

TECHNICAL FACT SHEET - 1,4-DIOXANE

At a Glance

- Flammable liquid and a fire hazard. Potentially explosive if exposed to light or air.
- Found at many federal facilities because of its widespread use as a stabilizer in certain chlorinated solvents, paint strippers, greases and waxes.
- Short-lived in the atmosphere, may leach readily from soil to groundwater, migrates rapidly in groundwater and is relatively resistant to biodegradation in the subsurface.
- Classified by EPA as "likely to be carcinogenic to humans" by all routes of exposure.
- Short-term exposure may cause eye, nose and throat irritation; long-term exposure may cause kidney and liver damage.
- Federal screening levels, state health-based drinking water guidance values and federal occupational exposure limits have been established.
- Modifications to existing sample preparation procedures may be required to achieve the increased sensitivity needed for detection of 1,4-dioxane.
- Common treatment technologies include advanced oxidation processes and bioremediation.
- No federal maximum contaminant level (MCL) has been established for 1,4dioxane in drinking water.

Introduction

This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Federal Facilities Restoration and Reuse Office (FFRRO), provides a summary of the emerging contaminant 1,4-dioxane, including physical and chemical properties; environmental and health impacts; existing federal and state guidelines; detection and treatment methods; and additional sources of information. This fact sheet is intended for use by site managers who may address 1,4-dioxane at cleanup sites or in drinking water supplies and for those in a position to consider whether 1,4-dioxane should be added to the analytical suite for site investigations.

1,4-Dioxane is a likely human 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 does not readily biodegrade in the environment.

What is 1,4-dioxane?

- 1,4-Dioxane is a synthetic industrial chemical that is completely miscible in water (EPA 2006; ATSDR 2012).
- Synonyms include dioxane, dioxan, p-dioxane, diethylene dioxide, diethylene oxide, diethylene ether and glycol ethylene ether (EPA 2006; ATSDR 2012; Mohr 2001).
- 1,4-Dioxane is unstable at elevated temperatures and pressures and may form explosive mixtures with prolonged exposure to light or air (EPA 2006; HSDB 2011).
- 1,4-Dioxane is a likely contaminant at many sites contaminated with certain chlorinated solvents (particularly 1,1,1-trichloroethane [TCA]) because of its widespread use as a stabilizer for chlorinated solvents (EPA 2013a; Mohr 2001). Historically, the main use (90 percent) of 1,4-dioxane was as a stabilizer of chlorinated solvents such as TCA (ATSDR 2012). Use of TCA was phased out under the 1995 Montreal Protocol and the use of 1,4-dioxane as a solvent stabilizer was terminated (ECJRC 2002; NTP 2016). Lack of recent reports for other previously reported uses suggest that many other industrial, commercial and consumer uses were also stopped.

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- It is a by-product present in many goods, including paint strippers, dyes, greases, antifreeze and aircraft deicing fluids, and in some consumer products (deodorants, shampoos and cosmetics) (ATSDR 2012; Mohr 2001).
- 1,4-Dioxane is used as a purifying agent in the manufacture of pharmaceuticals and is a by-
- product in the manufacture of polyethylene terephthalate (PET) plastic (Mohr 2001).
- Traces of 1,4-dioxane may be present in some food supplements, food containing residues from packaging adhesives or on food crops treated with pesticides that contain 1,4-dioxane (ATSDR 2012; DHHS 2011).

Exhibit 1: Physical and Chemical Properties of 1,4-Dioxane (ATSDR 2012)

Property	1,4-Dioxane
Chemical Abstracts Service (CAS) number	123-91-1
Physical description (physical state at room temperature)	Clear, flammable liquid with a faint, pleasant odor
Molecular weight (g/mol)	88.11
Water solubility	Miscible
Melting point (°C)	11.8
Boiling point (°C) at 760 mm Hg	101.1
Vapor pressure at 25°C (mm Hg)	38.1
Specific gravity	1.033
Octanol-water partition coefficient (log Kow)	-0.27
Organic carbon partition coefficient (log K _{oc})	1.23
Henry's law constant at 25 °C (atm-m ³ /mol)	4.80 X 10 ⁻⁶

Abbreviations: g/mol – grams per mole; $^{\circ}$ C – degrees Celsius; mm Hg – millimeters of mercury; atm-m³/mol – atmospherecubic meters per mole

Existence of 1,4-dioxane in the environment

- 1,4-Dioxane is typically found at some solvent release sites and PET manufacturing facilities (ATSDR 2012; Mohr 2001).
- It is short-lived in the atmosphere, with an estimated 1- to 3-day half-life due to photooxidation (ATSDR 2012; DHHS 2011).
- Migration to groundwater is weakly retarded by sorption of 1,4-dioxane to soil particles; it is expected to move rapidly from soil to groundwater (EPA 2006; ATSDR 2012).
- It is relatively resistant to biodegradation in water and soil, although recent studies have identified degrading bacteria (Inoue 2016; Pugazhendi 2015; Sales 2013).

