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1,4-DIOXANE WHITE PAPER

1,4-dioxane is a synthetic industrial chemical that is completely miscible in water. The largest sources of 1,4-dioxane in drinking water sources are wastewater discharge, unintended spills, leaks, and historical disposal practices of its host solvent, 1,1,1-trichloroethane (TCA). 1,4-dioxane readily dissolves into groundwater, and its movement is not retarded significantly by sorption to soil particles. It is highly mobile, recalcitrant to microbial degradation, and has a low tendency to volatilize from water. Conventional water treatment practices (e.g., coagulation, sedimentation, and filtration), aeration, GAC adsorption, ozone, UV, and biofiltration have proven to be ineffective at removing 1,4-dioxane from water. Advanced oxidation processes including a combination of hydrogen peroxide and ferrous iron, ozone and hydrogen peroxide, and UV and hydrogen peroxide have been shown to be effective for oxidizing 1,4-dioxane.

INDUSTRIAL USES OF 1,4-DIOXANE

1,4-dioxane is used as a stabilizer for chlorinated solvents such as TCA to reduce the degradation of important properties of TCA[1]. Along with its association with solvents, 1,4-dioxane is used in many products, including paint strippers, dyes, greases, varnishes, and waxes. It is also found as an impurity in antifreeze and aircraft deicing fluids as well as in some consumer products (deodorants, shampoos, and cosmetics). It is a by-product in the manufacture of polyethylene terephthalate (PET) plastic and is used as a purifying agent in the manufacture of pharmaceuticals. Finally, 1,4-dioxane residues may be present in manufactured food additives, 1,4-dioxane-containing food packaging materials, or on food crops treated with pesticides that contain 1,4-dioxane (such as vine-ripened tomatoes) (EPA Technical Factsheet, 2013).

HEALTH EFFECTS AND REGULATIONS

Based on evidence in humans and experimental animals, the International Agency for Research on Cancer classified 1,4-dioxane as being a Group B2 carcinogen (probable human carcinogen). Toxicological studies show an increased incidence of nasal cavity and liver carcinomas in rats, liver carcinomas in mice, and gall bladder carcinomas in guinea pigs. Currently, a number of international regulatory guidelines for 1,4-dioxane exist. The World Health Organization suggested a 50 ug/L drinking water threshold value for 1,4-dioxane , whereas the EPA National

[1] TCA production was discontinued in the 1990s due to its ozone depleting properties

Center for Environmental Assessment proposed a health-based advisory level of 3 ug/L in tap water. According to the EPA Integrated Risk Information System, cancer development could occur in 1 out of 1,000,000 people exposed to a concentration of 0.35 ug/L in drinking water over a lifetime. Therefore, UCMR3 set the minimum reporting level for 1,4-dioxane at 0.07 ug/L. In its drinking water regulations, the German Federal Environmental Agency suggested a precautionary guideline limit for weak or non-genotoxic compounds such as 1,4-dioxane of 0.1 ug/L in drinking water. In Japan, an environmental standard for 1,4-dioxane was promulgated at 50 ug/L. Finally, in the United States, several state governments have set varying advisory levels for 1,4-dioxane (Table 1).

Table 1 - Regulatory Guidelines for 1,4-Dioxane in Water

State	**Guideline**	**Concentration (ug/L)**
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
New York Dept. of Health	Drinking Water Standard	50
South Carolina	Drinking Water Health Advisory	70

OCCURRENCE

Occurrence of 1,4-dioxane in surface and groundwater has been reported throughout the United States and in countries such as Japan, Germany, the Netherlands, United Kingdom, and Canada. In Japan, 1,4-dioxane was found in 87% of samples from a survey of surface and groundwater samples at levels up to 95 ug/L. The largest sources of 1,4-dioxane in drinking water sources are wastewater discharge, unintended spills, leaks, and historical disposal practices of its host solvent, TCA. Unlike TCA, 1,4-dioxane readily dissolves into groundwater, and its movement is not retarded significantly by sorption to soil particles. It is highly mobile, recalcitrant to microbial degradation, and has a low tendency to volatilize from water. Recently 1,4-dioxane was included in the Final Third Drinking Water Contaminant Candidate List (CCL3), due to its probable impact as human carcinogen (B2), as classified by the International Agency for Research on Cancer. It is also on included on the third Unregulated Contaminant Monitoring Rule (UCMR3).

UCMR3 MONITORING

The ongoing UCMR3 monitoring will provide a large database to assist in the national occurrence of 1,4-dioxane. Monitoring of more than 5,000 public drinking water supplies began on January 1, 2013 for 28 contaminants. Results from the first year monitoring released in January 2014 are compiled in Table 2 for approximately 1,000 reporting utilities, resulting in ~7,100 samples for 1,4-dioxane (EPA UCMR3 Occurrence Database [2014]). The data, thus far, indicates that almost 12% of the samples have concentrations greater than the method detection level of 0.07 ug/L with 3.9% of samples exceeding 0.35 ug/L (EPA's reference concentration for 10^{-6} cancer risk) (See Figure 1). No samples exceeded 35 ug/L (EPA's reference concentration for 10^{-4} cancer risk). The maximum concentration detected was 9.2 ug/L.

