carcinogen (Agency for Toxic Substances and Disease Registry, 2005) and its accumulation may create a health issue that might not be a concern during the early stages of ground-water contaminated by TCE.

Degradation of the Chlorinated Alkanes

The degradation of chlorinated VOCs is fundamentally different from that of BTEX compounds (Wiedemeier and others, 1995). The chlorinated alkanes can be degraded by abiotic processes through hydrolysis or dehydrohalogenation or by biotic processes through reductive dechlorination or dichloroelimination. These degradation processes can proceed under either aerobic or anaerobic conditions (figs. 3–6; Vogel and McCarty, 1987a; Vogel, 1994). According to McCarty (1997), 111-TCA is the only chlorinated compound that can be degraded in ground water within 20 years under all likely ground-water or aquifer conditions.

Abiotic Transformation

Hydrolysis and dehydrohalogenation are two abiotic processes that may degrade chlorinated ethanes under either aerobic or anaerobic conditions. The tendency for a chlorinated ethane to degrade by hydrolysis depends on the ratio of chlorine to carbon atoms (fig. 2) or the location of chlorine atoms on the number 2 carbon in the compound. Chlorinated alkanes are more easily hydrolyzed when the chlorine-carbon ratio is less than two or when chlorine atoms are only located on the number 1 carbon atom (Vogel and McCarty, 1987b; Vogel, 1994). For example, chloroethane and 111-TCA have half-lives that are measured in days or months (Vogel and others, 1987; Vogel, 1994; table 14). Conversely, the more chlorinated ethanes such as 1,1,1,2-tetrachloroethane (PCA) and those with chlorine atoms on the number 2 carbon tend to have half-lives measured in decades or centuries (table 14). Dehydrohalogenation is the removal of one or two halogen atoms from an alkane (Vogel and McCarty, 1987a). The dehydrohalogenation of two chlorine atoms is called dichloroelimination.

Chen and others (1996) show that PCA can be abiotically transformed to TCE under methanogenic conditions (fig. 3). In addition, the abiotic degradation of 111-TCA has been well studied in the scientific literature (fig. 4; Jeffers and others, 1989; McCarty and Reinhard, 1993; Chen and others, 1996; McCarty, 1997). McCarty and Reinhard (1993) indicate that the transformation of 111-TCA by hydrolysis is about four times faster than by dehydrochlorination. During abiotic degradation, about 80 percent of 111-TCA is transformed to acetic acid by hydrolysis (McCarty, 1997), and the remaining 20 percent is transformed to 11-DCE by dehydrochlorination (table 7; Vogel and McCarty, 1987b; McCarty, 1997). The presence of 11-DCE in contaminated ground water is probably the result of the dehydrochlorination of 111-TCA (McCarty, 1997).
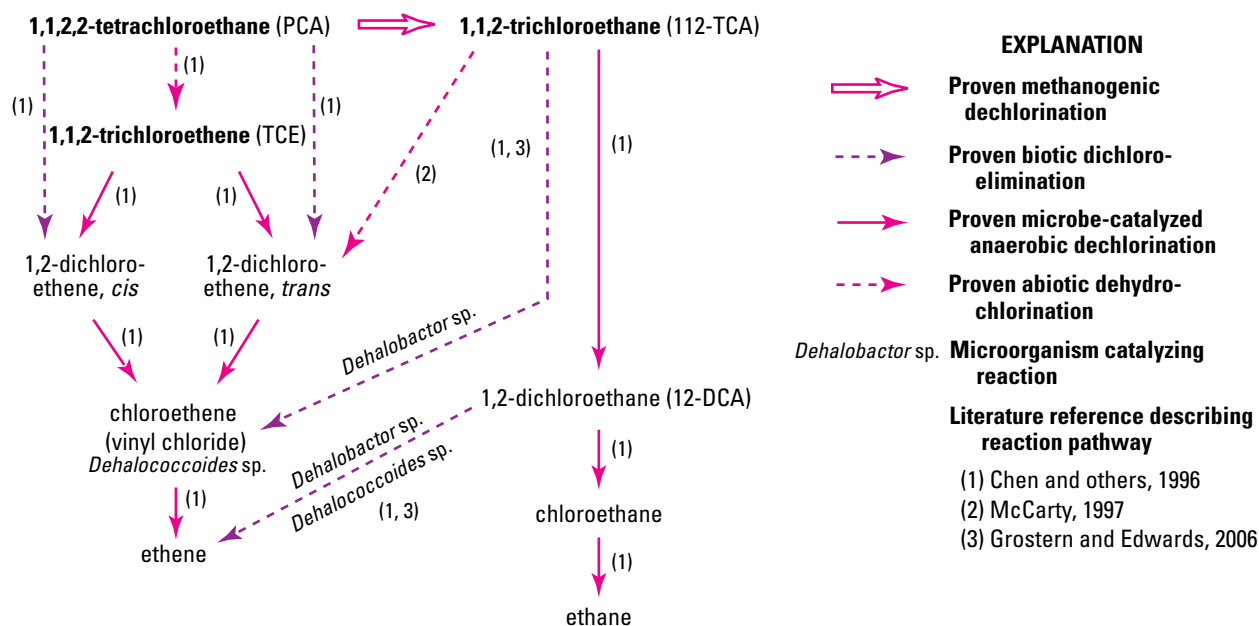
Figure 3.   Laboratory-derived pathway for the abiotic degradation, anaerobic, and methanogenic biodegradation of 1,1,2,2-tetrachloroethane; 1,1,2-trichloroethene; and 1,1,2-trichloroethane (modified from Chen and others, 1996).

Table 14.   Laboratory half-lifes and by-products of the abiotic degradation (hydrolysis or dehydrohalogenation) of chlorinated alkane compounds detected in ground water.

[IUPAC, International Union of Pure and Applied Chemistry; —, not applicable]

Compound (IUPAC name)[1]	Degradation by-products	Half-life	Literature reference
chloroethane	ethanol	44 days	Vogel and others, 1987
1,1-dichloroethane	—	61 years	Jeffers and others, 1989
1,2-dichloroethane	—	72 years	Jeffers and others, 1989
1,1,1-trichloroethane	acetic acid; 1,1-dichloroethane	1.1–2.5 years	Mabey and Mill, 1978; Jeffers and others, 1989; Vogel and McCarty, 1987a,b
1,1,2-trichloroethane	1,1-dichloroethane	140 years	Jeffers and others, 1989
1,1,1,2-tetrachloroethane	trichloroethene	47–380 years	Mabey and Mill, 1978; Jeffers and others, 1989
1,1,2,2-tetrachloroethane	1,1,2-trichloroethane; trichloroethene	146–292 days	Mabey and Mill, 1978; Jeffers and others, 1989

[1]International Union of Pure and Applied Chemistry, 2006

Abiotic pathway

1,1,1-trichloroethane

(10)

1,1-dichloroethene   acetic acid

Aerobic pathway

1,1,1-trichloroethane
(*Methylosinus trichosporium* OB3b,
Mycobacterium spp. TA5, 27)

(4, 5)

2,2,2-trichloroethanol

(6)

2,2,2-trichloroacetate
(*Pseudomonas* sp.)

(9)

(8)   (7)   2,2-dichloroacetate

carbon   oxalate
dioxide

Anaerobic pathway

1,1,1-trichloroethane
(*Clostridium* spp.,
Dehalobacter strain TCA1)

(1, 2)

1,1-dichloroethane

(2)

chloroethane

(3)

acetaldehyde

EXPLANATION

- - - → **Proven dehydrochlorination**

- - - → **Proven abiotic hydrolysis**

Proven microbe-catalyzed

⇒   Co-metabolism

→   Hydrolosis

Methylosinus trichosporium **Microorganism catalyzing reaction**

**Literature reference describing
reaction pathway**

(1) Egli and others, 1987
(2) Gälli and McCarty, 1989
(3) De Best and others, 1999
(4) Yagi and others, 1999
(5) Oldenhuis and others, 1989
(6) Newman and Wackett, 1997
(7) Motosugi and others, 1982
(8) Jun Oh, 2005
(9) De Wever and others, 2000
(10) McCarty, 1997

Figure 4.   Laboratory-derived pathway for the abiotic, aerobic, and anaerobic biodegradation of
1,1,1-trichloroethane (modified from Sands and others, 2005; Whittaker and others, 2005).

Aerobic Biodegradation

According to the degradation pathway constructed by Sands and others (2005) and Whittaker and others (2005), the dichloroethanes are not a by-product of 111-TCA or 112-TCA biodegradation under aerobic conditions (fig. 4). Apparently, the only source of 11-DCA and 12-DCA via a degradation pathway is the reductive dechlorination of 111-TCA and 112-TCA, respectively, under anaerobic conditions (figs. 3 and 4). Under aerobic conditions, however, 12-DCA can be degraded when used as a carbon source by microorganisms. The intermediate by-product of this degradation is chloroethanol, which is then mineralized to carbon dioxide and water (fig. 5; Stucki and others, 1983; Janssen and others, 1985; Kim and others, 2000; Hage and others, 2001).

1,2-dichloroethane, aerobic
(*xanthobacter autotrophicus* GJ10,
Ancylobacter aquaticus Ad20, AD25, AD27)

↓ (1)

2-chloroethanol

↓ (2)

choroacetaldehyde

↓ (3)

chloroacetic acid

↓ (4, 5)

glycolate

↓

intermediary metabolism
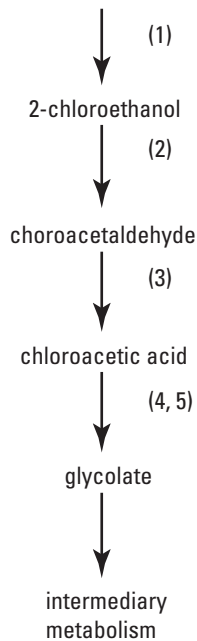
EXPLANATION

→   **Proven microbe-catalyzed oxidation reaction**

xanthobacter autotrophicus   **Microorganism catalyzing reaction**

Literature reference describing reaction pathway

(1) Verschueren and others, 1993
(2) Xia and others, 1996
(3) Liu and others, 1997
(4) Janssen and others, 1985
(5) Hisano and others, 1996

Figure 5. Laboratory-derived pathway for the aerobic biodegradation of 1,2-dichloroethane (modified from Renhao, 2005).

Anaerobic Biodegradation

While researching the scientific literature for their report, Wiedemeier and others (1998) did not find published studies describing anaerobic biodegradation of chlorinated ethanes in ground water. Since the publication of Wiedemeier and others (1998), however, numerous published studies describe the anaerobic biodegradation of chlorinated ethanes. McCarty (1997) indicates that carbon tetrachloride was transformed to chloroform under denitrifying conditions and mineralized to carbon dioxide and water under sulfate-reducing conditions (fig. 6). Adamson and Parkin (1999) show that under anaerobic conditions, carbon tetrachloride and 111-TCA tend to inhibit the degradation of each other. Adamson and Parkin (1999) also show that carbon tetrachloride was rapidly degraded by co-metabolism when acetate was the carbon source.

Chen and others (1996) describe how methanogenic conditions in a municipal sludge digester allowed the degradation of PCA to 112-TCA, and 112-TCA to 12-DCA through dehydrohalogenation (fig. 3). De Best and others (1999) report that co-metabolic transformations of 112-TCA will occur under methanogenic conditions. In this study, 112-TCA was degraded tochloroethane when sufficient amounts of the carbon source were present (fig. 3). This transformation was inhibited by the presence of nitrate, but not nitrite.

Dolfing (2000) discusses the thermodynamics of reductive dechlorination during the degradation of chlorinated hydrocarbons and suggests that fermentation of chloroethanes to ethane or acetate may be energetically more favorable than "classic" dechlorination reactions. Moreover, polychlorinated ethanes may degrade preferentially by reductive dechlorination under strongly reducing conditions. Dichloroelimination, however, may actually be the dominant degradation reaction for polychlorinated ethanes because more energy is available to microorganisms than is available during reductive dechlorination (Dolfing, 2000). During anaerobic biodegradation, the mean half-lifes of the chloroethane compounds can be as short as three days, in the case of 111-TCA, or as long as 165 days, in the case of 12-DCA (table 15).

Table 15.   Mean half-life in days for the anaerobic biodegradation of selected chlorinated alkane and alkene compounds.[1]

[(27), number of samples used to derive the mean value; —, not available]

Compound	All studies	Field/in situ studies
chloroethene	0.018 (27)	0.0073 (19)
1,2-dichloroethane	63-165 (2)	63–165 (2)
tetrachloroethene (PCE)	239–3,246 (36)	239 (16)
tetrachloromethane	47 (19)	40 (15)
1,1,1-trichloroethane	2.3–2.9 (28)	—
1,1,2-trichloroethane	47–139 (1)	—
trichloroethene (TCE)	1,210 (78)	277 (30)

[1]Aronson and Howard, 1997, p. 111

carbon tetrachloride
(Pseudomonas stutzeri KC, *Methanosarcina barkeri,*
Desulfobacterium autotrophicum, Moorella thermoacetica,
Methanoabacterium thermoautotrophicum)

Pathway 1   Pathway 2   Pathway 3

(1)   (2)   (1)   (1)

chloroform   thiophosgene   phosgene

(1)

dichloromethane   (2)   (1)   carbon
dioxide

(1)

methyl chloride   carbon
monoxide
(Methylococcus   formate
capsulatus;
Pseudomonas
aeruginosa)

(1)

methane

(1)   (3)   (4)

C_1 metabolic cycle

carbon
dioxide

EXPLANATION

→ **Proven microbe-catalyzed dechlorination**

--→ **Postulated microbe-catalyzed reductive pathway**

→ **Proven microbe-catalyzed reductive pathway**

Pseudomonas stutzeri **Microorganism catalyzing reaction**

thiophosgene **Postulated intermediate compound**

Literature reference describing reaction pathway
(1) Lee and others, 1999
(2) Krone and others, 1991
(3) Eggen and others, 1991
(4) Lamzin and others, 1992

Figure 6.   Laboratory-derived pathways for the anaerobic biodegradation of tetrachloromethane (carbon tetrachloride; modified from Ma and others, 2005; Sands and others, 2005).

