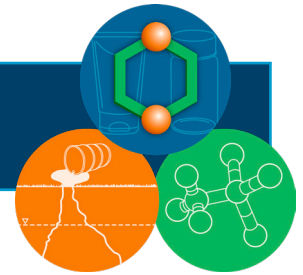




# History of Use and Potential Sources 1,4-Dioxane



## 1 Introduction

Researchers first synthesized 1,4-dioxane (Chemical Abstracts Service [CAS] Registry Number #123-91-1) in 1863 (Lourenço 1863) (Wurtz 1863), and it has since been used in a variety of industrial applications. It is estimated that 90% of this synthetic, organic compound (also known as dioxane, p-dioxane, diethylene oxide, and 1,4-diethylene dioxide and glycol) has been used to stabilize the chlorinated solvent 1,1,1-trichloroethane (1,1,1-TCA) (ATSDR 2012).

U.S. commercial manufacturing began at a small scale in 1929 (ACS 1929), with production increasing in 1951 and then spiking in the early 1970s and again in the mid-1980s. The decline in 1,4-dioxane production in the late 1970s to early 1980s tracks 1,1,1-TCA production; the spike in the mid-1980s occurred as companies phased out use of trichloroethylene (TCE) in favor of 1,1,1-TCA (Figure 1). By 1985, domestic 1,4-dioxane production was approximately 25 million pounds annually (Surprenant 2005). Approximately 90% of 1,4-dioxane produced was used to stabilize 1,1,1-TCA (ATSDR 2012). Production of 1,4-dioxane began to decline after 1985, partially as a result of conversion from Freon 113 use to 1,1,1-TCA use. Use of 1,1,1-TCA continued to decline substantially post-1995 after it was phased out as an “ozone-depleting material” pursuant to the 1987 Montreal Protocol (ATSDR 2012). In 2002, domestic annual production of 1,4-dioxane was estimated to be between 1 and 10 million pounds, and it has declined further since (HSDB 2010.).

The Interstate Technology and Regulatory Council (ITRC) has developed a series of six fact sheets to summarize the latest science and emerging technologies regarding 1,4-dioxane. The purpose of this fact sheet is to:

- review the history of 1,4-dioxane manufacturing and usage
- provide an overview of the potential sources of releases of 1,4-dioxane to the environment

Note: ITRC is developing a 1,4-dioxane guidance document for publication in late 2020. The guidance document will provide additional details on 1,4-dioxane history of use and potential sources.

