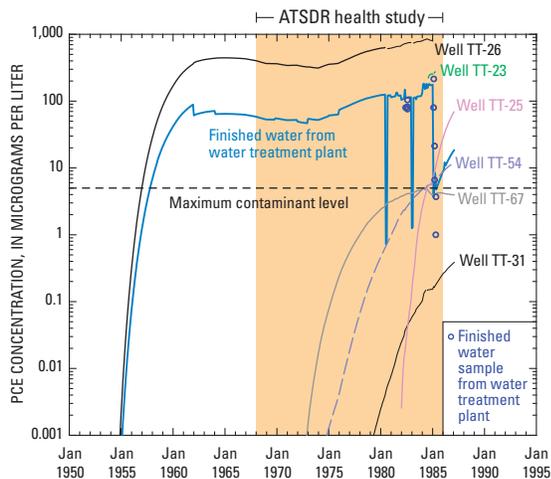# Analyses of Groundwater Flow, Contaminant Fate and Transport, and Distribution of Drinking Water at Tarawa Terrace and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina: Historical Reconstruction and Present-Day Conditions

Chapter D: Properties and Degradation Pathways of Common Organic Compounds in Groundwater

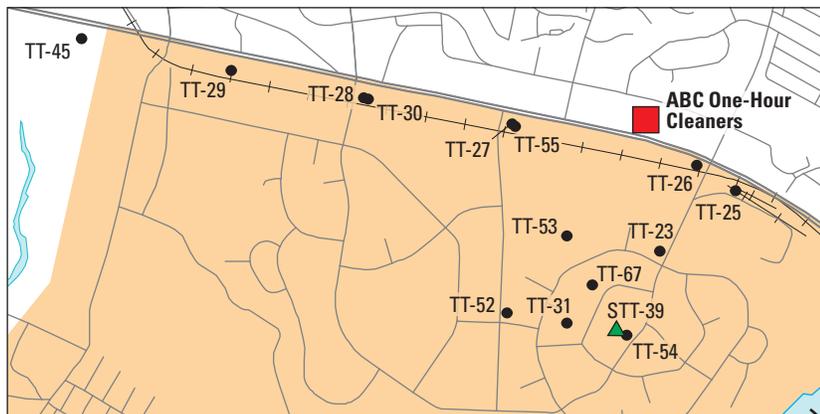ATSDR
AGENCY FOR TOXIC SUBSTANCES
AND DISEASE REGISTRY

Analyses of Groundwater Flow, Contaminant Fate and Transport, and Distribution of Drinking Water at Tarawa Terrace and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina: Historical Reconstruction and Present-Day Conditions

Chapter D: Properties and Degradation Pathways of Common Organic Compounds in Groundwater

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Foreword

The Agency for Toxic Substances and Disease Registry (ATSDR), an agency of the U.S. Department of Health and Human Services, is conducting an epidemiological study to evaluate whether in utero and infant (up to 1 year of age) exposures to volatile organic compounds in contaminated drinking water at U.S. Marine Corps Base Camp Lejeune, North Carolina, were associated with specific birth defects and childhood cancers. The study includes births occurring during the period 1968–1985 to women who were pregnant while they resided in family housing at the base. During 2004, the study protocol received approval from the Centers for Disease Control and Prevention Institutional Review Board and the U.S. Office of Management and Budget.

Historical exposure data needed for the epidemiological case-control study are limited. To obtain estimates of historical exposure, ATSDR is using water-modeling techniques and the process of historical reconstruction. These methods are used to quantify concentrations of particular contaminants in finished water and to compute the level and duration of human exposure to contaminated drinking water.

Final interpretive results for Tarawa Terrace and vicinity—based on information gathering, data interpretations, and water-modeling analyses—are presented as a series of ATSDR reports. These reports provide comprehensive descriptions of information, data analyses and interpretations, and modeling results used to reconstruct historical contaminant levels in drinking water at Tarawa Terrace and vicinity. Each topical subject within the water-modeling analysis and historical reconstruction process is assigned a chapter letter. Specific topics for each chapter report are listed below:

- **Chapter A**: Summary of Findings

- **Chapter B**: Geohydrologic Framework of the Castle Hayne Aquifer System

- **Chapter C**: Simulation of Groundwater Flow

- **Chapter D**: Properties and Degradation Pathways of Common Organic Compounds in Groundwater

- **Chapter E**: Occurrence of Contaminants in Groundwater

- **Chapter F**: Simulation of the Fate and Transport of Tetrachloroethylene (PCE) in Groundwater

- **Chapter G**: Simulation of Three-Dimensional Multispecies, Multiphase Mass Transport of Tetrachloroethylene (PCE) and Associated Degradation By-Products

- **Chapter H**: Effect of Groundwater Pumping Schedule Variation on Arrival of Tetrachloroethylene (PCE) at Water-Supply Wells and the Water Treatment Plant

- **Chapter I**: Parameter Sensitivity, Uncertainty, and Variability Associated with Model Simulations of Groundwater Flow, Contaminant Fate and Transport, and Distribution of Drinking Water

- **Chapter J**: Field Tests, Data Analyses, and Simulation of the Distribution of Drinking Water

- **Chapter K**: Supplemental Information

An electronic version of this report, *Chapter D: Properties and Degradation Pathways of Common Organic Compounds in Groundwater*, and its supporting information and data will be made available on the ATSDR Camp Lejeune Web site at *http://www.atsdr.cdc. gov/sites/lejeune/index.html*. Readers interested solely in a summary of this report or any of the other reports should refer to *Chapter A: Summary of Findings* that also is available at the ATSDR Web site.

Contents

Figures

Tables

Glossary and Abbreviations

Definitions of terms and abbreviations used throughout this report are listed below.

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, for example 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]

ATSDR   Agency for Toxic Substances and Disease Registry.

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]

BTEX   Benzene, toluene, ethylbenzene, and xylene; a group of VOCs found in petroleum hydrocarbons, such as gasoline, and other common environmental contaminants.

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.[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]

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]

IUPAC   International Union of Pure and Applied Chemistry.

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]

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 micro-organisms 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]

USEPA   U.S. Environmental Protection Agency.

USGS   U.S. Geological Survey.

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]

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

Conversion Factors

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

Analyses of Groundwater Flow, Contaminant Fate and Transport, and Distribution of Drinking Water at Tarawa Terrace and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina: Historical Reconstruction and Present-Day Conditions

Chapter D: Properties and Degradation Pathways of Common Organic Compounds in Groundwater

By Stephen J. Lawrence[1]

Abstract

Two of three water-distribution systems that have histori-cally supplied drinking water to family housing at U.S. Marine Corps Base Camp Lejeune, North Carolina, were contaminated with volatile organic compounds (VOCs). Tarawa Terrace was contaminated mostly with tetrachloroethylene, and Hadnot Point was contaminated mostly with trichloroethylene. Because scientific data relating to the harmful effects of VOCs on a child or fetus are limited, the Agency for Toxic Substances and Disease Registry (ATSDR), an agency of the U.S. Department of Health and Human Services, is conducting an epidemiologi-cal study to evaluate potential associations between in utero and infant (up to 1 year of age) exposures to VOCs in con-taminated drinking water at Camp Lejeune and specific birth defects and childhood cancers. The study includes births occur-ring during the period 1968–1985 to women who were preg-nant while they resided in family housing at Camp Lejeune. Because limited measurements of contaminant and exposure data are available to support the epidemiological study, ATSDR is using modeling techniques to reconstruct historical condi-tions of groundwater flow, contaminant fate and transport, and the distribution of drinking water contaminated with VOCs delivered to family housing areas.

This report, Chapter D, has been released previously as U.S. Geological Survey Open-File Report 2006–1338. It pro-vides abridged information describing the most salient proper-ties and biodegradation of 27 chlorinated volatile organic compounds detected during groundwater studies in the United States. This information is condensed from an extensive list of reports, papers, and literature published by the U.S. Govern-ment, various State governments, and peer-reviewed journals. The list includes literature reviews, compilations, and sum-maries describing volatile organic compounds in groundwater. 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 VOCs in groundwater is a major concern to all who use groundwater as a drinking water source because many of these compounds can adversely affect human health. Likewise, concern about VOCs in groundwater is shared by State and Federal regulatory agencies responsible for protect-ing the groundwater resource from contaminants and for pro-tecting 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 aca-demic 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 groundwater.

Purpose and Scope

The purpose of this report is to (1) list 27 VOCs fre-quently detected in groundwater, (2) cross-reference com-mon 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 groundwater. The goal of the report is not to supplant previously published litera-ture reviews on VOCs in groundwater, 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 groundwater in the United States.

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[1] U.S. Geological Survey Georgia Water Science Center, Atlanta, Georgia

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 groundwater studies of VOC. The 27 VOCs described in this report are among the VOCs commonly detected in aquifers and groundwater sources of drinking water in the United States (Zogorski et al. 2006).

The amount of academic, government, and popular literature addressing volatile organic compounds in groundwater 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 groundwater. Citations for several of these compilations and the information summarized are listed in Table D1. 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.

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 groundwater primarily deals with site-specific contamination, and the abiotic and microbial transformation, attenuation, and degradation observed in groundwater. 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 groundwater 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 groundwater and more attentive to contamination issues of areal, regional, or national importance (Grady 2003; Hamlin et al. 2002, 2005; Moran 2006; Zogorski et al. 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 groundwater.

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)

Table D1. List of selected publications providing literature reviews and summaries of volatile organic compound degradation and behavior in groundwater.

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

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

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 groundwater within a regulatory context. Moreover, each State and territory within the United States publishes scientific and regulatory literature regarding the occurrence of VOCs in groundwater 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 groundwater.

Naming Conventions and Descriptions of Volatile Organic Compounds in Groundwater

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* (USEPA 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 D2). 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.

Table D2. Names and synonyms of volatile organic compounds commonly detected in groundwater.

[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, phenylethane	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
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] IUPAC 2006
[2] USEPA 1995

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 D2). The alkyl radicals are the lower molecular weight alkanes minus one hydrogen atom (Table D3) 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 groundwater because the stability of the benzene ring is reduced and the ring is weakened (Borden et al. 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.

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 D3). 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 D3) on the second carbon would be named 2-ethyl septane (Figure D1). 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 (Figure D1).

Figure D1. Generic and International Union of Pure and Applied Chemistry (IUPAC) naming conventions for the same aliphatic compound.

Table D3. 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]	−0.5
		CH_3 CH_3C-- [t-butyl] CH_3	

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]IUPAC 2006

Sources of Volatile Organic Compounds Detected in Groundwater

A relatively large amount of literature exists that describes VOCs in groundwater at specific, known areas of contamination. Few documents, however, describe VOC contamination in a regional or national context. One report by Arneth et al. (1989) lists the top 15 VOCs detected in groundwater near landfills in the United States and in Germany (Table D4). This list shows that the VOCs contaminating groundwater 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 D4 (Table D5; Delzer and Ivahnenko 2003; Moran 2006; Zogorski et al. 2006). Although the number of VOCs analyzed in groundwater 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 D6). The 10 most commonly detected VOCs in the studies summarized in Tables D5 and D6 are methyl *tert*-butyl ether (MTBE), tetrachloroethene (PCE), 1,1,2-trichloroethene (TCE), methyl-

benzene (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), and the dimethyl-benzenes (*m*-, *o*-, *p*-xylenes)

Sources of Chlorinated Alkanes

The chlorinated solvents within the alkane group are listed in Table D2. The CVOCs are typically used in the manufacturing of industrial, chemical, electronic, and consumer goods (Smith et al. 1988; USEPA 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 D4. Volatile organic compounds ranked by those frequently detected in groundwater 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, tetrachloro-ethylene, 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 et al. 1989, p. 399
[2]IUPAC 2006

D6

Historical Reconstruction of Drinking-Water Contamination at Tarawa Terrace and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina

Table D5. Volatile organic compounds detected in regional and national groundwater 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, Groundwater in Wisconsin[1]	Groundwater in the Santa Ana River Basin, California[2]	Groundwater 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-dichloroethene [.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 et al. 2002)
[3]Zogorski et al. 2006
[4]1, 710–3,498 samples
[5]1,190–1,208 samples
[6]828–1,096 samples

Table D6. Volatile organic compounds detected in groundwater 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, 1958–1985[2]	U.S. Naval Undersea Warfare Center, Washington, D.C.[3]	Wright-Patterson Air Force Base, Ohio, 1993–1994[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-dichloroethene [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 et al. 2004)

[2] 607 samples (Sargent et al. 1986)

[3] 121–179 samples (Dinicola et al. 2002)

[4] 343 samples (Schalk et al. 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 (USEPA 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, printing 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 D2 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 groundwater (Tables D5 and D6). 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 (USEPA 2005b, Web page: *http://www.epa.gov/envirofw/html/emci/chemref/tetrachl.html*, accessed May 23, 2006). Most of the TCE used in the United States is for vapor degreasing of metal parts and some textiles (USEPA 2005b, Web page: *http://www.epa.gov/envirofw/html/emci/chemref/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 et al. 1988).

Four chlorinated benzenes commonly detected in groundwater 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 D5 and D6). 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 (USEPA 2005b, Web page: *http://www.epa.gov/envirofw/html/emci/chemref/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 D7). 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).

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

About 16 percent of a typical gasoline blend consists of BTEX compounds (collectively, benzene, toluene, ethlybenzene, and three xylene compounds; Table D7). Of the different components contained in gasoline, BTEX compounds are the largest group associated with human-health effects. Because

Table D7. 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 trialkylphenols, 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

of the adverse impact on human health, BTEX compounds are typically the fuel components analyzed in groundwater 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 groundwater (Tables D5 and D6). 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 groundwater (USEPA 2000b, 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 et al. 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 (USEPA 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 groundwater contamination. Tables D8 through D12 list basic physical properties of 27 VOCs detected in groundwater. 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 groundwater 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 groundwater 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 groundwater (Institute for Environmental Health 2004; Mackay et al. 1996; Saichek and Reddy 2005).

Degradation of Selected Volatile Organic Compounds in Groundwater

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 et al. 1999).

The degradation of VOCs in groundwater 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 et al. 1987). Table D13 summarizes these reactions. Oxidation-reduction reactions are the dominant mechanisms driving VOC degradation and most of these reactions are catalyzed by microorganisms (Azadpour-Keeley et al. 1999; Wiedemeier et al. 1998). 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 (Olaniran et al. 2004; Vogel et al. 1987). 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 (Figure D2). Degradation pathways are illustrated in Figures D3 through D19 for a subset of the compounds listed in Table D2. These figures are modifications of pathways described in the University of Minnesota's biodegradation/biocatalysis database (Ellis et al. 2006) accessible via the Internet at *http://umbbd.msi.umn.edu*, accessed May 23, 2006.

Table D8. Henry's Law constants for selected volatile organic compounds detected in groundwater.

[IUPAC, International Union of Physical and Applied Chemistry; kPa, kilopascals; m³, cubic meter; mol, mole; °C, degrees Celsius; —, not applicable]

IUPAC name[1]	Common or alternative name[2]	Henry's Law[3] constant (H) (kPa m³ 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]IUPAC 2006

[2]USEPA 1995

[3]Lide 2003

[4]Gossett 1987

[5]National Center for Manufacturing Sciences 2006

Table D9. Water-solubility data for selected volatile organic compounds detected in groundwater.

[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]IUPAC 2006

[2]USEPA 1995

[3]Lide 2003

[4]National Center for Manufacturing Sciences 2006

[5]Horvath 1982

[6]Lyman 1982

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Historical Reconstruction of Drinking-Water Contamination at Tarawa Terrace and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina

Table D10.   Density of selected volatile organic compounds detected in groundwater 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/cm³, 20°C)	
1,2,3-trichlorobenzene	1,2,6-trichlorobenzene	[4]1.690	↑ Increasing density (heavier than water)
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	1.440	
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	↓ Decreasing density (lighter than water)
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	

[1]IUPAC 2006

[2]USEPA 1995

[3]Lide 2003

[4]Chiou et al. 1983

Table D11. Octanol-water partition coefficients for selected volatile organic compounds detected in groundwater.

[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]IUPAC 2006

[2]USEPA 1995

[3]Sangster 1989

[4]Mackay et al. 1992a

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Historical Reconstruction of Drinking-Water Contamination at Tarawa Terrace and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina

Table D12. Soil-sorption partition coefficients for selected volatile organic compounds detected in groundwater.

[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]IUPAC 2006

[2]USEPA 1995

[3]Boyd et al. 1990

[4]Schwarzenbach and Westall 1981

[5]Chiou et al. 1983

[6]Chiou et al. 1979

[7]Seip et al. 1986

[8]Friesel et al. 1984

[9]Kile et al. 1996

[10]Garbarini and Lion 1986

[11]USEPA 1994

[12]USEPA 2005b, Web page: *http://www.epa.gov/envirofw/html/emci/chemref/12-dicl.html*, accessed August 3, 2006

Table D13. 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 et al. 1987, figure 1

Aquifer conditions (aerobic and anaerobic) and microbial metabolism (respiration, fermentation, and co-metabolism) control the environmental degradation of VOCs in groundwater. 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 et al. 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 et al. 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 et al. 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 groundwater (Azadpour-Keeley et al. 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 groundwater contaminated by TCE.