Degradation of the Chlorinated Alkenes

The primary degradation of the most common chlorinated alkenes is microbial reductive dechlorination under anaerobic conditions. However, biodegradation of certain chlorinated compounds—such as trichloroethene, the dichloroethenes, vinyl chloride, or chloroethane—can also proceed via oxidative pathways under aerobic conditions. Two forms (isomers) of dichloroethene occur in ground water as chemical by-products of PCE and TCE biodegradation (Wiedemeier and others, 1998; Olaniran and others, 2004). Abiotic degradation of PCA to TCE can occur in PCA-contaminated ground water (fig. 3; Chen and others, 1996).

Aerobic Biodegradation

Several studies have shown that chlorinated ethenes, with the exception of PCE, can degrade under aerobic conditions by oxidation (Hartmans and De Bont, 1992; Klier and others, 1999; Hopkins and McCarty, 1995; Coleman and others, 2002) and by co-metabolic processes (Murray and Richardson, 1993; Vogel, 1994; McCarty and Semprini, 1994). Studies describing the degradation of PCE under aerobic conditions were not found in the peer-reviewed literature. In one study, aerobic biodegradation of PCE was not measurable beyond analytical precision after 700 days of incubation (Roberts and others, 1986). Furthermore, Aronson and others (1999) indicate that

PCE is not degraded when dissolved oxygen (DO) is greater than 1.5 mg/L, the approximate boundary between aerobic and anaerobic conditions (Stumm and Morgan, 1996). Chen and others (1996) suggest the structure and oxidative state of PCE prevents its aerobic degradation in water.

According to the aerobic biodegradation pathway constructed by Whittaker and others (2005), the dichloroethenes are not a by-product of TCE degradation under aerobic conditions (fig. 4). Rather, TCE is degraded along three different pathways by different microorganisms (fig. 7). These pathways do not form any of the dichlorothene compounds and the only apparent source of 12-DCE is by the reductive dechlorination of TCE under anaerobic conditions (figs. 3 and 8). The compounds 12-DCE and VC, however, can be degraded under aerobic conditions by microorganisms utilizing the compounds as a primary carbon source (fig. 5; Bradley and Chapelle, 1998).

Although PCE is not known to degrade through co-metabolism under aerobic conditions, co-metabolism is known to degrade TCE, the dichloroethenes, and VC. The rate of co-metabolism increases as the degree of chlorination decreases on the ethene molecule (Vogel, 1994). During aerobic co-metabolism, the chlorinated alkene is indirectly dechlorinated by oxygenase enzymes produced when microorganisms use other compounds, such as BTEX compounds, as a carbon source (Wiedemeier and others, 1998). The co-metabolic degradation of TCE, however, tends to be limited to low concentrations of TCE because high concentrations in the milligram per liter range are toxic to microbes catalyzing this reaction (Wiedemeier and others, 1998). In field studies by Hopkins and McCarty (1995), VC is shown to degrade by co-metabolism under aerobic conditions when phenol and toluene were used as a carbon source.
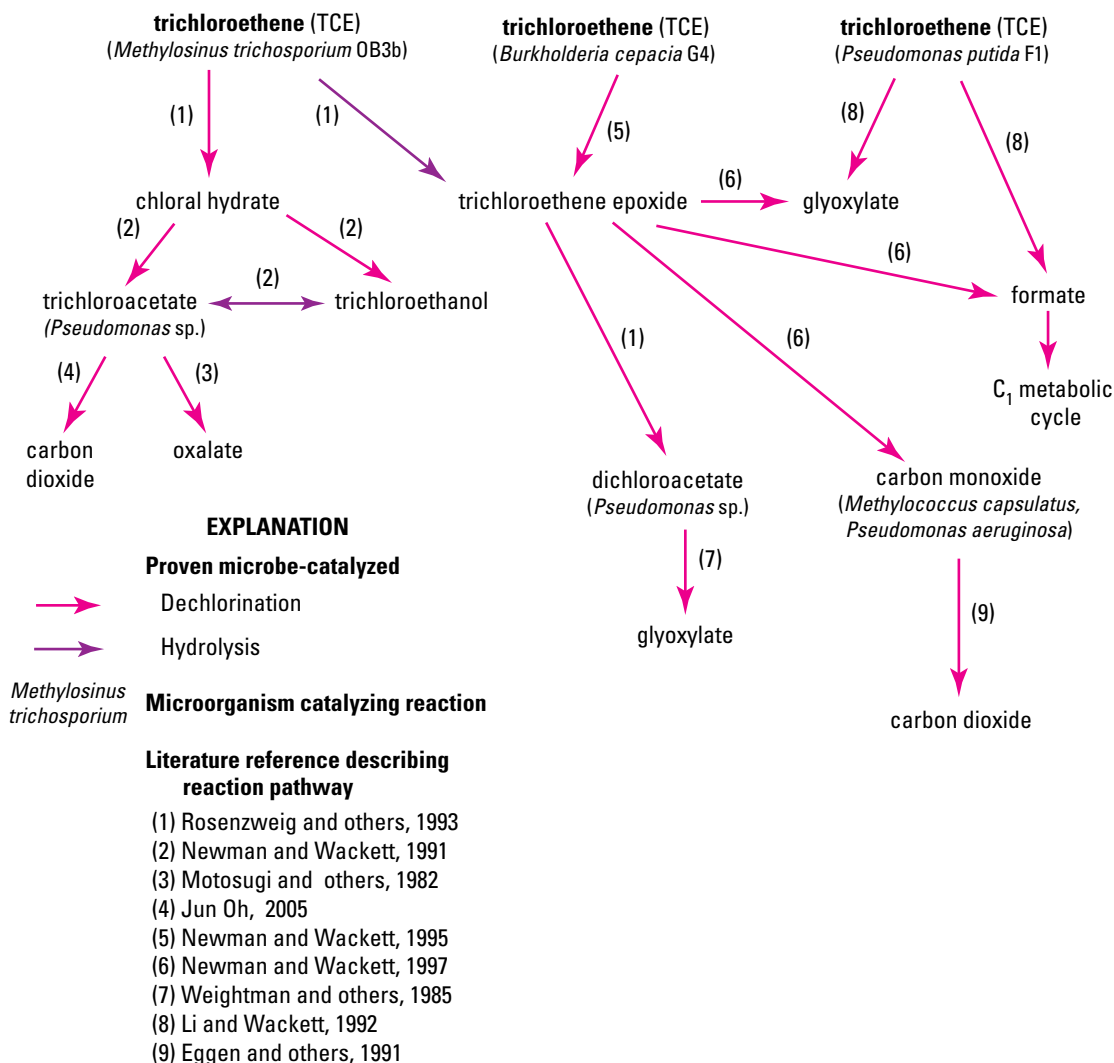

Figure 7.   Laboratory-derived pathways for the aerobic biodegradation of trichloroethene (modified from Whittaker and others, 2005).

Anaerobic Biodegradation

Many laboratory and field studies have shown that microorganisms degrade chlorinated ethenes under anaerobic conditions (Bouwer and others, 1981; Bouwer, 1994, Dolfing, 2000). Ground water is considered anoxic when the dissolved oxygen concentration falls below 1.0–1.5 mg/L (Stumm and Morgan, 1996; Christensen and others, 2000). Under anoxic conditions, anaerobic or facultative microbes will use nitrate as an electron acceptor, followed by iron (III), then sulfate, and finally carbon dioxide (methanogenesis; Chapelle and others, 1995; Wiedemeier and others (1998). As the concentration of each electron acceptor sequentially decreases, the redox potential of the ground water becomes greater (more negative) and biodegradation by reductive dechlorination is favored.

Anaerobic conditions in ground water can be determined by measuring the vertical and spatial concentrations of oxygen, iron (II), manganese (II), hydrogen sulfide, or methane in ground water and using that data as a qualitative guide to the redox status (Stumm and Morgan, 1996; Christensen and others, 2000). Other measurements of anaerobic conditions involving microorganism biomarkers include volatile fatty acids, ester-linked phospholipid fatty acid (PLFA), deoxyribonucleic acid (DNA), and ribonucleic acid (RNA) probes, and TEAP bioassay (Christensen and others, 2000). The reduction of iron (III) to iron (II), manganese (IV) to manganese (II), sulfate to hydrogen sulfide, and carbon dioxide to methane during the microbial reduction of chlorinated VOCs can have a major influence on the distribution of iron (II), manganese (II), hydrogen sulfide, and methane concentrations in ground water (Stumm and Morgan, 1996; Lovley, 1991; Higgo and others, 1996; Braun, 2004).

The highly chlorinated alkenes are commonly used as electron acceptors during anaerobic biodegradation and are reduced in the process (Vogel and others, 1987). The primary anaerobic process driving degradation of CVOCs, except VC, is reductive dechlorination (figs. 3 and 8; Bouwer and others, 1981; Bouwer, 1994). Tetrachloroethene and TCE are the most susceptible to reductive dechlorination because they are the most oxidized of the chlorinated ethenes; however, the more reduced (least oxidized) degradation by-products such as the dichloroethenes and vinyl chloride are less prone to reductive dechlorination. The main by-product of anaerobic biodegradation of the polychlorinated ethenes is VC (fig. 8), which is more toxic than any of the parent compounds (Agency for Toxic Substances and Disease Registry, 2004). The rate of reductive dechlorination tends to decrease as the reductive dechlorination of daughter products proceeds (Vogel and McCarty, 1985; Bouwer, 1994). Murray and Richardson (1993) suggest that the inverse relation between the degree of chlorination and the rate of reductive dechlorination may explain the accumulation of 12-DCE and VC in anoxic ground water contaminated with PCE and TCE. In addition, the anaerobic reduction of VC to ethene is slow and inefficient under weak reducing conditions, which favors the persistence of VC in anoxic ground water (Freedman and Gossett, 1989).
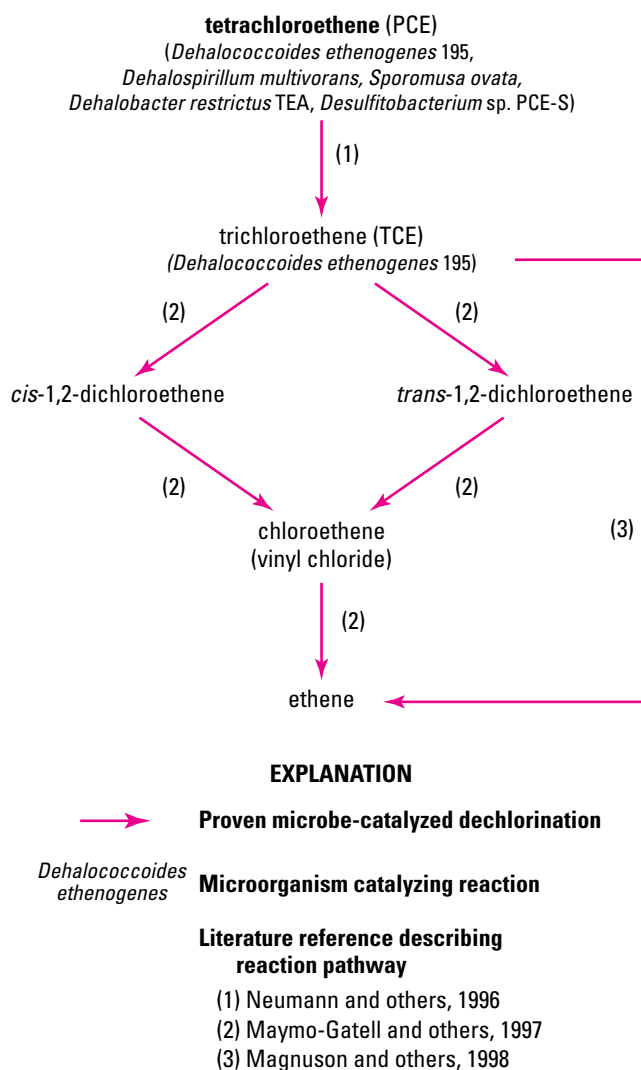
Figure 8. Laboratory-derived pathway for the anaerobic biodegradation of tetrachloroethene (modified from Ellis and Anderson, 2005).

Reductive dechlorination has been demonstrated under nitrate- and iron-reducing conditions (Wiedemeier and others, 1998). Reductive dechlorination of the CVOCs, however, may be more rapid and more efficient when oxidation-reduction (redox) conditions are below nitrate-reducing levels (Azadpour-Keeley and others, 1999). Sulfate-reducing and methanogenic ground-water conditions create an environment that facilitates not only biodegradation for the greatest number of CVOCs, but also more rapid biodegradation rates (Bouwer, 1994). Reductive dechlorination of DCE and VC is most apparent under sulfate reducing and methanogenic conditions (Wiedemeier and others, 1998). Anaerobic biodegradation rates for the chlorinated alkenes can be as short as 45 minutes, in the case of VC, to as long as 9 years for PCE (table 15).