## 1,4-DIOXANE TIMELINE AND HISTORICAL PRODUCTION

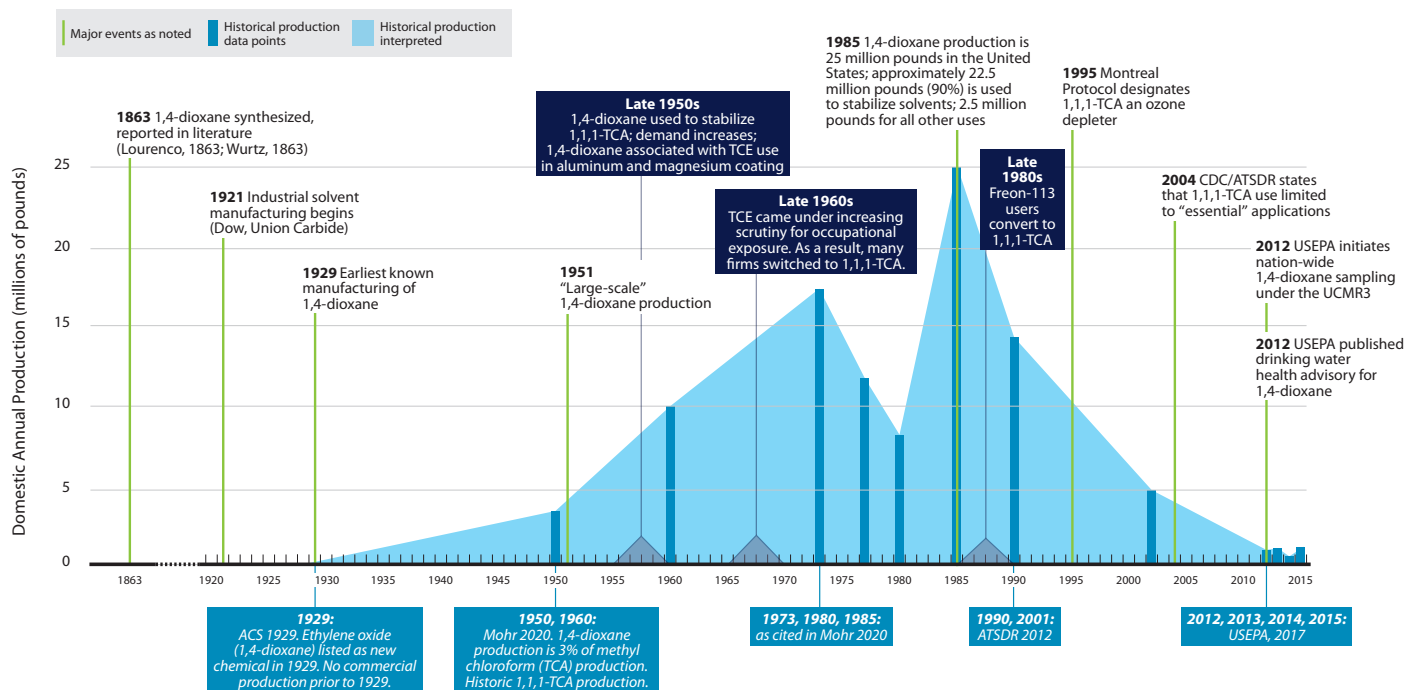


Figure 1. 1,4-Dioxane timeline and historic production

## History of Use and Potential Sources: 1,4-Dioxane *continued*

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In 2013, the U.S. Environmental Protection Agency (USEPA) included 1,4-dioxane on its list of candidate chemicals for consideration for national drinking water regulation and initiated sampling of 1,4-dioxane under the Third Unregulated Contaminant Monitoring Rule (UCMR3) (USEPA 2017). Additionally, the USEPA published a health advisory in 2012, and a year later, it classified 1,4-dioxane as a potential human carcinogen. For additional information on the UCMR3, please see the Regulatory Framework fact sheet. Officials have detected 1,4-dioxane in drinking water, soil, and groundwater throughout the world (EC 2010). Therefore, understanding the historical uses and sources of 1,4-dioxane is necessary to identify sites where further investigation may be required.

### Industrial and Consumer Uses of 1,4-Dioxane

Widespread use of 1,4-dioxane included, but was not limited to, the following:

**Solvent stabilizer:** Industry has used chlorinated solvents, such as 1,1,1-TCA and TCE, for degreasing and preparing materials (for example, for chrome plating and other coatings) and for repairing and maintaining equipment. Solvent stabilizers are often required to mitigate harmful reactions between solvents and metals, which form acids as the solvent decomposes. 1,1,1-TCA is highly reactive with a variety of metals (CD 2003), and manufacturers have historically stabilized this key solvent with 1,4-dioxane and other stabilizers. 1,1,1-TCA is an order of magnitude more reactive with aluminum than TCE (Archer and Stevens 1977) and therefore requires greater amounts of stabilizing agents. Over 90% of the 1,4-dioxane production in the mid-1980s was for stabilizing 1,1,1-TCA (Mohr et al. 2020). Companies sometimes market chlorinated solvents as formulations containing potentially complex mixtures of multiple solvents and stabilizing agents (Mohr et al. 2020). Figure 1 summarizes key milestones related to the historical production, use, and regulation of 1,4-dioxane as a stabilizing agent for chlorinated solvents. Details regarding regulations are contained in the Regulatory Framework fact sheet.