- It does not bioaccumulate, biomagnify, or bioconcentrate in the food chain (ATSDR 2012; Mohr 2001).
- 1,4-Dioxane is frequently present at sites with TCA contamination (Mohr 2001; Adamson 2014).
- It may migrate rapidly in groundwater, ahead of other contaminants (DHHS 2011; EPA 2006).
- Where delineated, 1,4-dioxane is frequently found within previously delineated chlorinated solvent plumes and existing monitoring networks (Adamson 2014).
- As of 2016, 1,4-dioxane had been identified at more than 34 sites on the EPA National Priorities List (NPL); it may be present (but samples were not analyzed for it) at many other sites (EPA 2016b).

What are the routes of exposure and the potential health effects of 1,4-dioxane?

- Exposure may occur through ingestion of contaminated food and water, or dermal contact. Worker exposures may include inhalation of vapors (ATSDR 2012; DHHS 2011; EU 2002).
- Potential exposure could occur during production and use of 1,4-dioxane as a stabilizer or solvent (DHHS 2011; EU 2002).
- Short-term exposure to high levels of 1,4-dioxane may result in nausea, drowsiness, headache, and irritation of the eyes, nose and throat (ATSDR 2012; EPA 2013b; NIOSH 2010; EU 2002). 1,4-Dioxane is readily absorbed through the lungs and gastrointestinal tract. Some 1,4-dioxane may also pass through the skin, but studies indicate that much of it will evaporate before it is absorbed. Distribution is rapid and uniform in the lung, liver, kidney, spleen, colon and skeletal muscle tissue (ATSDR 2012).
- 1,4-Dioxane is weakly genotoxic and reproductive effects in humans are unknown; however, a developmental study on rats indicated that 1,4-

- dioxane may be slightly toxic to the developing fetus (ATSDR 2012; Giavini and others 1985).
- Animal studies showed increased incidences of nasal cavity, liver and gall bladder tumors after exposure to 1,4-dioxane (ATSDR 2012; DHHS 2011; EPA IRIS 2013).
- EPA has classified 1,4-dioxane as "likely to be carcinogenic to humans" by all routes of exposure (EPA IRIS 2013).
- The U.S. Department of Health and Human Services states that "1,4-dioxane is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity from studies in experimental animals" (DHHS 2011).
- The National Institute for Occupational Safety and Health (NIOSH) considers 1,4-dioxane a potential occupational carcinogen (NIOSH 2010).
- The European Union has classified 1,4-dioxane as having limited evidence of carcinogenic effect (EU 2002).

Are there any federal and state guidelines and health standards for 1,4-dioxane?

- ❖ EPA's Integrated Risk Information System (IRIS) database includes a chronic oral reference dose (RfD) of 0.03 milligrams per kilogram per day (mg/kg/day) based on liver and kidney toxicity in animals and a chronic inhalation reference concentration (RfC) of 0.03 milligrams per cubic meter (mg/m³) based on atrophy and respiratory metaplasia inside the nasal cavity of animals (EPA IRIS 2013).
- The cancer risk assessment for 1,4-dioxane is based on an oral slope factor of 0.1 mg/kg/day and the drinking water unit risk is 2.9 x 10⁻⁶ micrograms per liter (μg/L) (EPA IRIS 2013).
- EPA risk assessments indicate that the drinking water concentration representing a 1 x 10⁻⁶ cancer risk level for 1,4-dioxane is 0.35 μg/L (EPA IRIS 2013).
- No federal maximum contaminant level (MCL) for drinking water has been established (EPA 2012).
- 1,4-Dioxane is included on the fourth drinking water contaminant candidate list and is included in the Third Unregulated Contaminant Monitoring Rule (EPA 2009; EPA 2016a).