Degradation of the Chlorinated Alkanes

The degradation of chlorinated VOCs is fundamentally different from that of BTEX compounds (Wiedemeier et al. 1995). The chlorinated alkanes can be degraded by abiotic processes through hydrolysis or dehydrohalogenation or by biotic processes through reductive dechlorination or dichloro-elimination. These degradation processes can proceed under either aerobic or anaerobic conditions (Figures D3–D6; Vogel 1994; Vogel and McCarty 1987a). According to McCarty (1997), 111-TCA is the only chlorinated compound that can be degraded in groundwater within 20 years under all likely groundwater 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 (Figure D2) 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 1994; Vogel and McCarty 1987b). For example, chloroethane and 111-TCA have half-lifes that are measured in days or months (Vogel 1994; Vogel et al. 1987; Table D14). 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-lifes measured in decades or centuries (Table D14). 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 et al. (1996) show that PCA can be abiotically transformed to TCE under methanogenic conditions (Figure D3). In addition, the abiotic degradation of 111-TCA has been well studied in the scientific literature (Figure D4; Chen et al. 1996; Jeffers et al. 1989; McCarty 1997; McCarty and Reinhard 1993). 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 D7; McCarty 1997; Vogel and McCarty 1987b). The presence of 11-DCE in contaminated groundwater is probably the result of the dehydrochlorination of 111-TCA (McCarty 1997).
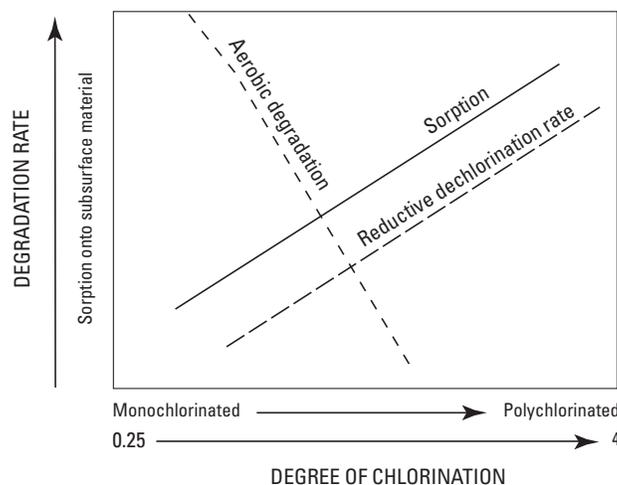
Figure D2. Relation between degree of chlorination and anaerobic reductive-dechlorination, aerobic degradation and sorption onto subsurface material (modified from Norris et al. 1993, p. 10–19). Degree of chlorination is number of chloride atoms divided by number of carbon atoms.
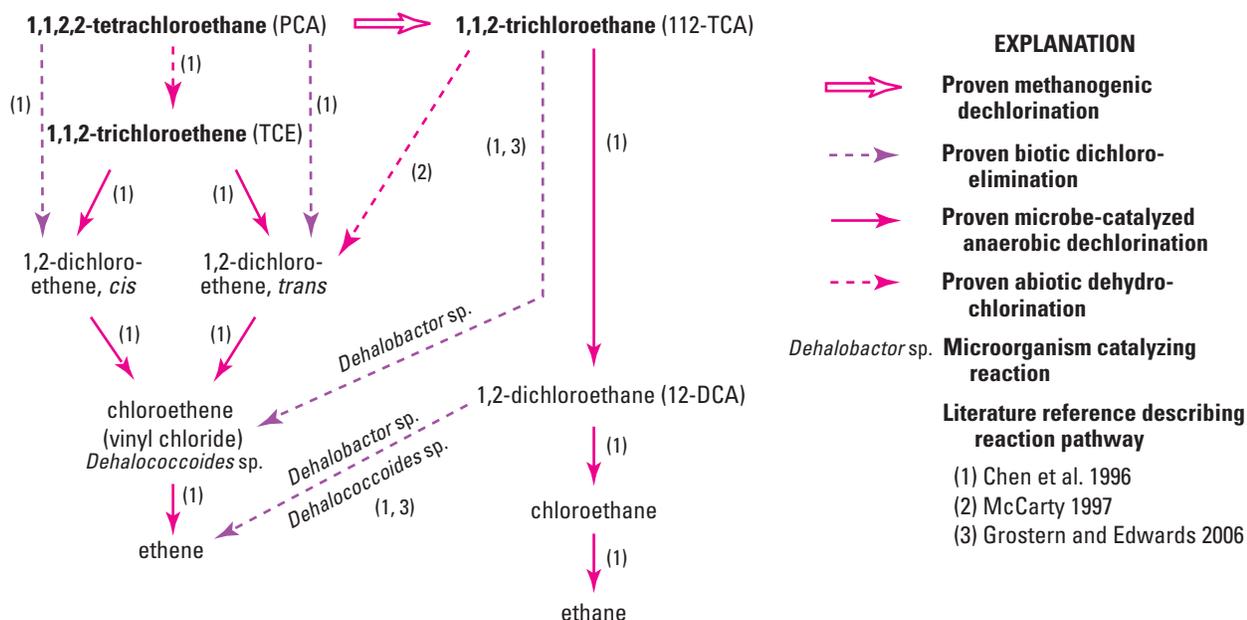
Figure D3. Laboratory-derived pathway for the abiotic degradation, anaerobic, and methanogenic biodegradation of 1,1,2,2-tetrachloroethane; 1,1,2-trichloroethene; and 1,1,2-trichloroethane (modified from Chen et al. 1996).

Table D14. Laboratory half-lifes and by-products of the abiotic degradation (hydrolysis or dehydrohalogenation) of chlorinated alkane compounds detected in groundwater.

[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 et al. 1987
1,1-dichloroethane	—	61 years	Jeffers et al. 1989
1,2-dichloroethane	—	72 years	Jeffers et al. 1989
1,1,1-trichloroethane	acetic acid; 1,1-dichloroethane	1.1–2.5 years	Jeffers et al. 1989; Mabey and Mill 1978; Vogel and McCarty 1987a, 1987b
1,1,2-trichloroethane	1,1-dichloroethane	140 years	Jeffers et al. 1989
1,1,1,2-tetrachloroethane	trichloroethene	47–380 years	Jeffers et al. 1989; Mabey and Mill, 1978
1,1,2,2-tetrachloroethane	1,1,2-trichloroethane; trichloroethene	146–292 days	Jeffers et al. 1989; Mabey and Mill, 1978

[1]IUPAC 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) → 2,2-dichloroacetate

(8) ╱   ╲ (7)

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

Figure D4.   Laboratory-derived pathway for the abiotic, aerobic, and anaerobic biodegradation of 1,1,1-trichloroethane (modified from Sands et al. 2005; Whittaker et al. 2005).

Aerobic Biodegradation

According to the degradation pathway constructed by Sands et al. (2005) and Whittaker et al. (2005), the dichloroethanes are not a by-product of 111-TCA or 112-TCA biodegradation under aerobic conditions (Figure D4). 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 (Figures D3 and D4). 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 (Figure D5; Hage et al. 2001; Janssen et al. 1985; Kim et al. 2000; Stucki et al. 1983).

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 et al. 1993
(2) Xia et al. 1996
(3) Liu et al. 1997
(4) Janssen et al. 1985
(5) Hisano et al. 1996

Figure D5. 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 et al. (1998) did not find published studies describing anaerobic biodegradation of chlorinated ethanes in groundwater. Since the publication of Wiedemeier et al. (1998), however, numerous published studies describe the anaerobic biodegradation of chlorinated ethanes. McCarty (1997) indicates that carbon tetrachloride was transformed to chlor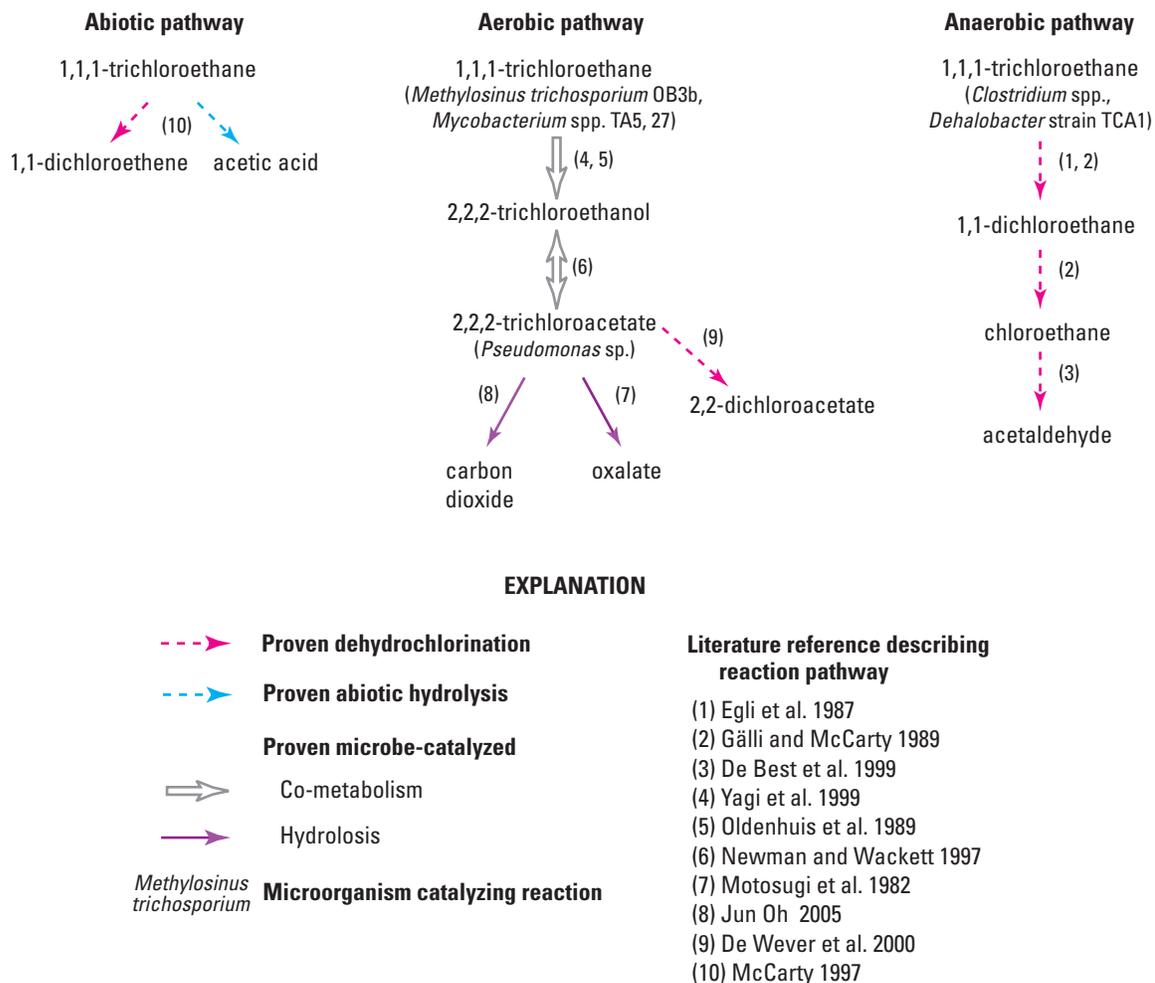oform under denitrifying conditions and mineralized to carbon dioxide and water under sulfate-reducing conditions (Figure D6). Adamson and Parkin (1999) show that under anaerobic conditions, carbon tetrachloride and 111-TCA tends to inhibit the degradation of each other. Adamson and Parkin (1999) also show that carbon tetrachloride was rapidly degraded by co-metabolism when acetate was the carbon source.

Chen et al. (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 (Figure D3). De Best et al. (1999) report that co-metabolic transformations of 112-TCA will occur under methanogenic conditions. In this study, 112-TCA was degraded to chloroethane when sufficient amounts of the carbon source were present (Figure D3). 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 an aerobic 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 D15).

Table D15. 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
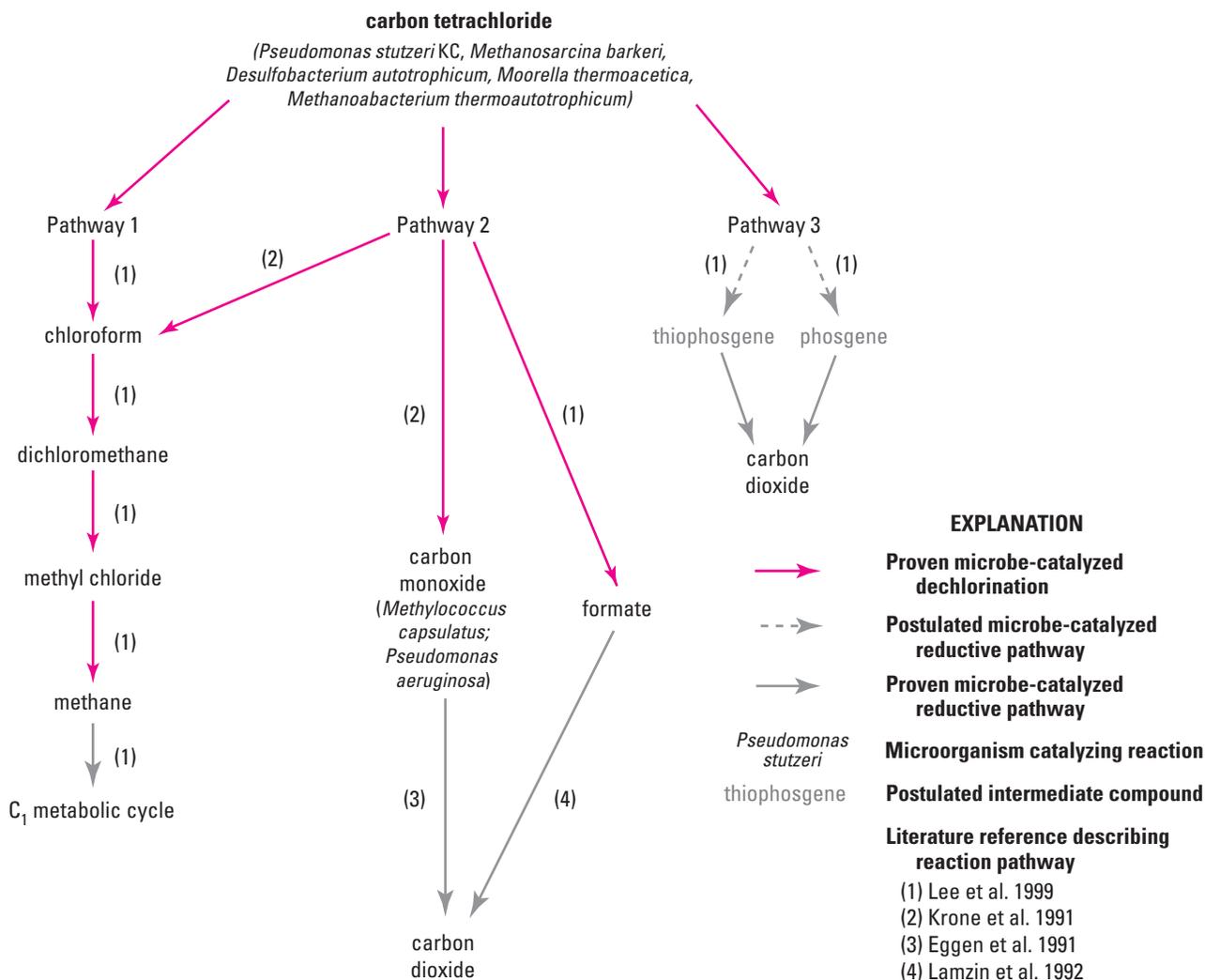
Figure D6. Laboratory-derived pathways for the anaerobic biodegradation of tetrachloromethane (carbon tetrachloride; modified from Ma et al. 2005; Sands et al. 2005).

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 groundwater as chemical by-products of PCE and TCE biodegradation (Olaniran et al. 2004; Wiedemeier et al. 1998). Abiotic degradation of PCA to TCE can occur in PCA-contaminated groundwater (Figure D3; Chen et al. 1996).

Aerobic Biodegradation

Several studies have shown that chlorinated ethenes, with the exception of PCE, can degrade under aerobic conditions by oxidation (Coleman et al. 2002; Hartmans and de Bont 1992; Hopkins and McCarty 1995; Klier et al. 1999) and by co-metabolic processes (McCarty and Semprini 1994; Murray and Richardson 1993; Vogel 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 et al. 1986). Furthermore, Aronson et al. (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 et al. (1996) suggest the structure and oxidative state of PCE prevents its aerobic degradation in water.

According to the aerobic biodegradation pathway constructed by Whittaker et al. (2005), the dichloroethenes are not a by-product of TCE degradation under aerobic conditions (Figure D4). Rather, TCE is degraded along three different pathways by different microorganisms (Figure D7). 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 (Figures D3 and D8). The compounds 12-DCE and VC, however, can be degraded under aerobic conditions by microorganisms utilizing the compounds as a primary carbon source (Figure D5; 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 et al. 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 et al. 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.

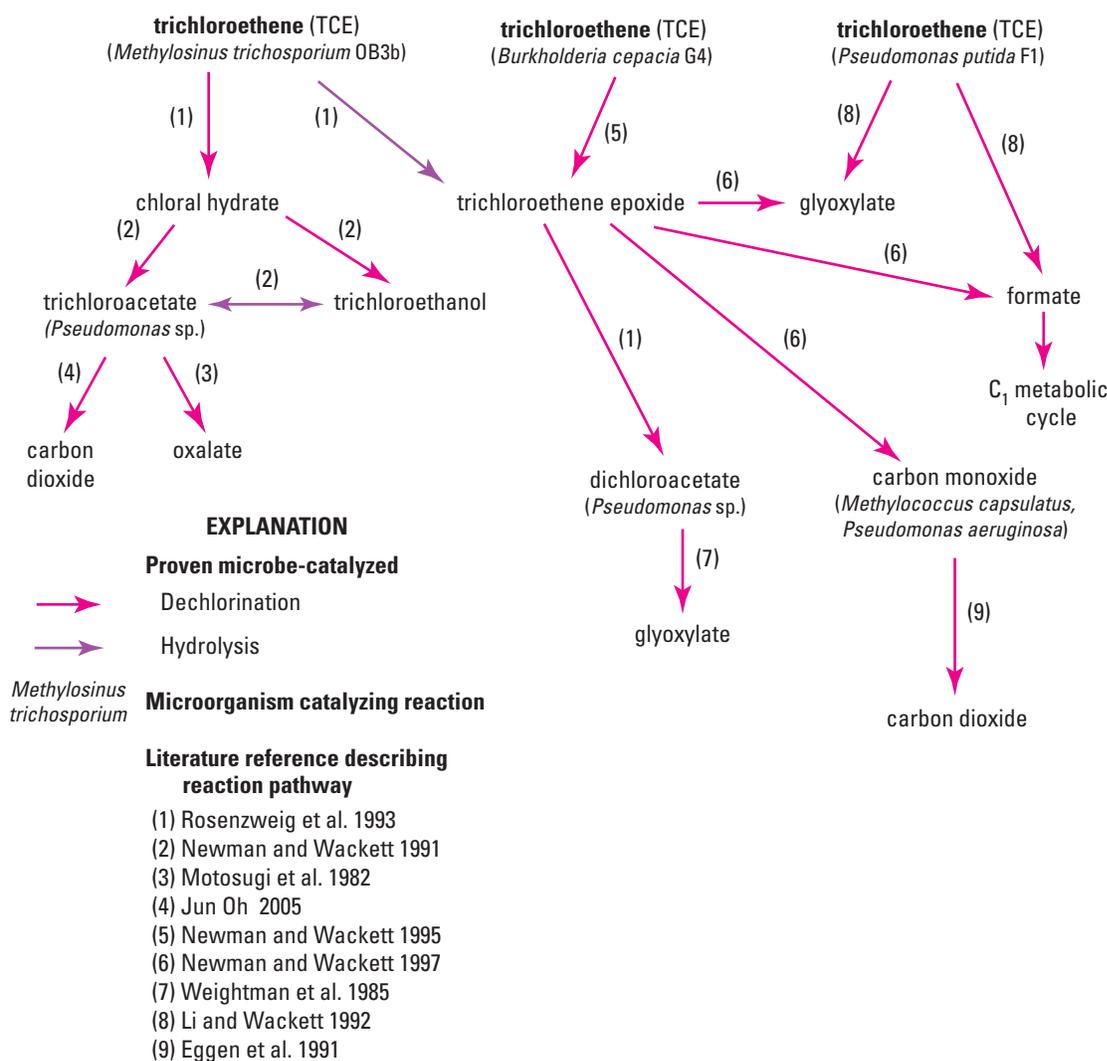**Figure D7.** Laboratory-derived pathways for the aerobic biodegradation of trichloroethene (modified from Whittaker et al. 2005).