Questions have been raised regarding whether 1,4-dioxane was used for stabilization of TCE. Mohr et al. (Mohr et al. 2020) provide extensive documentation regarding the use of 1,4-dioxane as a stabilizing agent for 1,1,1-TCA but do not identify any definitive evidence for using 1,4-dioxane as a stabilizing agent for TCE. The industry reportedly stabilized TCE when used with more reactive metals such as aluminum and magnesium (NYSPPI 2017), although 1,4-dioxane was not specifically identified as the stabilizer used. Given the increased use of 1,4-dioxane for chlorinated solvent stabilization since the late 1950s and the existence of many different TCE manufacturers throughout the twentieth century (Doherty 2000), it is possible that some stabilized TCE contained 1,4-dioxane. Notwithstanding the limited documentation of the use of 1,4-dioxane as a stabilizer in TCE, several empirical occurrence studies confirm the presence of 1,4-dioxane at sites with TCE in the groundwater (Anderson, Anderson, and Bower 2012); (Adamson et al. 2014); (Chiang et al. 2016); (Karges, Becker, and Püttmann 2018). Co-occurrence of 1,4-dioxane and TCE, in the absence of 1,1,1-TCA, could be due to something as simple as the use of both solvents at a site over time, coupled with TCE's greater recalcitrance, suggesting that 1,1,1-TCA was present in the past but has degraded completely from the site, leaving only TCE. ITRC will present additional information on this topic in the forthcoming 1,4-dioxane guidance document.

**Chemical process by-products:** 1,4-Dioxane occurs as an impurity in certain chemical processes, such as during polyethylene terephthalate (PET, aka polyester) production (Hovenkamp and Munting 1970). 1,4-Dioxane is also a by-product of some forms of acetate and ethoxylated surfactant production (Stepan 2006). Additionally, 1,4-dioxane may be produced during production of some consumer detergents, industrial detergents, and cleaning compounds—especially ones with components derived from ethoxylated surfactants. In some cases, these processes have been modified to remove the 1,4-dioxane (ATSDR 2012).

**Medical, pharmaceutical, and biotechnical uses:** 1,4-Dioxane has various uses in medical, pharmaceutical, and biotechnical industries. Scintillation cocktails—radio-labeled solutions used as tracers in the life sciences industry—can contain as much as 80% 1,4-dioxane (Bray 1960). Medical and research laboratories also used 1,4-dioxane as a solvent for dehydrating tissue and preparing slides for microscopy (Mossman 1937); (Shearer and Hunsicker 1980), preparing samples for analysis, and removing chrome-based fixative staining (Winsor 2006). Although some laboratories reclaimed the expensive 1,4-dioxane (Winsor 2006), often they discarded 1,4-dioxane-containing materials to wastewater systems or landfills after use.

**Plastics and polymers:** 1,4-Dioxane is directly used in and can be a by-product of certain sectors of the rubber and plastics industry. Manufacturers use 1,4-dioxane to make photosensitive resins and magnetic (recordings) tapes (RSC

## History of Use and Potential Sources: 1,4-Dioxane *continued*

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1992), acetate and cellulose triacetate (for example, reverse osmosis and kidney dialysis membranes) (Philippoff 2006), and acetate cigarette filters (Matsumura, Shimamoto, and Shibata 1997). The USEPA also identified 1,4-dioxane as a waste that can be produced as a manufacturing by-product from some rubber and plastics industrial facilities (USEPA 2005).

**Inks, paints, and coatings:** The industry has used 1,4-dioxane as a component of printing inks and paints since the 1950s (NYSPPPI 2017), either as a solvent (to help ink or paint adhere to plastic) or in conjunction with 1,1,1-TCA (a solvent in some paints) (Mohr et al. 2020). It was also present in the resins used to make paints and in paint strippers, fabric dyes, and some felt tip pens (Mohr et al. 2020).

**Adhesives:** 1,4-Dioxane has been used as an additive in adhesives (Wilke, Jann, and Brödner 2004) and as surface preparation prior to application of epoxy adhesives, and it may have been present as a contaminant in adhesives using 1,1,1-TCA as a solvent (HSDB 2010.). Based on the limited information that is available, 1,4-dioxane may still be used in adhesive applications or be present in historical adhesives.

**Aircraft deicing fluids:** 1,4-Dioxane has been used as an additive, or was an impurity, in antifreeze and aircraft deicing fluids (UC 1989).

