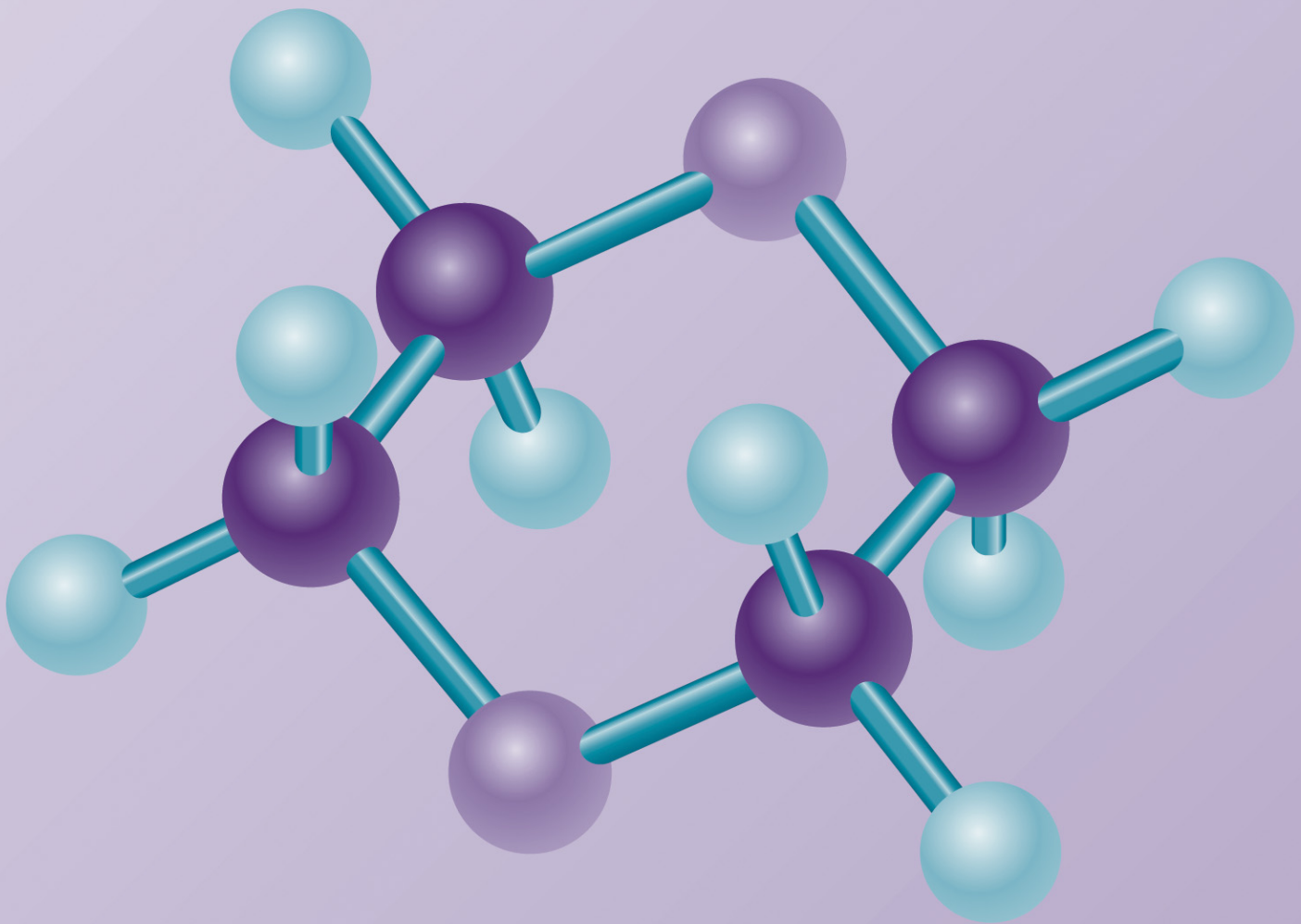




Treatment Technologies For 1,4-Dioxane: Fundamentals And Field Applications



Office of Solid Waste
and Emergency Response
(5203P)

EPA-542-R-06-009
December 2006
www.epa.gov/tio
<http://clu-in.org>

Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications

CONTENTS

<u>Section</u>	<u>Page</u>
ACRONYMS AND ABBREVIATIONS.....	ii
FOREWORD.....	iv
NOTICE AND DISCLAIMER.....	v
ACKNOWLEDGMENTS.....	v
EXECUTIVE SUMMARY.....	ES-1
1.0 INTRODUCTION.....	1-1
1.1 Overview of Dioxane Production and Environmental Occurrence.....	1-2
1.2 Properties and Behavior of Dioxane in the Environment.....	1-3
1.3 Characterization of Dioxane.....	1-4
1.4 Cleanup Goals and Standards.....	1-5
2.0 TREATMENT OF MEDIA CONTAINING DIOXANE.....	2-1
2.1 Treatment Technologies for Dioxane in Water.....	2-1
2.1.1 Advanced Oxidation (<i>Ex Situ</i>).....	2-1
2.1.2 Adsorption (GAC) (<i>Ex Situ</i>).....	2-5
2.1.3 Bioremediation.....	2-5
2.2 Treatment of Dioxane in Soil.....	2-6
2.3 Ongoing Research on Dioxane Treatment.....	2-6
3.0 REFERENCES.....	3-1
APPENDIX A INTERNET SOURCES FOR SUMMARY OF SELECTED U.S. ENVIRONMENTAL PROTECTION AGENCY AND STATE GUIDANCE FOR DIOXANE IN SOIL AND WATER.....	A-1

EXHIBITS

<u>Exhibit</u>	<u>Page</u>
1 Process and Product Uses of Dioxane.....	1-2
2 2002 Toxics Release Inventory Data for Dioxane and 1,1,1-Trichloroethane (all amounts in pounds).....	1-3
3 Molecular Structure of Dioxane.....	1-4
4 Properties of Dioxane and 1,1,1-Trichloroethane.....	1-4
5 Summary of Selected U.S. Environmental Protection Agency and State Guidance for Dioxane in Soil and Water (as of January 2005).....	1-6
6 Process Flow Diagram of a Typical Ozone/Hydrogen Peroxide Groundwater Treatment System.....	2-2
7 Summary of Full- and Pilot-Scale Treatment Projects for 1-4 Dioxane in Groundwater.....	2-7

ACRONYMS AND ABBREVIATIONS

µg/L	Micrograms per liter
AFB	Air Force Base
AOP	Advanced oxidation process
APT	Applied Process Technology, Inc.
ART	Accelerated Remediation Technologies, LLC
atm	Atmosphere
ATSDR	Agency for Toxic Substances and Disease Registry
CLU-IN	EPA Hazardous Waste Clean-Up Information Web site
DCE	Dichloroethene
EPA	U.S. Environmental Protection Agency
FRTR	Federal Remediation Technologies Roundtable
g	Grams
GAC	Granular activated carbon
GC	Gas chromatography
gpm	Gallon per minute
GRAC	Groundwater Resources Association of California
IARC	International Agency for Research on Cancer
IRIS	Integrated Risk Information System
K _{ow}	Octanol-water partition coefficient
L	Liter
Log K _{ow}	Log of the octanol-water partition coefficient
mg	Milligrams
mg/kg	Milligrams per kilogram
mg/kg/day	Milligrams per kilogram per day
mg/L	Milligrams per liter
mg/m ³	Milligrams per cubic meter
mL	Milliliter
mm Hg	Millimeters of mercury
MS	Mass spectrometry
ND	Non detect
NPDES	National Pollutant Discharge Elimination System
OSHA	Occupational Safety and Health Administration
PEL	Permissible exposure limit
ppm	Parts per million
PRG	Preliminary remediation goal
ROD	Record of decision
SERDP	Strategic Environmental Research and Development Program
SIM	Selected ion monitoring
SLAC	Stanford Linear Accelerator Center

TCA	Trichloroethane
TCE	Trichloroethylene
TRI	Toxics Release Inventory
USACE	U.S. Army Corps of Engineers
USDHHS	U.S. Department of Health and Human Services
UV	Ultraviolet
VOC	Volatile organic compound

FOREWORD

1,4-Dioxane is a solvent stabilizer frequently found at contaminated sites where methyl chloroform (1,1,1-trichloroethane) was used for degreasing. This report profiles the occurrence and properties of 1,4-dioxane and provides a summary of the available remedial technologies. The information presented should prove useful to project managers and other regulatory officials who oversee cleanup of contaminated groundwater, particularly where chlorinated solvents are the principal contaminant. Consultants, including hydrogeologists, remediation engineers, and modelers, should also find this report useful, as should water utility operators and regulators.

In recent years, the regulated community has become increasingly aware that 1,4-dioxane is likely to be present at sites where methyl chloroform is a contaminant. Although 1,4-dioxane has been a constituent of methyl chloroform wastes for decades, recent improvements to analytical methods allowed its detection in the parts per billion range beginning in 1997. Analysis of 1,4-dioxane often must be specifically requested. The common practice of analyzing by a limited list of available methods for regulatory compliance has precluded detection of 1,4-dioxane.

The properties that made 1,4-dioxane difficult to analyze in the past also make it difficult to treat. For example, 1,4-dioxane is fully miscible in water. As a hydrophilic contaminant, it is not, therefore, amenable to the conventional *ex situ* treatment technologies used for chlorinated solvents. Successful remedial technologies must take into account the challenging chemical and physical properties unique to 1,4-dioxane. This report profiles technologies that have been shown to successfully remove or eliminate 1,4-dioxane and examines other technologies currently under development.

1,4-Dioxane is among the most mobile organic contaminants in the saturated zone. As a result, it may be found farther downgradient than the leading edge of a solvent plume. The combination of a wider spatial occurrence and different requirements for treatment technologies make 1,4-dioxane a potentially problematic contaminant, particularly if it is discovered after site characterization and remedial design have already been completed. In some cases, discovery of 1,4-dioxane has necessitated expanded monitoring networks, larger capture zones, and the addition of new treatment technologies to the treatment train.

Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications should prove useful to all site managers faced with addressing 1,4-dioxane at a cleanup site or in drinking water supplies and to those in a position to consider whether 1,4-dioxane should be added to the analytical suite for site investigation.

NOTICE AND DISCLAIMER

This report has been funded by the U.S. Environmental Protection Agency (EPA) Office of Superfund Remediation and Technology Innovation (OSRTI) under Contract Number 68-W-02-034. Information in this report is derived from numerous sources, including personal communications with experts in the field. Not all the source documents have been peer reviewed. This report has undergone EPA and external review by subject-matter experts. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

If you have questions about this report, please contact Martha Otto, EPA OSRTI, at (703) 603-8853 or otto.martha@epa.gov.

A portable document format (pdf) version of *Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications* may be viewed or downloaded at the Hazardous Waste Clean-up Information (CLU-IN) system Web site at <http://clu-in.org/542R06009>. A limited number of printed copies are available free of charge and may be ordered via the Web site, by mail, or by fax from:

EPA/National Service Center for Environmental Publications
P.O. Box 42419
Cincinnati, OH 45242-2419
Telephone: (800) 490-9198
Fax: (301) 604-3408

ACKNOWLEDGMENTS

Special acknowledgement is given to the federal and state staff and other remediation professionals who provided information for this document. Their willingness to share their expertise on treatment technologies for 1,4-dioxane encourages the successful application of these technologies at other sites. Contributors to the report included EPA OSRTI, EPA Office of Solid Waste, EPA Office of Research and Development, EPA Office of Drinking Water, EPA Office of Prevention, Pesticides, and Toxic Substances, EPA Office of Emergency Management, EPA Groundwater Forum, Thomas Mohr of the Santa Clara Valley Water District of California, Reid Bowman of Applied Process Technology, Inc., John Horst of ARCADIS, Charles Drewry of Calgon Carbon Corporation, and Rula Deeb and Christine Cotton of Malcolm Pirnie, Inc. Additional acknowledgment is given to Thomas Mohr for authoring the foreword to the report.

EXECUTIVE SUMMARY

The cyclic ether 1,4-dioxane is a synthetic industrial chemical that is used as a solvent in products such as paints and lacquers and in processes such as organic chemical manufacturing. It was used in the past primarily with 1,1,1-trichloroethane (TCA), as a stabilizer and corrosion inhibitor, and has proven to be a contaminant of concern (a contaminant that poses a human health or environmental risk) at sites contaminated with TCA. It is a probable carcinogen and has been found in groundwater at sites throughout the United States. The physical and chemical properties and behavior of 1,4-dioxane create challenges for its characterization and treatment. It is highly mobile and has not been shown to readily biodegrade in the environment.

Groundwater investigations at solvent release sites have not typically included 1,4-dioxane as a target analyte because it was not detectable at low concentrations in a standard laboratory scan for volatile organic compounds. In addition, it was traditionally not regarded as a contaminant of concern. As a result, the U.S. Environmental Protection Agency (EPA) and many states have not promulgated cleanup levels that would mandate characterization or remediation of 1,4-dioxane at contaminated sites. Currently, no federal drinking water standard exists for 1,4-dioxane. Recent analytical improvements, however, have now made it possible for 1,4-dioxane to be detected at concentrations similar to other volatile organic compounds. As a result, based on a review of the risks posed, some states have now established enforceable cleanup goals for 1,4-dioxane. For example, in September 2004, Colorado became the first state to establish an enforceable standard for dioxane in groundwater and surface water. This standard is being phased in and requires facilities to have met a 6.1 micrograms per liter ($\mu\text{g/L}$) limit by March 2005 and a 3.2 $\mu\text{g/L}$ limit by March 2010.

This report provides fundamental information about 1,4-dioxane and field applications of viable treatment technologies to remove this contaminant from groundwater. 1,4-Dioxane's high solubility, low potential to partition from the dissolved phase

Key Findings:

- 1,4-Dioxane was used primarily in the past as a stabilizer in chlorinated solvents. It is now used for a wide variety of industrial purposes.
- 1,4-Dioxane is hydrophilic, is only minimally retarded in groundwater, and is not prone to sorption to soil. It is a good candidate for pump-and-treat remediation using *ex situ* treatment technologies tailored for its unique properties.
- A total of 15 projects were identified where 1,4-dioxane was treated in groundwater. Twelve of the 15 projects used *ex situ* advanced oxidation processes.
- Research is being conducted on technologies such as bioremediation and phytoremediation to assess their capability to treat 1,4-dioxane.

to vapor, and its low affinity for organic matter in soil combine to favor its occurrence dissolved in groundwater. As a result, treatment of 1,4-dioxane in soil is not commonly implemented and site-specific examples of soil treatment were not identified in the research conducted. However, a brief discussion is provided on potential technologies to treat soil contaminated with 1,4-dioxane.

This report focuses on treatment of contaminated groundwater. The report includes an overview of topics related to 1,4-dioxane, including its occurrence, physical and chemical properties, and treatability, as well as relevant policy and guidance. In addition, site-specific information about treatment of 1,4-dioxane is provided, as is information on technologies that show promise in treating 1,4-dioxane in the future.

Project managers, technology providers, consulting engineers, and members of academia can use this information to gain a better understanding of current treatment practices and the potential for new treatment technologies. This report includes information from EPA documents, journal articles, conference proceedings, and discussions with experts in remediation of 1,4-dioxane.

1.0 INTRODUCTION

This report provides fundamental information about 1,4-dioxane and field applications of technologies that can treat this contaminant in groundwater. Treatment of soil contaminated with 1,4-dioxane is also briefly discussed. References cited in bold type refer to peer-reviewed journal articles.

Synonyms for 1,4-dioxane are dioxane, *p*-dioxane, diethylene ether, diethylene dioxide, and glycol ethylene ether. Dioxane was used primarily as a stabilizer in chlorinated solvents, mainly for 1,1,1-trichloroethane (TCA), and is now used for a wide variety of industrial purposes. It stabilizes solvents by behaving as a Lewis Base and inhibiting reactions of the solvent with acids and metal salts that may degrade the properties of the solvent. It reacts or complexes with the active metal site, preventing degradation of the solvent. Dioxane has been added to many grades of TCA at 2 to 3 percent by volume, and in some instances, up to 8 percent (Mohr 2001).

Dioxane is a probable carcinogen and is found as a contaminant in water at sites throughout the United States (U.S. Department of Health and Human Services [USDHHS] 2002). The physical properties and behavior of dioxane, including its high mobility and persistence in the environment, make characterization and treatment of this chemical challenging. Its potential risks as a contaminant in groundwater have not been fully identified; the U.S. Environmental Protection Agency (EPA) and most states have not promulgated cleanup levels for dioxane.

EPA and the International Agency for Research on Cancer (IARC) classify dioxane as a Group B2 (probable human) carcinogen. It has a carcinogenic oral slope factor of 1.1E-2 milligrams/kilogram/day (mg/kg/day) and its toxicity is currently being reassessed under the EPA Integrated Risk Information System (IRIS) (EPA IRIS 2005; IARC 1999).

In 2001, the Santa Clara Valley Water District of California prepared a white paper on solvent stabilizers that provided background information on dioxane (Mohr 2001). The intent of this report is to provide an update to that information, present an overview of issues associated with characterization and remediation of dioxane, and discuss technology applications for treating water contaminated with this chemical. More information on cleanup of dioxane and links to additional resources can be found on the EPA Hazardous Waste Clean-Up Information (CLU-IN) Web site at <http://clu-in.org/contaminantfocus/default.focus/sec/1,4-Dioxane/cat/Overview/>.

1,4-Dioxane Toxicology

- There is sufficient evidence for the carcinogenicity of 1,4-dioxane in experimental animals. However, there is inadequate evidence in humans for the carcinogenicity of 1,4-dioxane. Therefore, EPA and IARC have classified 1,4-dioxane as a Group B2 (probable human) carcinogen (EPA IRIS 2005; IARC 1999).
- According to EPA's IRIS, the carcinogenic risk from oral exposure to dioxane is 1.1E-2 mg/kg/day.
- The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL)¹ for 1,4-dioxane is 360 milligrams per cubic meter (mg/m³) (OSHA 1998).

Further information on the toxicology of 1,4-dioxane can be found on the Web site for the Agency for Toxic Substances and Disease Registry (ATSDR) (<http://www.atsdr.cdc.gov/toxprofiles/tp187.html>).

¹ PEL is the concentration of a substance to which most workers can be exposed without adverse effects averaged over a normal 8-hour workday or a 40-hour workweek.

1.1 Overview of Dioxane Production and Environmental Occurrence

Exhibit 1 lists some of the common process and product uses for dioxane. Dioxane may be present at sites with TCA contamination because it was primarily used as a stabilizer for TCA (Mohr 2001). TCA frequently occurs in soil and groundwater at Superfund and other hazardous waste sites in the United States. In addition, the relatively high boiling point (101.1°C) of dioxane can increase its concentration in solvents during the solvent vapor degreasing process. In one study, concentrations of dioxane in spent TCA were measured as being nearly 70 percent greater than the dioxane concentration in new TCA (2.9 percent versus 1.7 percent by weight) (Joshi and others, 1989).

