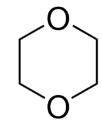
1,4-DIOXANE IN DRINKING WATER

Background



1,4-Dioxane

1,4-Dioxane is a widely used solvent, stabilizer, and purifying agent in a variety of industrial and commercial applications, such as in the manufacture of chlorinated solvents (e.g. 1,1,1-trichloroethane), in products such as adhesives, sealants, paint strippers, dyes, greases, varnishes, waxes, and in the manufacture of pharmaceuticals (U.S. EPA, 2014). In addition to its intentional uses, 1,4-dioxane is also found as impurities in consumer products such as deodorants, shampoos, and cosmetics, and as byproducts during the manufacture of polyethylene terephthalate (PET) plastic. Wastewater discharges, unintended spills, and historical disposal practices have been identified as some of the important sources of 1,4-dioxane in drinking water sources. The chemical is highly soluble in water and has a low sorption coefficient making them highly mobile in groundwater (Table 1). In addition, it is non-volatile and highly resistant to microbial degradation. Hence, conventional water treatment processes (coagulation, sedimentation, filtration) are not effective in removing 1,4-dioxane from waters.

Table 1. Physical and chemical properties of 1,4-dioxane.

Property	Value	Comment
Physical description at room temperature		Clear, flammable liquid with pleasant odor
Molecular weight	88.11 g/mol	
Water solubility	Highly miscible	High mobility in groundwater
Melting point	11.8 ºC	
Boiling point at 760 mm Hg	101.1 ºC	Removal by distillation is difficult and economically infeasible
Vapor pressure at 25 ºC	38.1	Low vapor pressure makes it difficult to remove via air stripping
Henry's law constant at 25 ºC	4.80×10^{-6}	
Organic carbon partition coefficient (log K_{OC})	1.23	Low partitioning makes it difficult to remove via adsorption (e.g. GAC)
Octanol-water partition coefficient (log K_{OW})	-0.27	

Health Concerns and Current Regulations

1,4-Dioxane is classified as probable human carcinogen based on sufficient evidence of carcinogenicity from animal studies (ATSDR, 2012). The chemical has been associated with increased incidences of nasal cavity, liver and gall bladder tumors in animal studies. A risk assessment performed by the U.S. EPA indicates that the drinking water level representing a 1 x 10^{-6} cancer risk for 1,4-dioxane is 0.35 µg L^{-1}. 1,4-Dioxane is a widespread contaminant in Long Island water supplies, with some of the nation's highest concentrations detected here (33 µg L^{-1}) (U.S. EPA, 2012). Analysis of the Unregulated Contaminant Monitoring Rule 3 data from the U.S. EPA revealed that 39 water districts/distribution areas in Long Island had detections of 1,4-dioxane greater than the EPA's cancer risk guideline level of 0.35 µg L^{-1} (CCE, 2017). Currently, there is no established federal maximum contaminant level (MCL) for 1,4-dioxane in drinking water. Based on the 1 in 10^{-6} cancer risk the EPA has calculated a screening level of 0.67 µg L^{-1} in tap water. Some U.S. states have their own clean-up or notification levels as shown in Table 2.

Advanced Oxidation Processes for 1,4-Dioxane Removal

Advanced oxidation processes (AOP) have been shown to be very effective in oxidizing 1,4-dioxane in drinking waters (Stefan and Bolton, 1998; Adams et al., 1994). AOP uses chemical reactions that generate highly reactive short-lived hydroxyl radicals (OH.) that can effectively oxidize organic contaminants. Some typical reactions that produce hydroxyl radicals are (i) ozone (O_3) and hydrogen peroxide (H_2O_2), (ii) O_3 and UV radiation, (iii) H_2O_2 and UV radiation, (iv) titanium dioxide (TiO_2) and UV radiation, and (v) combinations of these technologies. The inherent advantages of AOP over conventional treatment processes, such as adsorption or air stripping, are: (i) contaminants can be completely destroyed, (ii) contaminants that are not adsorbable or volatile can be destroyed, and (iii) oxidation by hydroxyl radicals are not contaminant-specific and hence can oxidize a wide range of compounds rapidly (in some cases this can be a disadvantage as the radicals are consumed by non-target compounds) (Crittenden et al. 2005). The typical chain of reactions showing complete destruction of organic pollutant using AOP is shown below:

Table 2. Summary of U.S. state standards for 1,4-dioxane

State	Standard	Level (μg L^{-1})
California	Notification Level	1
Colorado	Drinking Water Standard	3.2
Connecticut	Action Level	3
Maine	Maximum Exposure Guideline	4
Massachusetts	Guideline	0.3
New Hampshire	Proposed Risk-Based Remediation Value	3
South Carolina	Drinking Water Health Advisory	70
New Jersey	Ground Water Quality Standard	0.4
Florida	Drinking water guideline	0.35
New York	Drinking Water Standard	50*

* Unspecified Organic Contaminant standard. A drinking water quality council is currently working on setting a NYS drinking water standard for 1,4-dioxane.

Organic pollutant (1,4-dioxane) → aldehydes → carboxylic acids
→ carbon dioxide and mineral acids

These byproducts (aldehydes, carboxylic acids etc.) may accumulate in waters if insufficient hydroxyl radicals are generated during treatment. A summary of byproducts observed following AOP of 1,4-dioxane is provided in Table 3 (Stefan and Bolton, 1998).

Table 3. Observed byproducts during AOP of 1,4-Dioxane (Source: Crittenden et al. 2005)

Byproduct	Approximate Yield: Mole Byproduct per Mole 1,4-Dioxane, %
1,2-Ethanediol diformate, formic acid, oxalic acid, glycolic acid, acetic acid, formaldehyde, 1,2-ethanediol monoformate	10–30
Methoxyacetic acid, glyoxal	2–5
Acetaldehyde	<1

Research on 1,4-dioxane at the NYS Center for Clean Water Technology

Research at the New York State Center for Clean Water Technology is focused on developing and evaluating methods to remove emerging contaminants from drinking water supplies, with an initial focus on 1,4-dioxane. The Center has established a pilot program to test the effectiveness and feasibility of AOP and other alternative water treatment technologies to remove 1,4-dioxane from drinking waters. Though AOP technology has been widely studied under laboratory conditions, very few reports are available that evaluate their performances on larger scales (pilot- and full-scale systems). In order to commercialize and use such systems for the treatment of public drinking water, in-depth understanding of the system performance, optimum conditions, source water quality impacts, potential degradation pathways of 1,4-dioxane, and by-product formation in treated waters and in distribution systems are needed. Hence, in addition to the pilot program, research is being conducted to (i) understand the fate and transformation of 1,4-dioxane, and formation of other toxic reaction byproducts during AOP treatment, and (ii) test combination of other treatment techniques with AOP (e.g. Granular Activated Carbon (GAC), Biological Activated Carbon (BAC) etc.) to enhance the removal of 1,4-dioxane and their byproducts.

References

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