Degradation of the Chlorinated Benzenes

Several studies have shown that chlorinated benzene compounds containing up to four chlorine atoms can be degraded by microorganisms under aerobic conditions (Reineke and Knackmuss, 1984; Spain and Nishino, 1987; Sander and others, 1991). Under aerobic conditions, 1,2,4-trichlorobenzene (124-TCB; Haigler and others, 1988) and chlorobenzene (CB; Sander and others, 1991) are used as a primary carbon source during biodegradation by microorganisms such as *Burkholdia* and *Rhodococcus* species (Rapp and Gabriel-Jürgens, 2003). During biodegradation, these compounds are completely mineralized to carbon dioxide (CO_2) (van de Meer and others, 1991). Rapp and Gabriel-Jürgens (2003) also indicate that all of the dichlorobenzene isomers were biodegraded by the *Rhodococcus* bacterium. The biodegradation pathways for 124-TCB, 14-DCB, 12-DCB, and CB, under aerobic conditions are shown in figures 9 to 11, respectively. These pathways are similar to that of benzene, except that one chlorine atom is eventually eliminated through hydroxylation of the chlorinated benzene to form a chlorocatechol, then ortho cleavage of the benzene ring (van der Meer and others, 1998).

Calculated and published degradation half-lifes for the chlorobenzenes under aerobic conditions are shown in table 16. The compounds 124-TCB, 12-DCB, and CB lose 50 percent of their initial mass within 180 days (table 16). Conversely, Dermietzel and Vieth (2002) show that chlorobenzene was rapidly mineralized to CO_2 in laboratory and in situ microcosm studies, with complete mineralization ranging from 8 hours to about 17 days. In addition, the compound 14-DCB was completely mineralized within 25 days. Nevertheless, under the aerobic conditions of Dermietzel and Vieth (2002) study, 124-TCB, 12-DCB, and 13-DCB were only partially degraded after 25 days. In another laboratory-microcosm study by Monferran and others (2005), all isomers of DCB were mineralized to CO_2 within 2 days by the aerobe *Acidovorax avenae*.

Although Wiedemeir and others (1998) indicate that few studies existed that described the anaerobic degradation of the chlorobenzene compounds, a study by Ramanand and others (1993) did suggest that 124-TCB could be biodegraded to chlorobenzene with 14-DCB as an intermediate compound under anaerobic conditions. Moreover, Middeldorp and others (1997) show that 124-TCB was reductively dechlorinated to 14-DCB, then to chlorobenzene in a methanogenic laboratory microcosm in which chlorobenzene-contaminated sediment was enriched with lactate, glucose, and ethanol. These compounds served as carbon sources. Furthermore, the microbial consortia facilitating the dechlorination of 124-TCB also was able to degrade isomers of tetrachlorobenzene to other isomers of TCB and 12-DCB. More recent studies show that a strain of the bacterium, *Dehalococcoides,* can reductively dechlorinate 124-TCB under anaerobic conditions (Holscher and others, 2003; Griebler and others, 2004a). In addition, Adrian and others (1998) suggest that fermentation is the primary degradation process for the chlorobenzenes under anaerobic conditions. This study also showed that the co-metabolism of 124-TCB was inhibited by the presence of sulfate, sulfite, and molybdate.
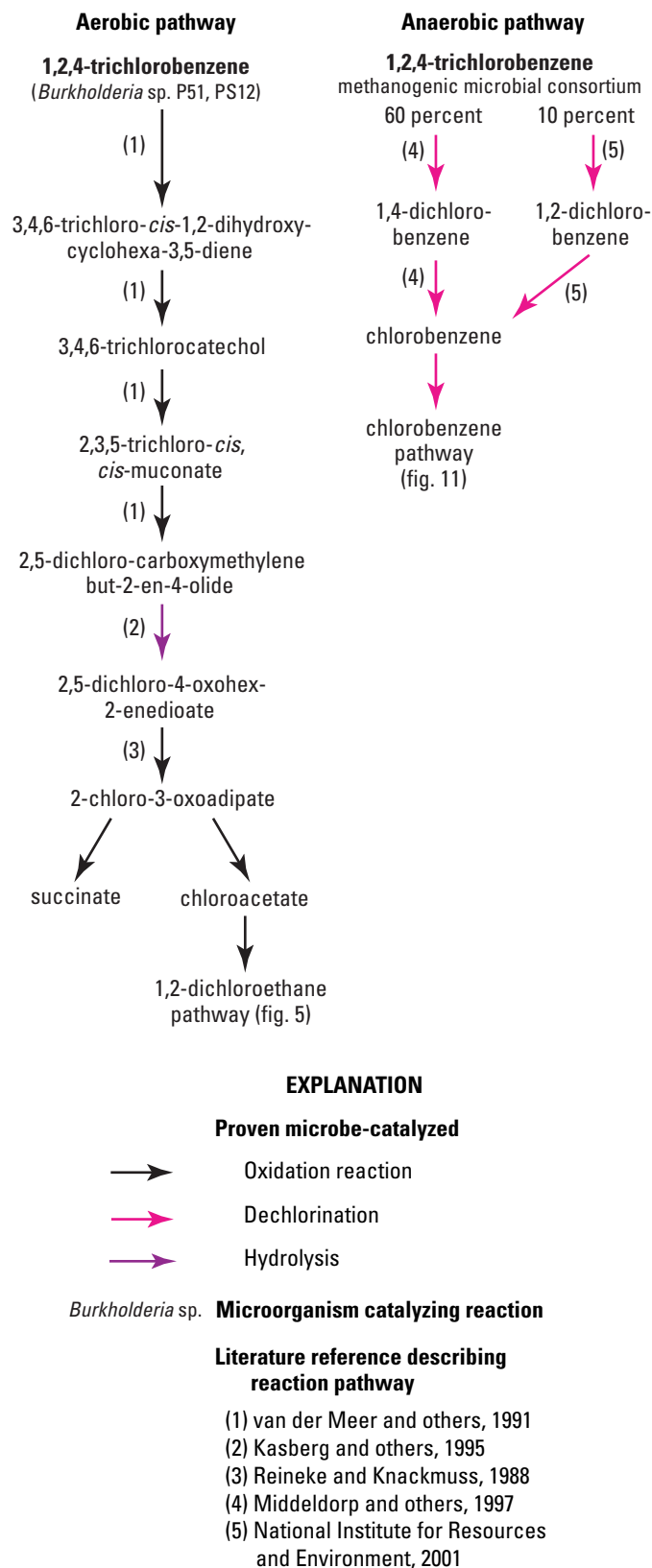

Figure 9. Laboratory-derived pathways for the aerobic and anaerobic biodegradation of 1,2,4-trichlorobenzene (modified from Yao, 2006).

Furthermore, Ramanand and others (1993) show that 124-TCB had declined by 63 percent within 30 days under anaerobic conditions. Dermietzel and Vieth (2002) show that the anaerobic biodegradation of 14-DCB was markedly slower under iron-reducing conditions than under aerobic conditions. In general, it appears that the biodegradation of the chlorinated benzenes is slower under anaerobic than under aerobic conditions.
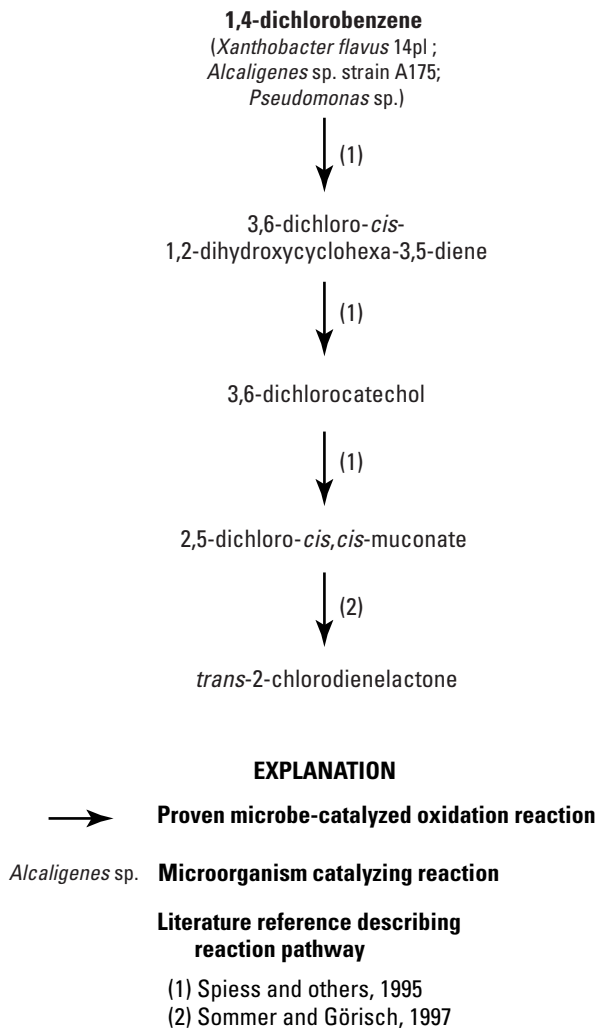
1,4-dichlorobenzene
(*Xanthobacter flavus* 14pl ;
Alcaligenes sp. strain A175;
Pseudomonas sp.)

↓ (1)

3,6-dichloro-*cis*-
1,2-dihydroxycyclohexa-3,5-diene

↓ (1)

3,6-dichlorocatechol

↓ (1)

2,5-dichloro-*cis,cis*-muconate

↓ (2)

trans-2-chlorodienelactone

EXPLANATION

→   **Proven microbe-catalyzed oxidation reaction**

Alcaligenes sp.   **Microorganism catalyzing reaction**

**Literature reference describing
reaction pathway**

(1) Spiess and others, 1995
(2) Sommer and Görisch, 1997

Figure 10.   Laboratory-derived pathway for the aerobic biodegradation of 1,4-dichlorobenzene (modified from Liu, 2006).
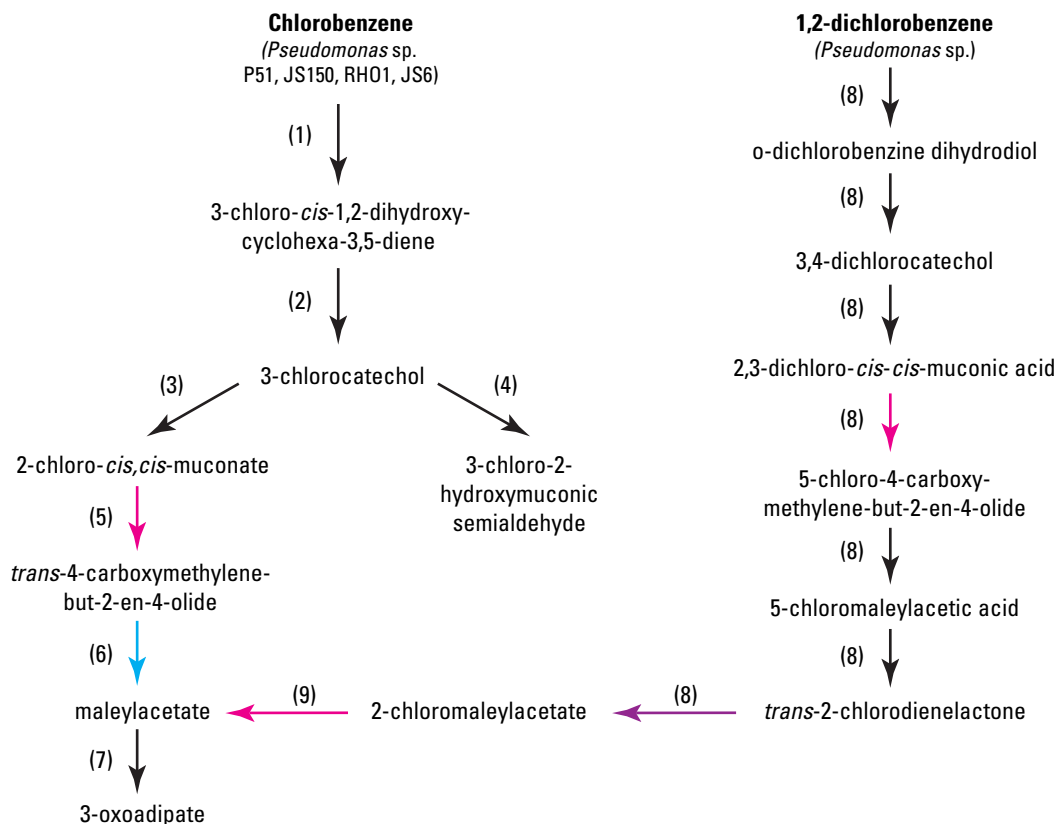
Degradation of the Gasoline Compounds

Laboratory and field studies have shown that microorganisms mediate the degradation (biodegradation) of the common gasoline compounds (MTBE and BTEX) under both aerobic and anaerobic conditions. Aerobic microorganisms readily oxidize BTEX compounds while using them as primary substrates. The biodegradation of BTEX compounds under various redox conditions is well documented in the scientific literature (Vogel and Grbić-Galić, 1986; Kuhn and others, 1988; Lovley and Lonergan, 1990; Evans and others, 1991a,b; Hutchins and others, 1991; Rabus and others, 1993; Edwards and Grbić-Galić, 1994; Fries and others, 1994; Rabus and Widdel, 1995; Anderson and others, 1998).