Exhibit 1: Process and Product Uses of Dioxane

Process Uses	<ul style="list-style-type: none"> Stabilizer in chlorinated solvents used for degreasing, electronics manufacturing, and metal finishing
	<ul style="list-style-type: none"> Solvent for specific applications in biological procedures (histology)
	<ul style="list-style-type: none"> Solvent used in impregnating cellulose acetate membranes used as filters
	<ul style="list-style-type: none"> Wetting and dispersing agent in textile process
	<ul style="list-style-type: none"> Solvent used in microscopy
	<ul style="list-style-type: none"> Reaction medium solvent in organic chemical manufacturing
	<ul style="list-style-type: none"> By-product formed during esterification of polyester

Exhibit 1: Process and Product Uses of Dioxane (continued)

Product Uses	<ul style="list-style-type: none"> Solvent in paints, lacquer, and varnish remover
	<ul style="list-style-type: none"> Solvent in stain and printing compositions
	<ul style="list-style-type: none"> Solvent in liquid scintillation counters
	<ul style="list-style-type: none"> Surface treating agent for artificial leather
	<ul style="list-style-type: none"> Impurity in antifreeze, including aircraft de-icing fluid formulations
	<ul style="list-style-type: none"> Impurity in some consumer products (such as deodorants, shampoos, and cosmetics) that incorporate ethoxylated fatty alcohol sulfates
	<ul style="list-style-type: none"> “Inert” ingredient in pesticides and fumigants
	<ul style="list-style-type: none"> Purifying agent in pharmaceuticals
	<ul style="list-style-type: none"> Solvent in resins, oils, rubber chemicals, sealants, adhesives, waxes, and cements

Sources: Mohr 2001 and USDHHS 2002

Information about the occurrence of dioxane in the environment is limited. In 2002, based on EPA’s Toxics Release Inventory (TRI) data, an estimated 1.15 million pounds of dioxane were released to the environment from facilities that produced, processed, or used the chemical in the United States (EPA 2003). As shown in Exhibit 2, the mass of dioxane released to the environment was more than four times the mass of TCA released, based on data from the 2002 TRI. Use of TCA was greatly reduced after the 1990 Montreal Protocol, which restricted emissions of ozone-degrading compounds. Currently, TCA is not widely used (Mohr 2005). TRI data serve as a general indicator of the amount of a particular chemical released to the environment, but should not be considered to be a comprehensive measure of the quantity released. Not all facilities that produce, process, or use a chemical report the quantity of its release because of the specific reporting requirements for TRI data collection.

**Exhibit 2: 2002 Toxics Release Inventory Data for Dioxane and 1,1,1-Trichloroethane
(all amounts are in pounds)**

Chemical	Surface Water Discharges ^a	Releases to Air ^b	Releases to Land ^c	Off-site Releases ^d	Total Releases
Dioxane	75,119	105,484	1,902	964,136	1,146,641
1,1,1-TCA	99	234,013	38,399	1,182	273,693

Source: EPA 2003

Notes:

^a Include discharges to streams, rivers, lakes, oceans, and other bodies of water. Include releases from confined sources or open trenches. Releases caused by runoff are also reportable to TRI under this category.

^b Include fugitive and point-source emissions. Fugitive emissions include equipment leaks, evaporative losses from surface impoundments and spills, and releases from building ventilation systems. Point-source air emissions occur through confined air streams such as stack, vents, ducts, or pipes.

^c Refer to the incorporation of waste into the soil where the waste degrades in the soil.

^d Sum of off-site disposal to Class I underground injection wells, Resource Conservation and Recovery Act Subtitle C landfills, and other landfills.

1.2 Properties and Behavior of Dioxane in the Environment

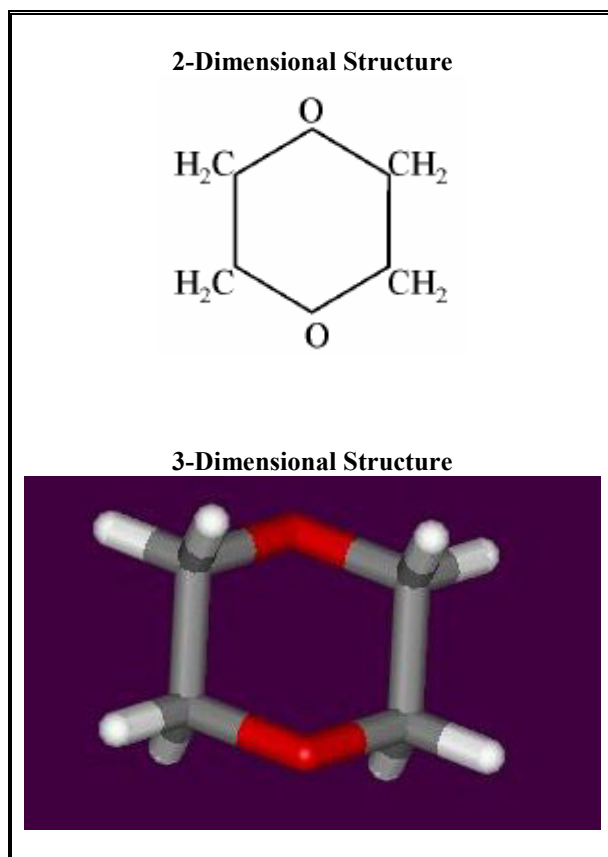
The compound dioxane is a cyclic ether with a chemical formula of $C_4H_8O_2$ and a molecular weight of 88.1. Its two oxygen atoms, each with free electrons, make it hydrophilic and miscible in water. In addition, it has virtually no dipole moment because of its symmetrical structure, as shown in Exhibit 3. In its pure form, dioxane is a colorless, flammable liquid with a faint odor. It is a peroxidizable compound, capable of reacting with atmospheric oxygen to form potentially explosive peroxides (ATSDR 2004). Exhibit 4 summarizes selected properties of dioxane and TCA that are relevant to site characterization and remediation. Because of its properties, dioxane has been shown to migrate rapidly in the environment. It can evaporate from dry soil, but laboratory column studies have shown that dioxane can also rapidly diffuse through even low-permeability soils such as silts and clays, driven by partitioning into the soil moisture as a result of its low octanol-water partition coefficient (K_{ow}) (Mohr 2001; Walsom and Tunnicliffe 2002).

Dioxane can migrate rapidly in groundwater and will dissolve almost completely because it is fully miscible. Once dissolved, the chemical's transport in groundwater is only weakly retarded by sorption to soil particles or suspended

sediments because of its low K_{ow} (Zenker and others 2003). In addition, its low Henry's Law constant prevents it from volatilizing from the dissolved to the vapor phase. Although it is relatively unaffected by sorptive mechanisms in an aquifer, dioxane can diffuse into static pore water (the pore fraction that does not participate in fluid migration), creating the appearance of retardation. Depending on the relative volume of static to migratory pore water, the resulting mass of dioxane that can be stored in the static pore water can be significant (Horst 2005). As a result, a plume of dioxane can persist after the source has been removed or controlled.

Because of its physical and chemical properties, dioxane plumes have been documented to measure twice the length of the associated solvent plumes and to affect an area up to six times greater (Walsom and Tunnicliffe 2002). Therefore, defining, capturing, and remediating a plume of dioxane in groundwater are considerably more challenging than the same activities for the associated plume of chlorinated solvent (Walsom and Tunnicliffe 2002).

Exhibit 3: Molecular Structure of Dioxane



Source: USDHHS 2003

1.3 Characterization of Dioxane

As a result of the limitations in the analytical methods used for dioxane, it has been difficult to evaluate the occurrence of the chemical in the environment. Conventional analytical methods used by commercial laboratories produced sensitivity levels for the chemical that were about 100 times greater than those of other volatile organic compounds (VOC) because of dioxane's low Henry's Law constant and vapor pressure (Mohr 2001). Routine analysis of VOCs uses a purge-and-trap device to separate the analytes from the matrix and gas chromatography (GC) to identify the analytes. Once they have been identified, one of the following can be used to quantitate the analytes: flame ionization detector (SW-846 Method 8015) or mass spectrometer (MS) (SW-846 Method 8260, and water methods 624 and 1624).

Exhibit 4: Properties of Dioxane and 1,1,1-Trichloroethane

Property	Dioxane	1,1,1-TCA
Molecular Weight	88.1	133.4
Melting Point (°C at 760 mm Hg)	11.8	-30.4
Boiling Point (°C at 760 mm Hg)	101.1	74.1
Flash Point (°C at 760 mm Hg)	5 to 18	none
Density (g/mL at 20°C)	1.0329	1.3
Water Solubility (mg/L at 20°C)	Miscible	950
Vapor Density (air = 1)	3.03	4.54
Octanol-Water Partition Coefficient (K_{ow})	0.27	2.49
Vapor Pressure (mm Hg at 20°C)	30	100
Henry's Law Constant (atm m ³ /mole)	4.88×10^{-6}	0.0172

Source: CHEMFATE, 2003

Notes: atm = atmosphere; L = liter; mL = milliliter; mm Hg = millimeters of mercury; g = grams; mg = milligrams

For 1,4-dioxane, better sample preparative procedures must be used to achieve increased sensitivity. Purging at elevated temperatures allows more dioxane to be removed from water (as described in SW-846 Method 5030C). Use of other high temperature sample preparation techniques, such as equilibrium headspace analysis (SW 846 Method 5021), vacuum distillation (SW 846 Method 8261A) (EPA 2000), and azeotropic distillation (SW 846 Method 5031) also improve the recovery of dioxane. One common variant in analyzing dioxane involves improving the sensitivity of the MS detector by using selected-ion monitoring (SIM) (Lancaster 2003).

ATSDR provides a general review of the available analytical methods for dioxane in all media in "Toxicological Profile for 1,4-Dioxane. Draft for Public Comment" (ATSDR 2004).

1.4 Cleanup Goals and Standards

Currently, there is no federal drinking water standard for dioxane. However, several EPA regions and states have developed guidance for characterizing and remediating dioxane in soil and water. In September 2004, Colorado became the first state to establish an enforceable standard for dioxane in groundwater and surface water. This standard is being phased in and requires facilities to have met a 6.1 µg/L limit by March 2005 and a 3.2 µg/L limit by March 2010. Three EPA regions and several other states also have set screening levels for dioxane based on carcinogenic risk; however, these goals are not currently enforceable. Drinking water action levels and health advisories are often used by state regulators to establish appropriate cleanup goals, and dioxane is listed in regulatory cleanup orders in many states as a result. Although a legal or regulatory enforcement level is absent in all states except Colorado, dioxane can be subject to regulation through cleanup requirements (Mohr 2001, 2005).

Exhibit 5 provides examples of EPA and state guidance for dioxane in soil and water. The guidance was identified during a review of readily available information on the Internet and is current as of September 2006. Information was available for three EPA regions and 14 states. Various types of goals are presented, including risk-based standards, preliminary remediation goals (PRG), and medium-specific concentrations. A risk-based goal of 6.1 µg/L has been established for dioxane in tap water in EPA Regions 3, 6, and 9; however this level does not constitute a regulatory standard. Exhibit 5 is not intended as a comprehensive compilation of federal and state cleanup levels for dioxane. Appendix A lists the Internet sources used to compile this exhibit.

