Emerging Over a Century: The Status and Regulatory Climate of 1,4-dioxane as a Contaminant of Emerging Concern, and Treatment Options

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Introduction

Cited by the U.S. EPA as "likely to be carcinogenic to humans,"[1] 1,4-dioxane has been used in industrial and commercial applications for over a century, including as a stabilizer in chlorinated solvents, paint strippers, greases and waxes, and as a purifying agent in pharmaceutical production. 1,4-dioxane is difficult to detect in the environment, biodegrades very slowly in water and soil, and moves quickly into and via groundwater, explaining why it has been found in drinking water supplies, groundwater and surface water throughout the world.

Despite its long history, 1,4-dioxane's effects are still being evaluated. This article investigates the status of 1,4-dioxane as an emerging contaminant in drinking water systems and surface water, the federal and state regulatory climate, and the availability and efficacy of treatment options.

Summary Bullet Points:

- 1,4-dioxane is a synthetic chemical, historically used as a stabilizer for industrial solvents, predominantly 1,1,1-trichloroethane (TCA), from the 1950s through the 1990s.
- Highly soluble in water and a likely carcinogen, 1,4-dioxane has migrated from hazardous waste sites and landfills and infiltrated drinking water supplies and surface water.

[1] U.S. Environmental Protection Agency. Integrated Risk Information System (IRIS) on 1,4-Dioxane. National Center for Environmental Assessment, Office of Research and Development, Washington, DC. 1999.

- There is no federal limit on 1,4-dioxane in drinking water, and treatment is challenging.

1,4-dioxane (also known as dioxane, p-dioxane, diethylene oxide, 1,4-diethylene dioxide, and glycol ethylene ether) is a synthetic organic compound used in various industrial applications. Researchers first synthesized 1,4-dioxane in 1863. In 1985, about 90% of the 1,4-dioxane produced was for use as a stabilizer for the chlorinated solvent 1,1,1-trichloroethane (1,1,1-TCA). 1,4-dioxane is a byproduct present in many goods, including paint strippers, dyes, greases, antifreeze and aircraft deicing fluids, and in some consumer products (e.g., deodorants, shampoos and cosmetics).[,2] A 2008 survey found a range of 1-12 parts per million (ppm) 1,4-dioxane in about 20 percent of products tested.[3] A 2018 FDA survey of children's cosmetic products containing ingredients associated with 1,4-dioxane contamination found approximately 2 percent had levels of 1,4-dioxane above 10 ppm.

1,4-dioxane received increased scrutiny in the early 2000s after EPA initiated a reassessment of its toxicity and began developing cleanup guidelines. However, 1,4-dioxane is still regarded as an "emerging contaminant," even though it has been in use for over 160 years. Despite a long record of use, a contaminant may be considered "emerging" because of the discovery of a new source or pathway to humans.

Environmental Transport and Toxicity

1,4-dioxane is highly mobile through environmental media (atmosphere, soil, surface water, groundwater, etc.). Once released to the environment, 1,4-dioxane is not retained in soil or sediments due its poor sorbability but rather leaches away from its source through these media to groundwater and may discharge to surface water. Humans are generally exposed to 1,4-dioxane via water or air by ingestion, inhalation, and, less significantly, through dermal absorption.

For residential populations, the primary exposure route for 1,4-dioxane is likely ingestion of contaminated water from public and private water supplies. In toxicity studies, laboratory rodents given 1,4-dioxane in their drinking water developed liver cancer, leading to the U.S.

[2] Mohr, T.K.G. 2001. "1,4-Dioxane and Other Solvent Stabilizers White Paper." Santa Clara Valley Water District of California. San Jose, California.

[3] Hardy J. Chou, Perry G. Wang, Wanlong Zhou, and Alexander J. Krynitsky, "Determination of 1,4-Dioxane in Cosmetic Products." Poster session presented at 124th AOAC Annual Meeting; 2010 Sept. 26-29; Orlando, Fl.

Environmental Protection Agency's (EPA) determination that 1,4-dioxane is likely to be carcinogenic to humans through all routes of exposure. From 2013–2015, EPA required all drinking water systems serving more than 10,000 people to sample for 1,4-dioxane and, in 2023, EPA released a draft supplement to the risk evaluation for 1,4-dioxane, which considered additional exposure pathways excluded from the earlier risk evaluation.

Regulatory Climate

Currently, there is no federal drinking water standard (i.e., a Maximum Contaminant Level [MCL]) for 1,4-dioxane despite its widespread presence in drinking water systems. EPA has stated in a non-enforceable Health Advisory (HA) that a concentration of 35 micrograms per liter (μg/L) of 1,4-dioxane should not be exceeded in drinking water, corresponding to an estimated incremental lifetime cancer risk to an exposed individual of 1 in 10,000 (i.e., 1E-04). As a result, state-level agencies have started regulating 1,4-dioxane, leading to a patchwork of criteria and guidance in the absence of a federal MCL. The present 1,4-dioxane regulatory landscape for drinking water consists of widely-varying state-promulgated standards and regulations, ranging from 0.3 μg/L (Massachusetts) to 7.2 μg/L (Michigan).