Although early studies concluded that MTBE was recalcitrant to aerobic biodegradation (Squillace and others, 1997), more recent studies show that, once initiated, the aerobic biodegradation of MTBE is relatively rapid (Deeb and others, 2000), but markedly slower than BTEX degradation. In addition, the anaerobic biodegradation of MTBE is known to proceed, although slowly, under a variety of redox conditions. Until recently, however, little was known about specific pathways involved in the anaerobic degradation of MTBE.

Aerobic Biodegradation of BTEX Compounds

Laboratory and field studies show that microorganisms mediate the biodegradation of BTEX compounds under aerobic conditions (table 17; Aronson and others, 1999). The microbially catalyzed oxidation reaction between dissolved oxygen and BTEX is thermodynamically favored because BTEX compounds are in a highly reduced state and the preferred terminal electron acceptor (TEA) is oxygen (Brown and others, 1996). The microbially catalyzed oxidation of BTEX compounds requires 3.1 milligrams per liter (mg/L) of dissolved oxygen (DO) to 1 mg/L of a BTEX compound (Aronson and Howard, 1997). Some studies show that the rate of biodegradation tends to slow when DO concentrations are less than about 1–2 parts per million (ppm; equal to milligrams per liter, mg/L; Chiang and others, 1989; Salanitro, 1993). During laboratory studies in which the initial DO concentration was at least 8 mg/L, individual BTEX compounds or a BTEX mixture biodegraded rapidly to low concentrations until the DO concentration was less than 2 mg/L; At this threshold, biodegradation was rate limited, rather than substrate limited, because of the low DO concentration (Salanitro, 1993).

Chlorobenzene
(Pseudomonas sp.
P51, JS150, RHO1, JS6)

(1) ↓

3-chloro-*cis*-1,2-dihydroxy-
cyclohexa-3,5-diene

(2) ↓

3-chlorocatechol

(3) ↙   (4) ↘

2-chloro-*cis,cis*-muconate   3-chloro-2-
hydroxymuconic
semialdehyde

(5) ↓

trans-4-carboxymethylene-
but-2-en-4-olide

(6) ↓

maleylacetate   ←(9)—   2-chloromaleylacetate   ←(8)—   *trans*-2-chlorodienelactone

(7) ↓

3-oxoadipate

1,2-dichlorobenzene
(Pseudomonas sp.)

(8) ↓

o-dichlorobenzine dihydrodiol

(8) ↓

3,4-dichlorocatechol

(8) ↓

2,3-dichloro-*cis-cis*-muconic acid

(8) ↓

5-chloro-4-carboxy-
methylene-but-2-en-4-olide

(8) ↓

5-chloromaleylacetic acid

(8) ↓

trans-2-chlorodienelactone

EXPLANATION

Proven microbe-catalyzed

→ Oxidation reaction

→ Dechlorination

→ Hydrolysis

→ Hydration

Pseudomonas sp. **Microorganism
catalyzing reaction**

**Literature reference describing
reaction pathway**

(1) Werlen and others, 1996
(2) Mason and Geary, 1990
(3) Broderick and O'Halloran, 1991
(4) Riegert and others, 1998
(5) Hammer and others, 1993
(6) Pathak and Ollis, 1990
(7) Kaschabek and Reineke, 1995
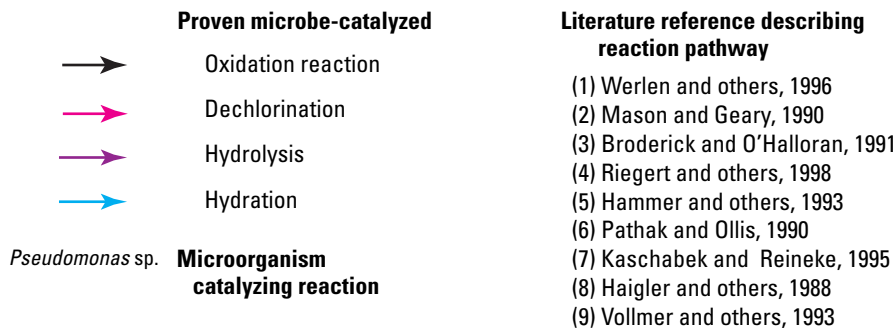(8) Haigler and others, 1988
(9) Vollmer and others, 1993

Figure 11.   Laboratory-derived pathway for the aerobic biodegradation of chlorobenzene and 1,2-dichlorobenzene (modified from McLeish, 2005).

Aerobic microorganisms readily oxidize BTEX compounds while using them as primary substrates. The oxidation of BTEX compounds can proceed via several pathways (figs. 12–16). In one laboratory column study, methanol was added to a BTEX mixture to identify possible co-metabolic pathways. The methanol was not used as the primary substrate and appeared to depress the biodegradation of BTEX compounds (Hubbard and others, 1994). This study showed that BTEX degradation was not a result of co-metabolism. Benzene has been shown to degrade completely to carbon dioxide (mineralization; Gibson and others, 1968; Gibson and Subramanian, 1984; Edwards and Grbić-Galić, 1992). More recent laboratory experiments show that catechol is an intermediate compound in the benzene pathway (fig. 12). Five separate degradation pathways have been identified for toluene under aerobic conditions (fig. 13). One of these pathways shares a common intermediate compound (3-methylcatechol) with the degradation of *o*- and *m*-xylene (figs. 12 and 13). The pathway for *p*-xylene follows a similar pattern, but differs in the intermediate compounds formed. This difference is caused by the position of the methyl group on the benzene ring of *p*-xylene (fig. 14). The aerobic biodegradation of ethylbenzene follows three pathways depending on the microorganism using ethylbenzene as its carbon source (fig. 15). Based on laboratory and field microcosm studies, biodegradation of BTEX under aerobic conditions is more rapid in gasoline-contaminated aquifer sediments than in uncontaminated aquifer sediments (Aronson and others, 1999; table 17).

Table 16. Laboratory or environmental half-lifes and by-products for the aerobic and anaerobic biodegradation of selected chlorinated benzene compounds detected in ground water.

[IUPAC, International Union of Pure and Applied Chemistry; CO_2, carbon dioxide; DCB, dichlorobenzene]

Compound (IUPAC name)[1]	Degradation by-products	Half-life (days)	Literature reference
Aerobic conditions			
chlorobenzene	3-chlorocatechol, CO_2	69–150	Rathbun, 1998; McLeish, 2005
1,2-dichlorobenzene	chlorobenzene	28–180	Rathbun, 1998
1,4-dichlorobenzene	chlorobenzene	28–180	Rathbun, 1998
1,2,4-trichlorobenzene	succinate, chloroacetate	28–180	Rathbun, 1998; Renhao, 2005; Yao, 2006
Anaerobic conditions			
chlorobenzene	CO_2	280–580	Rathbun, 1998; Monferran and others, 2005
1,2-dichlorobenzene	CO_2	119–722	Rathbun, 1998
1,4-dichlorobenzene	chlorobenzene	112–722	Rathbun, 1998; Yao, 2006
1,2,4-trichlorobenzene	1,4-DCB, chlorobenzene	112–722	Rathbun, 1998; Yao, 2006

[1]International Union of Pure and Applied Chemistry, 2006

A nationwide survey of VOCs in ground water showed that toluene, representing BTEX compounds, was detected more frequently in oxic rather than in anoxic ground water (Squillace and Moran, 2006). In other studies, the loss of BTEX compounds along ground-water flowpaths was inversely related to dissolved-oxygen concentration, indicating that microbial activity (respiration) was related to BTEX degradation (Donaldson and others, 1990; Huesemann and Truex, 1996).

Morasch and others (2001, 2002), using stable isotope fractionation data, concluded that quantifying aerobic microbial degradation of BTEX in oxic environments may not be possible. Moreover, laboratory studies have shown that ethylbenzene can inhibit the microbial degradation of benzene, toluene, and the xylenes and does so until all of the ethylbenzene is degraded (Deeb and Alvarez-Cohen, 2000).
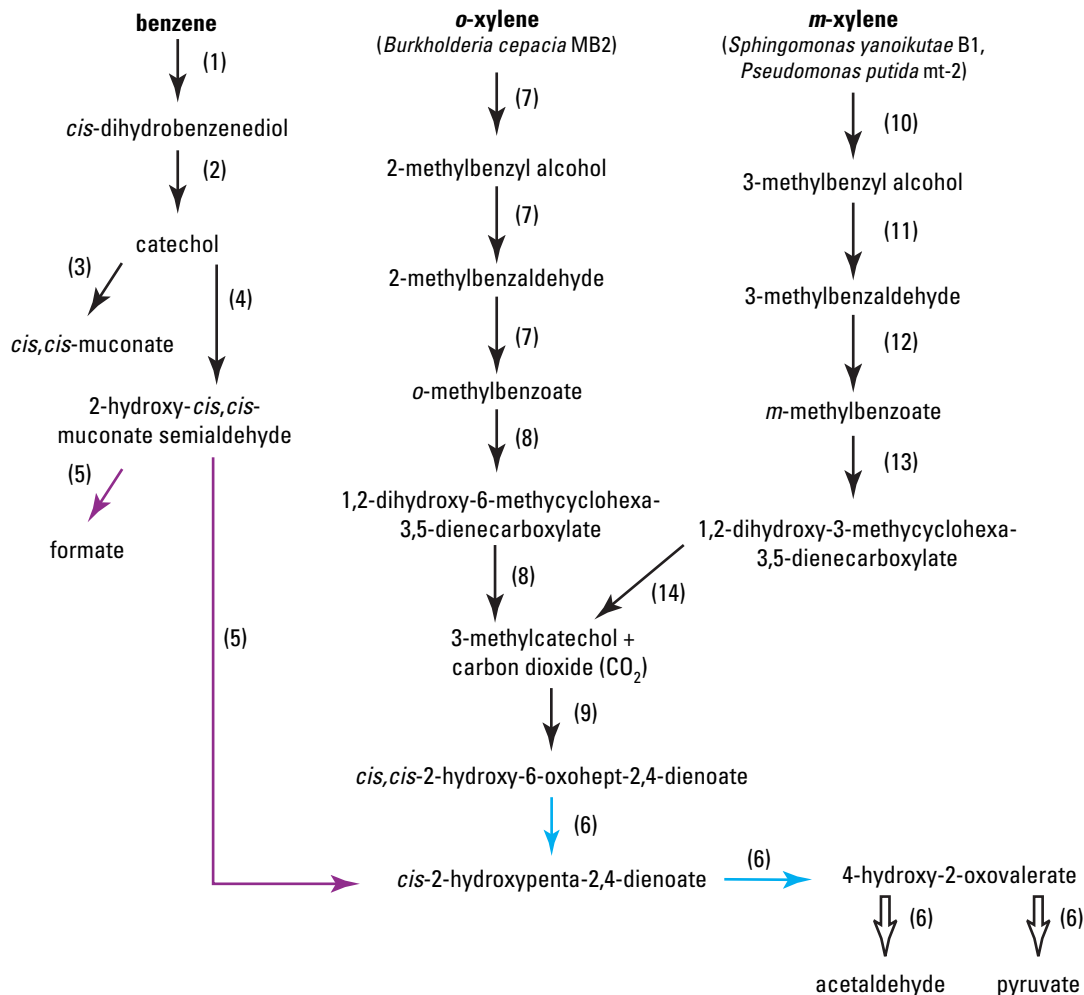
Anaerobic Biodegradation of BTEX Compounds

During anaerobic biodegradation, BTEX compounds are used metabolically as electron donors (carbon source, primary substrate) by select microbial populations to produce the energy for cell growth (Aronson and Howard, 1997). BTEX degradation can be limited by the availability of terminal electron acceptors such as nitrate, sulfate, carbon dioxide, or iron (III) in the aquifer (Lovley and others, 1989; Lovley and others, 1995). These electron acceptors, however, commonly exist in ground water at sufficient levels for these reactions to proceed (Lovley and Lonergan, 1990; Kuhn and others, 1988). Figure 16 shows the anaerobic biodegradation pathways for BTEX compounds.

Anaerobic biodegradation of benzene appears to be more aquifer specific than that for the other monoaromatic hydrocarbons. Current data indicates that biodegradation may not occur at all sites (Aronson and Howard, 1997). Some of these studies show that benzene resists anaerobic metabolism in the field (Reinhard and others, 1984; Barbaro and others, 1992) and in laboratory enrichments established with sewage sludge, aquifer sediments, and contaminated soils (Krumholz and others, 1996; Barbaro and others, 1992).

Conversely, several ground-water studies have shown that BTEX degradation rates decline in a sequence from mildly reducing conditions (nitrate reduction zone, Hutchins and others, 1991) to strongly reducing conditions (methanogenesis) in shallow aquifers (Kazumi and others, 1997; Lu and others, 1999; Roychoudhury and Merrett, 2005). Furthermore, other studies show that when conditions are favorable, benzene (and other BTEX compounds) can be oxidized to carbon dioxide under highly reducing conditions. For example, benzene was rapidly mineralized under sulfate-reducing conditions in marine and freshwater sediments, and in aquifer sediments (Lovley and Lonergan, 1990; Edwards and Grbić-Galić, 1992; Lovley and others, 1995; Phelps and others, 1996; Coates and others, 1996a,b; Weiner and Lovley, 1998).