GRAC's Ninth Symposium in its *Series on Groundwater Contaminants – 1,4-Dioxane and Other Solvent Stabilizer Compounds in the Environment*

In December 2003, the Groundwater Resources Association of California (GRAC) held a symposium in San Jose, California, on 1,4-dioxane and other solvent stabilizer compounds in the environment. The symposium addressed the following issues:

- Nature and extent of 1,4-dioxane occurrence in the environment
- Survey of 1,4-dioxane occurrence at solvent release sites in the San Francisco Bay area
- Case studies of the Pall-Gelman Sciences site and the Stanford Linear Accelerator site
- Updated evaluation of the carcinogenic potential of 1,4-dioxane
- Biological treatment options, *in situ* reactive zone strategies, and in-well air stripping for 1,4-dioxane removal
- Ozone-peroxide advanced oxidation treatment of 1,4-dioxane in water
- Legal aspects of emerging contaminants

A synopsis of some of the presentations at the symposium is available at the following Web site: <http://www.grac.org/dioxanemain.html>.

**Exhibit 5: Summary of Selected U.S. Environmental Protection Agency and State Guidance for Dioxane in Soil and Water
(as of September 2006)**

EPA Region or State	Type of Guidance	Matrix	Concentration
Region 3	Risk-Based Concentrations	Tap Water	6.1 µg/L
		Soil	260 mg/kg (Industrial) 58 mg/kg (Residential) 0.0013 to 0.0026 mg/kg (Groundwater Protection)
Region 6	Human Health Medium-Specific Screening Levels	Tap Water	6.1 µg/L
		Soil	170 to 520 mg/kg (Industrial) 44 mg/kg (Residential)
Region 9	Preliminary Remediation Goals	Tap Water	6.1 µg/L
		Soil	160 mg/kg (Industrial) 44 mg/kg (Residential)
Arizona	Soil Remediation Levels	Soil	1,700 mg/kg (Nonresidential) 400 mg/kg (Residential)
California	Health-Based Advisory Levels	Drinking Water	3 µg/L
		Soil	0.0018 mg/kg (Residential and Industrial)
Colorado	Water Quality Standard	Groundwater and Surface Water	6.1 µg/L by March 2005; 3.2 µg/L by March 2010
Delaware	Uniform Risk-Based Remediation Standards (Guidance)	Groundwater	6 µg/L
		Soil	0.6 mg/kg (Critical Water Resource Area) 58 to 520 mg/kg (Non-critical Water Resource Area)
Florida	Soil Cleanup Target Levels	Soil	38 mg/kg (Direct Exposure – Commercial/Industrial) 23 mg/kg (Direct Exposure – Residential) 0.01 mg/kg (Leachability – Groundwater) 0.5 mg/kg (Leachability – Surface Water)
		Groundwater	3.2 µg/L
Iowa	Standard for Soil	Soil	280 mg/kg (Statewide Standard)
Maine	Maximum Exposure Guideline	Drinking Water	32 µg/L
Michigan	Generic Cleanup Criteria and Screening Levels	Drinking Water	350 µg/L (Industrial) 85 µg/L (Residential)
		Soil	7 mg/kg (Drinking Water Protection – Industrial) 56 mg/kg (Groundwater – Surface Water Interface – Industrial) 2,400 to 3,400 mg/kg (Direct Contact – Industrial) 34,000 mg/kg (Groundwater Contact Protection – Industrial)

**Exhibit 5: Summary of Selected U.S. Environmental Protection Agency and State Guidance for Dioxane in Soil and Water
(as of September 2006) (continued)**

EPA Region or State	Type of Guidance	Matrix	Concentration
			56 mg/kg (Groundwater – Surface Water Interface – Residential) 530 mg/kg (Direct Contact – Residential) 34,000 mg/kg (Groundwater Contact – Residential) 1.7 mg/kg (Drinking Water Protection – Residential) 97,000 mg/kg (Soil Saturation Concentration)
Missouri	Target Concentrations	Groundwater	3 µg/L
		Soil	150 to 590 mg/kg (Direct Exposure) 0.01 mg/kg (Leaching to Groundwater)
Pennsylvania	Medium-Specific Concentrations for Organic Regulated Substances in Groundwater	Groundwater	5.6 µg/L (Used Aquifers – Residential) 24 µg/L (Used Aquifers – Nonresidential) 56 µg/L (Nonuse Aquifers – Residential) 240 µg/L (Nonuse Aquifers – Nonresidential)
			210 to 240 mg/kg (Direct Contact – Nonresidential.) 0.31 to 240 mg/kg (Groundwater Protection – Nonresidential)
		Soil	41 mg/kg (Direct Contact – Residential) 0.0073 to 56 mg/kg (Groundwater Protection – Residential)
South Carolina	Drinking Water Regulation and Health Advisory	Drinking Water	70 µg/L (Monthly average)
Texas	Protected Concentration Levels	Groundwater	18.6 µg/L (Commercial/Industrial) 8.3 µg/L (Residential)
			2,600 mg/kg (Total Combined Pathways – Industrial) 0.36 mg/kg (Groundwater Protection – Industrial)
		Soil	552 mg/kg (Total Combined Pathways – Residential) 0.083 mg/kg (Groundwater Protection – Residential)
			290 to 29,000 mg/kg (Industrial) 1,000 to 100,000 mg/kg (Residential)
West Virginia	Risk-Based Concentrations	Groundwater	6.1 µg/L
		Soil	5,200 mg/kg (Industrial) 58 mg/kg (Residential)
Wyoming	Soil Cleanup Level	Soil	44 mg/kg (Residential)

Source: Internet sources reviewed in September 2006. (Appendix A lists the Internet sources used to compile this summary.)

Notes:

mg/kg = milligrams per kilogram

µg/L= micrograms per liter

2.0 TREATMENT OF MEDIA CONTAINING DIOXANE

The physical and chemical properties of dioxane discussed in Section 1.0 create challenges for removing this compound from water. Dioxane is well suited to removal by groundwater extraction because of its high solubility and low degree of partitioning to organic matter in soil. However, the relatively low Henry's Law constant of dioxane makes technologies such as air stripping generally ineffective in treating the chemical in water. Its low adsorptive capacity also limits the effectiveness of treatment by granular activated carbon (GAC), although one full-scale GAC application was identified. As discussed in Section 1.0, bench-scale studies indicate that biodegradation of dioxane is possible, but information on field applications of this technology is limited (Zenker and others 2003).

Technologies that are effective for treating chlorinated solvents are often ineffective for treating dioxane because the properties of dioxane differ from those of chlorinated solvents. To date, the number and types of technologies available to treat dioxane are limited; however, research is under way to test and evaluate additional treatment technologies for this contaminant. This report provides information about three technologies that have been used to treat dioxane at the pilot and full scale levels:

- Advanced oxidation (*ex situ*)
- Adsorption (GAC) (*ex situ*)
- Bioremediation

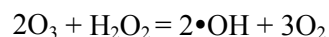
As discussed previously, dioxane in soil tends to readily partition to groundwater and does not sorb to soil particles. Therefore, groundwater is the primary medium of concern for this contaminant. The following sections present information about technologies applicable for treating dioxane and include site-specific examples where available. Section 2.1 addresses full- and pilot-scale treatment applications for dioxane in water; Section 2.2 briefly discusses potential technologies for treating dioxane in soil; and Section 2.3 presents information on research in bioremediation and phytoremediation.

2.1 Treatment Technologies for Dioxane in Water

This section discusses applications of advanced oxidation (*ex situ*), GAC adsorption (*ex situ*), and bioremediation to treat dioxane in water.

2.1.1 Advanced Oxidation (*Ex Situ*)

Advanced oxidation processes (AOP) are commercially available for aboveground treatment of dioxane in water. The technology can be used independently or as a pre- or post-treatment step in a remediation process. AOPs use hydroxyl radicals, which are powerful oxidizers, to sequentially oxidize organic contaminants to carbon dioxide, water, and residual chloride (Mohr 2001; Berman and others 1998; Walsom and Tunnicliffe 2002). Two common AOPs include hydrogen peroxide with ultraviolet (UV) light, and hydrogen peroxide with ozone. UV light causes the release of hydroxyl radicals from hydrogen peroxide added to contaminated water. Hydroxyl radicals are also generated when ozone is mixed with hydrogen peroxide, even in the absence of UV light, as shown in the equation below.



Other AOPs include hydrogen peroxide with ferrous iron (Fenton's reagent) and ozone with UV light. However, no sites where these processes have been used for dioxane treatment were identified in the research conducted for this report. Exhibit 6 shows a process flow diagram of a typical ozone/hydrogen peroxide groundwater treatment system.