**Automotive fluids:** Manufacturers included 1,4-dioxane in brake fluids, brake cleaning fluids, loosening fluids, and rust remover (Mohr et al. 2020). Although some of the 1,4-dioxane was present because 1,1,1-TCA was used in these materials, 1,4-dioxane concentrations were higher than expected (Valvoline 1991); (CRC 1987) compared to 1,1,1-TCA concentrations; therefore, 1,4-dioxane may have served other purposes in these applications.

**Consumer products:** 1,4-Dioxane is commonly present in raw materials used in the production of many consumer products, including cleaners, detergents, shampoo, and cosmetics. These include ethoxylated surfactants and other ingredients, including products containing propylene glycols (Johnson 2001); (Pundlik, Sitharaman, and Kaur 2001). Many consumer product manufacturing processes have been modified to reduce 1,4-dioxane concentrations.

**Other uses:** Officials have identified 1,4-dioxane in a wide variety of products. The Agency for Toxic Substances and Disease Registry (ATSDR 2012) found evidence of 1,4-dioxane use in wood pulping, fumigants, laboratory applications, and polymerization (ATSDR 2012). Other uses have included racing fuels (ProSystems 2002), fire retardant production (BCC 2002), medical device production (Wypych 2001), contraceptives (FDA 1997), and art restoration (Mohr et al. 2020).

## Sources of Contaminaton

Researchers have found that the occurrence of 1,4-dioxane in the environment is primarily caused by the use and disposal of associated chlorinated solvents. The following sections provide a more in-depth review of the sources of 1,4-dioxane releases to the environment.

The main sources of 1,4-dioxane in U.S. drinking water supplies are wastewater discharge, unintended spills or leaks, and historical disposal practices associated with 1,1,1-TCA (WRF 2014). 1,4-Dioxane can enter the environment through wastewater and air discharges at sites that produce, process, and use it. This production, processing, or use may be of either (1) chlorinated solvents, or other chemicals in which 1,4-dioxane is a chemical additive, or (2) industrial-grade 1,4-dioxane products (that is, technical grade >95% 1,4-dioxane or American Chemical Society [ACS] reagent grade >99% 1,4-dioxane). At some manufacturing facilities, or facilities that conduct disposal through incineration, 1,4-dioxane may be released via emissions. In groundwater, 1,4-dioxane contamination is principally associated with 1,1,1-TCA releases, wastewater disposal via groundwater recharge, and effluent water reuse. Elevated 1,4-dioxane levels have also been found in landfill leachates due to landfilling materials that contain 1,4-dioxane. More details are provided in the following sections.

**Wastewater (wastewater treatment plant, industrial wastewater treatment plant, and septic system):** 1,4-Dioxane is likely to be present in wastewater discharges to publicly owned treatment works (POTWs) due to the widespread use of 1,4-dioxane in consumer products (such as personal care products and detergents) (NYSPPPI 2017). Legacy contamination and nonpoint sources may also contribute to releases of 1,4-dioxane into the environment. One study of domestic wastewater effluents from 40 different wastewater treatment plants indicated non-detect (<0.30 micrograms per liter [ $\mu\text{g/L}$ ]) to 3.30  $\mu\text{g/L}$  1,4-dioxane levels, with a mean of 1.11 0.60  $\mu\text{g/L}$  (Simonich et al. 2013). Septic leach field effluent, reclaimed water, and sewer line exfiltration to groundwater sources may result in groundwater and downgradient surface waters as nonpoint sources. Effluent from industrial facilities and wastewater treatment plants is also a potential source of 1,4-dioxane in surface water.

## History of Use and Potential Sources: 1,4-Dioxane *continued*

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**Landfills:** Landfill waste materials and leachate pose a potential source of 1,4-dioxane release to the environment. In one evaluation, 1,4-dioxane was found in 70% of landfills that receive incinerator wastes and 38% of landfills receiving noncombustible waste (NYSPPPI 2017). Another evaluation that compiled multiple studies indicated a range of 1,4-dioxane levels in 38 landfills from 1 ug/L to 22,000 ug/L (Mohr et al. 2020). In 2000, the USEPA conducted a survey to review the chemistry of landfill leachate in the United States. The survey revealed the presence of 1,4-dioxane in leachate from Construction and Demolition (C&D), Resource Conservation and Recovery Act (RCRA) Subtitle D (solid waste) and hazardous waste landfills (USEPA 2000). ITRC will present additional information in the forthcoming 1,4-dioxane guidance document.