Anaerobic Biodegradation

Many laboratory and field studies have shown that microorganisms degrade chlorinated ethenes under anaerobic conditions (Bouwer 1994; Bouwer et al. 1981; Dolfing 2000). Groundwater is considered anoxic when the dissolved oxygen concentration falls below 1.0–1.5 mg/L (Christensen et al. 2000; Stumm and Morgan 1996). 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 et al. 1995; Wiedemeier et al. 1998). As the concentration of each electron acceptor sequentially decreases, the redox potential of the groundwater becomes greater (more negative) and biodegradation by reductive dechlorination is favored.

Anaerobic conditions in groundwater can be determined by measuring the vertical and spatial concentrations of oxygen, iron (II), manganese (II), hydrogen sulfide, or methane in groundwater and using that data as a qualitative guide to the redox status (Christensen et al. 2000; Stumm and Morgan 1996). 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 et al. 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 groundwater (Braun 2004; Higgo et al. 1996; Lovley 1991; Stumm and Morgan 1996).

The highly chlorinated alkenes are commonly used as electron acceptors during anaerobic biodegradation and are reduced in the process (Vogel et al. 1987). The primary anaerobic process driving degradation of CVOCs, except VC, is reductive dechlorination (Figures D3 and D8; Bouwer 1994; Bouwer et al. 1981). 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 (Figure D8), 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 (Bouwer 1994; Vogel and McCarty 1985). 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 groundwater 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 groundwater (Freedman and Gossett 1989).

EXPLANATION

→ **Proven microbe-catalyzed dechlorination**

Dehalococcoides ethenogenes **Microorganism catalyzing reaction**

Literature reference describing reaction pathway
(1) Neumann et al. 1996
(2) Maymo-Gatell et al. 1997
(3) Magnuson et al. 1998

Figure D8. 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 et al. 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 et al. 1999). Sulfate-reducing and methanogenic groundwater 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 et al. 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 D15).

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 et al. 1991). Under aerobic conditions, 1,2,4-trichlorobenzene (124-TCB; Haigler et al. 1988) and chlorobenzene (CB; Sander et al. 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 et al. 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 D9 to D11, 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 et al. 1998).

Calculated and published degradation half-lifes for the chlorobenzenes under aerobic conditions are shown in Table D16. The compounds 124-TCB, 12-DCB, and CB lose 50 percent of their initial mass within 180 days (Table D16). 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 et al. (2005), all isomers of DCB were mineralized to CO_2 within 2 days by the aerobe *Acidovorax avenae*.

Although Wiedemeier et al. (1998) indicate that few studies existed that described the anaerobic degradation of the chlorobenzene compounds, a study by Ramanand et al. (1993) did suggest that 124-TCB could be biodegraded to chlorobenzene with 14-DCB as an intermediate compound under anaerobic conditions. Moreover, Middeldorp et al. (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 (Griebler et al. 2004a; Holscher et al. 2003). In addition, Adrian et al. (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.
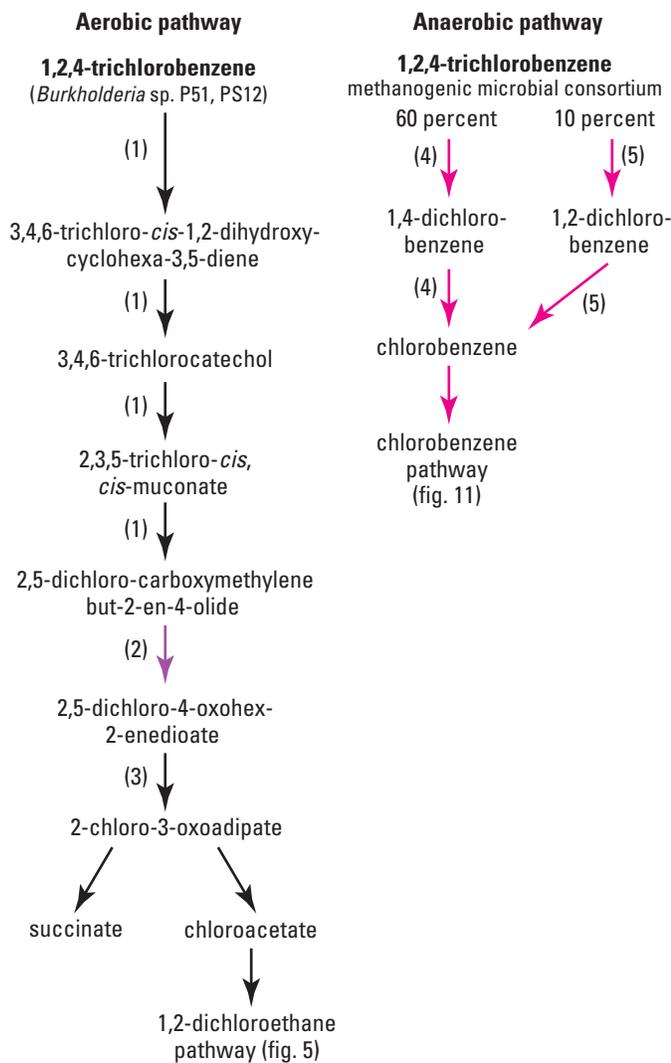
Furthermore, Ramanand et al. (1993) show that 124-TCB had declined by 63 percent within 30 days under anaerobic conditions. Dermietzel and Vieth (2002) show that the anaerobic biodegradation of 14-DCB was markedly slower under iron-reducing conditions than under aerobic conditions. In general, it appears that the biodegradation of the chlorinated benzenes is slower under anaerobic than under aerobic conditions.

Table D16. Laboratory or environmental half-lifes and by-products for the aerobic and anaerobic biodegradation of selected chlorinated benzene compounds detected in groundwater.

[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 et al. 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]IUPAC 2006

D24

Historical Reconstruction of Drinking-Water Contamination at Tarawa Terrace and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina

Aerobic pathway

1,2,4-trichlorobenzene
(*Burkholderia* sp. P51, PS12)

(1) ↓

3,4,6-trichloro-*cis*-1,2-dihydroxy-
cyclohexa-3,5-diene

(1) ↓

3,4,6-trichlorocatechol

(1) ↓

2,3,5-trichloro-*cis*,
cis-muconate

(1) ↓

2,5-dichloro-carboxymethylene
but-2-en-4-olide

(2) ↓

2,5-dichloro-4-oxohex-
2-enedioate

(3) ↓

2-chloro-3-oxoadipate

↙   ↘

succinate   chloroacetate

↓

1,2-dichloroethane
pathway (fig. 5)

Anaerobic pathway

1,2,4-trichlorobenzene
methanogenic microbial consortium

60 percent   10 percent

(4) ↓   (5) ↓

1,4-dichloro-   1,2-dichloro-
benzene   benzene

(4) ↓   (5) ↙

chlorobenzene

↓

chlorobenzene
pathway
(fig. 11)

EXPLANATION

Proven microbe-catalyzed

→ Oxidation reaction

→ Dechlorination

→ Hydrolysis

Burkholderia sp. **Microorganism catalyzing reaction**

**Literature reference describing
reaction pathway**

(1) van der Meer et al. 1991
(2) Kasberg et al. 1995
(3) Reineke and Knackmuss 1988
(4) Middeldorp et al. 1997
(5) National Institute for Resources
      and Environment 2001

Figure D9. Laboratory-derived pathways for the aerobic
and anaerobic biodegradation of 1,2,4-trichlorobenzene
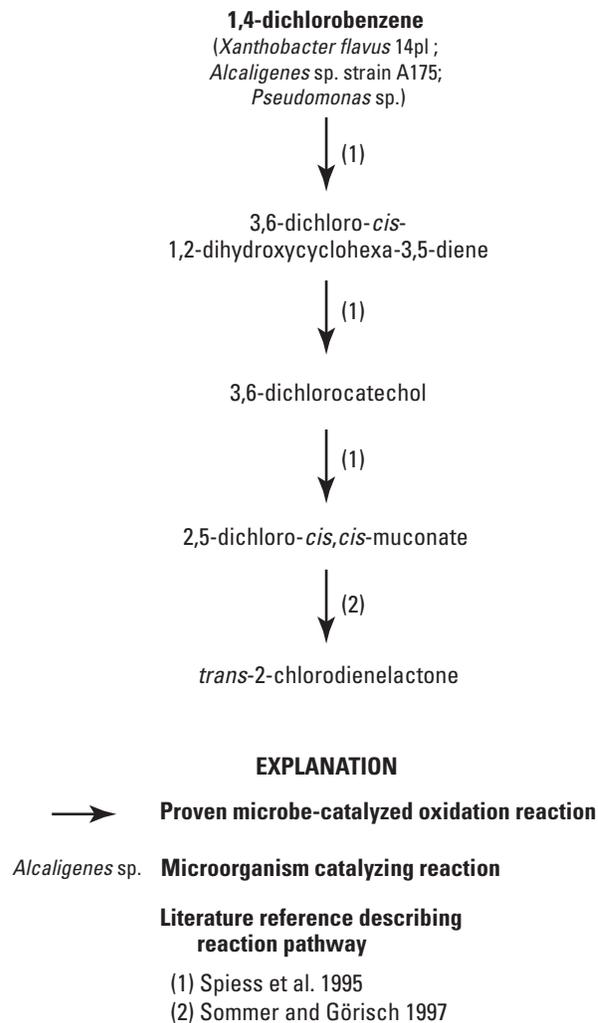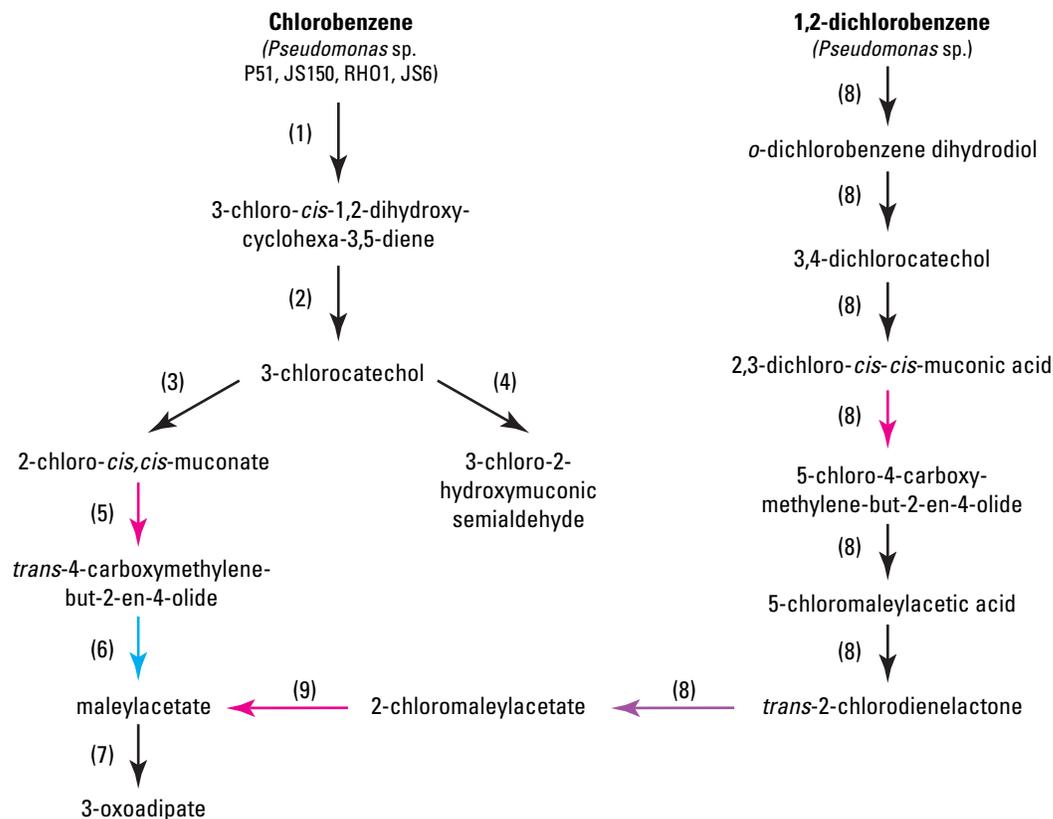(modified from Yao 2006).

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 et al. 1995
(2) Sommer and Görisch 1997

Figure D10. Laboratory-derived pathway for the
aerobic biodegradation of 1,4-dichlorobenzene
(modified from Liu 2006).

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-dichlorobenzene 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)

EXPLANATION

Proven microbe-catalyzed

→ Oxidation reaction

→ Dechlorination

→ Hydrolysis

→ Hydration

Pseudomonas sp. **Microorganism
catalyzing reaction**

**Literature reference describing
reaction pathway**

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

Figure D11. Laboratory-derived pathway for the aerobic biodegradation of chlorobenzene
and 1,2-dichlorobenzene (modified from McLeish 2005).

D26

**Historical Reconstruction of Drinking-Water Contamination at Tarawa Terrace
and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina**

Degradation of 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 (Anderson et al. 1998; Edwards and Grbić-Galić 1994; Evans et al. 1991a, 1991b; Fries et al. 1994; Hutchins et al. 1991; Kuhn et al. 1988; Lovley and Lonergan 1990; Rabus et al. 1993; Rabus and Widdel 1995; Vogel and Grbić-Galić 1986).

Although early studies concluded that MTBE was recalcitrant to aerobic biodegradation (Squillace et al. 1997), more recent studies show that, once initiated, the aerobic biodegradation of MTBE is relatively rapid (Deeb et al. 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 D17; Aronson et al. 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 et al. 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 et al. 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).

Aerobic microorganisms readily oxidize BTEX compounds while using them as primary substrates. The oxidation of BTEX compounds can proceed via several pathways (Figures D12–D16). 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 et al. 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; Edwards and Grbić-Galić 1992; Gibson et al. 1968; Gibson and Subramanian 1984). More recent laboratory experiments show that catechol is an intermediate

Table D17. 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 groundwater.[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 et al. 1999

[2]American Petroleum Institute 1994

[3]Alvarez et al. 1998

[4]Anid et al. 1993

[5]Kemblowski et al. 1987

[6]Nielsen et al. 1996
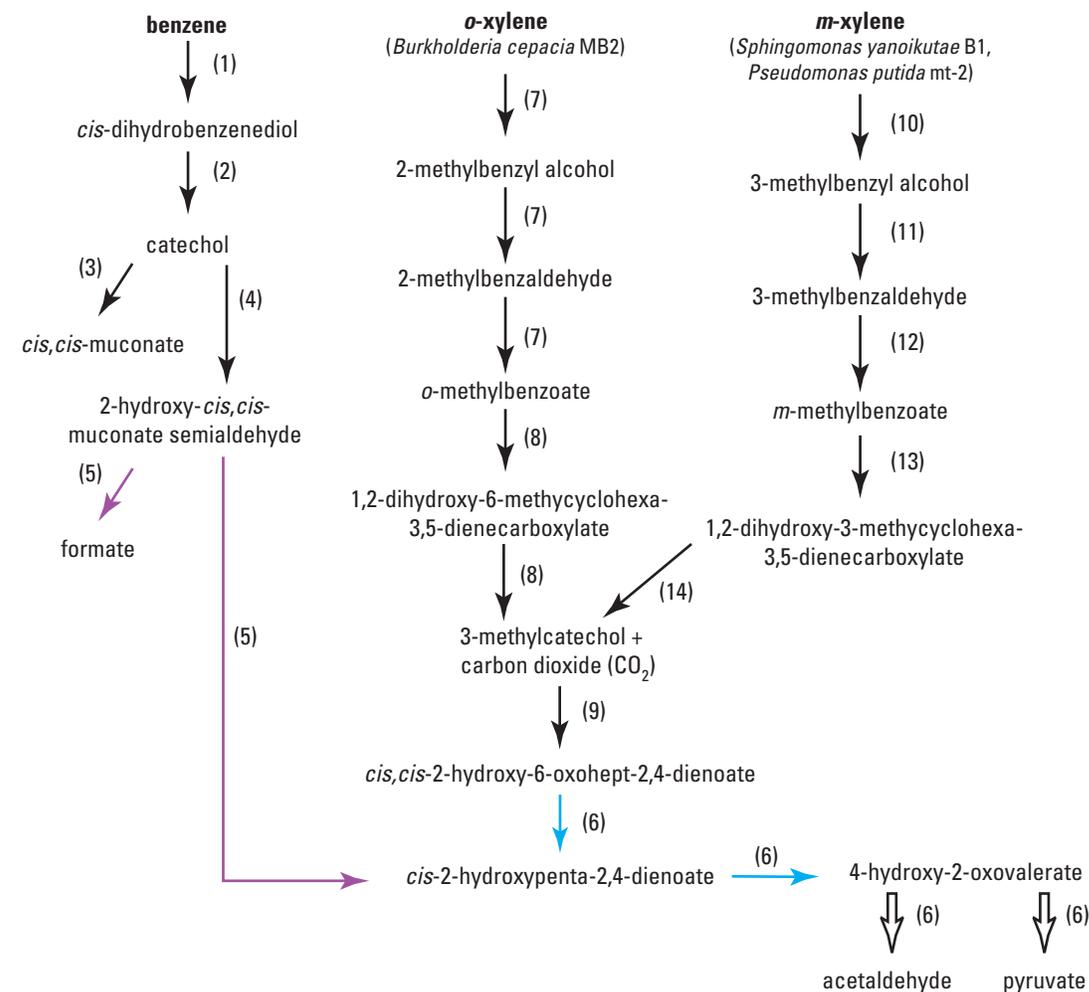
[7]McCarty et al. 1998

[8]Barker et al. 1987

[9]Hubbard et al. 1994

[10]Holm et al. 1992

[11]Thomas et al. 1990

[12]Laboratory microcosm

[13]Fenner et al. 2000

benzene

(1)

cis-dihydrobenzenediol

(2)

catechol

(3)

cis,cis-muconate

(4)

2-hydroxy-*cis,cis*-muconate semialdehyde

(5)

formate

(5)

o-xylene
(*Burkholderia cepacia* MB2)

(7)

2-methylbenzyl alcohol

(7)

2-methylbenzaldehyde

(7)

o-methylbenzoate

(8)

1,2-dihydroxy-6-methycyclohexa-3,5-dienecarboxylate

(8)

m-xylene
(*Sphingomonas yanoikutae* B1,
Pseudomonas putida mt-2)

(10)

3-methylbenzyl alcohol

(11)

3-methylbenzaldehyde

(12)

m-methylbenzoate

(13)

1,2-dihydroxy-3-methycyclohexa-3,5-dienecarboxylate

(14)

3-methylcatechol +
carbon dioxide (CO_2)

(9)

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

(6)

cis-2-hydroxypenta-2,4-dienoate

(6)

4-hydroxy-2-oxovalerate

(6)

(6)

acetaldehyde

pyruvate

EXPLANATION

Proven microbe-catalyzed

Oxidation reaction

Hydrolysis

Hydration

Reaction, unspecified

Burkholderia
cepacia

**Microorganism catalyzing
reaction**

Literature reference describing reaction pathway

(1) Zamanian and Mason 1987
(2) Mason and Geary 1990
(3) Ngai et al. 1990
(4) Cerdan et al. 1994
(5) Horn et al. 1991
(6) Lau et al. 1994
(7) Jorgensen et al. 1995

(8) Higson and Focht 1992
(9) Kukor and Olsen 1991
(10) Suzuki et al. 1991
(11) Katagiri et al. 1967
(12) Chalmers and Fewson 1989
(13) Harayama et al. 1986
(14) Neidle et al. 1992

Figure D12. Laboratory-derived pathways for the aerobic biodegradation of benzene, *o*-, and *m*-xylene (modified from Hyatt and Jun Oh 2005; Jun Oh 2005).