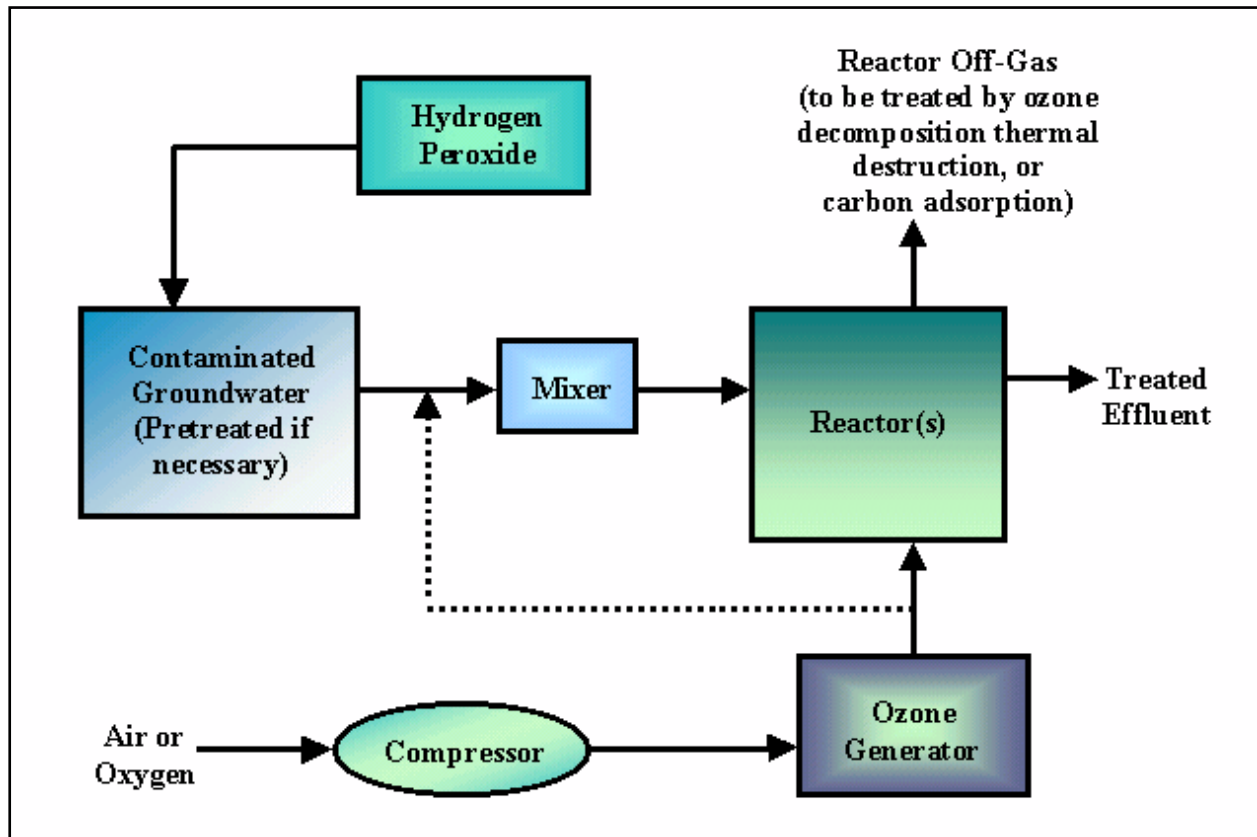
Hydrogen Peroxide with UV Light

Four projects were identified that used an AOP system that consisted of UV light for treatment of dioxane. The four projects were conducted at full scale at the following sites: McClellan Air Force Base (AFB) in Sacramento, California; Gloucester Landfill in Ontario, Canada; Charles George Landfill in Tyngsborough, Massachusetts; and the Pall-Gelman Sciences site in Ann Arbor, Michigan. Full-scale remediation of dioxane in groundwater was conducted at McClellan AFB in California using an AOP system consisting of

hydrogen peroxide and UV light. The system was originally installed to treat vinyl chloride contamination and was shut down after concentrations of vinyl chloride dropped below the maximum contaminant level. The system was then tested to evaluate whether it was capable of treating dioxane and it proved effective. The

system was restarted in October 2003 and treated approximately 2.7 million gallons of groundwater each month. The system reduced the concentrations of dioxane to below the EPA Region 9 tap water PRG of 6.1 µg/L and is no longer in operation (Zabaneh 2004; Gronstal 2006).

Exhibit 6: Process Flow Diagram of a Typical Ozone/Hydrogen Peroxide Groundwater Treatment System



Source: Federal Remediation Technologies Roundtable (FRTR) 2006

An AOP consisting of hydrogen peroxide and UV light is being used to treat dioxane in groundwater at the Gloucester Landfill site in Ontario, Canada. The site served as a municipal waste dump from approximately 1957 to 1980 and as a disposal area for federal laboratory, university, and hospital wastes from 1969 to 1980. Chemicals from the wastes seeped into the groundwater, contaminating a shallow, unconfined aquifer and a deep, confined aquifer. A 29-well pump-and-treat system has been operated at the site since 1992 to contain the contaminant plume and remove the contaminant mass from the aquifers. The system pumps and

treats approximately 132 gallons per minute (gpm) from the deep aquifer and 61 gpm from the shallow aquifer. The extracted groundwater is treated at the site using the following process: adding acid to the influent groundwater to reduce the pH to an optimal level for treatment, passing the groundwater through a series of UV lamps in the presence of hydrogen peroxide to destroy target contaminants, and adding sodium hydroxide to raise the pH again (the exact pH value was not provided). After sodium hydroxide has been added, the treated groundwater is reinjected at one or more of five locations upgradient of the site.

Pall-Gelman Sciences Site – UV Light and Hydrogen Peroxide Treatment System Details

A treatment system using UV light and hydrogen peroxide was applied at the Pall-Gelman Sciences site. Eighteen purge wells, including a 4,479-foot long horizontal well, were used to extract and divert groundwater. Purged water was mixed with sulfuric acid (a 93 percent solution by volume) in a lined pretreatment pond known as the “Red Pond” to lower the pH to 3.8. Earlier studies showed a pH of 3.8 to be optimal for hydrogen peroxide chemical reactions in conjunction with UV light.

In the first step of treatment, a 50 percent hydrogen peroxide solution was injected into the treatment line and mixed with groundwater by a static mixer. Water then passed through a multiple-chamber UV system consisting of 22 lamps, where it was exposed to UV radiation for approximately 5 seconds. After UV and hydrogen peroxide treatment, the pH of the treated water was raised to approximately 6.9 by adding sodium hydroxide (40 percent by volume) to meet the surface water discharge requirement of 6.5 to 9.0. Sodium bisulfate also was added to remove excess hydrogen peroxide before the water was discharged to an on-site holding pond known as the “Green Pond.” The water was monitored daily to ensure compliance with state requirements before it was released into an unnamed tributary of Honey Creek, which flows into the Huron River.

Large volumes of reactive chemicals were required for treating groundwater using the UV and hydrogen peroxide treatment system. The electrical demand also was high, averaging \$850 per day. The overall treatment cost for the system was approximately \$3.50 per 1,000 gallons. For these reasons, the site owner converted the UV and hydrogen peroxide system to an ozone and hydrogen peroxide-based technology in 2005 to reduce hydrogen peroxide consumption by 50 percent and eliminate the need for sulfuric acid and sodium hydroxide. Treatment costs using this new system were anticipated to be approximately \$1.50/1,000 gallons (Brode and others 2005).

Performance data for the system were not available (Ludwig 1997).

An AOP consisting of UV-hydrogen peroxide oxidation was used to treat landfill leachate and

contaminated groundwater at the Charles George Landfill, a Superfund site in Massachusetts. The contaminated liquid was extracted downgradient of the capped landfill and pumped to a 3.6-million-gallon storage lagoon, where it was treated. Initial concentrations of dioxane in the liquid were not provided; however, the system was able to reduce the concentration to 7 µg/L to meet the standard for surface water discharge specified in the record of decision (ROD) (U.S. Army Corps of Engineers [USACE] 2004).

Dioxane was unintentionally released into the subsurface in the 1960s at the Pall-Gelman Sciences site in Michigan. The source of the contamination was a manufacturer of micro-porous filters. The manufacturer used dioxane as a solvent for cellulose acetate, which was a component of specific membrane filters made at the site. The chemical was released into the subsurface primarily through a state-permitted, unlined treatment pond that was used to treat and dispose process wastes. Dioxane was eliminated from the manufacturing process in the mid-1980s (GRAC 2003). Groundwater samples collected at that time contained concentrations of dioxane as high as 221,000 µg/L.

Dioxane migrated into a complex sequence of glacial outwash deposits that form highly transmissive aquifers at the site. Once it reached these aquifer systems, the dioxane migrated more than 2 miles from the source areas in multiple plumes. This release constituted one of the nation’s largest releases of dioxane to groundwater (Tetra Tech EM Inc. [Tetra Tech] 2003).

Groundwater at the Pall-Gelman Sciences site was routinely monitored at 50 to 100 locations. Treatment system influent concentrations ranged from 3,000 to 4,000 µg/L and effluent concentrations ranged from nondetect to 10 µg/L. The method detection limit was 1.0 µg/L. Although treatment has only slightly reduced the areal extent of the plumes, 2 billion gallons of groundwater have been purged, treated, and discharged since 1997, and more than 60,000 pounds of dioxane have been removed from the contaminated aquifers. The concentration of dioxane within the plumes has also decreased. (GRAC 2003; Brode and others 2005).

Hydrogen Peroxide with Ozone

Eight projects that involved the treatment of dioxane in groundwater at five sites using a hydrogen peroxide-and-ozone-based system (HiPOx) were identified. A full-scale HiPOx system was built and installed as a pre-treatment step to remove dioxane and reduce chlorinated solvent concentrations in the contaminated groundwater at a confidential site in South El Monte, California. Initially, the system was operated using one well at 500 gpm and used three ozone injectors with 8-inch, static mixers. Later, a second well was added and the system flow rate was increased to 1,000 gpm. The system lowered the dioxane concentration from 4.6 µg/L in the influent to less than 1 µg/L in the effluent. The analytical method that was used was not specified (Bowman and others 2003; GRAC 2003).

Dioxane was found in extraction wells that fed an air stripper that was already in operation to remove chlorinated solvents from groundwater at a confidential site in City of Industry, California. Pilot tests showed that the HiPOx system could reduce the concentration of dioxane from 610 µg/L in the influent to 9.5 µg/L in the effluent (Bowman and others 2003). Pilot data were used to configure a commercial-scale unit that reduces the influent concentration of dioxane of 320 µg/L to an effluent concentration below the detection limit of 1 µg/L. The analytical method that was used was not specified. The commercial unit was installed in February 2002 and operates at a flow rate of 45 gpm (Bowman and others 2003; GRAC 2003; Applied Process Technology, Inc. [APT], 2005a).

The concentration of dioxane in the effluent from an air stripping and carbon adsorption treatment system was 15 µg/L, while the statutory discharge limit was 5 µg/L at the Middlefield-Ellis-Whisman Superfund Site in Mountain View, California. The air stripper and GAC system were replaced with a 50-gpm HiPOx unit that began operation in December 2003. The concentration of dioxane in the system effluent has been consistently reduced to below the detection limit of 1 µg/L. As of October 2006, the effluent concentration remains non-detect. The analytical method used was EPA Method 8270-SIM (Boarer and Milne, 2004).