The state-to-state variation is due to four factors:

- Scaling. Some states (e.g., Massachusetts) have adopted EPA's HA, but at a risk range of 1 in 1 million (i.e., 1E-06); i.e., 0.35 μ/L, based on EPA's Regional Screening Level, resulting in the 2-orders of magnitude difference between the HA and the state's standard;
- The residential drinking water goal is calculated using equations based on different critical effects (e.g., Michigan);
- An MCL is based on more than potential exposure risk. The MCLG, or Maximum Contaminant Level Goal, is a non-enforceable health goal based on how much of the contaminant can be present with no health risk. The MCL is then set as close to the MCLG as possible, while accounting for difficulties in measuring small quantities of a contaminant, a lack of available treatment technologies, or the potential costs of treatment outweighing the public health benefits of a lower MCL. These additional considerations can vary from state to state (e.g., California – 1 μg/L; Connecticut – 3 μg/L, etc.); and

- Most states have no 1,4-dioxane drinking water regulations or enforceable guidance.

Further, the type of regulation or guidance can differ state-to-state, including:

- Notification Levels – drinking water supply systems must notify state officials and customers when the level of a constituent approaches or exceeds a pre-determined value (e.g., California);
- Advisory – there is an established concentration limit but no action is required if concentrations exceed that value (e.g., Massachusetts);
- MCL – promulgated maximum amounts of a contaminant that may be present and must be routinely evaluated by treatment facilities (New York); and
- Clean Up – investigation and remediation are required if concentrations exceed the threshold (e.g., New Hampshire).

Therefore, drinking water aquifers around the U.S. contaminated with 1,4-dioxane continue to go unregulated or are inconsistently regulated, resulting in a variety of exposure risks.

Some states and cities have sued 1,4-dioxane manufacturers in the absence of a regulatory scheme. For example, in March 2023, the New Jersey Department of Environmental Protection filed a lawsuit against the Dow Chemical Co., Ferro Corp., and Vulcan Materials Co., as well as other unnamed companies, for "injuries to natural resources of the State, including groundwater and surface water, as a result of releases of 1,4-dioxane into the environment…and causing widespread contamination of the State's natural resources." The lawsuit alleges the companies knew the suspected human carcinogen would "significantly pollute drinking water supplies, render drinking water unusable and unsafe, threaten the public health and welfare, and harm other natural resources."

Additionally, the city of Pittsboro, North Carolina, sued Apollo Chemical and others for discharging 1,4-dioxane and per- and polyfluorinated alkyl substances into the Haw River and its tributaries. Ten years ago, these chemicals were found to have migrated into Pittsboro's drinking water supplies but no regulation has been adopted to-date to regulate the use and manufacture of these contaminants. Currently, Pittsboro is spending enormous sums on specialized treatment systems and customers are bearing the costs.

Discharges to Surface Water

1,4-dioxane can enter a publicly owned treatment works as a constituent of industrial and domestic wastewater. Most wastewater treatment plants are not designed for the removal of 1,4-dioxane, so it can pass through the treatment system and enter surface waters within the effluent discharge. EPA has not published surface water quality criteria for 1,4-dioxane protective of human health and the environment under Section 304(a) of the Clean Water Act, but some wastewater permits do specify discharge limits. For example, to industries and wastewater treatment plants discharging to the Cape Fear River Basin in North Carolina have reissued National Pollutant Discharge Elimination System (NPDES) permits containing an in-stream target value of 0.35 μg/L in surface waters classified as water supplies, or at the boundary of a water supply water for sources above a drinking water classification, and 80 μg/L in all other surface waters. Other examples can be found in states such as Pennsylvania and Illinois.

Treatment Technologies

1,4-dioxane's high miscibility and low volatility makes it challenging to remove from polluted water. Often, advanced treatment beyond conventional remediation approaches is required to remove 1,4-dioxane. According to the Interstate Technology Regulatory Council, there are three treatment processes that have varying degrees of efficacy in treating 1,4-dioxane:

- Advanced oxidation processes (AOPs);
- Ozone (under certain conditions); and
- Reverse osmosis (RO).

AOPs are a group of technologies that use the highly reactive hydroxyl radical to destructively remove organic contaminants and are the only fully demonstrated technologies available for 1,4-dioxane treatment in drinking water and groundwater. Additionally, ozone (under some conditions) and RO were found to remove 1,4-dioxane at various efficacies in laboratory studies and full-scale plants. For groundwater (including drinking water) and wastewater treatment systems impacted by 1,4-dioxane, a combination of pre-treatment and treatment options will need to be evaluated by engineers experienced in water quality and treatment technologies.

As an example, engineers at environmental consultant AlterEcho recently evaluated two tandem remedial processes for addressing a groundwater plume containing 1,4-dioxane: *in situ* chemical oxidation and *ex situ* advanced oxidation processes. These processes were bench-tested and field pilot-tested and a comparative analysis of each technology was performed to ensure compliance with statutory requirements and technical and policy considerations. To date, AlterEcho's engineering team has completed a design for two additional groundwater extraction, treatment and reinjection systems, utilizing advanced oxidation units for the treatment of 1,4-dioxane and are currently installing them in tandem with existing VOC groundwater treatment systems. After installation, the O&M Team will need to operate, maintain and monitor the systems for several years until cleanup standards are achieved.

Conclusions

Although considered an emerging contaminant, 1,4-dioxane has been used for over 160 years and has been found as a ubiquitous contaminant of water. To date, the federal government has not promulgated standards for 1,4-dioxane in drinking water, leaving states to create a patchwork of regulations and guidance that vary widely. Advanced treatment technologies are required to treat 1,4-dioxane because of its unique physical properties. Given the growing, but uneven, state regulatory involvement and heightened awareness at the federal level, it appears that 1,4-dioxane is poised to migrate from emerging contaminant to worrisome toxic pollutant in the years ahead.

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