D28

**Historical Reconstruction of Drinking-Water Contamination at Tarawa Terrace
and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina**

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)   (5)   (10)   (12)

benzaldehyde

3-methylcatechol + carbon dioxide (CO_2)

4-hydroxy-
benzaldehyde

(3)   (6)   (13)

benzoate

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

4-hydroxy-
benzoate

benzoate
pathway

(7)

cis-2-hydroxypenta-
2,4-dienoate

vanillin pathway

m-cresol pathway
(fig. 17)

(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 et al. 1993
(3) Inoue et al. 1995
(4) Shields et al. 1995
(5) Olsen et al. 1994
(6) Kukor and Olsen 1991
(7) Menn and others 1991

(8) Lau et al. 1994
(9) Wackett et al. 1988
(10) Simpson et al. 1987
(11) Yen et al. 1991
(12) McIntire et al. 1986
(13) Bossert et al. 1989

Figure D13. Laboratory-derived pathways for the aerobic biodegradation of toluene (modified from Wackett and Zeng 2004).
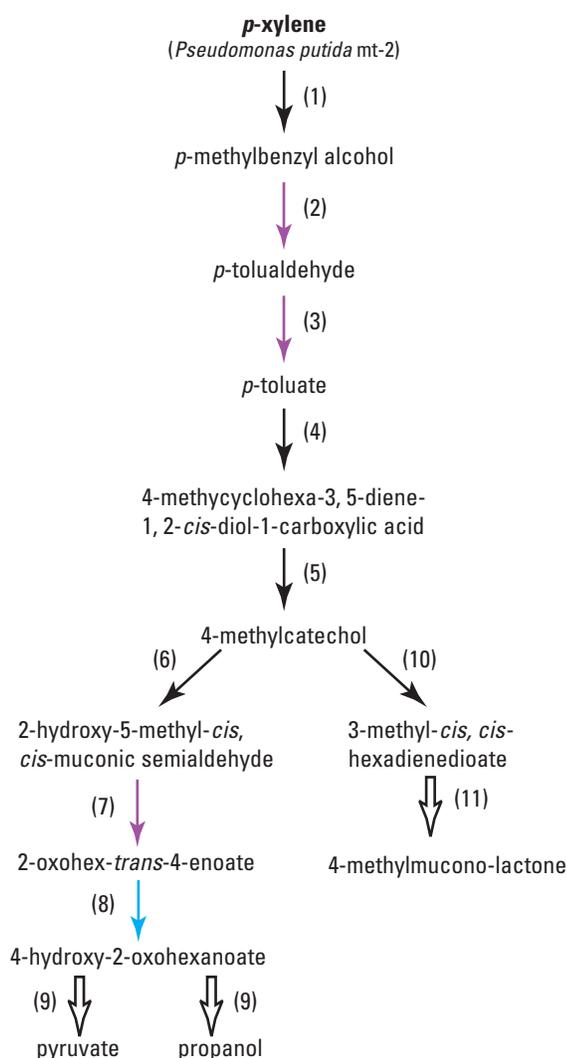
***p*-xylene**
(*Pseudomonas putida* mt-2)

↓ (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 et al. 1995   (8) Harayama et al. 1989
(3) Shaw and Harayama 1990   (9) Platt et al. 1995
(4) Walsh et al. 1983   (10) Murakami et al. 1997
(5) Whited et al. 1986   (11) Helin et al. 1995
(6) Cerdan et al. 1994

Figure D14.   Laboratory-derived pathways for the aerobic biodegradation of *p*-xylene (modified from Mili and Stephens 2006).

compound in the benzene pathway (Figure D12). Five separate degradation pathways have been identified for toluene under aerobic conditions (Figure D13). One of these pathways shares a common intermediate compound (3-methylcatechol) with the degradation of *o*- and *m*-xylene (Figures D12 and D13). 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 (Figure D14). The aerobic biodegradation of ethylbenzene follows three pathways depending on the microorganism using ethylbenzene as its carbon source (Figure D15). 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 et al. 1999; Table D17).

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

Morasch et al. (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 et al. 1989, 1995). These electron acceptors, however, commonly exist in groundwater at sufficient levels for these reactions to proceed (Kuhn et al. 1988; Lovley and Lonergan 1990). Figure D16 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 (Barbaro et al. 1992; Reinhard et al. 1984) and in laboratory enrichments established with sewage sludge, aquifer sediments, and contaminated soils (Krumholz et al. 1996; Barbaro et al. 1992).
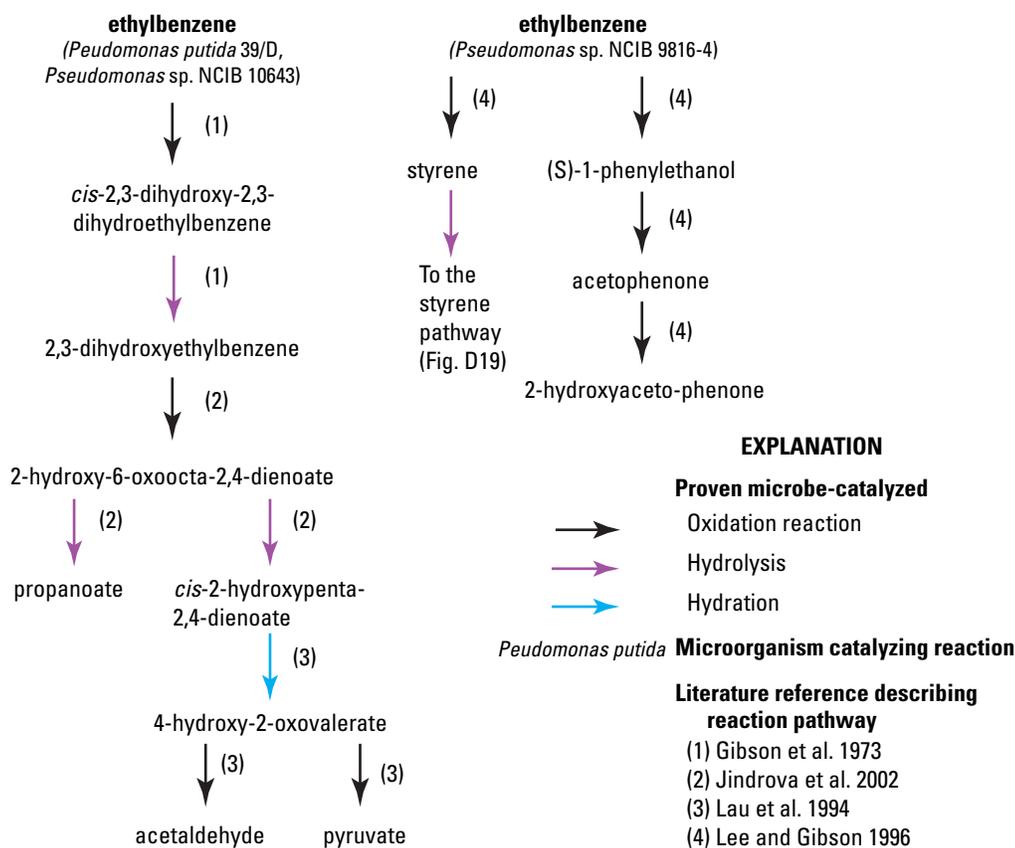
Figure D15. Laboratory-derived pathway for the aerobic biodegradation of ethylbenzene (modified from McLeish 2005).

Conversely, several groundwater studies have shown that BTEX degradation rates decline in a sequence from mildly reducing conditions (nitrate reduction zone, Hutchins et al. 1991) to strongly reducing conditions (methanogenesis) in shallow aquifers (Kazumi et al. 1997; Lu et al. 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 (Coates et al. 1996a, 1996b; Edwards and Grbić-Galić 1992; Lovley et al. 1995; Lovley and Lonergan 1990; Phelps et al. 1996; 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 et al. 1992a 1992b; Table D18). The anaerobic biodegradation of BTEX compounds in groundwater was conclusively shown in situ by Griebler et al. (2004b) using compound-specific isotope analysis and signature metabolites analysis. Figure D16 shows the anaerobic pathway for BTEX compounds developed from the intermediate compounds identified in groundwater samples by Griebler et al. (2004b).

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 (Alexander, 1973; Smith et al. 2003). Although early studies concluded that MTBE was recalcitrant to biodegradation (Squillace et al. 1997), more recent studies show that, once initiated, the aerobic biodegradation of MTBE is relatively rapid (Deeb et al. 2000), but markedly slower than BTEX degradation (Table D17). MTBE may appear to persist in contaminated groundwater if groundwater 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 et al. 2000, 2005). Wilson et al. (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.

Table D18. 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 et al. 2000

[3]Wilson et al. 2005

Although some studies concluded that MTBE degrades slowly in aerobic environments (Squillace et al. 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 et al. 1999, 2001). A study by Landmeyer et al. (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 groundwater.

Although three different bacteria are able to aerobically degrade MTBE via two different pathways (Figure D17; 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 et al. 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 D17). 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 et al. 1999; Drogos and Diaz 2000; Kane et al. 2001; Sedran et al. 2002).

Anaerobic Biodegradation of Methyl *Tert*-butyl Ether

The anaerobic biodegradation of MTBE is known to proceed, although slowly, under methanogenic (Wilson et al. 2000; Wilson et al. 2005), sulfate-reducing (Somsamak et al. 2001), iron-reducing (Finneran and Lovley 2001), and nitrate-reducing (Bradley et al. 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 et al. 2001; Kuder et al. 2005).

In a six-state groundwater study, Kolhatkar et al. (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 et al. (2002) confirmed the anaerobic degradation of MTBE and TBA in anoxic groundwater 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.
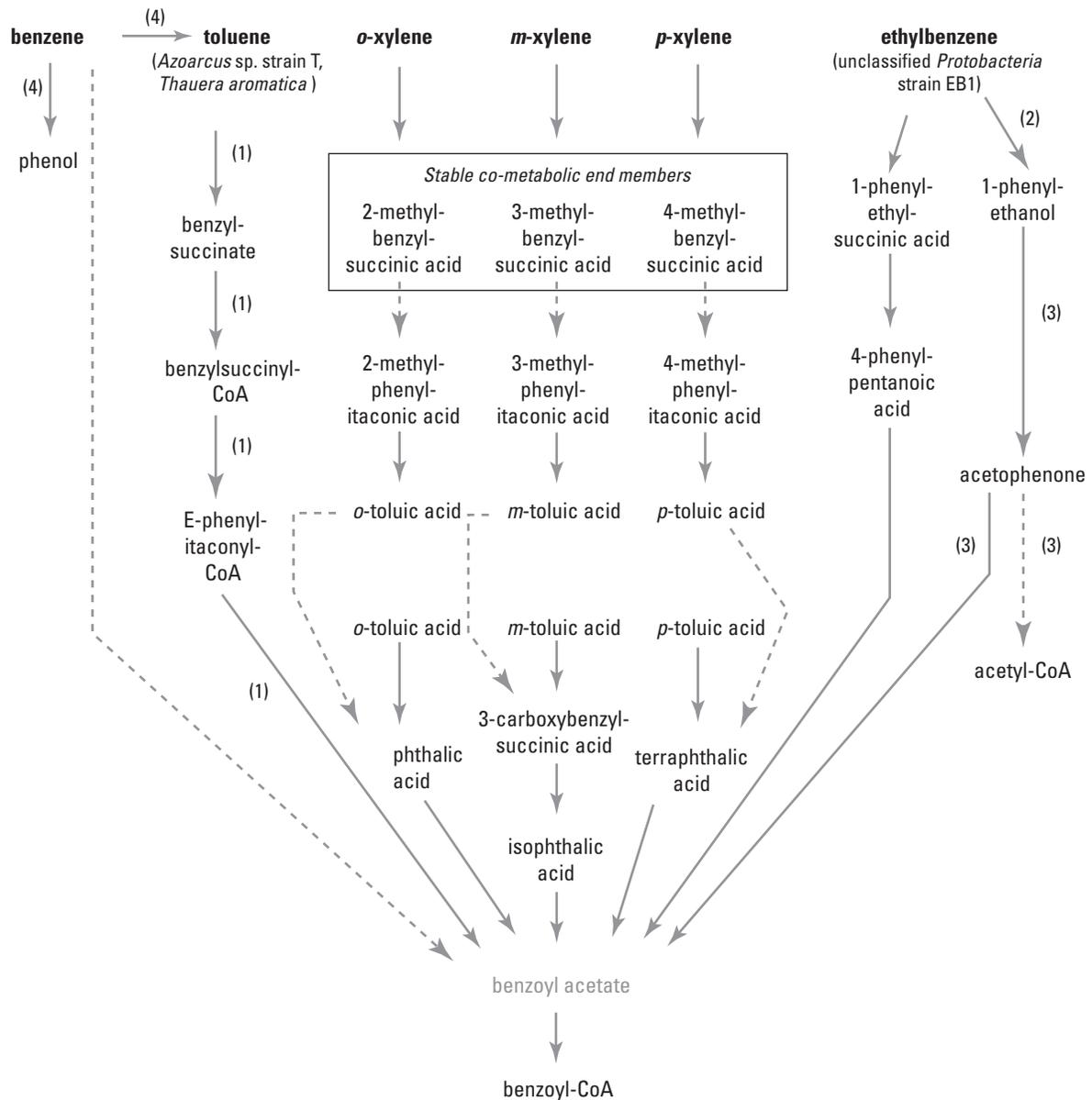
Figure D16. Field and laboratory-derived pathways for the anaerobic biodegradation of the BTEX compounds—benzene, toluene, ethylbenzene, and xylene (modified from Edwards and Grbić-Galić 1994; and Griebler et al. 2004b).
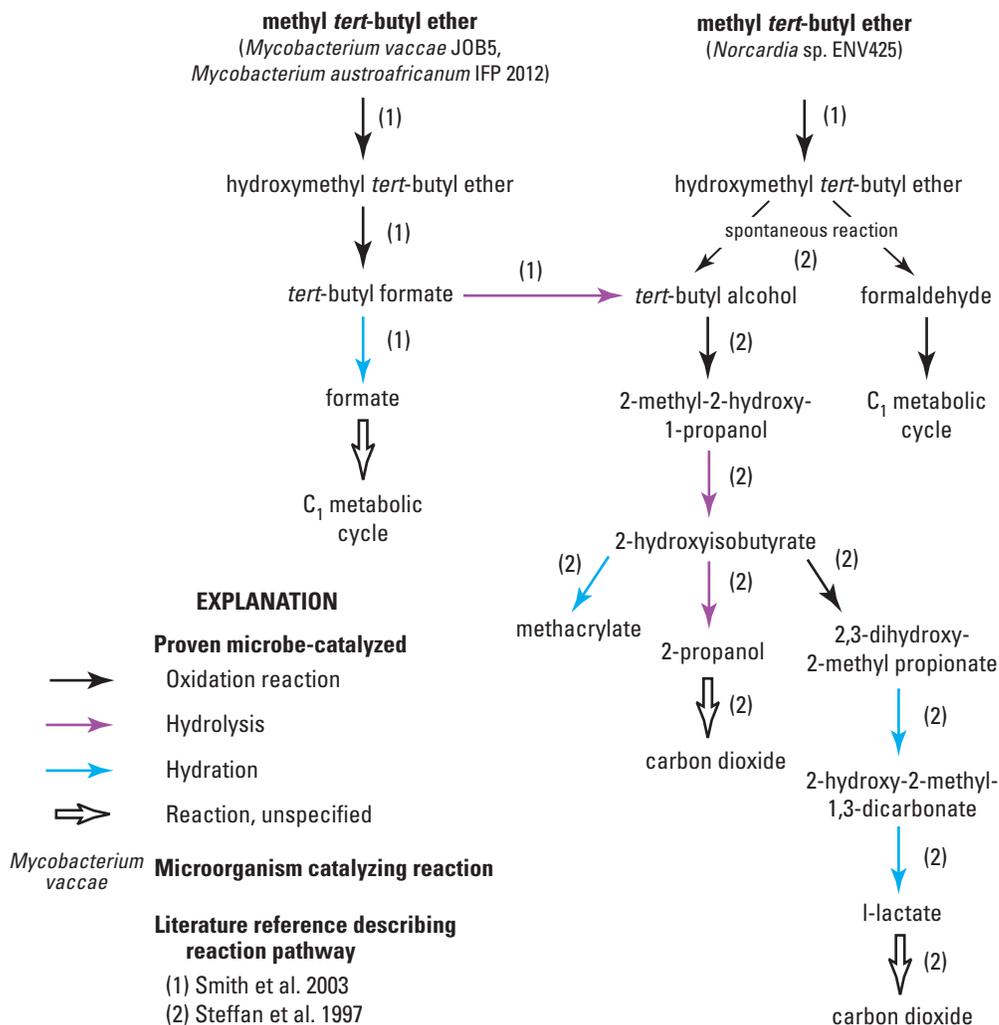
Figure D17. Laboratory-derived pathway for the aerobic biodegradation of methyl *tert*-butyl ether (modified from Pedersen and Essenberg 2005).
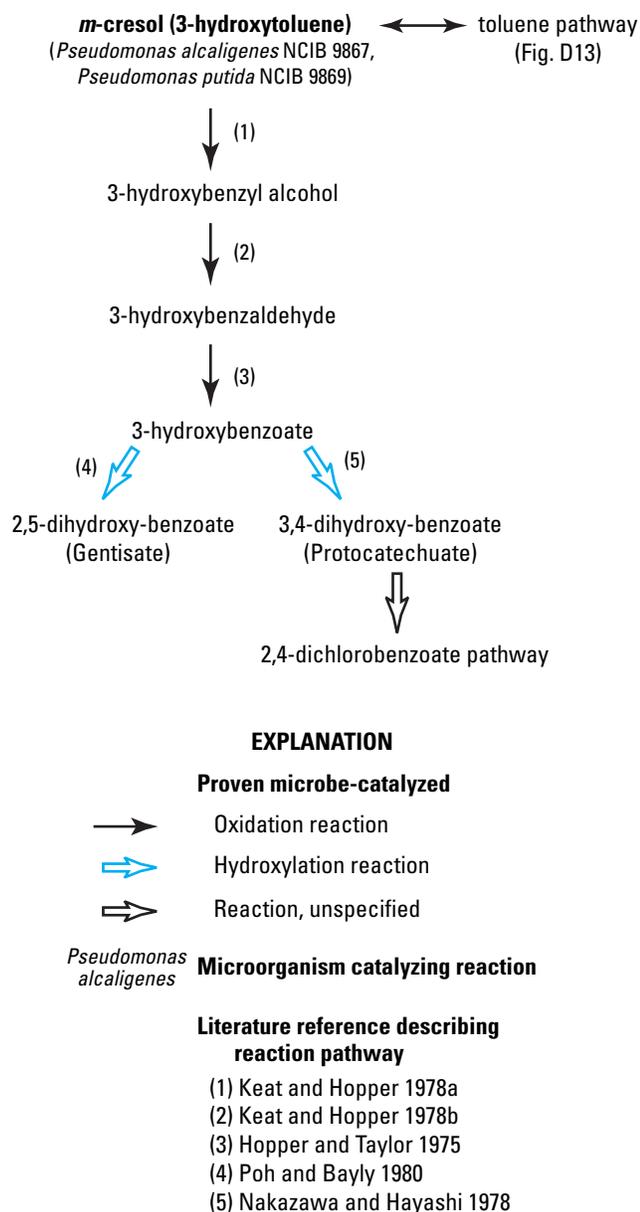
D34

Historical Reconstruction of Drinking-Water Contamination at Tarawa Terrace and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina

m-cresol (3-hydroxytoluene) ⟷ toluene pathway (Fig. D13)
(*Pseudomonas alcaligenes* NCIB 9867,
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 D18. Laboratory-derived pathway for the aerobic biodegradation of *m*-cresol (modified from Sakai et al. 2005).

styrene
(*Exophiala jeanselmei,*
Pseudomonas putida CA-3)

(1) ↓

styrene oxide

(1) ↓

phenylacetaldehyde

(1) ↓

phenylacetate

(2) ⇓

2-hydroxyphenylacetate

(2) ⇓

homogentisate

(3) ↓

4-maleylacetoacetate

(4) ↓

fumarylacetoacetate

(5) ↙   ↘

fumarate   acetoacetate

styrene
(*Rhodococcus rhodochrous*
NCIMB 13259)

(6) ↓

styrene *cis*-glycol

(6) ↓

3-vinylcatechol

(6) ↓

2-hydroxy-6-oxo-octa-trienoate

↙ (7)   ↘

acrylate   2-hydroxypenta-2,4-dienoate

(7) ↓

4-hydroxy-2-oxovalerate

↙   ↘

acetaldehyde   pyruvate

EXPLANATION

Proven microbe-catalyzed

→ Oxidation reaction

⇨ Hydroxylation reaction

→ Hydrolysis

→ Hydration

Exophiala jeanselmei **Microorganism catalyzing reaction**

Literature reference describing reaction pathway

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

Figure D19. Laboratory-derived pathways for the aerobic biodegradation of styrene (modified from Kraus et al. 2005).