Carbon adsorption and air stripping systems were in place to treat tetrachloroethene and TCA at a confidential industrial site in the Pacific Northwest. In 2002, dioxane was discovered at levels of up to 200 µg/L. A 20-gpm HiPOx unit was installed in April 2003 as a post-treatment to the carbon system and air stripper. The concentration of dioxane in the effluent has been reduced to below 6 µg/L (APT 2005b).

A treatment train that consisted of GAC and an undisclosed treatment system removed chlorinated solvents from groundwater at an industrial site in Orange County, California. In addition, a coagulation step was used to meet discharge requirements for suspended solids at the site. In 2003, dioxane was detected at concentrations of approximately 170 µg/L. The National Pollutant Discharge Elimination System (NPDES) permit at this site called for reduction of dioxane to below 3 µg/L. A 10-gpm mobile HiPOx field demonstration unit was used in tests on site. The demonstration showed that the dioxane could be reduced to meet the 3 µg/L permit requirement and a stationary 10-gpm HiPOx unit was installed in March 2004. The HiPOx unit is currently in operation and is reducing the concentration of dioxane to below 3 µg/L, and is also reducing 1,1-dichloroethylene (DCE) at 8 µg/L and trichloroethene (TCE) at 3 µg/L each to below 1 µg/L. The GAC system was retained at the effluent of the HiPOx system to remove other VOCs, such as TCA. The coagulation step was also retained (APT 2005c). The performance data for the Middlefield-Ellis-Whisman Superfund site and the industrial site in Orange County, California, do not appear to indicate a relationship between the flow rate of the HiPOx system and the reduction in contaminant concentrations achieved. Further research is required to better understand the effect of the system flow rate on treatment efficiency.

Limitations of AOPs

Although AOPs are capable of reducing the concentration of dioxane, potential limitations need to be considered before the technology can be implemented. Some of these limitations are listed below:

- If the dioxane-contaminated water contains bromide, ozone will oxidize it to bromate. IARC has classified bromate as a Group B2 (probable human) carcinogen. Therefore, the potential to form bromate must be considered and the production of bromate should be reduced as much as possible. These reductions may be achieved by adding ammonia or by decreasing the pH (Horst 2005).
- The potential formation of AOP decomposition products such as aldehydes and organic acids (Burgess 2005).
- If UV light is used as part of the oxidation process, the aqueous stream being treated must provide for good transmission of the light; high turbidity interferes with the oxidation reaction and should be reduced before treatment (FRTR 2006).
- Advanced oxidation reactions rely on contact between the oxidant and contaminant, which can limit the ability of the oxidation system to handle contaminant concentrations significantly above 1 milligram per liter (mg/L) without multiple units in series (Horst 2005)
- Free radical scavengers (for example, hydroxyl scavengers such as carbonate and bicarbonate) can inhibit contaminant destruction efficiency (Horst 2005; FRTR 2005).

2.1.2 Adsorption (GAC) (*Ex Situ*)

Adsorption involves concentrating contaminants on the surface of a sorbent such as GAC, thereby reducing the concentration of those contaminants in the liquid being treated. GAC was used to treat solvents in groundwater at the Stanford Linear Accelerator Center (SLAC) site in Menlo Park, California, before dioxane was discovered. It was later found that dioxane was present in the groundwater at concentrations ranging from a few $\mu\text{g/L}$ to 1,000s of $\mu\text{g/L}$. The concentration of dioxane was the highest at the location of a former underground storage tank (reported as high as 7,300 $\mu\text{g/L}$). Adsorption using GAC was found to remove the dioxane despite expectations based on the properties of the contaminant. Analytical results of influent and effluent water samples

collected from the treatment system showed that although the influent water has historically contained dioxane at concentrations as high as 1,500 $\mu\text{g/L}$, the compound was not present in the effluent water samples analyzed. The unexpected result could be attributed to low influent concentrations to the treatment system, very low flow rates (0.5 gpm), or possible biodegradation of dioxane on carbon surfaces in the presence of tetrahydrofuran, another constituent of the influent to the GAC (GRAC 2003).

2.1.3 Bioremediation

Ex situ bioremediation of groundwater involves putting contaminants in the extracted groundwater in contact with microorganisms in attached or suspended growth biological reactors. *Ex situ* bioremediation was selected to treat dioxane in groundwater at the Lowry Landfill Superfund site near Denver, Colorado. Between 1960 and 1980, the site was used for co-disposal of industrial and municipal solid wastes. Industrial waste liquids that contained spent solvents, which included dioxane, were placed in unlined pits and subsequently contaminated shallow groundwater. The ROD issued for the site required collection and treatment of landfill leachate and shallow groundwater emanating from the landfill mass.

Numerous treatability studies were conducted to evaluate potential treatment options for dioxane in the collected groundwater. A fixed-film, biological process was pilot tested in a continuous-flow configuration using Kaldnes media at temperatures of 15°C and 25°C. Kaldnes is a buoyant plastic media engineered in a wheel shape, allowing a small amount of water flow to circulate the media throughout the vessel. The pilot system successfully treated between 0.4 and 0.7 gpm of extracted groundwater that contained 8,000 to 12,000 $\mu\text{g/L}$ of dioxane; the effluent concentrations were less than 200 $\mu\text{g/L}$. Similar results were obtained at both temperatures. Extensive testing indicated that dioxane was degraded as a co-metabolite in the presence of tetrahydrofuran (Zenker and others 2000). A full-scale, fixed-film, moving-bed, biological treatment system was deployed at the site in December 2003 (GRAC 2003). Performance data for the full-scale system were not available in the references used for this report.

Exhibit 7 at the end of Section 2.0 summarizes 15 projects for the treatment of dioxane in groundwater. The timeframe for the projects (where this information was provided) ranges from July 1998 to the present.

2.2 Treatment of Dioxane in Soil

Dioxane typically migrates through soil rapidly and enters groundwater because it has a relatively high solubility and boiling point and a low log K_{ow} and Henry's Law constant. When it is present in soil, however, its physical properties indicate that it is theoretically volatile enough to be removed *in situ* using soil vapor extraction or *ex situ* with thermal desorption, even though its vapor pressure is lower than many VOCs. A factor to consider if a soil vapor extraction system is used is that dioxane will likely partition to the soil pore water in the vadose zone. The system should therefore be able to eliminate soil moisture to be effective (Horst 2005). Dioxane should also theoretically be amenable to removal from soil *in situ* or *ex situ* using cosolvent extraction with water as a solvent because of its hydrophilic characteristic. No full- or pilot-scale projects that involved treatment of dioxane in soil were identified from the sources reviewed for this report.

2.3 Ongoing Research on Dioxane Treatment

Research is being conducted on various technologies to assess whether they are capable of treating dioxane. These technologies include bioremediation using various strains of bacteria and phytoremediation.

The primary evidence for biodegradation of dioxane is from aerobic systems. Biodegradation pathways can be broken down into two categories:

1. Metabolic degradation (where dioxane serves as the primary growth substrate); at least four bacterial species are known to metabolically degrade dioxane under aerobic conditions: *Amycolata* sp. Strain CB1190, *Mycobacterium vaccae*, and two strains of *Rhodococcus* sp.
2. Cometabolic degradation (where dioxane is not the primary growth substrate but is degraded in the presence of other metabolites);

examples include degradation in the presence of a structural analog, such as tetrahydrofuran (Horst 2005).

In addition to the pilot-scale bioremediation project described in Section 2.1.3, a bench-scale study was conducted to evaluate the ability of a *Amycolata* sp. Strain CB1190, to degrade dioxane in industrial sludge obtained from a site in Darlington, South Carolina. CB1190 was able to degrade dioxane at a rate of 0.33 mg of dioxane/minute/mg of protein and mineralize 59.5 percent of the dioxane to carbon dioxide. This rate of degradation indicates that CB1190 has the potential to contribute to a practical and economical process for bioremediation of dioxane-contaminated groundwater and waste streams (Parales and others 1994).

In another bench-scale bioremediation study, bacterial inocula were isolated from dioxane-contaminated groundwater obtained from a Massachusetts Brownfields site. The bacteria were enriched using standard microbiological subculturing techniques, and the enrichment serum bottles were incubated under butane for a 4-week period. A microcosm study of the bottles indicated that butane was consumed and that dioxane was degraded from concentrations as high as 7.7 mg/L to sub- μ g/L concentrations within a 48-hour period as a result of the biostimulation. Butane biostimulation enhances contaminant destruction by encouraging the naturally occurring bacteria that are already acclimated to site conditions to flourish. This study demonstrates the potential for bioremediation of dioxane using butane biostimulation (GRAC 2003).

The ability of bioremediation to address dioxane contamination is being evaluated in various other bench-scale studies. Some of these studies are being funded by the Strategic Environmental Research and Development Program (SERDP) and are aimed at developing a mechanistic understanding of the enzymes, pathways, and kinetics of dioxane biodegradation; identifying and isolating new dioxane degrading microbes; identifying the products of dioxane biodegradation by studying degradation pathways in pure bacterial cultures; and confirming that the same biodegradation pathways occur in active environmental samples (Steffan 2005; Alvarez-Cohen 2005).