The rate of anaerobic biodegradation of BTEX compounds was quickest under sulfate-reducing conditions in laboratory and field/in situ studies (Beller and others, 1992a,b; table 18). The anaerobic biodegradation of BTEX compounds in ground water was conclusively shown in situ by Griebler and others (2004b) using compound-specific isotope analysis and signature metabolites analysis. Figure 16 shows the anaerobic pathway for BTEX compounds developed from the intermediate compounds identified in ground-water samples by Griebler and others (2004b).
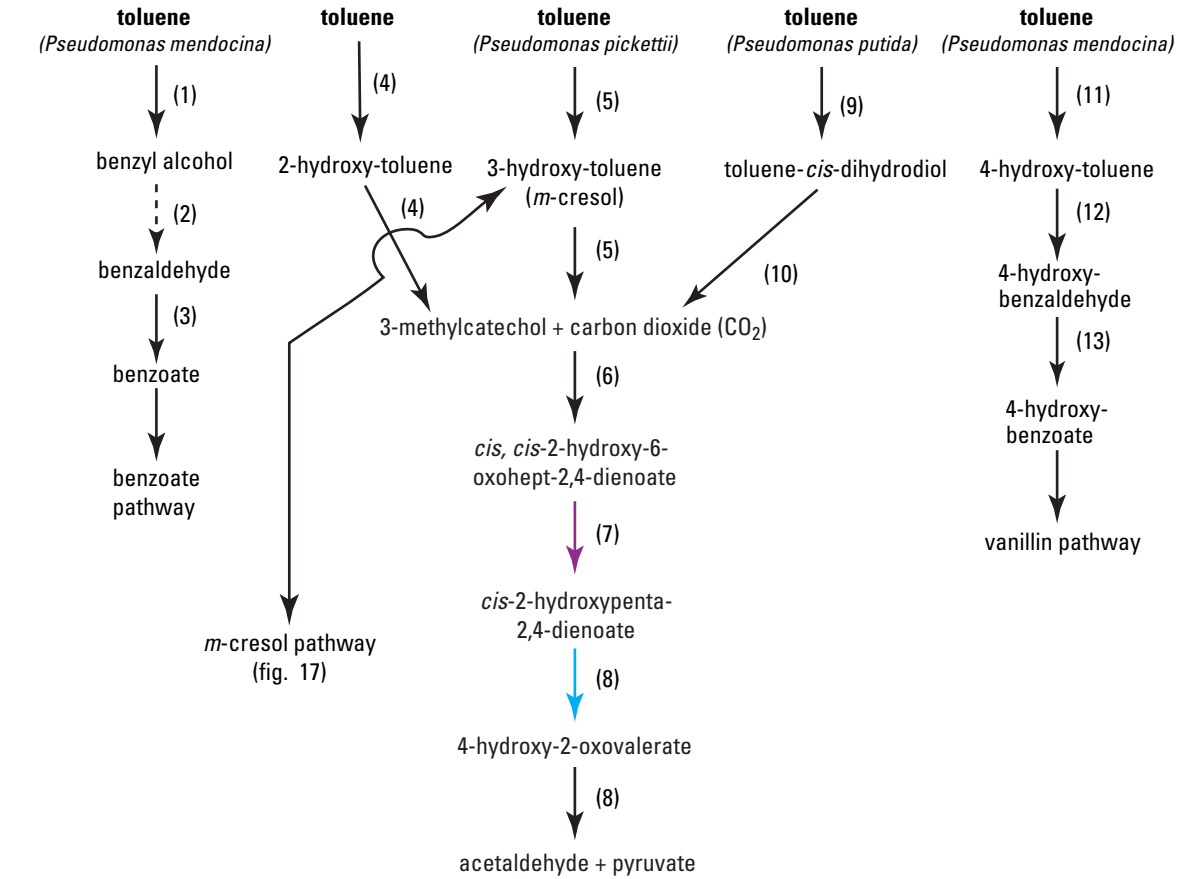
Figure 12. Laboratory-derived pathways for the aerobic biodegradation of benzene, *o*-, and *m*-xylene (modified from Hyatt and Jun Oh, 2005; Jun Oh, 2005).

toluene
(Pseudomonas mendocina)

toluene

toluene
(Pseudomonas pickettii)

toluene
(Pseudomonas putida)

toluene
(Pseudomonas mendocina)

(1)

(4)

(5)

(9)

(11)

benzyl alcohol

2-hydroxy-toluene

3-hydroxy-toluene
(*m*-cresol)

toluene-*cis*-dihydrodiol

4-hydroxy-toluene

(2)

(4)

(4)

(5)

(10)

(12)

benzaldehyde

3-methylcatechol + carbon dioxide (CO_2)

4-hydroxy-
benzaldehyde

(3)

(5)

(13)

benzoate

(6)

4-hydroxy-
benzoate

benzoate
pathway

cis, cis-2-hydroxy-6-
oxohept-2,4-dienoate

(7)

vanillin pathway

m-cresol pathway
(fig. 17)

cis-2-hydroxypenta-
2,4-dienoate

(8)

4-hydroxy-2-oxovalerate

(8)

acetaldehyde + pyruvate

EXPLANATION

Proven microbe-catalyzed

→ Oxidation reaction

→ Hydrolysis

→ Hydration

Pseudomonas mendocina **Microorganism catalyzing reaction**

Literature reference describing reaction pathway

(1) Shaw and Harayama, 1992
(2) Shaw and others, 1993
(3) Inoue and others, 1995
(4) Shields and others, 1995
(5) Olsen and others, 1994
(6) Kukor and Olsen, 1991
(7) Menn and others, 1991

(8) Lau and others, 1994
(9) Wackett and others, 1988
(10) Simpson and others, 1987
(11) Yen and others, 1991
(12) McIntire and others, 1986
(13) Bossert and others, 1989

Figure 13.   Laboratory-derived pathways for the aerobic biodegradation of toluene
(modified from Wackett and Zeng, 2004).

p-xylene
(*Pseudomonas putida* mt-2)

↓ (1)

p-methylbenzyl alcohol

↓ (2)

p-tolualdehyde

↓ (3)

p-toluate

↓ (4)

4-methycyclohexa-3, 5-diene-
1, 2-*cis*-diol-1-carboxylic acid

↓ (5)

4-methylcatechol

(6) ↙   ↘ (10)

2-hydroxy-5-methyl-*cis*,   3-methyl-*cis, cis*-
cis-muconic semialdehyde   hexadienedioate

(7) ↓   ↓ (11)

2-oxohex-*trans*-4-enoate   4-methylmucono-lactone

(8) ↓

4-hydroxy-2-oxohexanoate

(9) ↓   ↓ (9)

pyruvate   propanol
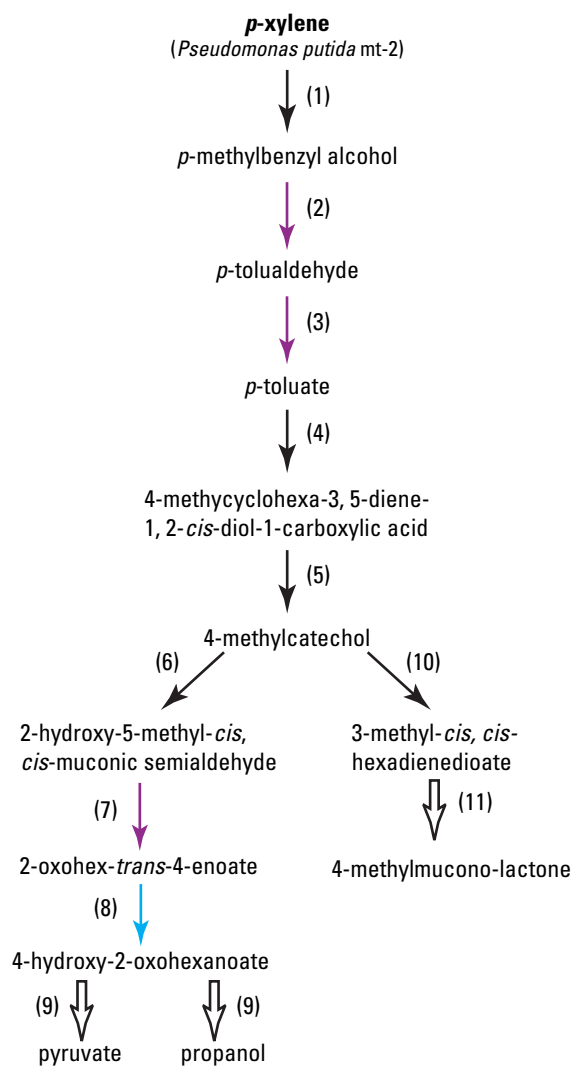
EXPLANATION

Proven microbe-catalyzed

→   Oxidation reaction

→   Hydrolysis

→   Hydration

⇒   Reaction, unspecified

Pseudomonas putida   **Microorganism catalyzing reaction**

Literature reference describing reaction pathway

(1) Shaw and Harayama, 1992   (7) Diaz and Timmis, 1995
(2) Biegert and others, 1995   (8) Harayama and others, 1989
(3) Shaw and Harayama, 1990   (9) Platt and others, 1995
(4) Walsh and others, 1983   (10) Murakami and others, 1997
(5) Whited and others, 1986   (11) Helin and others, 1995
(6) Cerdan and others, 1994

Figure 14.   Laboratory-derived pathways for the aerobic biodegradation of p-xylene (modified from Mili and Stephens, 2006).

Aerobic Biodegradation of Methyl *Tert*-butyl Ether

The compound methyl *tert*-butyl ether contains ether bonds and branched hydrocarbon skeletons (*tert*-butyl branch) that are common to compounds that persist in the environment (Smith and others, 2003; Alexander, 1973). Although early studies concluded that MTBE was recalcitrant to biodegradation (Squillace and others, 1997), more recent studies show that, once initiated, the aerobic biodegradation of MTBE is relatively rapid (Deeb and others, 2000), but markedly slower than BTEX degradation (table 17). MTBE may appear to persist in contaminated ground water if ground-water studies are concluded too quickly, especially in areas where MTBE is a new contaminant. This time lag before degradation begins is the time it takes the microorganisms in the aquifer to adapt and begin to use MTBE as a carbon source (Drogos and Diaz, 2000; Wilson and others, 2000, 2005). Wilson and others (2005), using data from various studies, show that microorganisms capable of degrading MTBE take from 10 to 500 times longer to double their population than do those microbes that degrade BTEX compounds. Therefore, the capacity for the natural attenuation of MTBE depends on the age of the contamination and the presence of microorganisms capable of assimilating MTBE.

Although some studies concluded that MTBE degrades slowly in aerobic environments (Squillace and others, 1997), other more recent studies show that MTBE is easily degraded under the proper conditions. For example, in a laboratory study of lake and streambed sediments collected from 11 sites across the United States, MTBE completely degraded within 50 days (Bradley and others, 1999, 2001). A study by Landmeyer and others (2001) clearly shows that MTBE was recalcitrant under anaerobic conditions during 2 weeks of monitoring, but rapidly degraded when oxygen was added to a small, discrete flowpath in shallow ground water.

Although three different bacteria are able to aerobically degrade MTBE via two different pathways (fig. 17; Pedersen and Essenberg, 2005), the exact mechanisms driving MTBE degradation are not well known. *Tert*-butyl alcohol (TBA) is a commonly detected by-product of aerobic MTBE degradation (Steffan and others, 1997). Aerobic biodegradation rates for MTBE are difficult to find in the literature, but those that are published indicate that the rates are substantially slower than those for BTEX compounds (table 17). Some studies indicate that the degradation of MTBE may be inhibited by the presence of BTEX compounds (Deeb and Alvarez-Cohen, 2000); however, others indicate that BTEX compounds do not inhibit MTBE degradation (Aronson and others, 1999; Drogos and Diaz, 2000; Kane and others, 2001; Sedran and others, 2002).

ethylbenzene
(Peudomonas putida 39/D,
Pseudomonas sp. NCIB 10643)

(1)

cis-2,3-dihydroxy-2,3-dihydroethylbenzene

(1)

2,3-dihydroxyethylbenzene

(2)

2-hydroxy-6-oxoocta-2,4-dienoate

(2)   (2)

propanoate   *cis*-2-hydroxypenta-2,4-dienoate

(3)

4-hydroxy-2-oxovalerate

(3)   (3)

acetaldehyde   pyruvate

ethylbenzene
(Pseudomonas sp. NCIB 9816-4)

(4)   (4)

styrene   (S)-1-phenylethanol

(4)

To the styrene pathway (fig. 19)   acetophenone

(4)