References Cited

Adamson DT, Parkin GF. Biotransformation of Mixtures of Chlorinated Aliphatic Hydrocarbons by an Acetate-Grown Methanogenic Enrichment Culture. Water Research 1999;33(6):1482–1494.

Adrian L, Manz W, Szewzyk U, Gorisch H. Physiological Characterization of a Bacterial Consortium Reductively Dechlorinating 1,2,3- and 1,2,4-Trichlorobenzene. Applied and Environmental Microbiology. 1998;64(2):496–503.

Agency for Toxic Substances and Disease Registry. Toxicological Profile of 1,1,2-Trichloroethane. Atlanta, Georgia: U.S. Department of Health and Human Services; 1989. Report No.: TP-148.

Agency for Toxic Substances and Disease Registry. Toxicological Profile of Chlorobenzene. Atlanta, Georgia: U.S. Department of Health and Human Services; 1990a. Report No.: TP-131.

Agency for Toxic Substances and Disease Registry. Toxicological Profile for 1,4-Dichlorobenzene. Atlanta, Georgia: U.S. Department of Health and Human Services; 1990b. Report No.: TP-10.

Agency for Toxic Substances and Disease Registry. Toxicological Profile for 1,1-Dichloroethane. Atlanta, Georgia: U.S. Department of Health and Human Services; 1990c. Report No.: TP-133.

Agency for Toxic Substances and Disease Registry. Toxicological Profile for Chloroethane. Atlanta, Georgia: U.S. Department of Health and Human Services; 1998. Report No.: TP-105.

Agency for Toxic Substances and Disease Registry. Toxicological Profile of 1,2-Dichloroethane. Atlanta, Georgia: U.S. Department of Health and Human Services; 2001. Report No.: TP-38.

Agency for Toxic Substances and Disease Registry. Draft Toxicological Profile for 1,1,1-Trichloroethane. Atlanta, Georgia: U.S. Department of Health and Human Services; 2004. Report No.: TP-70.

Agency for Toxic Substances and Disease Registry. Draft Toxicological Profile for Benzene. Atlanta, Georgia: U.S. Department of Health and Human Services; 2005. Report No.: TP-3.

Alexander M. Nonbiodegradable and Other Recalcitrant Molecules. Biotechnology and Bioengineering. 1973;15: 611–647.

Alvarez PJJ, Cronkhite LA, Hunt CS. Use of Benzoate to Establish Reactive Buffer Zones for Enhanced Attenuation of BTX Migration—Aquifer Column Experiments. Environmental Science and Technology. 1998;32(8):509–515.

American Petroleum Institute. Transport and Fate of Dissolved Methanol, Methyl-tertiary-butyl-ether, and Monoaromatic Hydrocarbons in a Shallow Sand Aquifer. American Petroleum Institute, Health Environmental Science Department; 1994a. API Publication No.: 4601.

Anderson RT, Rooney-Varga JN, Gaw CV, and Lovley DR. Anaerobic Benzene Oxidation in the Fe (III) Reduction Zone of Petroleum-Contaminated Aquifers. Environmental Science and Technology. 1998;32(9):1222–1229.

Anid PJ, Alvarez PJJ, and Vogel TM. Biodegradation of Monoaromatic Hydrocarbons in Aquifer Columns Amended with Hydrogen Peroxide and Nitrate. Water Research. 1993;27(4):685–691.

Archer WL. Other Chloroethanes. In: Kirk-Othmer Encyclopedia of Chemical Technology. 3rd ed. 1979;5:722–742.

Arneth JD, Gerald M, Kerndorff H, and Schleyer R. The 15 Most Frequently Detected Organic Compounds in Ground Water at Waste Disposal Sites in Germany and the U.S. In: Baccini P, editor. The Landfill—Reactor and Final Storage, Swiss Workshop on Land Disposal of Solid Wastes Gerzensee, March 14–17, 1988: Lecture Notes in Earth Sciences. New York: Springer–Verlag, Inc.; 1989.

Aronson D, and Howard PH. Anaerobic Biodegradation of Organic Chemicals in Groundwater—A Summary of Field and Laboratory Studies. Final report prepared for the American petroleum Institute by Environmental Science Center, Syracuse Research Corporation. North Syracuse, New York; 1997.

Aronson D, Citra M, Shuler K, Printup H, and Howard PH. 1999, Aerobic Biodegradation of Organic Chemicals in Environmental Media—A Summary of Field and Laboratory Studies. Prepared for the U.S. Environmental Protection Agency by Environmental Science Center, Syracuse Research Corporation. North Syracuse, New York, SRC TR 99-002; 1999.

Australian Department of Environment and Heritage. National Pollutant Inventory, Volatile Organic Compound Definition and Information, version 2.4. Department of Environment and Heritage, Commonwealth of Australia. 2003. [cited 2006 February 23]; Available from *http://www.npi.gov. au/handbooks/pubs/voc.pdf*

Azadpour-Keeley A, Russell HH, and Sewell GW. Microbial Processes Affecting Monitored Natural Attenuation of Contaminants in the Subsurface. Ada, Oklahoma: National Risk Management Research Laboratory, Subsurface Protection and Remediation Division, Robert S. Kerr Environmental Research Center; 1999. Report No.: EPA/540/S-99/001.

Ball HA, Johnson HA, Reinhard M, and Spormann AM. Initial Reactions in Anaerobic Ethylbenzene Oxidation by a Denitrifying Bacterium, Strain EB1. Journal of Bacteriology. 1996;178(19):5755–5761.

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Historical Reconstruction of Drinking-Water Contamination at Tarawa Terrace and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina

Barbaro JR, Barker JF, Lemon LA, and Mayfield CI. Biotransformation of BTEX under Anaerobic, Denitrifying Conditions—Field and Laboratory Observations. Journal of Contaminant Hydrology. 1992;11:245–272.

Barbaro JR, and Neupane PP. Distribution and Mass Loss of Volatile Organic Compounds in the Surficial Aquifer at Sites FT03, LF13, and WP14/LF15, Dover Air Force Base, Delaware, November 2000–February 2001: U.S. Geological Survey Water-Resources Investigations Report 02-4121; 2001.

Barker JF, Patrick GC, and Major D. Natural Attenuation of Aromatic Hydrocarbons in a Shallow Sand Aquifer. Groundwater Monitoring and Remediation. 1987;7(1):64–72.

Beek B, volume editor. Biodegradation and Persistence. In: Hutzinger O, editor. Reactions and Processes—The Handbook of Environmental Chemistry. v. 2k. Berlin, Germany: Springer–Verlag; 2001: 320 p.

Beller HR, Grbić-Galić D, and Reinhard M. Microbial Degradation of Toluene under Sulfate-Reducing Conditions and the Influence of Iron on the Process. Applied and Environmental Microbiology. 1992a;58(3):786–793.

Beller HR, Reinhard M, and Grbić-Galić D. Metabolic By-Products of Anaerobic Toluene Degradation by Sulfate-Reducing Enrichment Cultures. Applied and Environmental Microbiology. 1992b;58(9):3192–3195.

Beller HR, and Spormann AM. Anaerobic Activation of Toluene and *o*-Xylene by Addition to Fumarate in Denitrifying Strain T. Journal of Bacteriology. 1997;179(3):670–676.

Biegert T, Altenschmidt U, Eckerskorn C, and Fuchs G. Purification and Properties of Benzyl Alcohol Dehydrogenase from a Denitrifying *Thauera* sp. Archives of Microbiology. 1995;163(6):418–423.

Borden RC, Melody JH, Shafer MB, and Barlaz MA. Anaerobic Biodegradation of BTEX in Aquifer Material. U.S. Environmental Protection Agency. 1997; Report No.: EPA/600/S-97/003, 9 p.

Bossert ID, Whited G, Gibson DT, and Young LY. Anaerobic Oxidation of *p*-Cresol Mediated by a Partially Purified Methylhydroxylase from a Denitrifying Bacterium. Journal of Bacteriology. 1989;171(6):2956–2962.

Bouwer EJ. Bioremediation of Chlorinated Solvents Using Alternate Electron Acceptors. In: Norris RD, Hinchee RE, Brown R, McCarty PL, Semprini L, Wilson JT, Kampbell DH, Reinhard M, Bouwer EJ, Borden RC, Vogel TM, Thomas JM, and Ward CH, editors. Groundwater Cleanup through Bioremediation, Handbook of Bioremediation. Boca Raton, Florida: Lewis Publishers; 1994.

Bouwer EJ, Rittman BE, and McCarty RL. Anaerobic Degradation of Halogenated 1- and 2-Carbon Organic Compounds. Environmental Science and Technology. 1981;15(5):596–599.

Boyd SA, Xiangcan J, and Lee JF. Sorption of Non-ionic Organic Compounds by Corn Residues from a No-Tillage Field. Journal of Environmental Quality. 1990;19(4):734–738.

Bradley PM, and Chapelle FH. Effect of Contaminant Concentration on Aerobic Microbial Mineralization of DCE and VC in Stream-Bed Sediments. Environmental Science and Technology. 1998;32(5):553–557.

Bradley PM, Landmeyer JE, and Chapelle FH. Aerobic Mineralization of MTBE and *tert*-Butyl Alcohol by Stream-Bed Sediment Microorganisms. Environmental Science and Technology. 1999;33(11):1877–1879.

Bradley PM, Landmeyer JE, and Chapelle FH. Widespread Potential for Microbial MTBE Degradation in Surface-Water Sediments. Environmental Science and Technology. 2001;35(4):658–662.

Braun CL. Reductive Dechlorination of Chlorinated Ethenes under Oxidation-Reduction Conditions and Potentiometric Surfaces in Two Trichloroethene-Contaminated Zones at the Double Eagle and Fourth Street Superfund Sites in Oklahoma City, Oklahoma: U.S. Geological Survey Scientific Investigations Report 2004–5050; 2004.

Broderick JB, and O'Halloran TV. Overproduction, Purification, and Characterization of Chlorocatechol Dioxygenase, a Non-Heme Iron Dioxygenase with Broad Substrate Tolerance. Biochemistry. 1991;30(29):7349–7358.

Brown RA, Hinchee RE, Norris RD, and Wilson JT. Bioremediation of Petroleum Hydrocarbons—A Flexible, Variable Speed Technology. Bioremediation Journal. 1996;6(4):95–108.

Brown TL, and LeMay HE Jr. Chemistry—The Central Science. Englewood Cliffs, New Jersey: Prentice-Hall, Inc.; 1977.

Cerdan P, Wasserfallen A, Rekik M, Timmis KN, and Harayama S. Substrate Specificity of Catechol 2,3-Dioxygenase Encoded by TOL Plasmid pWW0 of *Pseudomonas putida* and Its Relationship to Cell Growth. Journal of Bacteriology. 1994;176(19):6074–6081.

Chalmers RM, and Fewson CA. Purification and Characterization of Benzaldehyde Dehydrogenase I from *Acinetobacter calcoaceticus*. Biochemical Journal. 1989;263(3):913–919.

Chapelle FH, McMahon PB, Dubrovsky NM, Fujii RF, Oaksford ET, and Vroblesky DA. Deducing the Distribution of Terminal Electron-Accepting Processes in Hydrologically Diverse Groundwater Systems. Water Resources Research. 1995;31:359–371.

Chen C, Puhakka JA, and Ferguson JF. Transformation of 1,1,2,2-Tetrachloroethane under Methanogenic Conditions. Environmental Science and Technology. 1996;30(2):542–547.

References Cited

Chiang CY, Salanitro JP, Chai EY, Colthart JD, and Klein CL. Aerobic Biodegradation of Benzene, Toluene, and Xylene in a Sandy Aquifer—Data Analysis and Computer Modeling. Ground Water. 1989;27(6):823–834.

Chiou CT, Peters LJ, and Freed VH. A Physical Concept of Soil-Water Equilibria for Nonionic Organic Compounds. Science. 1979;206:831–832.

Chiou CT, Porter PE, and Schmedding DW. Partition Equilibria of Nonionic Organic Compounds between Soil Organic Matter and Water. Environmental Science and Technology. 1983;17(4):227–231.

Christensen TH, Bjerg PL, Banwart SA, Jakobsen R, Heron G, and Albrechtsen H. Characterization of Redox Conditions in Groundwater Contaminant Plumes. Journal of Contaminant Hydrology. 2000;45:165–241.

Coates JD, Anderson RT, and Lovley DR. Oxidation of Polycyclic Aromatic Hydrocarbons under Sulfate-Reducing Conditions. Applied and Environmental Microbiology. 1996a;62(3):1099–1101.

Coates JD, Anderson RT, Woodward JC, Phillips EJP, and Lovley DR. Anaerobic Hydrocarbon Degradation in Petroleum-Contaminated Harbor Sediments under Sulfate-Reducing and Artificially Imposed Iron-Reducing Conditions. Environmental Science and Technology. 1996b;30(9):2784–2789.

Coleman NV, Mattes TE, Gossett JM, and Spain JC. Phylogenetic and Kinetic Diversity of Aerobic Vinyl-Chloride-Assimilating Bacteria from Chlorinated-Ethene Contaminated Sites. Applied and Environmental Microbiology. 2002;68(12):6162–6171.

Cox HH, Faber BW, Van Heiningen WN, Radhoe H, Doddema HJ, and Harder W. Styrene Metabolism in *Exophiala jeanselmei* and Involvement of a Cytochrome P-450-Dependent Styrene Monooxygenase. Applied and Environmental Microbiology. 1996;62(4):1471–1474.

Crawford RL. Degradation of Homogentisate by Strains of *Bacillus and Moraxella*. Canadian Journal of Microbiology. 1976;22(2):276–280.

De Best JH, Hage A, Doddema HJ, Janssen DB, and Harder W. Complete Transformation of 1,1,1-Trichloroethane to Chloroethane by a Methanogenic Mixed Population. Applied Microbiology and Biotechnology. 1999;51:277–283.

Deeb RA, and Alvarez-Cohen L. Aerobic Biotransformations of Gasoline Aromatics in Multicomponent Mixtures. Bioremediation Journal. 2000;4(1):1–9.

Deeb RA, Stocking AJ, Alvarez-Cohen L, and Kavanaugh MC. MTBE and TBA Biodegradation: A Current Review. In: Proceedings of the 2000 Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation, Special Focus—Natural Attenuation and Gasoline Oxygenates; 2000 November 15–17; Anaheim, California: National Ground Water Association; 2000:50–51.

Delzer GC, and Ivahnenko T. Occurrence and Temporal Variability of Methyl *tert*-Butyl Ether (MTBE) and Other Volatile Organic Compounds in Select Sources of Drinking Water—Results of the Focused Survey. U.S. Geological Survey Water-Resources Investigations Report 02-4084; 2003.

Dermietzel J, and Vieth A. Chloroaromatics in Groundwater—Chances of Bioremediation. Environmental Geology. 2002;41(6):683–689.

De Wever H, Cole JR, Fettig MR, Hogan DA, and Tiedje JM. Reductive Dehalogenation of Trichloroacetic Acid by *Trichlorobacter thiogenes* gen. nov., sp. nov. Applied and Environmental Microbiology. 2000;66(6):2297–2301.

Diaz E, and Timmis KN. Identification of Functional Residues in a 2-Hydroxymuconic Semialdehyde Hydrolase—A New Member of the α/β Hydrolase-Fold Family of Enzymes which Cleaves Carbon-Carbon Bonds. Journal of Biological Chemistry. 1995;270(11):6403–6411.

Dinicola RS, Cox SE, Landmeyer JE, and Bradley PM. Natural Attenuation of Chlorinated Volatile Organic Compounds in Ground Water at Operable Unit 1, Naval Undersea Warfare Center, Division Keyport, Washington. U.S. Geological Survey Water-Resources Investigations Report 02-4119; 2002.

Dolfing J. Energetics of Anaerobic Degradation Pathways of Chlorinated Aliphatic Compounds. Microbial Ecology. 2000;40:2–7.

Donaldson SG, Miller CM, and Miller WW. Volatilization of Gasoline Constituents from Soil—A Remedial Investigation. In: Proceedings of the National Outdoor Action Conference on Aquifer Restoration: Ground Water Monitoring and Geophysical Methods 4; 1990:721–735.

Drogos DL, and Diaz AF. Exploring the Environmental Issues of Mobile, Recalcitrant Compounds in Gasoline: Preprints of Extended Abstracts: American Chemical Society Symposium; 2000 March 26–30; San Francisco, California; 2000;40(1):238–240.