- EPA's drinking water equivalent level is 1 mg/L (EPA 2012). EPA has calculated a screening level of 0.46 μg/L for tap water, based on a 1 in 10⁻⁶ lifetime excess cancer risk (EPA 2017b).
- EPA established a 1-day health advisory of 4.0 milligrams per liter (mg/L) and a 10-day health advisory of 0.4 mg/L in drinking water for a 10-kilogram child and a lifetime health advisory of 0.2 mg/L in drinking water (EPA 2012).
- EPA has calculated a residential soil screening level (SSL) of 5.3 milligrams per kilogram (mg/kg) and an industrial SSL of 24 mg/kg. The soil-togroundwater risk-based SSL is 9.4 x 10⁻⁵ mg/kg (EPA 2017b).
- EPA has calculated a residential air screening level of 0.56 micrograms per cubic meter (μg/m³) and an industrial air screening level of 2.5 μg/m³ (EPA 2017b).
- A reportable quantity of 100 pounds has been established under the Comprehensive Environmental Response, Compensation, and Liability Act (EPA 2011).
- The Occupational Safety and Health Administration (OSHA) established a permissible

exposure limit (PEL) for 1,4-dioxane of 100 parts per million (ppm) or 360 mg/m³ as an 8-hour time weighted average (TWA). While OSHA has established a PEL for 1,4-dioxane, OSHA has recognized that many of its PELs are outdated and inadequate for ensuring the protection of worker health. OSHA recommends that employers follow the California OSHA limit of 0.28 ppm, the NIOSH recommended exposure limit of 1 ppm as a 30-minute ceiling, or the American Conference of Governmental Industrial Hygienists threshold limit value of 20 ppm (OSHA 2017).

Various states have established drinking water and groundwater guidelines, including the following:

State	Guideline (μg/L)	Source
Alaska	77	AL DEC 2016
California	1.0	Cal/EPA 2011
Colorado	0.35	CDPHE 2017
Connecticut	3.0	CTDPH 2013
Delaware	6.0	DE DNR 1999
Florida	3.2	FDEP 2005
Indiana	7.8	IDEM 2015
Maine	4.0	MEDEP 2016
Massachusetts	0.3	MADEP 2004
Mississippi	6.09	MS DEQ 2002
New Hampshire	0.25	NH DES 2011
New Jersey	0.4	NJDEP 2015
North Carolina	3.0	NCDENR 2015
Pennsylvania	6.4	PADEP 2011
Texas	9.1	TCEQ 2016
Vermont	3.0	VTDEP 2016
Washington	0.438	WA ECY 2015
West Virginia	6.1	WV DEP 2009

What detection and site characterization methods are available for 1,4-dioxane?

- As a result of the limitations in the analytical methods to detect 1,4-dioxane, it has been difficult to identify its occurrence in the environment. The miscibility of 1,4-dioxane in water causes poor purging efficiency and results in high detection limits (ATSDR 2012; EPA 2006; Mohr 2001).
- The Contract Laboratory Program SOW SOM02.3 includes a CRQL of 2.0 μg/L in water, 67 μg/kg in low soil and 2,000 μg/kg in medium soil (EPA 2013c).
- Conventional analytical methods can detect 1,4-dioxane only at concentrations 100 times greater than the concentrations of volatile organic compounds. Modifications of existing analytical methods and their sample preparation procedures may be needed to achieve lower detection limits for 1,4-dioxane (EPA 2006; Mohr 2001).
- High-temperature sample preparation techniques improve the recovery of 1,4-dioxane. These techniques include purging at elevated temperature (EPA SW-846 Method 5030); equilibrium headspace analysis (EPA SW-846

- Method 5021); vacuum distillation (EPA SW-846 Method 8261); and azeotropic distillation (EPA SW-846 Method 5031) (EPA 2006).
- NIOSH Method 1602 uses gas chromatography flame ionization detection (GC-FID) to determine the concentration of 1,4-dioxane in air (ATSDR 2012; NIOSH 2010).
- EPA SW-846 Method 8015D uses gas chromatography (GC) to determine the concentration of 1,4-dioxane in environmental samples. Samples may be introduced into the GC column by a variety of techniques including the injection of the concentrate from azeotropic distillation (EPA SW-846 Method 5031). The lower quantitation limits for 1,4-dioxane in aqueous matrices by azeotropic microdistillation are 12 μg/L (reagent water), 15 μg/L (groundwater) and 16 μg/L (leachate) (EPA 2003).
- EPA SW-846 Method 8260B detects 1,4-dioxane in a variety of solid waste matrices using GC and mass spectrometry (MS). The detection limit

- depends on the instrument and choice of sample preparation method (ATSDR 2012).
- A laboratory study is underway to develop a passive flux meter (PFM) approach to enhance the capture of 1,4-dioxane in the PFM sorbent to improve accuracy. Results to date show that the PFM is capable of quantifying low absorbing compounds such as 1,4-dioxane (DoD SERDP 2013b).
- EPA Method 1624 uses isotopic dilution gas chromatography – mass spectrometry (GC-MS) to detect 1,4-dioxane in water, soil and municipal discharges. The detection limit for this method is 10 μg/L (ATSDR 2012; EPA 2001b).
- EPA SW-846 Method 8270 uses liquid-liquid extraction and isotope dilution by capillary column GC-MS. This method is often modified for the detection of low levels of 1,4-dioxane in water (EPA 2007).