2-hydroxyaceto-phenone

EXPLANATION

Proven microbe-catalyzed

→ Oxidation reaction

→ Hydrolysis

→ Hydration

Peudomonas putida **Microorganism catalyzing reaction**

Literature reference describing reaction pathway
(1) Gibson and others, 1973
(2) Jindrova and others, 2002
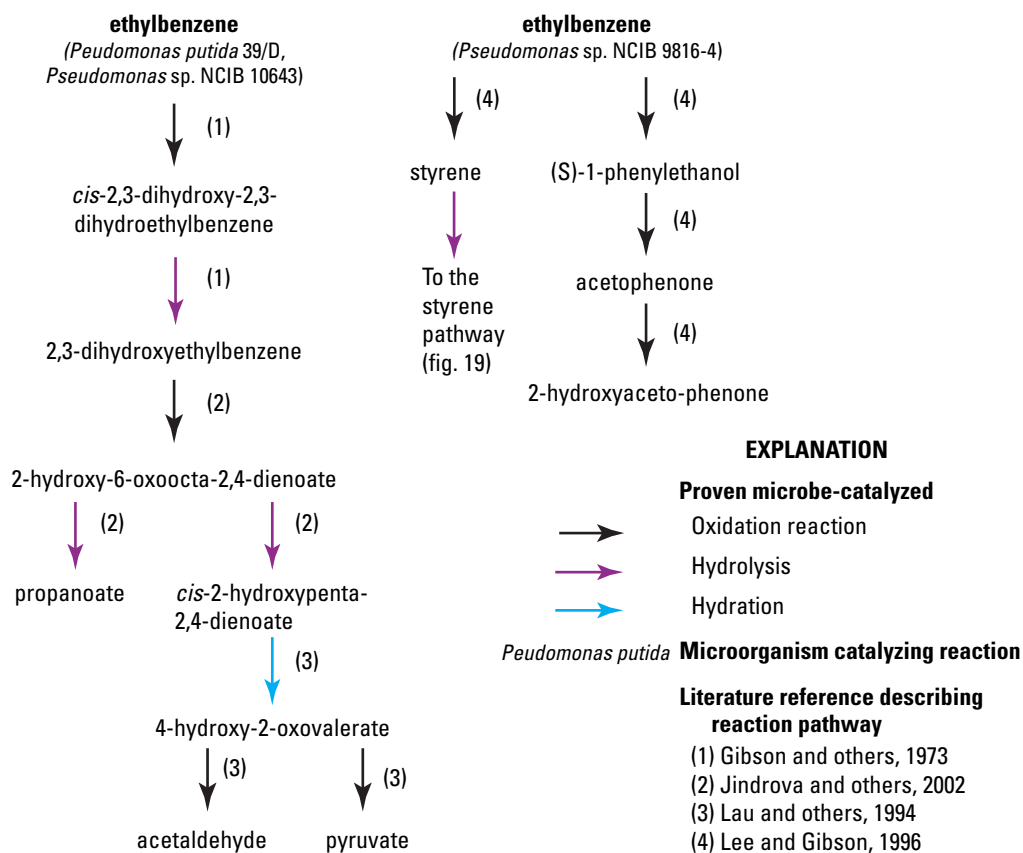(3) Lau and others, 1994
(4) Lee and Gibson, 1996

Figure 15. Laboratory-derived pathway for the aerobic biodegradation of ethylbenzene (modified from McLeish, 2005).

Anaerobic Biodegradation of Methyl *Tert*-butyl Ether

The anaerobic biodegradation of MTBE is known to proceed, although slowly, under methanogenic (Wilson and others, 2000; Wilson and others, 2005), sulfate-reducing (Somsamak and others, 2001), iron-reducing (Finneran and Lovley, 2001), and nitrate-reducing (Bradley and others, 2001) conditions. Little is presently known, however, about the pathway of MTBE biodegradation under any of these conditions, although it has been suggested that anaerobic biodegradation could be initiated by a hydrolytic mechanism (O'Reilly and others, 2001; Kuder and others, 2005).

In a six-state ground-water study, Kolhatkar and others (2000) observed the degradation of MTBE and TBA in anoxic zones near 76 gas stations. Using data from four of those sites, degradation rates were calculated for MTBE and TBA. These degradation rates ranged from 0.0011 to 0.0271 day^{-1} for MTBE and 0.0151 to 0.0351 day^{-1} for TBA. MTBE and TBA degradation were observed only at sites that were methanogenic (dissolved methane >0.5 mg/L). Furthermore, these sites were depleted in sulfate relative to background concentrations. Kolhatkar and others (2002) confirmed the anaerobic degradation of MTBE and TBA in anoxic ground water using stable carbon isotope analysis. This study also concludes that the anaerobic biodegradation rates of MTBE and TBA may exceed those estimated for aerobic biodegradation.

Table 17.   Average half-life for the aerobic biodegradation of the fuel compounds BTEX and methyl *tert*-butyl ether to carbon dioxide in an uncontaminated and contaminated matrix of aquifer sediments and ground water.[1]

[—, no studies referenced; <, less than]

Compound	Median[1] primary degradation rate (day^{-1})	Average half-life in uncontaminated matrix (days)			Average half-life in contaminated matrix (days)		
		Field setting[2]	Laboratory column[3]	Laboratory microcosm	Field setting	Laboratory column[4]	In situ microcosm
benzene	0.096	238	1.5	408	[5]58	[3]1−2.3	[6,10]3−31
toluene	.20	[8]135−238	4−7	[8,9]40−60	[7]5	2.3	[6]4.5−7
ethylbenzene	.113	238	—	[9]60−139	—	2.3	[13,11]11
m-, *p*-xylene	.054	238	—	[8,9]31−60	—	.350	[12,11]3.5−11
o-xylene	.054	238	1−4	[9]12−25	—	2.3	[6,10]14−83
methyl *tert*-butyl ether	[12].0039	—	—	—	—	—	[13]<365

[1] Aronson and others, 1999

[2] American Petroleum Institute, 1994

[3] Alvarez and others, 1998

[4] Anid and others, 1993

[5] Kemblowski and others, 1987

[6] Nielsen and others, 1996

[7] McCarty and others, 1998

[8] Barker and others, 1987

[9] Hubbard and others, 1994

[10] Holm and others, 1992

[11] Thomas and others, 1990

[12] Laboratory microcosm

[13] Fenner and others, 2000

Table 18.   Mean half-life in days for the anaerobic biodegradation of the fuel compounds BTEX, and methyl *tert*-butyl ether, *tert*-butyl alcohol under various reducing conditions.[1]
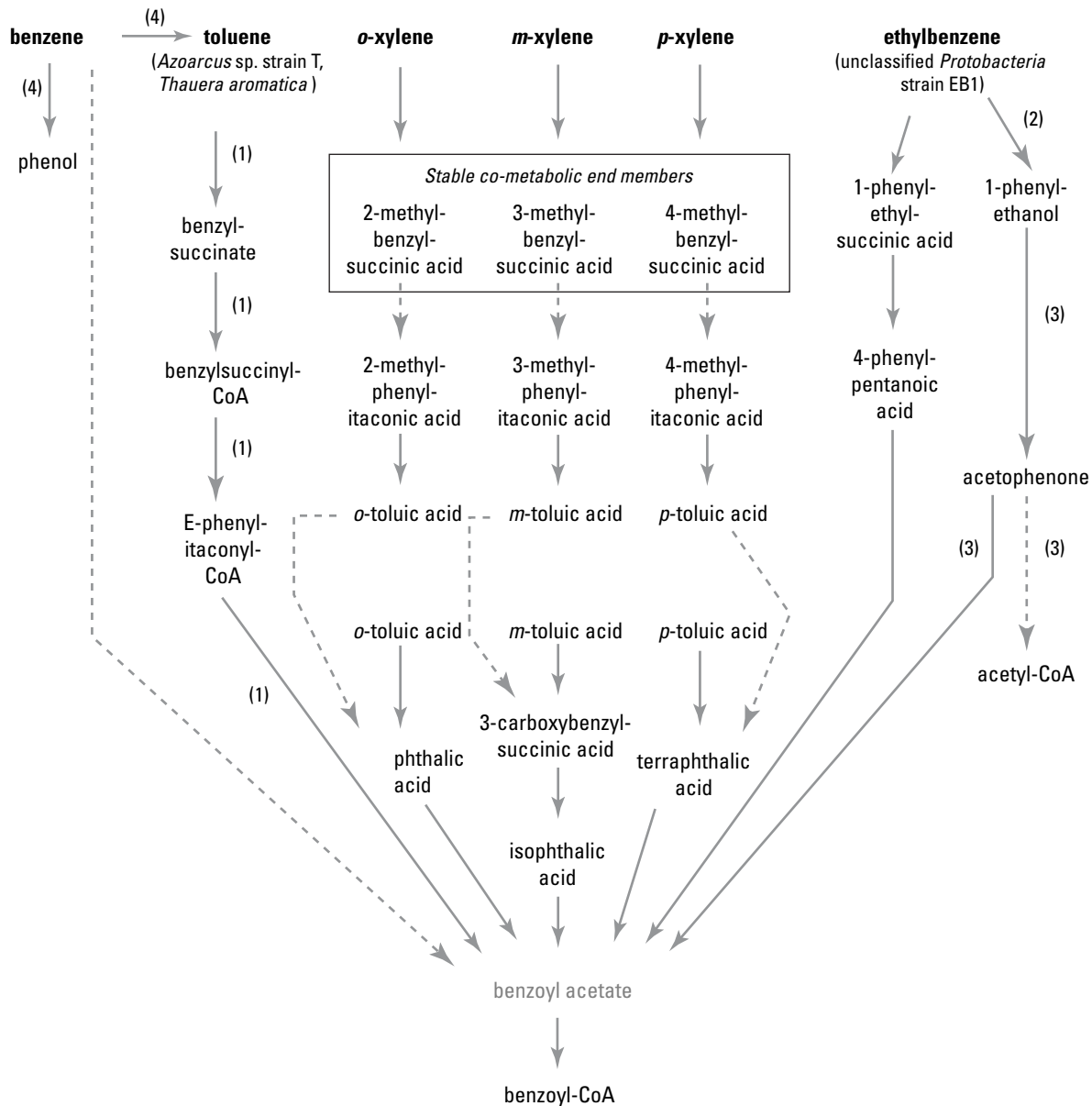
[(46), number of samples used to derive the mean value; MTBE, methyl *tert*-butyl ether; TBA, *tert*-butyl alcohol; —, not available]

Environmental condition	Benzene	Toluene	Ethylbenzene	*o*-Xylene	*m*-Xylene	*p*-Xylene	MTBE	TBA
Field/in situ studies	210 (41)	12 (46)	46 (37)	33 (33)	43 (34)	46 (26)	—	—
Nitrate-reducing studies	97 (38)	13 (42)	104 (28)	108 (46)	113 (35)	108 (29)	—	—
Iron-reducing studies	140 (11)	516 (10)	1,828 (4)	1,822 (8)	1,822 (8)	1,822 (8)	—	—
Sulfate-reducing studies	50 (9)	61 (14)	197 (7)	109 (9)	141 (8)	198 (5)	—	—
Methanogenic studies	61 (16)	50 (24)	229 (8)	304 (14)	317 (10)	406 (7)	[2,3]30−7,302	[2,3]15−502

[1] Aronson and Howard, 1997, p. 16

[2] Kolhatkar and others, 2000

[3] Wilson and others, 2005

benzene   (4)→   **toluene**
(*Azoarcus* sp. strain T,
Thauera aromatica)

o-xylene   **m-xylene**   **p-xylene**

ethylbenzene
(unclassified *Protobacteria*
strain EB1)

(4)

phenol

(1)

benzyl-
succinate

Stable co-metabolic end members

2-methyl-
benzyl-
succinic acid

3-methyl-
benzyl-
succinic acid

4-methyl-
benzyl-
succinic acid

1-phenyl-
ethyl-
succinic acid

(2)

1-phenyl-
ethanol

(1)

benzylsuccinyl-
CoA

2-methyl-
phenyl-
itaconic acid

3-methyl-
phenyl-
itaconic acid

4-methyl-
phenyl-
itaconic acid

4-phenyl-
pentanoic
acid

(3)

(1)

E-phenyl-
itaconyl-
CoA

o-toluic acid   m-toluic acid   p-toluic acid

acetophenone

o-toluic acid   m-toluic acid   p-toluic acid

(1)

(3)   (3)

phthalic
acid

3-carboxybenzyl-
succinic acid

terraphthalic
acid

acetyl-CoA

isophthalic
acid

benzoyl acetate

benzoyl-CoA

EXPLANATION

Proven microbe-catalyzed
→   Reductive pathway

- - →   **Postulated microbe-catalyzed
reductive pathway**

Azoarcus sp.   **Microorganism catalyzing reaction**

benzoyl acetate   **Postulated compound from other experiments**

**Literature reference describing
reaction pathway**

(1) Beller and Spormann, 1997
(2) Kniemeyer and Heider, 2001
(3) Ball and others, 1996
(4) Ulrich and others, 2005