Exhibit 7: Summary of Full- and Pilot-Scale Treatment Projects for Dioxane in Groundwater

Site Name, Location	Initial Contaminant Concentration (µg/L) ¹	Final Contaminant Concentration (µg/L) ¹	Scale	Technology	Period of Operation	Cleanup Goal (µg/L)	Operating Parameter(s)	Source
Advanced Oxidation Processes (AOP) (<i>Ex Situ</i>)								
WP 68, McClellan AFB, Sacramento, CA	64.1 (samples collected in September 2004)	16.5 (samples collected in September 2004) < 6.1 (samples collected after September 2004)	Full	UV-hydrogen peroxide	October 2003 to date unknown	6.1 (EPA tap water PRG)	NA	Zabaneh 2004
Gloucester Landfill, Ontario, Canada	NA	NA	Full	UV-hydrogen peroxide	1992 to present	NA	Addition of acid to reduce pH; passing groundwater through series of UV lamps in presence of hydrogen peroxide; addition of caustic to increase pH	Ludwig 1997
Charles George Landfill, Tyngsborough, MA	NA	7	Full	UV-hydrogen peroxide	NA	NA	NA	USACE 2004
Pall-Gelman Sciences, Ann Arbor, MI	3,000 to 4,000	ND to 10	Full	UV-hydrogen peroxide	NA	NA	Addition of acid to lower pH; injection with 50 percent hydrogen peroxide solution; passing groundwater through series of UV lamps; addition of caustic to increase pH	GRAC 2003
Confidential Site, South El Monte, CA	20.2	< 2	Pilot	HiPOx (ozone + hydrogen peroxide) <i>pre-treatment</i> for air stripping	July to August 1998	< 3	9.4 ppm ozone; 14.2 ppm hydrogen peroxide; 18-reactor system	Bowman and others 2003; GRAC 2003

Exhibit 7: Summary of Full- and Pilot-Scale Treatment Projects for 1,4-Dioxane in Groundwater (continued)

Site Name, Location	Initial Contaminant Concentration (µg/L) ¹	Final Contaminant Concentration (µg/L) ¹	Scale	Technology	Period of Operation	Cleanup Goal (µg/L)	Operating Parameter(s)	Source
	4.6	0.85	Full	HiPOx (ozone + hydrogen peroxide) <i>pre-treatment</i> for air stripping	August 2000 to September 2004	< 3	3.1 ppm ozone; 6.9 ppm hydrogen peroxide; 3-reactor system (pre-treatment step for GAC treatment)	
Confidential Site, City of Industry, CA	610	9.5	Pilot	HiPOx (ozone + hydrogen peroxide) <i>pre-treatment</i> for air stripping	August 2000 to January 2001	< 3	NA	Bowman and others 2003; GRAC 2003; APT 2005a
	320	<0.95	Full	HiPOx (ozone + hydrogen peroxide) <i>post-treatment</i> for air stripping	February 2001 to present	< 3	70 gpm at startup; eventually reduced to 50 gpm	
Middlefield-Ellis-Whisman Superfund Site, Mountain View, CA	15	< 0.94	Full	HiPOx (ozone + hydrogen peroxide)	December 2003 to present	5 (statutory discharge limit)	50 gpm	Boarer and Milne 2004
Confidential Site, Pacific Northwest	200	< 6	Full	HiPOx (ozone + hydrogen peroxide) <i>post-treatment</i> for carbon and air stripping	April 2003 to present	< 6	20 gpm	APT 2005b
Confidential Site, Orange County, CA	170	< 3	Pilot	HiPOx (ozone + hydrogen peroxide)	January 2004	< 3	10 gpm	APT 2005c
			Full	HiPOx (ozone + hydrogen peroxide) <i>pre-treatment</i> for GAC	March 2004 to present			
GAC Adsorption								
SLAC, Menlo Park, CA (Former Underground Storage Tank Area)	7,300	NA	Full	GAC	NA	NA	NA	GRAC 2003

Exhibit 7: Summary of Full- and Pilot-Scale Treatment Projects for 1,4-Dioxane in Groundwater (continued)

Site Name, Location	Initial Contaminant Concentration (µg/L) ¹	Final Contaminant Concentration (µg/L) ¹	Scale	Technology	Period of Operation	Cleanup Goal (µg/L)	Operating Parameter(s)	Source
Bioremediation								
Lowry Landfill Superfund Site, Aurora, CO	8,000 to 12,000	< 200	Pilot	Bioremediation (fixed film bioreactor using Kaldnes media)	NA	NA	NA	GRAC 2003
	NA	NA	Full					

Notes:

¹ Based on available data, initial and final contaminant concentrations for projects with treatment trains may be for the entire train or for technologies within the train that were intended to treat dioxane.

NA = Not available in information reviewed

ND = Nondetect

gpm = Gallons per minute

ppm = Parts per million

A study of the relationship between enhancing biodegradability and oxidizing dioxane using ozone and hydrogen peroxide showed a linear correlation. The initial dioxane solutions exhibited negligible or near-zero biological oxygen demand (an indicator of biodegradation) with the biological seed employed. This finding confirmed that dioxane is not readily biodegradable and may not be removed effectively using conventional biological methods. The concentration of dioxane in the solution decreased and biological oxygen demand increased with each treatment of ozone and hydrogen peroxide, indicating partial oxidation of dioxane and transformation of this compound into more biodegradable intermediates (Suh and Mohseni 2004).

Phytoremediation has also been investigated to assess its suitability for removing dioxane in groundwater. Phytoremediation as it applies to dioxane is a relatively new remedial approach, and many of the associated removal and degradation pathways are being studied. Phytoremediation relies on multiple processes to remove contaminants from groundwater. Examples include the uptake of contaminated water, after which dioxane may be metabolized or volatilized from plant leaves (phytovolatilization), and the biodegradation of dioxane in the rhizosphere (root zone).

Papers published on the potential for phytoremediation of dioxane have evaluated the usefulness of various plants and trees, such as hybrid poplars. **Aitchison and others 2000** states that removal of 54 percent of dioxane in contaminated water was achieved within 9 days in hydroponic environments by using hybrid poplar cuttings. Most of the removal (about 36 percent) was attributed to phytovolatilization. New research is examining the possibility of bioaugmenting the phytoremediation process with the bacterium *Amycolata sp.* Strain CB 1190 to enhance *in situ* biodegradation in the rhizosphere (**Kelley and others 2001**). Other studies have shown that phytoremediation is a viable alternative for dioxane in groundwater, although the technology's effectiveness may be limited to shallow groundwater where contamination is confined to a limited depth within the root zone of

the trees (up to about 15 feet deep for hybrid poplars) (EPA 2001). Aboveground hydroponic treatment systems may also be suitable for removing dioxane from extracted groundwater for low-flow groundwater treatment regimens. Phytoremediation may also serve to provide long-term stabilization of dioxane-contaminated soil that would otherwise require excavation and stockpiling (GRAC 2003).

Photocatalysis is another emerging process used to treat dioxane. As opposed to hydrogen peroxide and UV light, where high energy photons are used to cleave the peroxide molecule and generate hydroxyl radicals, photocatalysis with titanium dioxide (TiO₂) uses the full spectrum of UV light to activate the TiO₂ catalyst, thereby creating organic destruction pathways. Purifics ES Inc. uses this technology in its Photo-CAT product line (Powell 2006).

Another company, Accelerated Remediation Technologies, LLC (ART), uses in-well technology combining *in situ* air stripping, air sparging, soil vapor extraction, enhanced bioremediation, and dynamic subsurface groundwater circulation to treat dioxane contamination. The in-well technology was able to reduce dioxane concentrations by up to 90 percent within 3 months during a pilot study conducted in North Carolina by Delta Environmental, Inc. (Odah and others 2005).

3.0 REFERENCES

- Agency for Toxic Substances and Disease Registry (ATSDR). 2004. "Toxicological Profile for 1,4-Dioxane. Draft for Public Comment." Available online at <http://www.atsdr.cdc.gov/toxprofiles/tp187.html>. September.
- Aitchison, E.W., Sara L. Kelley, Pedro Alvarez, and Jerald L. Schnoor. 2000. "Phytoremediation of 1,4-Dioxane by Hybrid Poplar Trees." *Water Environmental Research*. Volume 72, Number 3. Pages 313 through 321. <http://www.ingentaconnect.com/content/wef/wer/2000/00000072/00000003/art00008;jsessionid=dh4bhdclak8jb.alice>.
- Alvarez-Cohen, L. 2005. "Oxygenase-Catalyzed Biodegradation of Emerging Water Contaminants: 1,4-Dioxane and N-Nitrosodimethylamine." In: Partners in Environmental Technology Technical Symposium & Workshop. Strategic Environmental Research and Development Program/Environmental Security Technology Certification Program (SERDP/ ESTCP). November 29-December 1. http://www.serdp.org/research/CU/CU_1417.pdf.
- Applied Process Technology, Inc. (APT). 2005a. City of Industry, CA: HiPOx Industrial Site Remediation." *HiPOx: The Best Solution for Removing 1,4-Dioxane From Groundwater*, Rev. C. Page 7-3.
- APT, Inc. 2005b. "Pacific Northwest: HiPOx Industrial Site Remediation." *HiPOx: The Best Solution for Removing 1,4-Dioxane From Groundwater*, Rev. C. Page 7-6.
- APT, Inc. 2005c. "Orange County, CA: HiPOx Industrial Site Remediation." *HiPOx: The Best Solution For Removing 1,4-Dioxane from Groundwater*, Rev. C. Page 7-5.
- Berman, M., M. Darrow, C. DeMai, T. Gretarsson, P. Karakelian, T. Krantz, and R. Martel. 1998. "Remedial Design for the Cornell University Radioactive Waste Disposal Site, Ithaca, New York." May.
- Boarer, J.E., and R. Milne. 2004. "1,4-Dioxane Treatment in Mountain View, California." *Pollution Engineering*. July. http://www.aptwater.com/assets/news_articles/Article-PE0704.pdf#search=%22dioxane%20treatment%20pollution%20engineering%22.
- Bowman, R.H., P. Miller, M. Purchase, and R. Schoellerman. 2003. "Ozone-Peroxide Advanced Oxidation Water Treatment System for Treatment of Chlorinated Solvents and 1,4-Dioxane." *NGWA Conference on MTBE: Assessment, Remediation, and Public Policy*. Baltimore, Maryland. June 6.
- Brode, J., F. Fotouhi, and S. Kolon. 2005. "Ultraviolet and Hydrogen Peroxide Treatment Removes 1,4-Dioxane from Multiple Aquifers." *Technology News and Trends*. January. <http://clu-in.org/products/newsletters/tnandt/view.cfm?issue=0105.cfm>.
- Burgess, M. EPA. 2005. Comments on draft "Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications."
- CHEMFATE. 2003. Database Listing for 1,1,1-Trichloroethane. <http://www.syrres.com/esc/chemfate.htm>.
- Federal Remediation Technologies Roundtable (FRTR). 2006. "Remediation Technologies Screening Matrix and Reference Guide." Version 4.0. <http://www.frtr.gov/matrix2/>.
- Gronstal, D. McClellan AFB. 2006. Telephone conversation with Sankalpa Nagaraja, Tetra Tech EM Inc., regarding the dioxane treatment system at McClellan AFB. October 20.