**Improper waste disposal:** Waste solvents containing 1,4-dioxane have been historically released through improper disposal in unlined lagoons, ponds, and trenches, and illegal dumping of drums or liquid solvents. For example, 1,4-dioxane has been discovered in groundwater at concentrations of more than 250 mg/L at a San Jose, California, solvent recycling facility through inadvertent releases as well as improper disposal (ATSDR 2012). At Air Force Plant 44 in Tucson, Arizona, chlorinated solvent waste from degreasing operations was disposed of in an unlined lagoon between 1966 and 1970 (ET 2000).

**Other releases:** Accidental releases, such as those from leaking pipes, storage tanks, and drums, as well as from inadvertent spills, are also common sources of chlorinated solvent and associated 1,4-dioxane releases to the environment. A case study on the Seymour Recycling Corporation Superfund Site in Indiana documents USEPA enforcement actions related to 60,000 55-gallon drums and 98 bulk storage tanks containing a variety of wastes, including substantial quantities of chlorinated solvent waste containing 1,4-dioxane (Mohr et al. 2020). Releases of 1,4-dioxane to the environment can also be caused by intentional applications of products containing 1,4-dioxane, such as use of deicing fluids or pesticides.

## Presence in Environmental Media

1,4-Dioxane has been found in a wide range of media during investigations, as described in several case studies in Mohr et al. (Mohr et al. 2020). The following sections briefly describe the most common media and whether 1,4-dioxane is likely to be of environmental concern in those media. More details regarding the fate and transport of 1,4-dioxane can be found in the Environmental Fate, Transport, and Investigation Strategies fact sheet.

**Groundwater:** Spills of solvents and improper disposal of still bottoms (condensate waste) from solvent recycling at electronics manufacturing, metals fabrication, and other industrial sites in the 1960s, 1970s, and 1980s is often the source of 1,4-dioxane and chlorinated solvent contamination in groundwater. Given the evidence that solvent stabilizer concentrate in still bottoms (condensate waste), 1,4-dioxane is likely to be present at these sites.

**Surface water:** Sampling under the UCMR3 (USEPA 2017) indicated that approximately 10% of surface water sources had detections of 1,4-dioxane, suggesting relatively widespread impacts from releases to surface water from wastewater plants and other industrial discharges.

**Soil and sediment:** Because of its high solubility in water, low vapor pressure, and minimal sorption to organic carbon, as evidenced by a low Log KOC of 1.23 (Mohr et al. 2020), 1,4-dioxane is not often found at levels of concern in soil. Laboratory column and field studies Priddle and Jackson (1991); (Liu et al. 2000) determined retardation factors between 1.1 and 1.2, suggesting that 1,4-dioxane would move through a soil column close to the rate of water (such as precipitation). This suggests minimal 1,4-dioxane retention in soils.

**Air:** 1,4-Dioxane may be released to air during its production, its use (ATSDR 2012), and the processing of other chemicals (such as pharmaceuticals or pesticides). In 1984, the concentration of 1,4-dioxane ranged from 0.1–0.4 microgram per cubic meter ( $\mu\text{g}/\text{m}^3$ ) in ambient air sampled in the United States. The research contains no information on the source of the 1,4-dioxane detected or the locations of the air sampling (EC 2010). In air, 1,4-dioxane remains as a vapor but degrades through reactions with photochemically produced hydroxyl radicals with an estimated half-life of a few days (USEPA 2014). Because the use of 1,4-dioxane has declined in recent years, current levels of 1,4-dioxane in ambient air are likely to be lower than the levels reported in the 1980s or earlier. However, recent national surveys are unavailable.

### 4 References

The references cited in this fact sheet, and the other ITRC 1,4-Dioxane fact sheets, are included in one combined list that is available on the ITRC web site.

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