Figure 16. Field and laboratory-derived pathways for the anaerobic biodegradation
of the BTEX compounds—benzene, toluene, ethylbenzene, and xylene (modified from
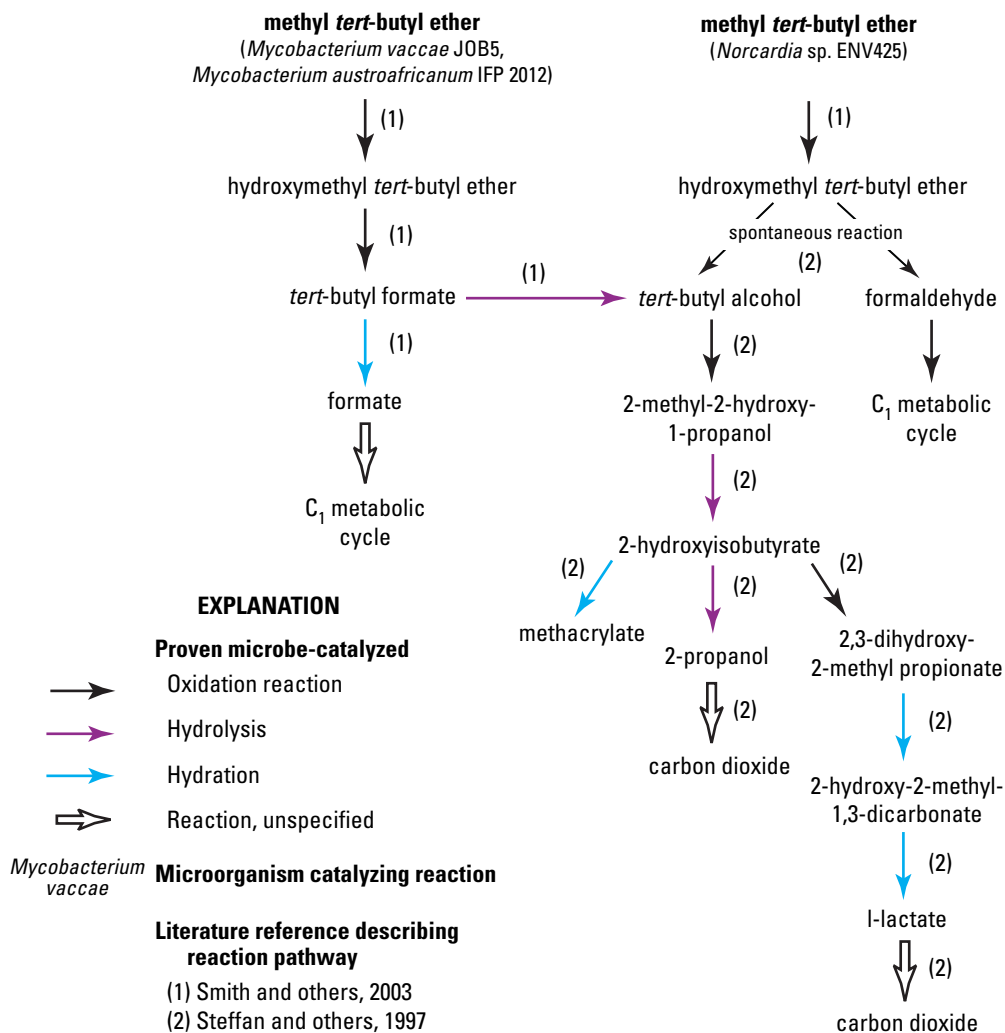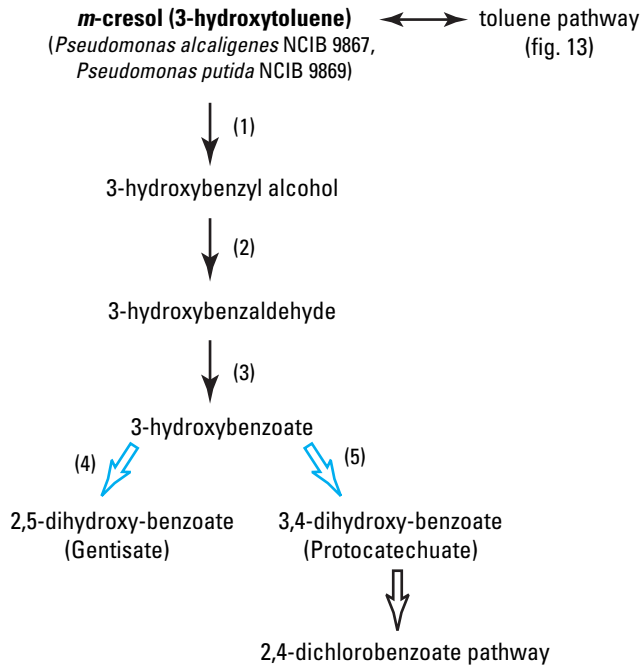Edwards and Grbić-Galić, 1994; and Griebler and others, 2004b).

Figure 17. Laboratory-derived pathway for the aerobic biodegradation of methyl *tert*-butyl ether (modified from Pedersen and Essenberg, 2005).

m-cresol (3-hydroxytoluene) ⟷ toluene pathway
(*Pseudomonas alcaligenes* NCIB 9867, (fig. 13)
Pseudomonas putida NCIB 9869)

↓ (1)

3-hydroxybenzyl alcohol

↓ (2)

3-hydroxybenzaldehyde

↓ (3)

3-hydroxybenzoate

(4) ↙   ↘ (5)

2,5-dihydroxy-benzoate   3,4-dihydroxy-benzoate
(Gentisate)   (Protocatechuate)

⇩

2,4-dichlorobenzoate pathway

EXPLANATION

Proven microbe-catalyzed

→   Oxidation reaction

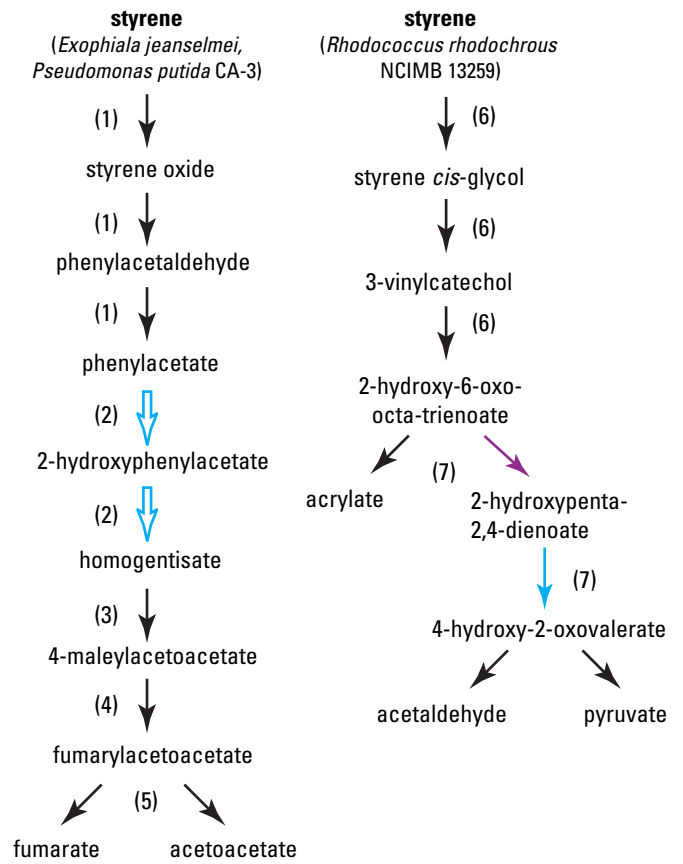⇨   Hydroxylation reaction

⇨   Reaction, unspecified

Pseudomonas alcaligenes   **Microorganism catalyzing reaction**

**Literature reference describing
reaction pathway**

(1) Keat and Hopper, 1978a
(2) Keat and Hopper, 1978b
(3) Hopper and Taylor, 1975
(4) Poh and Bayly, 1980
(5) Nakazawa and Hayashi, 1978

Figure 18. Laboratory-derived pathway for the aerobic biodegradation of *m*-cresol (modified from Sakai and others, 2005).

styrene   **styrene**
(*Exophiala jeanselmei,*   (*Rhodococcus rhodochrous*
Pseudomonas putida CA-3)   NCIMB 13259)

(1) ↓   ↓ (6)

styrene oxide   styrene *cis*-glycol

(1) ↓   ↓ (6)

phenylacetaldehyde   3-vinylcatechol

(1) ↓   ↓ (6)

phenylacetate   2-hydroxy-6-oxo-
              octa-trienoate

(2) ⇩   ↙   ↘ (7)

2-hydroxyphenylacetate   acrylate   2-hydroxypenta-
                         2,4-dienoate

(2) ⇩   ↓ (7)

homogentisate   4-hydroxy-2-oxovalerate

(3) ↓   ↙   ↘

4-maleylacetoacetate   acetaldehyde   pyruvate

(4) ↓

fumarylacetoacetate

↙ (5) ↘

fumarate   acetoacetate

EXPLANATION

Proven microbe-catalyzed

→   Oxidation reaction

⇨   Hydroxylation reaction

→   Hydrolysis

→   Hydration

Exophiala jeanselmei   **Microorganism catalyzing reaction**

**Literature reference describing
reaction pathway**

(1) Cox and others, 1996
(2) Olivera and others, 1994
(3) Fernandez-Canon and Penalva,1995
(4) Hagedorn and Chapman,1985
(5) Crawford,1976
(6) Warhurst and others, 1994
(7) Lau and others, 1994

Figure 19. Laboratory-derived pathways for the aerobic biodegradation of styrene (modified from Kraus and others, 2005).

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Glossary

Sources: [1]International Union of Pure and Applied Chemistry, 2006; [2]U.S. Environmental Protection Agency, 2004; [3]Wiedemeier and others, 1998; [4]U.S. Geological Survey, 2006; [5]Brown and LeMay, 1977

A

abiotic   Not associated with living organisms. Synonymous with abiological.[1]

abiotic transformation   Process in which a substance in the environment is modified by nonbiological mechanisms.[1]

absorption   The penetration of atoms, ions, or molecules into the bulk mass of a substance.[2]

adsorption   The retention of atoms, ions, or molecules onto the surface of another substance.[2]

aerobe   An organism that needs oxygen for respiration and hence for growth.[1]

aerobic   An environment or process that sustains biological life and growth, or occurs only when free (molecular) oxygen is present.[2]

aerobic conditions   Conditions for growth or metabolism in which the organism is sufficiently supplied with oxygen.[1]

alcohols   Compounds in which a hydroxy group, –OH, is attached to a saturated carbon atom R3COH. The term *hydroxyl* refers to the radical species, HO.[1]

aldehydes   Compounds RC(=O)H, in which a carbonyl group is bonded to one hydrogenatom and to one R group[1]. R represents a functional group such as an alkyl group (methyl or ethyl radical).[1]

aliphatic compounds   A broad category of hydrocarbon compounds distinguished by a straight, or branched, open chain arrangement of the constituent carbon atoms, excluding aromatic compounds. The carbon-carbon bonds may be either single or multiple bonds. Alkanes, alkenes, and alkynes are aliphatic hydrocarbons.[2]

alkanes   The homologous group of linear (acyclic) aliphatic hydrocarbons having the general formula C_nH_{2n+2}. Alkanes can be straight chains, branched chains, or ring structures, sometimes called paraffins.[1]

alkenes   Acyclic branched or unbranched hydrocarbons having one carbon–carbon double bond and the general formula C_nH_{2n}, sometimes called olefins.[1]

alkyl groups   Univalent groups derived from alkanes by removal of a hydrogen atom from any carbon atom with the general form of $–C_nH_{2n+1}$. The groups derived by removal of a hydrogen atom from a terminal carbon atom of unbranched alkanes form a subclass called normal alkyl (n-alkyl) groups $H[CH_2]_n$.[1]

alkyl radicals   Carbon-centered radicals derived formally by removal of one hydrogen atom from an alkane, e.g., CH_3CH_2—(ethyl radical).[1]

alkynes   The group of acyclic branched or unbranched hydrocarbons having a carbon-carbon triple bond that have the general formula C_nH_{2n-2}.[1]

ambient   The surrounding environment and prevailing conditions.[2]

anaerobe   An organism that does not need free-form oxygen for growth. Many anaerobes are even sensitive to free oxygen.[1]

anaerobic   A biologically-mediated process or condition not requiring molecular or free oxygen.[1]

analyte   The component of a system to be analyzed.[1] For example, chemical elements or ions in ground-water sample.[2]

anoxic   An environment without oxygen.[2]

aquifer   A water-bearing layer of soil, sand, gravel, rock or other geologic formation that will yield usable quantities of water to a well under normal hydraulic gradients or by pumpage.[3]

aromatic   A group of organic compounds that are cyclic, contain resonant carbon-carbon double bonds in the form of at least one 6-carbon benzene ring.[2] In the traditional sense, "having a chemistry typified by benzene."[1]

attenuation   The set of human-made or natural processes that either reduce or appear to reduce the amount of a chemical compound as it migrates away from one specific point towards another point in space or time. For example, the apparent reduction in the amount of a chemical in a ground-water plume as it migrates away from its source. Degradation, dilution, dispersion, sorption, or volatilization are common processes of attenuation.[2]

B

biodegradation   Transformation of substances into new compounds through biochemical reactions or the actions of microorganisms, such as bacteria. Typically expressed in terms of a rate constant or half-life.[2]

biota   Living organisms.[2]

breakdown product   A compound derived by chemical, biological, or physical action on a chemical compound. The breakdown is a process which may result in a more toxic or a less toxic compound and a more persistent or less persistent compound than the original compound.[2]

C

carbon   Element number 6 in the periodic table of elements. For a description of the various types of carbon as a solid, the term carbon should be used only in combination with an additional noun or a clarifying adjective (that is, organic carbon).[1]

catabolism   The breakdown of complex molecules into simpler ones through the oxidation of organic substrates to provide biologically available energy (for example, ATP, adenosine triphosphate).[1]

catalysis   The process where a catalyst increases the rate of a chemical reaction without modifying the overall standard Gibbs energy change in the reaction.[1]

catalyst   Substances that increases the rate of a chemical reaction. The catalyst is both a reactant and product of the reaction. The words catalyst and catalysis should not be used when the added substance reduces the rate of reaction (see inhibitor).[1]

chemical bond   The forces acting among two atoms or groups of atoms that lead to the formation of an aggregate with sufficient stability to make it convenient for the chemist to consider it as an independent "molecular species."[1]

chemical induction (coupling)   When one reaction accelerates another in a chemical system there is said to be chemical induction or coupling. Coupling is caused by an intermediate or by-product of the inducing reaction that participates in a second reaction. Chemical induction is often observed in oxidation–reduction reactions.[1]

chemical reaction   A process that results in the interconversion of chemical species. Chemical reactions may be elementary reactions or stepwise reactions.[1]

chlorinated solvent   A volatile organic compound containing chlorine. Some common solvents are trichloroethylene, tetrachloroethylene, and carbon tetrachloride.[2]