Edwards EA, and Grbić-Galić D. Complete Mineralization of Benzene by Aquifer Microorganisms under Strictly Anaerobic Conditions. Applied and Environmental Microbiology. 1992;58(8):2663–2666.

Edwards EA, and Grbić-Galić D. Anaerobic Degradation of Toluene and *o*-Xylene by a Methanogenic Consortium. Applied and Environmental Microbiology. 1994;60(1):313–322.

Eggen RI, Geerling AC, Jetten MS, de Vos WM. Cloning, Expression, and Sequence Analysis of the Genes for Carbon Monoxide Dehydrogenase of *Methanothrix soehngenii*. Journal of Biological Chemistry. 1991;266(11):6883–6887.

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Historical Reconstruction of Drinking-Water Contamination at Tarawa Terrace and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina

Egli C, Scholtz R, Cook AM, and Leisinger T. Anaerobic Dechlorination of Tetrachloromethane and 1,2-Dichloroethane to Degradable Products by Pure Cultures of *Desulfobacterium* sp. and *Methanobacterium* sp. FEMS Microbiology Letters. 1987;43:257–261.

Ellis L, and Anderson S. Tetrachloroethene Pathway Map (Anaerobic)—University of Minnesota Biocatalysis/Biodegradation Database. 2005 [cited 2006 April 10]; Available from *http://umbbd.msi.umn.edu/tce2/tce2_map.html*

Ellis LBM, Roe D, and Wackett LP. University of Minnesota Biocatalysis/Biodegradation Database: The First Decade, Nucleic Acids Research. 2006;34(Database issue): D517–D521.

Evans PJ, Mang DT, Kim KS, and Young LY. Anaerobic Degradation of Toluene by a Denitrifying Bacterium. Applied and Environmental Microbiology. 1991a;57(4):1139–1145.

Evans PJ, Mang DT, and Young LY. Degradation of Toluene and *m*-Xylene and Transformation of *o*-Xylene by Denitrifying Enrichment Cultures. Applied and Environmental Microbiology. 1991b;57(2):450–454.

Fenner K, Scheringer M, and Hüngerbuhler K. Persistence of Parent Compounds and Transformation Products in a Level IV Multimedia Model. Environmental Science and Technology. 2000;34(17):3809–3817.

Fernandez-Canon JM, and Penalva MA. Molecular Characterization of a Gene Encoding a Homogentisate Dioxygenase from *Aspergillus nidulans* and Identification of its Human and Plant Homologues. Journal of Biological Chemistry. 1995;270(36):21199–21205.

Finneran KT, and Lovley DR. Anaerobic Degradation of Methyl-*tert*-butyl Ether (MTBE) and *tert*-Butyl Ether (TBA). Environmental Science and Technology. 2001;35(10):1785–1790.

Freedman DL, and Gossett JM. Biological Reductive Dechlorination of Tetrachloroethylene and Trichloroethylene to Ethylene under Methanogenic Conditions. Applied and Environmental Microbiology. 1989;55(9):2144–2151.

Fries MR, Zhou J, Chee-Sanford J, and Tiedje JM. Isolation, Characterization, and Distribution of Denitrifying Toluene Degraders from a Variety of Habitats. Applied and Environmental Microbiology. 1994;60(8):2802–2810.

Friesel P, Milde G, and Steiner B. Interactions of Halogenated Hydrocarbons with Soils. Fresenius Zeitschrift fuer Analytische Chemie. 1984;319:160–164.

Gälli R, and McCarty PL. Biotransformation of 1,1,1-Trichloroethane, Trichloromethane, and Tetrachloromethane by a *Clostridium* sp. Applied and Environmental Microbiology. 1989;55(4):837–844.

Garbarini DR, and Lion LW. Influence of the Nature of Soil Organics on the Sorption of Toluene and Trichloroethylene. Environmental Science and Technology. 1986;20(12):1263–1269.

Gibson DT, Koch JR, and Kallio RE. Oxidative Degradation of Aromatic Hydrocarbons by Microorganisms—I. Enzymatic Formation of Catechol from Benzene. Biochemistry. 1968;7(7):2653–2662.

Gibson DT, Gschwendt B, Yeh WK, and Kobal VM. Initial Reactions in the Oxidation of Ethylbenzene by *Pseudomonas putida.* Biochemistry. 1973;12(8):1520–1528.

Gibson DT, and Subramanian V. Microbial Degradation of Aromatic Hydrocarbons. In: Gibson DT, editor. Microbial Degradation of Organic Compounds. New York: Marcel Dekker, Inc.; 1984:181–252.

Gossett JM. Measurement of Henry's Law Constants for C_1 and C_2 Chlorinated Hydrocarbons. Environmental Science and Technology. 1987;28(2):202–208.

Grady SJ. A National Survey of Methyl *tert*-Butyl Ether and Other Volatile Organic Compounds in Drinking-Water Sources—Results of the Random Survey. U.S. Geological Survey Water-Resources Investigations Report 02-4079; 2003.

Griebler C, Adrian L, Meckenstock RU, and Richnow HH. Stable Carbon Isotope Fractionation during Aerobic and Anaerobic Transformation of Trichlorobenzene. FEMS Microbiology Ecology. 2004a;48(3):313–321.

Griebler C, Safinowski M, Vieth A, Richnow HH, and Meckenstock RU. Combined Application of Stable Carbon Isotope Analysis and Specific Metabolites Determination for Assessing In-situ Degradation of Aromatic Hydrocarbons in a Tar Oil-Contaminated Aquifer. Environmental Science and Technology. 2004b;38(2):617–631.

Grostern A, and Edwards EA. Growth of *Dehalobacter* and *Dehalococcoides* spp. during Degradation of Chlorinated Ethanes. Applied and Environmental Microbiology. 2006;72(1):428–436.

Guertal WR, Stewart M, Barbaro JR, and McHale TJ. Analytical Results from Ground-Water Sampling Using a Direct-Push Technique at the Dover National Test Site, Dover Air Force Base, Delaware, June–July 2001. U.S. Geological Survey Open-File Report 03-380; 2004.

Hage JC, Kiestra FD, and Hartmans S. Co-metabolic Degradation of Chlorinated Hydrocarbons by *Pseudomonas* sp. Strain DCA1. Applied Microbiology and Biotechnology. 2001;57(4):548–554.

Hagedorn SR, and Chapman PJ. Glutathione-Independent Maleylacetoacetate Isomerase in Gram-Positive Bacteria. Journal of Bacteriology. 1985;163(2):803–805.

References Cited

Haigler BE, Nishino SF, and Spain JC. Degradation of 1,2-Dichlorobenzene by a *Pseudomonas* sp. Applied and Environmental Microbiology. 1988;54(2):294–301.

Hamlin SN, Belitz K, Kraja S, and Dawson B. Ground-Water Quality in the Santa Ana Watershed, California—Overview and Data Summary. U.S. Geological Survey Water-Resources Investigations Report 02-4243; 2002.

Hamlin SN, Belitz K and Johnson T. Occurrence and Distribution of Volatile Organic Compounds and Pesticides in Ground Water in Relation to Hydrogeologic Characteristics and Land Use in the Santa Ana Basin, Southern California. U.S. Geological Survey Scientific Investigations Report 2005-5032; 2005.

Hammer A, Hildenbrand T, Hoier H, Ngai K-L, Schlömann M, and Stezowski JJ. Crystallization and Preliminary X-ray Data of Chloromuconate Cycloisomerase from Alcaligenes Eutrophus JMP134 (pJP4). Journal of Molecular Biology. 1993;232(1):305–307.

Harayama S, Rekik M, and Timmis KN. Genetic Analysis of a Relaxed Substrate Specificity Aromatic Ring Dioxygenase, Toluate 1,2-Dioxygenase, Encoded by TOL Plasmid pWW0 of *Pseudomonas putida*. Molecular and General Genetics. 1986;202(2):226–234.

Harayama S, Rekik M, Ngai KL, and Ornston LN. Physically Associated Enzymes Produce and Metabolize 2-Hydroxy-2,4-dienoate, a Chemically Unstable Intermediate Formed in Catechol Metabolism via Meta Cleavage in *Pseudomonas putida*. Journal of Bacteriology. 1989;171(11):6251–6258.

Harper C, and Liccione JJ. Toxicological Profile for Gasoline. 1995. [cited 2006 May 26]: U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, p. 107; Available from *http://www.atsdr.cdc.gov*

Hartmans S, and De Bont JA. Aerobic Vinyl Chloride Metabolism in Mycobacterium Aurum L1. Applied and Environmental Microbiology. 1992;58(4):1220–1226.

Helin S, Kahn PC, Guba BL, Mallows DG, and Goldman A. The Refined X-ray Structure of Muconate Lactonizing Enzyme from *Pseudomonas putida* PRS2000 at 1.85 A Resolution. Journal of Molecular Biology. 1995;254(5):918–941.

Higgo JJW, Nielsen PH, Bannon MP, Harrison I, and Christensen TH. Effect of Geochemical Conditions on Fate of Organic Compounds in Groundwater. Environmental Geology. 1996;27(4):335–346.

Higson FK, and Focht DD. Degradation of 2-Methylbenzoic Acid by *Pseudomonas cepacia* MB2. Applied and Environmental Microbiology. 1992;58(1):194–200.

Hisano T, Hata Y, Fujii T, Liu J-Q, Kurihara T, Esaki N, and Soda K. Crystal Structure of L-2-haloacid Dehalogenase from *Pseudomonas* sp. YL. Journal of Biological Chemistry. 1996;271(34):20322–20330.

Holbrook MT. Carbon Tetrachloride. In: Kroschwitz JI, and Howe-Grant M, editors. Kirk-Othmer Encyclopedia of Chemical Technology; v. 5, 4th ed.; New York: John Wiley & Sons; 1992:1062–1072.

Holm PE, Nielsen PH, Albrechtsen H-J, and Christensen TH. Importance of Unattached Bacteria and Bacteria Attached to Sediment in Determining Potentials for Degradation of Xenobiotic Organic Contaminants in an Aerobic Aquifer. Applied and Environmental Microbiology. 1992;58(9):3020–3026.

Holscher T, Gorisch H, and Lorenz A. Reductive Dehalogenation of Chlorobenzene Congeners in Cell Extracts of *Dehalococcoides* sp., Strain CBDB1. Applied and Environmental Microbiology. 2003;69(5):2999–3001.

Hopkins GD, and McCarty PL. Field Evaluation of In Situ Aerobic Cometabolism of Trichloroethylene and Three Dichloroethylene Isomers Using Phenol and Toluene as the Primary Substrates. Environmental Science and Technology. 1995;29(6):1628–1637.

Hopper DJ, and Taylor DG. Pathways for the Degradation of *m*-Cresol and *p*-Cresol by *Pseudomonas putida*. Journal of Bacteriology; 1975;122(1):1–6.

Horn JM, Harayama S, and Timmis KN. DNA Sequence Determination of the TOL Plasmid (pWW0) xylGFJ Genes of *Pseudomonas putida*—Implications for the Evolution of Aromatic Catabolism. Molecular Microbiology. 1991;5(10):2459–2474.

Horvath AL. Halogenated Hydrocarbons—Solubility-Miscibility with Water. New York: Marcel Dekker, Inc.; 1982:494–495.

Howard PH, Boethling RS, Jarvis WF, Meylan WM, and Michalenko EM. Handbook of Environmental Degradation Rates. 2nd printing. Chelsea, Michigan: Lewis Publishers; 1991.

Hubbard CE, Barker JF, and Vandegriendt M. Transport and Fate of Dissolved Methanol, Methyl-tertiary-butyl-ether, and Monoaromatic Hydrocarbons in a Shallow Sand Aquifer, Appendix H—Laboratory Biotransformation Studies. Washington, D.C.: American Petroleum Institute, Health Environmental Science Department, API Publication Number 4601; 1994.

Huesemann MH, and Truex MJ. The Role of Oxygen Diffusion in Passive Bioremediation of Petroleum Contaminated Soils. Journal of Hazardous Materials. 1996;51(1–3):93–113.

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Historical Reconstruction of Drinking-Water Contamination at Tarawa Terrace and Vicinity, U.S. Marine Corps Base Camp Lejeune, North Carolina

Hutchins SR, Sewell GW, Kovacs DA, and Smith GA. Biodegradation of Aromatic Hydrocarbons by Aquifer Microorganisms under Denitrifying Conditions. Environmental Science and Technology. 1991;25(1):68–76.

Hyatt BA, and Jun Oh D. *m*-Xylene Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2005. [cited 2006 April 3]; Available from *http://umbbd.msi. umn.edu/mxy/mxy_map.html*

Inoue J, Shaw JP, Rekik M, and Harayama S. Overlapping Substrate Specificities of Benzaldehyde Dehydrogenase (the xylC Gene Product) and 2-Hydroxymuconic Semialdehyde Dehydrogenase (the xylG Gene Product) Encoded by TOL Plasmid pWW0 of *Pseudomonas putida*. Journal of Bacteriology. 1995;177(5):1196–1201.

Institute for Environmental Health. A Screening Method for Ranking Chemicals by Their Fate and Behavior in the Environment and Potential Toxic Effects in Humans Following Non-occupational Exposure (Web Report W14). 2004. [cited 2006 March 28]; Leicester, United Kingdom: MRC Institute for Environment and Health; Available from *http://www.silsoe.cranfield.ac.uk/ieh/*

International Union of Pure and Applied Chemistry. Compendium of Chemical Terminology. 2006. [cited 2006 August 8]; Available from *http://www.iupac.org/ publications/compendium/index.html*

Janssen DB, Scheper A, Dijkhuizen L, and Witholt B. Degradation of Halogenated Aliphatic Compounds by *Xanthobacter autotrophicus* GJ10. Applied and Environmental Microbiology. 1985;49(3):673–677.

Jeffers PM, Ward LM, Woytowitch LM, and Wolfe NL. Homogeneous Hydrolysis Rate Constants for Selected Chlorinated Methanes, Ethanes, Ethenes, and Propanes. Environmental Science and Technology. 1989;23(8):965–969.

Jindrova E, Chocová M, Demnerová K, and Brenner V. Bacterial Aerobic Degradation of Benzene, Toluene, Ethylbenzene and Xylene. Folia Microbiologica (Praha). 2002;47(2):83–93.

Jorgensen C, Nielsen B, Jensen BK, and Mortensen E. Transformation of *o*-Xylene to *o*-Methyl Benzoic Acid by a Denitrifying Enrichment Culture Using Toluene as the Primary Substrate. Biodegradation. 1995;6(2):141–146.

Jun Oh D. *o*-Xylene Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2005. [cited 2006 April 4]; Available from *http://umbbd.msi.umn.edu/ oxy/oxy_map.html*

Kane SR, Beller HR, Legler TC, Koester CJ, Pinkart HC, Halden RU, and Happel AM. Aerobic Biodegradation of Methyl *tert*-Butyl Ether by Aquifer Bacteria from Leaking Underground Storage Tank Sites. Applied and Environmental Microbiology. 2001;67(12):5824–5829.

Kasberg T, Daubaras DL, Chakrabarty AM, Kinzelt D, and Reineke W. Evidence that Operons tcb, tfd, and clc Encode Maleylacetate Reductase, the Fourth Enzyme of the Modified Ortho Pathway. Journal of Bacteriology. 1995;177(13):3885–3889.

Kaschabek SR, and Reineke W. Maleylacetate Reductase of *Pseudomonas* sp. Strain B13—Specificity of Substrate Conversion and Halide Elimination. Journal of Bacteriology. 1995;177(2):320–325.

Katagiri M, Takemori S, Nakazawa K, Suzuki H, and Akagi K. Benzyl Alcohol Dehydrogenase, a New Alcohol Dehydrogenase from *Pseudomonas* sp. Biochimica et Biophysica Acta. 1967;139(1):173–176.

Kazumi J, Caldwell ME, Suflita JM, Lovley DR, and Young, LY. Anaerobic Degradation of Benzene in Diverse Anoxic Environments. Environmental Science and Technology. 1997;31(3):813–818.

Keat MJ, and Hopper DJ. *p*-Cresol and 3,5-Xylenol Methylhydroxylases in *Pseudomonas putida* N.C.I.B. 9896. Biochemistry Journal. 1978a;175(2):649–658.

Keat MJ, and Hopper DJ. The Aromatic Alcohol Dehydrogenases in *Pseudomonas putida* N.C.I.B. 9869 Grown on 3,5-Xylenol and *p*-Cresol. Biochemistry Journal. 1978b;175(2):659–667.

Kemblowski MW, Salanitro JP, Deeley GM, and Stanley CC. Fate and Transport of Residual Hydrocarbon in Ground Water—A Case Study. In: Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water Conference: National Water Well Association and American Petroleum Institute, Houston, Texas; 1987. p. 207–231.

Kile DE, Chiou CT, Zhou H, Li H, and Xu O. Partition of Nonpolar Organic Pollutants from Water to Soil and Sediment Organic Matters. Environmental Science and Technology. 1996;29(5):1401–1406.

Kim Y, Arp DJ, and Semprini L. Chlorinated Solvent Cometabolism by Butane-Grown Mixed Culture. Journal of Environmental Engineering. 2000;126:934–942.

Klier NJ, West RJ, and Donberg PA. Aerobic Biodegradation of Dichloroethylenes in Surface and Subsurface Soils. Chemosphere. 1999;38(5):1175–1188.

Kniemeyer O, and Heider J. Ethylbenzene Dehydrogenase, a Novel Hydrocarbon-Oxidizing Molybdenum/Iron-Sulfur/Heme Enzyme. Journal of Biological Chemistry. 2001;276(24):21381–21386.

Kolhatkar R, Wilson JT, and Dunlap LE. Evaluating Natural Biodegradation of MTBE at Multiple UST Sites. In: Proceedings of the 2000 Petroleum Hydrocarbons and Organic Chemicals in Ground Water—Prevention, Detection, and Remediation—Special Focus, Natural Attenuation and Gasoline Oxygenates; 2000 November 15–17; Anaheim, California: National Ground Water Association; 2000; p. 32–49.

Kolhatkar R, Kuder T, Philp P, Allen J, and Wilson JT. Use of Compound-Specific Stable Carbon Isotope Analyses to Demonstrate Anaerobic Biodegradation of MTBE in Groundwater at a Gasoline Release Site. Environmental Science and Technology. 2002;36(23):5139–5146.

Kraus D, Lind KE, Marconi A, and McLeish R. Styrene Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2005. [cited 2006 April 10]; Available from *http://umbbd.msi.umn.edu/sty/sty_map.html*

Krone UE, Thauer RK, Hogenkamp HPC, and Steinbach K. Reductive Formation of Carbon Monoxide from CCl4 and FREONs 11, 12, and 13 Catalyzed by Corrinoids. Biochemistry. 1991;30(10):2713–2719.

Krumholz LR, Caldwell ME, and Suflita JM. Biodegradation of "BTEX" Hydrocarbons under Anaerobic Conditions. In: Crawford RL, and Crawford DL, editors. Bioremediation—Principles and Applications. New York: Cambridge University Press; 1996. p. 61–99.