- EPA Method 522 uses solid phase extraction and GC-MS with selected ion monitoring for the detection of 1,4-dioxane in drinking water with detection limits as low as 0.02 µg/L (EPA 2008).
- GC-MS detection methods using solid phase extraction followed by desorption with an organic solvent have been developed to remove 1,4dioxane from the aqueous phase. Detection limits as low as 0.03 μg/L have been achieved by passing the aqueous sample through an activated carbon column, following by elution with acetonedichloromethane (ATSDR 2012; Kadokami and others 1990).
- Lab studies indicate effective methods for monitoring growth of dioxane-degrading bacteria in culture (Gedalanga 2014).
- Studies are underway to develop and assess methods for performing compound-specific isotope analysis (CSIA) on low levels of 1,4-dioxane in groundwater (DoD SERDP 2016).

What technologies are being used to treat 1,4-dioxane?

- Pump-and-treat remediation can treat dissolved 1,4-dioxane in groundwater and control groundwater plume migration, but requires ex-situ treatment tailored for the unique properties of 1,4dioxane (e.g., its low octanol-water partition coefficient makes 1,4-dioxane hydrophilic) (EPA 2006; Kiker and others 2010).
- Commercially available advanced oxidation processes using hydrogen peroxide with ultraviolet light or ozone can be used to treat 1,4-dioxane in wastewater (Asano and others 2012; EPA 2006).
- Peroxone and iron activated persulfate oxidation of 1,4-dioxane might aid in the cleanup of VOCcontaminated sites (Eberle 2015; Zhong 2015; Li 2016; SERDP 2013d).
- In-situ chemical oxidation can be successfully combined with bioaugmentation for managing dioxane contamination (DoD SERDP 2013d; Adamson 2015).
- Ex-situ bioremediation using a fixed-film, movingbed biological treatment system is also used to treat 1,4-dioxane in groundwater (EPA 2006).
- Electrical resistance heating may be an effective treatment method (Oberle 2015).
- Phytoremediation is being explored as a means to remove the compound from shallow groundwater. Pilot-scale studies have demonstrated the ability of hybrid poplars to take up and effectively

- degrade or deactivate 1,4-dioxane (EPA 2001a, 2013a; Ferro and others 2013).
- Microbial degradation in engineered bioreactors has been documented under enhanced conditions or where selected strains of bacteria capable of degrading 1,4-dioxane are cultured, but the impact of the presence of chlorinated solvent cocontaminants on biodegradation of 1,4-dioxane needs to be further investigated (EPA 2006, 2013a; Mahendra and others 2013).
- Results from a 2012 laboratory study found 1,4-dioxane-transforming activity to be relatively common among monooxygenase-expressing bacteria; however, both TCA and 1,1-dichloroethene inhibited 1,4-dioxane degradation by bacterial isolates (DoD SERDP 2012).
- Isobutane-metabolizing bacteria can consistently degrade low (<100 ppb) concentrations of 1,4dioxane, often to concentrations <1 ppb. These organisms also can degrade many chlorinated cocontaminants such as TCA and 1,1-dichoroethene (1,1-DCE) (DoD SERDP 2013c).
- Ethane effectively serves as a cometabolite for facilitating the biodegradation of 1,4-dioxane at relevant field concentrations (DoD SERDP 2013f).
- Biodegradation rates are subject to interactions among transition metals and natural organic ligands in the environment. (Pornwongthong 2014; DoD SERDP 2013e).

- Photocatalysis has been shown to remove 1,4-dioxane in aqueous solutions. Laboratory studies documented that the surface plasmon resonance of gold nanoparticles on titanium dioxide (Au TiO2) promotes the photocatalytic degradation of 1,4-dioxane (Min and others 2009; Vescovi and others 2010).
- Other in-well combined treatment technologies being assessed include air sparging; soil vapor extraction (SVE); enhanced bioremediation-
- oxidation; and dynamic subsurface groundwater circulation (Odah and others 2005).
- 1,4-Dioxane was reduced by greater than 90 percent in the treatment zone with no apparent downward migration of 1,4-dioxane using enhanced or extreme SVE, which uses a combination of increased air flow, sweeping with drier air, increased temperature, decreased infiltration and more focused vapor extraction to enhance 1,4-dioxane remediation in soils (DoD SERDP 2013a).

Where can I find more information about 1,4-dioxane?

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