- Groundwater Resources Association of California (GRAC). 2003. "1,4-Dioxane and Other Solvent Stabilizer Compounds in the Environment." *The Ninth Symposium in GRAC's Series on Groundwater Contaminants*. San Jose, California. December 10.
<http://www.grac.org/dioxanemain.html>.
- Korst, J.F. ARCADIS. 2005. Comments on draft "Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications."
- International Agency for Research on Cancer (IARC). 1999. "Re-Evaluation of Some Organic Chemicals, Hydrazine and Hydrogen Peroxide." *Monographs on the Evaluation of the Carcinogenic Risk of Chemicals to Man*. Volume 71. Pages 589 through 602.
<http://monographs.iarc.fr/ENG/Monographs/vol71/volume71.pdf>.
- Joshi, S.B., B.A. Donahue, A.R. Tarrer, J.A. Guin, M.A. Rahman, and B.L. Brady. 1989. "Methods for Monitoring Solvent Condition and Maximizing Its Utilization – STP 1043." *The American Society for Testing and Materials (ASTM)*. Philadelphia, Pennsylvania. 1989. Page 80 through 103.
- Kelley, S.L., E.W. Aitchison, M. Deshpande, J.L. Schooner, and P.J. Alvarez. 2001. "Biodegradation of 1,4-Dioxane in Planted and Unplanted Soil: Effect of Bioaugmentation with *Amycolata* sp. CB 1190." *Water Research*. Volume 35, Number 16. Pages 3791 through 3800.
- Lancaster Laboratories, Inc. 2003. "GC/MS Groups Aid Clients with 1,4-Dioxane Analyses." Fall.
<http://www.lancasterlabs.com/whatsnew/envpersp/fall2003/1-4dioxane.htm>.
- Ludwig, R. 1997. "Pumping and Treatment of Groundwater at the Gloucester Landfill Site." In: *Site Remediation Technologies: A Reference Manual*. Contaminated Sites Management Working Group. March.
http://www.ec.gc.ca/etad/csmwg/pub/site_me m/en/xb_e.htm.
- Mohr, T.K.G. Santa Clara Valley Water District of California. 2001. "Solvent Stabilizers White Paper." Prepublication Copy. San Jose, California. June 14.
http://www.valleywater.org/water/Water_Quality/Protecting_your_water/Solvents/PDFs/SolventStabilizers.pdf#search=%22Solvent%20Stabilizers%20White%20Paper%22.
- Mohr, T.K.G. 2005. Comments on draft "Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications."
- Occupational Safety and Health Administration (OSHA). 1998. "Occupational Safety and Health Standards, Toxic and Hazardous Substances." 29 *Code of Federal Regulations* 1910.1000.
- Odah, M.M., R. Powell, and D.J. Riddle. June. 2005. "ART in-well technology proves effective in treating 1,4-dioxane contamination." *Remediation Journal*. Volume 15, Issue 3. Pages 51 through 64.
- Parales, R.E., J.E. Adamus, N. White, and H.D. May. 1994. "Degradation of 1,4-Dioxane by an Actinomycete in Pure Culture." *Applied and Environmental Microbiology*. Volume 60, Number 12. Pages 4527 through 4530.
<http://aem.asm.org/cgi/content/abstract/60/12/4527>.
- Powell, T. January 2006. Photo-Cat Case Histories & Technology Briefing.
www.purifics.com.
- Steffan, R.J. 2005. "Biodegradation of 1,4-Dioxane". In: *Partners in Environmental Technology Technical Symposium & Workshop*. SERDP/ESTCP. November 29 - December 1.
<http://www.serd.org/Symposium/index.cfm#lastyear>.
- Suh, J.H. and M. Mohseni. 2004. "A Study on the Relationship Between Biodegradability Enhancement and Oxidation of 1,4-Dioxane Using Ozone and Hydrogen Peroxide." *Water Research*. Volume 38. Pages 2596 through 2604.

- Tetra Tech EM Inc. (Tetra Tech). 2003. Teleconference with Thomas K.G. Mohr, Santa Clara Valley Water District of California. July 2.
- U.S. Army Corps of Engineers (USACE). 2004. "Innovative Technology Success Stories: Charles George Landfill." http://hq.environmental.usace.army.mil/tool_info/it/success/charles2/charles2.html.
- USDHHS. 2002. "Report on Carcinogens." Public Health Service, National Toxicology Program. Tenth Edition. December. <http://ehp.niehs.nih.gov/roc/toc10.html>.
- USDHHS. 2003. National Toxicology Program Web site. <http://ntp.niehs.nih.gov/index.cfm?objectid=0703C9B2-9F3B-C96D-D7039F6B47F18098>.
- U.S. Environmental Protection Agency (EPA). 2000. "Method 8261. Volatile Organic Compounds by Vacuum Distillation in Combination with Gas Chromatography/Mass Spectroscopy (VD/GC/MS)." In SW-846 Draft Update IVB. November. <http://www.epa.gov/sw-846/pdfs/8261.pdf>.
- EPA. 2001. "Brownfields Technology Primer: Selecting and Using Phytoremediation for Site Cleanup." EPA 542-R-01-006. July. <http://www.brownfieldstsc.org>.
- EPA. 2003. Toxics Release Inventory Explorer. <http://www.epa.gov/triexplorer>.
- EPA Integrated Risk Information System (IRIS). 2005. "1,4-Dioxane (CASRN 123-91-1)." <http://www.epa.gov/IRIS/subst/0326.htm>.
- Walsom, G and B. Tunnicliffe. 2002. "1,4-Dioxane – A Little Known Compound." *Environmental Science and Engineering Magazine*. May. <http://www.esemag.com/0502/tca.html>.
- Zabaneh, M. 2004. E-mail to Martha Otto, U.S. Environmental Protection Agency Headquarters, Regarding the Advanced Oxidation System to Treat 1,4-Dioxane at McClellan Air Force Base. November 15.
- Zenker, M.J., R. C. Borden, and M.A. Barlaz. 2000. "Cometabolism of Poorly Biodegradable Ethers in Engineered Bioreactors". In: *Bioremediation and Phytoremediation of Chlorinated and Recalcitrant Compounds*, pg. 421. Proceedings of the Second International Conference on Remediation of Chlorinated and Recalcitrant Compounds. Monterey, California. <http://www.battelle.org/BookStore/BookTemplate.aspx?ISBN=1-57477-098-5>.
- Zenker, M.J., R.C. Borden, and M.A. Barlaz. 2003. "Occurrence and Treatment of 1,4-Dioxane in Aqueous Environments." *Environmental Engineering Science*. Volume 20, Number 5. Pages 423 through 432. http://www.aptwater.com/assets/tech_papers/Paper-Zenker.pdf.

APPENDIX A

INTERNET SOURCES FOR SUMMARY OF SELECTED U.S. ENVIRONMENTAL PROTECTION AGENCY AND STATE GUIDANCE FOR DIOXANE IN SOIL AND WATER

EPA Region or State	Internet Source
Region 3	EPA Region 3 Risk-Based Concentration Table http://www.epa.gov/reg3hwmd/risk/human/rbc/rbc0406.pdf
Region 6	EPA Region 6 Human Health Medium-Specific Screening Levels http://www.epa.gov/earth1r6/6pd/rcra_c/pd-n/screenvalues.pdf
Region 9	EPA Region 9 PRG http://www.epa.gov/region09/waste/sfund/prg/files/02table.pdf
Arizona	Arizona Administrative Code, Title 18, Chapter 7 http://www.azsos.gov/public_services/title_18/18-07.htm
California	California Health-Based Advisory Levels, Table A http://www.swrcb.ca.gov/rwqcb2/RBSL/SFRWQCB%20RBSLs%20Vol.1(December%202001).pdf
Colorado	Colorado Department of Public Health and Environment, Water Quality Control Commission Regulations http://www.cdphe.state.co.us/op/regs/waterregs/100241basicstandardsforgroundwater.pdf
Delaware	Remediation Standards Guidance Under the Delaware Hazardous Substance Cleanup Act http://www.dnrec.state.de.us/dnrec2000/Divisions/AWM/sirb/DOCS/PDFS/Misc/RemStnd.pdf
Florida	University of Florida http://fdep.ifas.ufl.edu/TTable2.pdf
Iowa	Standards for Soil, Iowa Land Recycling Program http://www.iowadnr.com/land/consites/lrp/conLRP.html
Maine	Maximum Exposure Guidelines for Drinking Water http://mainegov-images.informe.org/dhhs/eohp/wells/megtable.pdf
Michigan	Rule744Table.pdf, Rule748Table.pdf, and Rule746Table.pdf http://www.michigan.gov/deq/0,1607,7-135-3311-58095--,00.html
Missouri	Cleanup Levels for Missouri http://www.dnr.state.mo.us/alpd/hwp/pub468b.pdf
Pennsylvania	Effective Statewide Health Standard MSCs http://www.pacode.com/secure/data/025/chapter250/s250.708.html
Texas	Texas State Cleanup Levels, Search Engine http://www.pela.com/SCLs/TCLSearch.asp
West Virginia	West Virginia Voluntary Remediation and Redevelopment Act http://www.dep.state.wv.us/Docs/3200_RemediationGuidanceVersion2-1.pdf
Wyoming	Soil Cleanup Level Look-up Table Under the Voluntary Remediation Program http://deq.state.wy.us/volremedi/downloads/Fact%20Sheet%2012%20Jan05/F%20S%2012%2001-06-05%20clean.pdf



United States
Environmental Protection Agency
(5203P)
Washington D.C. 20460

Official Business
Penalty for Private Use \$300

Treatment Technologies For 1,4-Dioxane: Fundamentals And Field Applications

Office of Solid Waste and
Emergency Response

EPA-542-R-06-009
December 2006
www.epa.gov/tio
<http://clu-in.org>