***cis, trans* isomers**   The difference in the positions of atoms (or groups of atoms) relative to a reference plane in an organic molecule. In a *cis*-isomer, the atoms are on the same side of the molecule, but are on opposite sides in the *trans*-isomer. Sometimes called stereoisomers, these arrangements are common in alkenes and cycloalkanes.[1]

co-metabolism   The simultaneous metabolism of two compounds, in which the degradation of the second compound (the secondary substrate) depends on the presence of the first compound (the primary substrate). For example, in the process of degrading methane, some bacteria can degrade chlorinated solvents that would otherwise not be degraded under the same conditions.[2]

concentration   Composition of a mixture characterized in terms of mass, amount, volume or number concentration with respect to the volume of the mixture.[1]

conservative constituent or compound   One that does not degrade, is unreactive, and its movement is not retarded within a given environment (aquifer, stream, contaminant plume, and so forth).[4]

constituent   An essential part or component of a system or group (that is, an ingredient of a chemical mixture). For instance, benzene is one constituent of gasoline.[4]

covalent bond   A region of relatively high electron density between atomic nuclei that results from sharing of electrons and that gives rise to an attractive force and a characteristic internuclear distance. Carbon-hydrogen bonds are covalent bonds.[1]

D

daughter product   A compound that results directly from the degradation of another. For example *cis*-1,2-dichloroethene (12-cDCE)is commonly a daughter product of trichloroethene (TCE) degradation. This is a term that has currently (2006) fallen out of general use. See metabolic by-product.[3]

dehydrohalogenation   Removal of hydrogen and halide ions from an alkane resulting in the formation of an alkene.[3]

denitrification   Bacterial reduction of nitrate to nitrite to gaseous nitrogen or nitrous oxides under anaerobic conditions.[4]

density (ρ)   The ratio of the mass of a substance to the mass of an equal volume of distilled water at 4 degrees Celsius. Since the mass of one milliliter (ml) of water at 4 degrees Celsius is exactly 1 gram, the specific gravity (unitless) is numerically equivalent to its density (in grams per ml).[1]

detection limit (in analysis)   The minimum single result that, with a stated probability, can be distinguished from a representative blank value during the laboratory analysis of substances such as water, soil, air, rock, biota, tissue, blood, and so forth.[1]

dichloroelimination   Removal of two chlorine atoms from an alkane compound and the formation of an alkene compound within a reducing environment.[4]

dihaloelimination   Removal of two halide atoms from an alkane compound and the formation of an alkene compound within a reducing environment.[3]

diols   Chemical compounds that contain two hydroxy (--OH) groups, generally assumed to be, but not necessarily, alcoholic. Aliphatic diols are also called glycols.[1]

downgradient   In the direction of decreasing static hydraulic head (potential).[4]

E

electron acceptor   A compound capable of accepting electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron acceptors are compounds that are relatively oxidized and include oxygen, nitrate, iron (III), manganese (IV), sulfate, carbon dioxide, or in some cases chlorinated aliphatichydro-

carbons such as perchloroethene (PCE), TCE, DCE, and vinyl chloride.[2]

electron donor   A compound capable of supplying (giving up) electrons during oxidation-reduction reactions. Microorganisms obtain energy by transferring electrons from electron donors such as organic compounds (or sometimes reduced inorganic compounds such as sulfide) to an electron acceptor. Electron donors are compounds that are relatively reduced and include fuel hydrocarbons and native organic carbon.[3]

electronegativity   Concept introduced by Nobel Laureate Linus Pauling as the power of an atom to attract electrons to itself.[1]

elimination   Reaction where two groups such as chlorine and hydrogen are lost from adjacent carbon atoms and a double bond is formed in their place.[3]

endergonic reaction   A chemical reaction that requires energy to proceed. A chemical reaction is endergonic when the change in free energy is positive.[3]

enzyme   Macromolecules, mostly proteins or conjugated proteins produced by living organisms, that facilitate the degradation of a chemical compound (catalyst). In general, an enzyme catalyzes only one reaction type (reaction specificity) and operates on only one type of substrate (substrate specificity).[1, 4]

epoxidation   A reaction wherein an oxygen molecule is inserted in a carbon-carbon double bond and an epoxide is formed.[3]

epoxides   A subclass of epoxy compounds containing a saturated three-membered cyclic ether. See epoxy compounds.[1]

epoxy compounds   Compounds in which an oxygen atom is directly attached to two adjacent or nonadjacent carbon atoms in a carbon chain or ring system; thus cyclic ethers.[1]

F

facultative anaerobes   Microorganisms that use (and prefer) oxygen when it is available, but can also use alternate electron acceptors such as nitrate under anaerobic conditions when necessary.[3]

fermentation   Microbial metabolism in which a particular compound is used both as an electron donor and an electron acceptor resulting in the production of oxidized and reduced daughter products.[3]

functional group   An atom, or a group of atoms attached to the base structure of a compound that has similar chemical properties irrespective of the compound to which it is a part. It defines the characteristic physical and chemical properties of families of organic compounds.[1]

G

H

half-life ($t_{1/2}$)   The time required to reduce the concentration of a chemical to 50 percent of its initial concentration. Units are typically in hours or days.[2]

halide   An element from the halogen group. These include fluorine, chlorine, bromine, iodine, and astatine.[5]

halogen   Group 17 in the periodic table of the elements. These elements are the reactive nonmetals and are electronegative.[5]

Henry's Law   The relation between the partial pressure of a compound and the equilibrium concentration in the liquid through a proportionality constant known as the Henry's Law constant.[4]

Henry's Law constant   The concentration ratio between a compound in air (or vapor) and the concentration of the compound in water under equilibrium conditions.[4]

heterogeneous   Varying in structure or composition at different locations in space.[4]

heterotrophic   Organisms that derive carbon from organic matter for cell growth.[4]

homogeneous   Having uniform structure or composition at all locations in space.[4]

hydration   The addition of a water molecule to a compound within an aerobic degradation pathway.[5]

hydrogen bond   A form of association between an electronegative atom and a hydrogen atom attached to a second, relatively electronegative atom. It is best considered as an electrostatic interaction, heightened by the small size of hydrogen, which permits close proximity of the interacting dipoles or charges.[1]

hydrogenation   A process whereby an enzyme in certain microorganisms catalyzes the hydrolysis or reduction of a substrate by molecular hydrogen.[2]

hydrogenolysis   A reductive reaction in which a carbon-halogen bond is broken, and hydrogen replaces the halogen substituent.[3]

hydrolysis   A chemical transformation process in which a chemical reacts with water. In the process, a new carbon-oxygen bond is formed with oxygen derived from the water molecule, and a bond is cleaved within the chemical between carbon and some functional group.[1]

hydroxylation   Addition of a hydroxyl group to a chlorinated aliphatic hydrocarbon.[3]

I

inhibition   The decrease in rate of reaction brought about by the addition of a substance (inhibitor), by virtue of its effect on the concentration of a reactant, catalyst, or reaction intermediate.[1]

in situ   In its original place; unmoved; unexcavated; remaining in the subsurface.[4]

J

K

L

lag phase   The growth interval (adaption phase) between microbial inoculation and the start of the exponential growth phase during which there is little or no microbial growth.[1]

M

measurement   A description of a property of a system by means of a set of specified rules, that maps the property onto a scale of specified values, by direct or "mathematical" comparison with specified reference(s).[1]

metabolic by-product (by-product)   A product of the reaction between an electron donor and an electron acceptor. Metabolic by-products include volatile fatty acids, daughter products of chlorinated aliphatic hydrocarbons, methane, and chloride.[3]

metabolism   The entire physical and chemical processes involved in the maintenance and reproduction of life in which nutrients are used to generate energy and in the process degrade to simpler molecules (catabolism), which by themselves may be used to form more complex molecules (anabolism).[1]

methanogens   Strictly anaerobic archaebacteria, able to use only a very limited spectrum of substrates (for example, molecular hydrogen, formate, methanol, methylamine, carbon monoxide or acetate) as electron donors for the reduction of carbon dioxide to methane.[1]

methanogenic   The formation of methane by certain anaerobic bacteria (methanogens) during the process of anaerobic fermentation.[4]

microcosm   A diminutive, representative system analogous to a larger system in composition, development, or configuration.[4]

microorganisms   Microscopic organisms that include bacteria, protozoans, yeast, fungi, mold, viruses, and algae.[4]

mineralization   The release of inorganic chemicals from organic matter in the process of aerobic or anaerobic decay.[4]

monoaromatic   Aromatic hydrocarbons containing a single benzene ring.[4]

N

nucleophile   A chemical reagent that reacts by forming covalent bonds with electronegative atoms and compounds.[4]

nutrients   Major elements (for example, nitrogen and phosphorus) and trace elements (including sulfur, potassium, calcium, and magnesium) that are essential for the growth of organisms.[3]

O

octanol-water partition coefficient (K_{OW})   The equilibrium ratio of a chemical's concentration in octanol (an alcoholic compound) to its concentration in the aqueous phase of a two-phase octanol/water system, typically expressed in log units (log K_{OW}). K_{OW} provides an indication of a chemical's solubility in fats (lipophilicity), its tendency to bioconcentrate in aquatic organisms, or sorb to soil or sediment.[2]

order of reaction   A chemical rate process occurring in systems for which concentration changes (and hence the rate of reaction) are not themselves measurable, provided it is possible to measure a chemical flux.[1]

organic carbon (soil) partition coefficient (K_{OC})   The proportion of a chemical sorbed to the solid phase, at equilibrium in a two-phase, water/soil or water/sediment system expressed on an organic carbon basis. Chemicals with higher K_{OC} values are more strongly sorbed to organic carbon and, therefore, tend to be less mobile in the environment.[2]

oxidation   In general, a reaction in which electrons are transferred from a chemical to an oxidizing agent, or where a chemical gains oxygen from an oxidizing agent.[2]

P

Q

R

rate   Derived quantity in which time is a denominator quantity. Rate of x is dx/dt.[1]

rate constant, k   See order of reaction.[1]

rate-controlling step (rate-limiting step, rate-determining step)   The elementary reaction having the largest control factor exerts the strongest influence on the rate (v). A step having a control factor much larger than any other step is said to be rate-controlling.[1]

recalcitrant   Unreactive, nondegradable, refractory.[4]

redox   Reduction-oxidation reactions. Oxidation and reduction occur simultaneously; in general, the oxidizing agent gains electrons in the process (and is reduced) while the reducing agent donates electrons (and is oxidized).[2]

reduction   In general, a reaction in which electrons are transferred to a chemical from a reducing agent, or where oxygen is removed from a chemical.[2]

respiration   The process of coupling oxidation of organic compounds with the reduction of inorganic compounds, such as oxygen, nitrate, iron (III), manganese (IV), and sulfate.[2]

S

solvolysis   Generally, a reaction with a solvent, involving the rupture of one or more bonds in the reacting solute. More specifically the term is used for substitution, elimination, or fragmentation reactions in which a solvent species is the nucleophile (hydrolysis, if the solvent is water or alcoholysis, if the solvent is an alcohol).[1]

stable   As applied to chemical species, the term expresses a thermodynamic property, which is quantitatively measured by relative molar standard Gibbs energies. A chemical species A is more stable than its isomer B if $\Delta rGo > 0$ for the (real or hypothetical) reaction A $\rightarrow$ B, under standard conditions.[1]

substrate   Component in a nutrient medium, supplying microorganisms with carbon (C-substrate), nitrogen (N-substrate) as "food" needed to grow.[1]

T

terminal electron acceptor (TEA)   A compound or molecule that accepts an electron (is reduced) during metabolism (oxidation) of a carbon source. Under aerobic conditions molecular oxygen is the terminal electron acceptor. Under anaerobic conditions a variety of terminal electron acceptors may be used. In order of decreasing redox potential, these TEAs include nitrate, manganic manganese, ferric iron, sulfate, and carbon dioxide. Microorganisms preferentially utilize electron acceptors that provide the maximum free energy during respiration. Of the common terminal electron acceptors listed above, oxygen has the highest redox potential and provides the most free energy during electron transfer.[4]

U

unsaturated zone   The zone between land surface and the capillary fringe within which the moisture content is less than saturation and pressure is less than atmospheric. Soil pore spaces also typically contain air or other gases. The capillary fringe is not included in the unsaturated zone.[4]

upgradient   In the direction of increasing potentiometric (piezometric) head.[4]

V

vadose zone   The zone between land surface and the water table within which the moisture content is less than saturation (except in the capillary fringe) and pressure is less than atmospheric. Soil pore spaces also typically contain air or other gases. The capillary fringe is included in the vadose zone.[4]

vapor pressure (Pv)   The force per unit area exerted by a vapor in an equilibrium state with its pure solid, liquid, or solution at a given temperature. Vapor pressure is a measure of a substance's propensity to evaporate. Vapor pressure increases exponentially with an increase in temperature. Typical units are millimeter of mercury (mm Hg), torr, or inches of mercury (in. Hg).[2]

W

water solubility (S)   The maximum amount of a chemical that can be dissolved in a given amount of pure water at standard conditions of temperature and pressure. Typical units are milligrams per liter (mg/L), gallons per liter (g/L), or pounds per gallon (lbs/gal).[2]

X

Y

Z