Kuder T, Wilson JT, Kaiser P, Kolhatkar R, Philp P, and Allen J. Enrichment of Stable Carbon and Hydrogen Isotopes during Anaerobic Biodegradation of MTBE—Microcosm and Field Evidence. Environmental Science and Technology. 2005;39(23):213–220.

Kuhn EP, Zeyer J, Eicher P, and Schwarzenbach RP. Anaerobic Degradation of Alkylated Benzenes in Denitrifying Laboratory Aquifer Columns. Applied and Environmental Microbiology. 1988;54(2):490–496.

Kukor JJ, and Olsen RH. Genetic Organization and Regulation of a Meta Cleavage Pathway for Catechols Produced from Catabolism of Toluene, Benzene, Phenol, and Cresols by *Pseudomonas pickettii* PK01. Journal of Bacteriology. 1991;173(15):4587–4594.

Lamzin VS, Aleshin AE, Strokopytov BV, Yukhnevich MG, Popov VO, Harutyunyan EH, and Wilson KS. Crystal Structure of NAD-Dependent Formate Dehydrogenase. European Journal of Biochemistry. 1992;206(2):441–452.

Landmeyer JE, Chapelle FH, Herlong HH, and Bradley PM. Methyl *tert*-Butyl Ether Biodegradation by Indigenous Aquifer Microorganisms under Natural and Artificial Oxic Conditions. Environmental Science and Technology. 2001;35(6):1118–1126.

Lau PCK, Bergeron H, Labbé D, Wang Y, Brousseau R, and Gibson DT. Sequence and Expression of the todGIH Genes Involved in the Last Three Steps of Toluene Degradation by *Pseudomonas putida* F1. Gene. 1994;146(1):7–13.

Lee C-H, Lewis TA, Paszczynski A, and Crawford RL. Identification of an Extracellular Catalyst of Carbon Tetrachloride Dehalogenation from *Pseudomonas stutzeri* Strain KC as Pyridine-2,6-bis(thiocarboxylate). Biochemical and Biophysical Research Communications. 1999;261(3):562–566.

Lee K, and Gibson DT. Toluene and Ethylbenzene Oxidation by Purified Naphthalene Dioxygenase from *Pseudomonas* sp. Strain NCIB 9816-4. Applied and Environmental Microbiology. 1996;62(9):3101–3106.

Li S, and Wackett LP. Trichloroethylene Oxidation by Toluene Dioxygenase. Biochemical and Biophysical Research Communication. 1992;185(1):443–451.

Lide DR. CRC Handbook of Chemistry and Physics. 84th ed. New York: CRC Press Ltd.; 2003, p. 8–93—8–115, 15–14—15–18.

Liu J. 1,4-Dichlorobenzene Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2006. [cited 2006 October 25]; Available from *http://umbbd.msi.umn.edu/dcz/dcz_map.html*

Liu ZJ, Sun YJ, Rose J, Chung YJ, Hsiao CD, Chang WR, Kuo I, Perozich J, Lindahl R, Hempel J, and Wang BC. The First Structure of an Aldehyde Dehydrogenase Reveals Novel Interactions between NAD and the Rossmann Fold. Nature Structural Biology. 1997;4(4):317–326.

Lovley DR, Baedecker MJ, Lonergan DJ, Cozzarelli IM, Phillips EJP, and Siegel DI. Oxidation of Aromatic Contaminants Coupled to Microbial Iron Reduction. Nature (London). 1989;339:297–299.

Lovley DR, and Lonergan DJ, Anaerobic Oxidation of Toluene, Phenol, and *p*-Cresol by the Dissimilatory Iron-Reducing Organism, GS-15. Applied and Environmental Microbiology. 1990;56(6):1858–1864.

Lovley DR. Dissimilatory Fe (III) and Mn (IV) Reduction. Microbiological Review. 1991;55(2):259–287.

Lovley DR, Coates JD, Woodward JC, and Phillips EJP. Benzene Oxidation Coupled to Sulfate Reduction. Applied and Environmental Microbiology. 1995;61(3):953–958.

Lu G, Clement TP, Zheng C, and Wiedemeier TH. Natural Attenuation of BTEX Compounds—Model Development and Field-Scale Application. Ground Water. 1999;37(5):707–715.

Lyman WJ. Adsorption Coefficient for Soils and Sediments. In: Lyman WJ, Reehl WF, and Rosenblatt DH, editors. Handbook of Chemical Property Estimation Methods—Environmental Behavior of Organic Compounds. New York: McGraw-Hill Book Company; 1982. p. 4–l—5–29.

Ma J, Kale Y, and Ellis L. C$_1$ Metabolic Cycle Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2005. [cited 2006 April 3]; Available from *http://umbbd.msi.umn.edu/C1cyc/C1cyc_map.html*

Mabey WR, and Mill T. Critical Review of Hydrolysis of Organic Compounds in Water under Environmental Conditions. Journal of Physical and Chemical Reference Data. 1978;7(2):383–415.

Mackay D, Shiu WY, and Ma KC. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals—Volume I, Monoaromatic Hydrocarbons, Chlorobenzenes, and PCBs. Chelsea, Michigan: Lewis Publishers; 1992a.

Mackay D, Shiu WY, and Ma KC. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals—Volume II, Polynuclear Aromatic Hydrocarbons, Polychlorinated Dioxins, and Dibenzofurans. Chelsea, Michigan: Lewis Publishers; 1992b.

Mackay D, Di Guardo A, Paterson S, Kicsi G, and Cowan CE. Assessing the Fate of New and Existing Chemicals—A Five-Stage Process. Environmental Toxicology and Chemistry. 1996;15(9):1618–1626.

Mackay D. Finding Fugacity Feasible, Fruitful, and Fun. Environmental Toxicology and Chemistry. 2004;23(10):2282–2289.

Magnuson JK, Stern RV, Gossett JM, Zinder SH, and Burris DR. Reductive Dechlorination of Tetrachloroethene to Ethene by a Two-Component Enzyme Pathway. Applied and Environmental Microbiology. 1998;64(4):1270–1275.

Mason JR, and Geary PJ. cis-1,2-Dihydroxycyclohexa-3,5-diene (NAD) Oxidoreductase (cis-Benzene Dihydrodiol Dehydrogenase) from Pseudomonas putida NCIB 12190. Methods in Enzymology. 1990;188:134–137.

Maymo-Gatell X, Chien Y-T, Gossett JM, and Zinder SH. Isolation of a Bacterium that Reductively Dechlorinates Tetrachloroethene to Ethene. Science. 1997;276(5318):1568–1571.

McCarty PL, and Reinhard M. Biological and Chemical Transformations of Halogenated Aliphatic Compounds in Aquatic and Terrestrial Environments in the Biochemistry of Global Change. In: Oremland RS, editor. The Biogeochemistry of Global Change—Radioactive Trace Gases. New York: Chapman and Hall, Inc.; 1993; p. 839–852.

McCarty PL, and Semprini L. Ground-Water Treatment for Chlorinated Solvents. In: Norris RD, Hinchee RE, Brown R, McCarty PL, Semprini L, Wilson JT, Kampbell DH, Reinhard M, Bouwer EJ, Borden RC, Vogel TM, Thomas JM, and Ward CH, editors. Groundwater Cleanup through Bioremediation—Handbook of Bioremediation. Boca Raton, Florida: Lewis Publishers, Inc.; 1994.

McCarty PL. Biotic and Abiotic Transformations of Chlorinated Solvents in Ground Water. In: Proceedings of the Symposium on Natural Attenuation of Chlorinated Organics in Ground Water; 1996 September 11–13; Dallas, Texas: U.S. Environmental Protection Agency, Report No. EPA/540/R-97/504; 1997, p. 7–11.

McCarty PL, Goltz MN, Hopkins GD, Dolan ME, Allan JP, Kawakami BT, and Carrothers TJ. Full Scale Evaluation of In Situ Cometabolic Degradation of Trichloroethylene in Groundwater through Toluene Injection. Environmental Science and Technology. 1998;32:88–100.

McIntire W, Singer TP, Smith AJ, and Mathews FS. Amino Acid and Sequence Analysis of the Cytochrome and Flavo-Protein Subunits of p-Cresol Methylhydroxylase. Biochemistry. 1986;25(20):5975–5981.

McLeish R. Ethylbenzene Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2005. [cited 2006 April 5]; Available from http://umbbd.msi.umn.edu/ethb2/ethb2_map.html

Menn FM, Zylstra GJ, and Gibson DT. Location and Sequence of the todF Gene Encoding 2-Hydroxy-6-oxohepta-2,4-dienoate Hydrolase in Pseudomonas putida F1. Gene. 1991;104(1):91–94.

Middeldorp PJM, De Wolf J, Zehnder AJB, and Schraa G. Enrichment and Properties of a 1,2,4-Trichlorobenzene-dechlorinating Methanogenic Microbial Consortium. Applied and Environmental Microbiology. 1997;63(4):1225–1229.

Mili J, and Stephens S. p-Xylene Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2006. [cited 2006 April 3]; Available from http://umbbd.msi.umn.edu/pxy/pxy_map.html

Monferran MV, Echenique JR, and Wunderlin DA. Degradation of Chlorobenzenes by a Strain of Acidovorax Avenae Isolated from a Polluted Aquifer. Chemosphere. 2005;61(1):98–106.

Moran MJ. Occurrence and Implications of Selected Chlorinated Solvents in Ground Water and Source Water in the United States and in Drinking Water in 12 Northeast and Mid-Atlantic States, 1993–2002. U.S. Geological Survey Scientific Investigations Report 2005–5268; 2006.

Moran MJ, Zogorski JS, and Squillace PJ. Occurrence and Implications of Methyl tert-Butyl Ether and Gasoline Hydrocarbons in Ground Water and Source Water in the United States and in Drinking Water in 12 Northeast and Mid-Atlantic States, 1993–2002. U.S. Geological Survey Water-Resources Investigations Report 03-4200; 2004.

Morasch B, Richnow HH, Schink B, and Meckenstock RU. Stable Hydrogen and Carbon Isotope Fractionation during Microbial Toluene Degradation—Mechanistic and Environmental Aspects. Applied and Environmental Microbiology. 2001;67(10):4842–4849.

Morasch B, Richnow HH, Schink B, Vieth A, and Meckenstock RU. Carbon and Hydrogen Stable Isotope Fractionation during Aerobic Bacterial Degradation of Aromatic Hydrocarbons. Applied and Environmental Microbiology. 2002;68(10):5191–5194.

Motosugi K, Esaki N, and Soda K. Purification and Properties of a New Enzyme, DL-2-haloacid Dehalogenase, from *Pseudomonas* sp. Journal of Bacteriology. 1982;150(2):522–527.

Murakami S, Kodama N, Shinke R, and Aoki K. Classification of Catechol 1,2-Dioxygenase Family—Sequence Analysis of a Gene for the Catechol 1,2-Dioxygenase Showing High Specificity for Methylcatechols from Gram+ Aniline-Assimilating *Rhodococcus erythropolis* AN-13. Gene. 1997;185(1):49–54.

Murray WD, and Richardson M. Progress toward the Biological Treatment of C_1 and C_2 Halogenated Hydrocarbons. Critical Reviews in Environmental Science and Technology. 1993;23(3):195–217.

Nakazawa T, and Hayashi E. Phthalate and 4-Hydroxyphthalate Metabolism in *Pseudomonas testosterone*—Purification and Properties of 4,5-Dihydroxyphthalate Decarboxylase. Applied and Environmental Microbiology. 1978;36(2): 264–269.

National Center for Manufacturing Sciences. SOLV-DB®, Online Database. 2006. [cited 2006 September 5]; Available from *http://solvdb.ncms.org/common01.idc*

National Institute for Resources and Environment. Database for Environmental Fate of Chemicals—Biodegradation Pathways of Chlorobenzenes in a Sediment Sample. 2001. [cited 2006 October 25]; National Institute for Resources and Environment, Ibaraki, Japan; Available from *http://www.aist.go.jp/RIODB/dbefc/nirefate/bio/CBZs_E.html*

Neidle E, Hartnett C, Ornston LN, Bairoch A, Rekik M, and Harayama S. *cis*-Diol Dehydrogenases Encoded by the TOL pWW0 Plasmid xylL Gene and the *Acinetobacter calcoaceticus* Chromosomal benD Gene Are Members of the Short-chain Alcohol Dehydrogenase Superfamily. European Journal of Biochemistry. 1992;204(1):113–120.

Newman LM, and Wackett LP. Fate of 2,2,2-Trichloroacetaldehyde (Chloral Hydrate) Produced during Trichloroethylene Oxidation by Methanotrophs. Applied and Environmental Microbiology. 1991;57(8):2399–2402.

Newman LM, and Wackett LP. Purification and Characterization of Toluene 2-Monooxygenase from *Burkholderia cepacia* G4. Biochemistry. 1995;34(43):14066–14076.

Newman LM, and Wackett LP. Trichloroethylene Oxidation by Purified Toluene 2-Monooxygenase—Products, Kinetics, and Turnover-Dependent Inactivation. Journal of Bacteriology. 1997;179(1):90–96.

Ngai KL, Neidle EL, and Ornston LN. Catechol and Chlorocatechol 1,2-Dioxygenases. Methods in Enzymology. 1990;188:122–126.

Nielsen PH, Bjerg PL, Nielsen P, Smith P, and Christensen TH. *In Situ* and Laboratory Determined First-Order Degradation Rate Constants of Specific Organic Compounds in an Aerobic Aquifer. Environmental Science and Technology. 1996;30(1):31–37.

Norris RD, Hinchee RE, Brown RA, McCarty PL, Semprini L, Wilson JT, Kampbell DH, Reinhard M, Bouwer EJ, Borden RC, Vogel TM, Thomas JM, and Ward CH. In-Situ Bioremediation of Groundwater and Geologic Material—A Review of Technologies. Washington, D.C.: U.S. Environmental Protection Agency; 1993. Report No.: EPA/600/R-93/124.

Olaniran AO, Pillay D, and Pillay B. Chloroethenes Contaminants in the Environment—Still a Cause for Concern. African Journal of Biotechnology. 2004;3(12):675–682.

Oldenhuis R, Vink RL, Janssen DB, and Witholt B. Degradation of Chlorinated Aliphatic Hydrocarbons by *Methylosinus trichosporium* OB3b Expressing Soluble Methane Monooxygenase. Applied and Environmental Microbiology. 1989;55(11):2819–2826.

Olivera ER, Reglero Á, Martinez-Blanco H, Fernández-Medarde A, Moreno MA, and Luengo JM. Catabolism of Aromatics in *Pseudomonas putida* U.—Formal Evidence that Phenylacetic Acid and 4-Hydroxyphenylacetic Acid Are Catabolized by Two Unrelated Pathways. European Journal of Biochemistry. 1994;221(1):375–381.

Olsen RH, Kukor JJ, and Kaphammer B. A Novel Toluene-3-Monooxygenase Pathway Cloned from *Pseudomonas pickettii* PKO1. Journal of Bacteriology. 1994;176(12):3749–3756.

O'Reilly KT, Moir ME, Taylor CD, Smith CA, and Hyman MR. Hydrolysis of *tert*-Butyl Methyl Ether (MTBE) in Dilute Aqueous Acid. Environmental Science and Technology. 2001;35(19):3954–3961.

Pathak D, and Ollis D. Refined Structure of Dienelactone Hydrolase at 1.8 Angstroms. Journal of Molecular Biology. 1990;214(2):497–525.

Pedersen CR, and Essenberg C. Methyl *tert*-Butyl Ether Pathway Map—University of Minnesota Biocatalysis/ Biodegradation Database. 2005. [cited 2006 March 15]; Available from *http://umbbd.msi.umn.edu/mtb/mtb_map.html*

Phelps CP, Kazumi J, and Young LY. Anaerobic Degradation of Benzene in BTX Mixtures Dependent on Sulfate Reduction. FEMS Microbiology Letters. 1996;145(3):433–437.

Platt A, Shingler V, Taylor SC, and Williams PA. The 4-Hydroxy-2-oxovalerate Aldolase and Acetaldehyde Dehydrogenase (Acylating) Encoded by the nahM and nahO Genes of the Naphthalene Catabolic Plasmid pWW60-22 Provide Further Evidence of Conservation of Meta-Cleavage Pathway Gene Sequences. Microbiology. 1995;141(9):2223–2233.

Poh CL, and Bayly RC. Evidence for Isofunctional Enzymes Used in *m*-Cresol and 2,5-Xylenol Degradation via the Gentisate Pathway in *Pseudomonas alcaligenes*. Journal of Bacteriology. 1980;143(1):59–69.

Rabus R, Nordhaus R, Ludwig W, and Widdel F. Complete Oxidation of Toluene under Strictly Anoxic Conditions by a New Sulfate-Reducing Bacterium. Applied Environmental Microbiology. 1993;59(5):1444–1451.

Rabus R, and Widdel F. Anaerobic Degradation of Ethylbenzene and Other Aromatic Hydrocarbons by New Denitrifying Bacteria. Archives of Microbiology. 1995;163(2):96–103.

Ramanand K, Balba MT, and Duffy J. Reductive Dehalogenation of Chlorinated Benzenes and Toluenes under Methanogenic Conditions. Applied and Environmental Microbiology. 1993;59(10):3266–3272.

Rapp P, and Gabriel-Jürgens LHE. Degradation of Alkanes and Highly Chlorinated Benzenes, and Production of Biosurfactants, by a Psychrophilic *Rhodococcus* sp. and Genetic Characterization of Its Chlorobenzene Dioxygenase. Microbiology. 2003;149(10):2879–2890.

Rathbun RE. Transport, Behavior, and Fate of Volatile Organic Compounds in Streams. U.S. Geological Survey Professional Paper 1589; 1998.

Reineke W, and Knackmuss HJ. Microbial Metabolism of Haloaromatics—Isolation and Properties of a Chlorobenzene-Degrading Bacterium. Applied and Environmental Microbiology. 1984;47(2):395–402.

Reineke W, and Knackmuss HJ. Microbial Degradation of Haloaromatics. Annual Review of Microbiology. 1988;42:263–287.

Reinhard M, Goodman NL, and Barker JF. Occurrence and Distribution of Organic Chemicals in Two Landfill Leachate Plumes. Environmental Science and Technology. 1984;18(12):953–961.

Renhao L. 1,2-Dichloroethane Pathway Map (Anaerobic)—University of Minnesota Biocatalysis/Biodegradation Database. 2005. [cited 2006 April 10]; Available from *http://umbbd.msi.umn.edu/dce/dce_map.html*

Riegert U, Heiss G, Fischer P, and Stolz A. Distal Cleavage of 3-Chlorocatechol by an Extradiol Dioxygenase to 3-Chloro-2-Hydroxymuconic Semialdehyde. Journal of Bacteriology. 1998;180(11):2849–2853.

Roberts PV, Goltz MN, and Mackay DM. A Natural Gradient Experiment on Solute Transport in a Sand Aquifer—III. Retardation Estimates and Mass Balances for Organic Solutes. Water Resources Research. 1986;22(13):2047–2058.

Rosenzweig AC, Frederick CA, Lippard SJ, and Nordlund P. Crystal Structure of a Bacterial Non-Haem Iron Hydroxylase that Catalyses the Biological Oxidation of Methane. Nature. 1993;366(6455):537–543.

Roychoudhury AN, and Merrett GL. Redox Pathways in a Petroleum Contaminated Shallow Sandy Aquifer—Iron and Sulfate Reductions. Science of the Total Environment. 2005;366(1):262–274.

Saichek RE, and Reddy KR. Electrokinetically Enhanced Remediation of Hydrophobic Organic Compounds in Soils—A Review. Critical reviews in Environmental Science and Technology. 2005;35(1):115–192.

Sakai K, Rowley M, Gairola P, and Stephens S. *m*-Cresol Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2005. [cited 2006 March 24]; Available from *http://umbbd.msi.umn.edu/mcr/mcr_map.html*

Salanitro JP. The Role of Bioattenuation in the Management of Aromatic Hydrocarbon Plumes in Aquifers. Ground Water Monitoring Review. 1993;Fall:150–161.

Sander P, Wittaich RM, Fortnagel P, Wilkes H, and Francke W. Degradation of 1,2,4-Trichloro- and 1,2,4,5-Tetrachlorobenzene by *Pseudomonas* Strains. Applied and Environmental Microbiology. 1991;57(5):1430–1440.

Sands T, Dodge T, and Fitzgerald M. 1,1,1-Trichloroethane (An/Aerobic) Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2005. [cited 2006 March 21]; Available from *http://umbbd.msi.umn.edu/tca/tca_map.html*

Sangster J. Octanol-Water Partition Coefficients of Simple Organic Compounds. Journal of Physical and Chemical Reference Data. 1989;18:1111–1230.

Sargent BP, Green JW, Harte PT, and Vowinkel EF. Ground-Water-Quality Data for Picatinny Arsenal, New Jersey, 1958–85: U.S. Geological Survey Open-File Report 86-58; 1986.

Schalk CW, Cunningham WL, Sarver KM, Timmins RM, Rowe GL, Wright PR, and Parnell JM. Results of the Base-wide Monitoring Program at Wright-Patterson Air Force Base, Ohio, 1993–1994: U.S. Geological Survey Water-Resources Investigations Report 96-4125; 1996.

Schwarzenbach RP, and Westall J. Transport of Nonpolar Organic Compounds from Surface Water to Groundwater—Laboratory Sorption Studies. Environmental Science and Technology. 1981;15(11):1360–1367.

Sedran MA, Pruden A, Wilson GJ, Suidan MT, and Venosa AD. Effect of BTEX on Degradation of MTBE and TBA by Mixed Bacterial Consortium. Journal of Environmental Engineering. 2002;128(9):830–835.

Seip HM, Alstad J, Carlberg GE, Martinsen K, and Skaane R. Measurement of Mobility of Organic Compounds in Soils. Science of the Total Environment. 1986;50(1):87–101.

Shaw JP, and Harayama S. Purification and Characterization of TOL Plasmid-Encoded Benzyl Alcohol Dehydrogenase and Benzaldehyde Dehydrogenase of *Pseudomonas putida*. European Journal of Biochemistry. 1990;191(3):705–714.

References Cited

Shaw JP, and Harayama S. Purification and Characterization of the NADH:acceptor Reductase Component of Xylene Monooxygenase Encoded by the TOL Plasmid pWW0 of *Pseudomonas putida* mt-2. European Journal of Biochemistry. 1992;209(1):51–61.

Shaw JP, Rekik M, Schwager F, and Harayama S. Kinetic Studies on Benzyl Alcohol Dehydrogenase Encoded by TOL Plasmid pWW0. Journal Biology Chemistry. 1993;268(15):10842–10850.

Shields MS, Reagin MJ, Gerger RR, Campbell R, and Somerville C. TOM, a New Aromatic Degradative Plasmid from *Burkholderia* (*Pseudomonas*) *cepacia* G4. Applied and Environmental Microbiology. 1995;61(4):1352–1356.

Simpson HD, Green J, Dalton H. Purification and Some Properties of a Novel Heat-Stable *cis*-Toluene Dihydrodiol Dehydrogenase. Biochemistry Journal. 1987;244(3):585–590.

Smith CA, O'Reilly KT, and Hyman MR. Characterization of the Initial Reactions during the Cometabolic Oxidation of Methyl *tert*-Butyl Ether by Propane-Grown *Mycobacterium vaccae* JOB5. Applied and Environmental Microbiology. 2003;69(2):796–804.

Smith JA, Witkowski PJ, and Fusillo TV. Manmade Organic Compounds in the Surface Waters of the United States—A Review of Current Understanding: U.S. Geological Survey Circular 1007; 1988.

Sommer C, and Görisch H. Enzymology of the Degradation of (Di)chlorobenzenes by *Xanthobacter flavus* 14p1. Archives of Microbiology. 1997;167(6):384–391.

Somsamak P, Cowan RM, and Häggblom MM. Anaerobic Biotransformation of Fuel Oxygenates under Sulfate-Reducing Conditions. FEMS Microbiology Ecology. 2001;37(3):259–264.

Spain JC, and Nishino SF. Degradation of 1,4-Dichlorobenzene by a *Pseudomonas* sp. Applied and Environmental Microbiology. 1987;53(3):1010–1019.

Spiess E, Sommer C, and Görisch H. Degradation of 1,4-Dichlorobenzene by *Xanthobacter flavus* 14p1. Applied and Environmental Microbiology. 1995;61(11):3884–3888.

Squillace PJ, Pankow JF, Korte NE, and Zorgorski JS. Review of the Environmental Behavior and Fate of Methyl *tert*-Butyl Ether. Environmental Toxicology and Chemistry. 1997;16(9):1836–1844.

Squillace PJ, and Moran MJ. Factors Associated with Sources, Transport, and Fate of Volatile Organic Compounds in Aquifers of the United States and Implications for Ground-Water Management and Assessments: U.S. Geological Survey Scientific Investigations Report 2005-5269; 2006.

Steffan RJ, McClay K, Vainberg S, Condee CW, and Zhang D. Biodegradation of the Gasoline Oxygenates Methyl *tert*-Butyl Ether, Ethyl *tert*-Butyl Ether, and *tert*-Amyl Methyl Ether by Propane-Oxidizing Bacteria. Applied and Environmental Microbiology. 1997;63(11):4216–4222.

Stucki G, Krebser U, and Leisinger T. Bacterial Growth on 1,2-Dichloroethane. Experientia. 1983;39(11):1271–1273.

Stumm W, and Morgan JJ. Aquatic Chemistry. 3rd ed. New York: John Wiley & Sons, Inc.; 1996.

Suzuki M, Hayakawa T, Shaw JP, Rekik M, and Harayama S. Primary Structure of Xylene Monooxygenase—Similarities to and Differences from the Alkane Hydroxylation System. Journal of Bacteriology. 1991;173(5):1690–1695.

Swoboda-Colberg NG. Chemical Contamination of the Environment—Sources, Types, and Fate of Synthetic Organic Chemicals. In: Young LY, and Cerniglia CE, editors. Microbial Transformations and Degradation of Toxic Organic Chemicals. New York: Wiley-Liss, Inc.; 1995. p. 27–74.

Thomas JM, Gordy VR, Fiorenza S, and Ward CH. Biodegradation of BTEX in Subsurface Materials Contaminated with Gasoline—Granger, Indiana. Water Science and Technology. 1990;22:53–62.

Ulrich AC, Beller HR, and Edwards EA. Metabolites Detected during Biodegradation of 13C6-Benzene in Nitrate-Reducing and Methanogenic Enrichment Cultures. Environmental Science and Technology. 2005;39(17):6681–6691.

U.S. Environmental Protection Agency. Chemical Summary for Methyl-*tert*-butyl Ether (CAS No. 1634-04-4). Washington, D.C.: Office of Pollution Prevention and Toxics, U.S. Environmental Protection Agency; Report No.: EPA 749-F-94-017a. 1994. [cited 2006 May 22]; Available from *http://www.epa.gov/chemfact/s_mtbe.txt*

U.S. Environmental Protection Agency. Contaminant Specific Fact Sheets, Volatile Organic Chemicals—Technical Version. U.S. Environmental Protection Agency, EPA 811-F-95-004-T. 1995. [cited 2006 January 11]; Available from *http://www.epa.gov/safewater/dwh/t-voc.html*

U.S. Environmental Protection Agency. Use and Distribution of MTBE and Ethanol, MTBE Fact Sheet #3. Washington, D.C.: Office of Underground Storage Tanks, U.S. Environmental Protection Agency, Report No.: EPA 510-F-97-016. 1998. [cited 2006 September 22]; Available from *http://www.epa.gov/swerust1/mtbe/mtbefs3.pdf*

U.S. Environmental Protection Agency. Requirements for Preparation, Adoption, and Submittal of Implementation Plans—Definitions, Code of Federal Regulations, Title 40, Volume 2, Parts 50 to 51, Section 51.100, revised as of July 1, 2000. Washington, D.C.: U.S. Environmental Protection Agency; 2000a.

U.S. Environmental Protection Agency. Report to Congress on a Compliance Plan for the Underground Storage Tank Program. Washington, D.C.: U.S. Environmental Protection Agency, Solid Waste and Emergency Response; 2000b. Report No.: EPA 510-R-00-001. [cited 2006 September 22]; Available from *http://www.epa.gov/swerust1/pubs/rtc_0600.pdf*

U.S. Environmental Protection Agency. How to Evaluate Alternative Cleanup Technologies for Underground Storage Tank Sites—A Guide for Corrective Action Plan Reviewers. U.S. Environmental Protection Agency; 2004. Report No.: EPA 510-B-95-007. [cited 2006 September 22]; Available from *http://www.epa.gov/swerust1/pubs/tums.htm*

U.S. Environmental Protection Agency. U.S. Environmental Protection Agency Underground Storage Tank Program, Corrective Action Measures Archive. 2005a. [cited 2006 April 27]; Available from *http://www.epa.gov/oust/cat/camarchv.htm*

U.S. Environmental Protection Agency. Technical Fact Sheets on Volatile Organic Compounds. 2005b. [cited 2006 September 23]; Available from *http://www.epa.gov/envirofw/html/emci/chemref/*

U.S. Geological Survey. National Water Quality Assessment Glossary. 2006. [cited 2006 September 23]; Available from *http://water.usgs.gov/nawqa/glos.html*

van der Meer JR, van Neerven AR, de Vries EJ, de Vos WM, and Zehnder AJ. Cloning and Characterization of Plasmid-Encoded Genes for the Degradation of 1,2-Dichloro-, 1,4-Dichloro-, and 1,2,4-Trichlorobenzene of *Pseudomonas* sp. Strain P51. Journal of Bacteriology. 1991;173(1):6–15.

van der Meer JR, Werlen C, Nishino SF, and Spain JC. Evolution of a Pathway for Chlorobenzene Metabolism Leads to Natural Attenuation in Contaminated Groundwater. Applied and Environmental Microbiology. 1998;64(11):4185–4193.

Verschueren HGK, Seljée F, Rozeboom HJ, Kalk KH, and Dijkstra BW. Crystallographic Analysis of the Catalytic Mechanism of Haloalkane Dehalogenase. Nature. 1993;363(6431):693–698.

Vogel TM, and McCarty PL. Biotransformation of Tetrachloroethylene to Trichloroethylene, Dichloroethylene, Vinyl Chloride, and Carbon Dioxide under Methanogenic Conditions. Applied and Environmental Microbiology. 1985;49(5):1080–1083.

Vogel TM, and Grbić-Galić D. Incorporation of Oxygen from Water into Toluene and Benzene during Anaerobic Fermentative Transformation. Applied and Environmental Microbiology. 1986;52(1):200–202.

Vogel TM, Criddle CS, and McCarty PL. Transformation of Halogenated Aliphatic Compounds. Environmental Science and Technology. 1987;21(8):722–736.

Vogel TM, and McCarty PL. Rate of Abiotic Formation of 1,1-Dichloroethylene from 1,1,1-Trichloroethane in Groundwater. Journal of Contaminant Hydrology. 1987a;1(3):299–308.

Vogel TM, and McCarty PL. Abiotic and Biotic Transformation of 1,1,1-Trichloroethane under Methanogenic Conditions. Environmental Science and Technology. 1987b;21(12):1208–1214.

Vogel TM. Natural Bioremediation of Chlorinated Solvents. In: Norris RD, Hinchee RE, Brown R, McCarty PL, Semprini L, Wilson JT, Kampbell DH, Reinhard M, Bouwer EJ, Borden RC, Vogel TM, Thomas JM, and Ward CH, editors. Handbook of Bioremediation. Boca Raton, Florida: Lewis Publishers; 1994. p. 201–222.

Vollmer MD, Stadler-Fritzsche K, and Schlömann M, Conversion of 2-Chloromaleylacetate in *Alcaligenes eutrophus* JMP134. Archives of Microbiology. 1993;159(2):182–188.

Wackett LP, Kwart LD, and Gibson DT. Benzylic Monooxygenation Catalyzed by Toluene Dioxygenase from *Pseudomonas putida*. Biochemistry. 1988;27(4):1360–1367.

Wackett LP, and Zeng Y. Toluene Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2004. [cited 2006 March 22]; Available from *http://umbbd.msi.umn.edu/tol/tol_map.html*

Walsh TA, Ballou DP, Mayer R, and Que L Jr. Rapid Reaction Studies on the Oxygenation Reactions of Catechol Dioxygenase. Journal of Biological Chemistry. 1983;258(23):14422–14427.

Warhurst AM, Clarke KF, Hill RA, Holt RA, and Fewson CA. Metabolism of Styrene by *Rhodococcus rhodochrous* NCIMB 13259. Applied and Environmental Microbiology. 1994;60(4):1137–1145.

Washington JW. Hydrolysis Rates of Dissolved Volatile Organic Compounds—Principles, Temperature Effects and Literature Review. Ground Water. 1995;33(3):415–424.

Weightman AJ, Weightman AL, and Slater JH. Toxic Effects of Chlorinated and Brominated Alkanoic Acids on *Pseudomonas putida* PP3—Selection at High Frequencies of Mutations in Genes Encoding Dehalogenases. Applied and Environmental Microbiology. 1985;49(6):1494–1501.

Weiner JM, and Lovley DR. Rapid Benzene Degradation in Methanogenic Sediments from a Petroleum-Contaminated Aquifer. Applied and Environmental Microbiology. 1998;64(5):1937–1939.

Werlen C, Kohler HP, and van der Meer JR. The Broad Substrate Chlorobenzene Dioxygenase and *cis*-Chlorobenzene Dihydrodiol Dehydrogenase of *Pseudomonas* sp. Strain P51 Are Linked Evolutionarily to the Enzymes for Benzene and Toluene Degradation. Journal of Biological Chemistry. 1996;271(8):4009–4016.

References Cited

Whited GM, McCombie WR, Kwart LD, and Gibson DT. Identification of *cis*-Diols as Intermediates in the Oxidation of Aromatic Acids by a Strain of *Pseudomonas putida* that Contains a TOL Plasmid. Journal of Biochemistry. 1986;166(3):1028–1039.

Whittaker M, Monroe D, Jun Oh D, and Anderson S. Trichloroethylene Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2005. [cited 2006 March 21]; Available from *http://umbbd.msi.umn.edu/tce/tce_map.html*

Wiedemeier TH, Wilson JT, Kampbell DH, Miller RN, and Hansen JE. Technical Protocol for Implementing Intrinsic Remediation with Long-Term Monitoring for Natural Attenuation of Fuel Contamination Dissolved in Groundwater. U.S. Air Force Center for Environmental Excellence, Technology Transfer Division, Brooks Air Force Base, San Antonio, Texas; 1995.

Wiedemeier TH, Swanson MA, Moutoux DE, Gordon EK, Wilson JT, Wilson BH, Kampbell DH, Haas PE, Miller RN, Hansen JE, and Chapelle FH. Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water. Cincinnati, Ohio: U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Office of Research and Development; 1998. Report No.: EPA/600/R-98/128.

Wilson JT, Cho JS, Wilson BH, and Vardy JA. Natural Attenuation of MTBE in the Subsurface under Methanogenic Conditions. Ada, Okla.: U.S. Environmental Protection Agency, National Risk Management Research Laboratory. Report No.: EPA/600/R-00/006. 2000. [cited 2006 September 21]; Available from *http://www.epa.gov/ada/download/reports/mtbereport.pdf*

Wilson JT, Kaiser PM, and Adair C. Monitored Natural Attenuation of MTBE as a Risk Management Option at Leaking Underground Storage Tank Sites. U.S. Environmental Protection Agency. Report No.: EPA/600/R-044/179. 2005. [cited 2006 September 21]; Available from *http://www.epa.gov/ORD/NRML/pubs/600r04179/600r04179.htm*

Wisconsin Department of Natural Resources. Fiscal Year 2001 Groundwater Quality Monitoring Plan. Madison, Wisconsin: Wisconsin Department of Natural Resources; 2000.

Xia Z, Dai W, Zhang Y, White SA, Boyd GD, and Mathews SF. Determination of the Gene Sequence and the Three-Dimensional Structure at 2.4 Angstroms Resolution of Methanol Dehydrogenase from *Methylophilus* W3A1. Journal of Molecular Biology. 1996;259(3):480–501.

Yagi O, Hashimoto A, Iwasaki K, and Nakajima M. Aerobic Degradation of 1,1,1-Trichloroethane by *Mycobacterium* spp. Isolated from Soil. Applied and Environmental Microbiology. 1999;65(10):4693–4696.

Yao G. 1,2,4-Trichlorobenzene (an/aerobic) Pathway Map—University of Minnesota Biocatalysis/Biodegradation Database. 2006. [cited 2006 June 14]; Available from *http://umbbd.msi.umn.edu/tbz/tbz_map.html*

Yen KM, Karl MR, Blatt LM, Simon MJ, Winter RB, Fausset PR, Lu HS, Harcourt AA, and Chen KK. Cloning and Characterization of a *Pseudomonas mendocina* KR1 Gene Cluster Encoding Toluene-4-monooxygenase. Journal of Bacteriology. 1991;173(17):5315–5327.

Zamanian M, and Mason JR. Benzene Dioxygenase in *Pseudomonas putida*—Subunit Composition and Immuno-Cross-Reactivity with Other Aromatic Dioxygenases. Biochemical Journal. 1987;244(3):611–616.

Zogorski JS, Carter JM, Ivahnenko T, Lapham WW, Moran MJ, Rowe BL, Squillace PJ, and Toccalino PL. The Quality of Our Nation's Waters—Volatile Organic Compounds in the Nation's Ground Water and Drinking-Water Supply Wells. U.S. Geological Survey Circular 1292; 2006. [cited 2006 September 21]; Available from *http://pubs.usgs.gov/circ/circ1292/*

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Chapter D: Properties and Degradation Pathways of Common Organic Compounds in Groundwater