Table 2. First Year of 1,4-dioxane Occurrence Summary

Number of Samples	7,171
Maximum Concentration (ug/L)	9.23
Number of Results > MRL	854
% of Results > MRL	11.9%
Number of Results > Reference Concentration	277
% of Results > Reference Concentration	3.9%

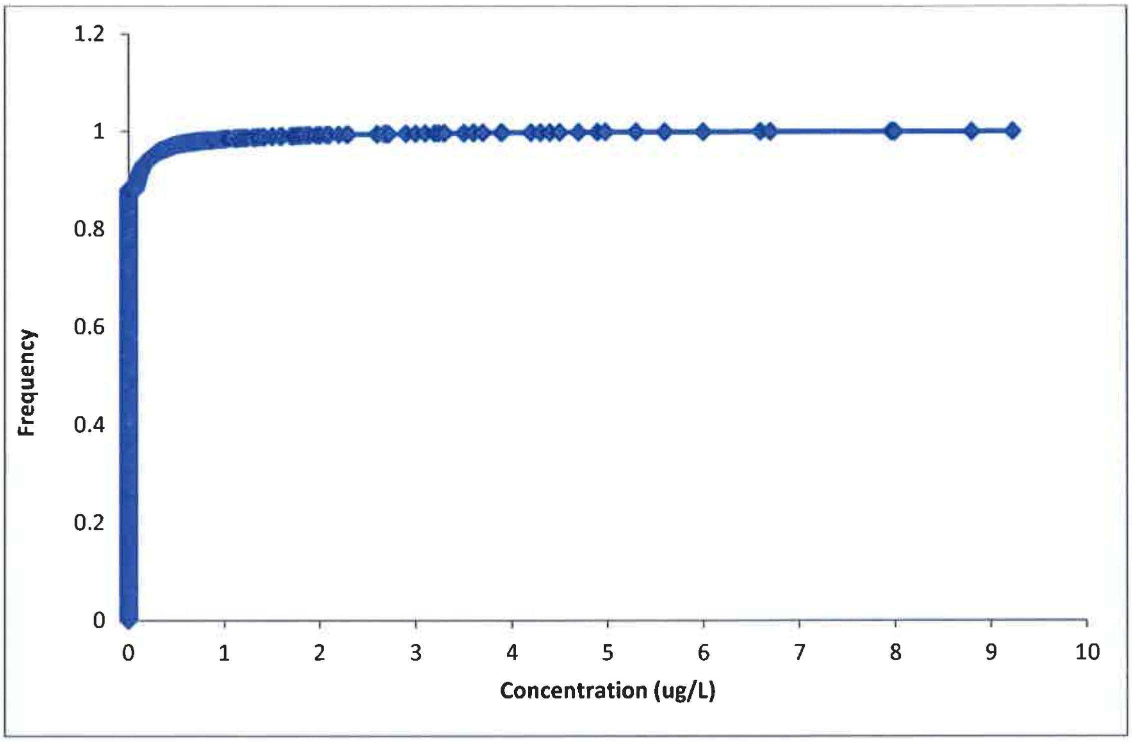

Figure 1. First Year of 1,4-dioxane Occurrence from UCMR3 Database

TREATMENT

Once released into the environment, the physical and chemical properties of 1,4-dioxane make it not only persistent, but difficult to treat (see Table 3 for its physical and chemical properties). Current conventional water treatment practices (e.g., coagulation, sedimentation, and filtration) have proven to be relatively ineffective at removing 1,4-dioxane from water. Its low Henry's Law Constant indicates it will not readily volatilize out of water making it difficult to remove using aeration. Additionally, the unfavorable octanol-water partition coefficient and organic carbon partition coefficient imply that 1,4-dioxane is hydrophilic and cannot be efficiently adsorbed onto activated carbon. Despite the fact that 1,4-dioxane biodegradation has been achieved through bioaugmentation and the use of enriched microbial cultures, limited studies show that conventional biological treatment takes considerable time due to its resistance to biodegradation. Several studies tested ozone or hydrogen peroxide alone for 1,4-dioxane removal and found very minimal removal due to a low reaction rate constant. Finally, in one study, riverbank filtration was shown to be ineffective for removing 1,4-dioxane.

Advanced oxidation processes (AOPs) have been shown to be effective for removing 1,4-dioxane. A combination of hydrogen peroxide and ferrous iron, ozone and hydrogen peroxide, and UV and hydrogen peroxide were found to effectively oxidize 1,4-dioxane.

Other processes shown to be effective for removing 1,4-dioxane include photocatalysis using titanium dioxide, sonication with or without UV irradiation, zero-valent iron, distillation, and electrolysis. However, these techniques have very limited drinking water application and can be prohibitively expensive.

Table 3. Physical and Chemical Properties of 1,4-Dioxane (EPA Technical Factsheet, 2013)

Property	**Value**
CAS Number	000123-91-1
Physical Description (physical state at room temperature)	Flammable liquid with a faint, pleasant odor
Molecular weight (g/mol)	88.11
Water solubility (mg/L at 25°C)	Soluble in water ($4.31 x 10^5$ mg/L)
Boiling point (°C)	101.1 °C at 760 mm Hg
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 Koc)	1.23
Henry's law constant at 25 oC (atm cm^3/mol)	4.80 X 10-6

RESOURCES

CDC 1,4-Dioxane Information Page, http://www.cdc.gov/niosh/topics/1,4-dioxane/

EPA Health Effects Notebook for Hazardous Air Pollutants, 1,4-Dioxane (1,4-Diethyleneoxide), http://www.epa.gov/ttn/atw/hlthef/dioxane.html

EPA Integrated Risk Information System (IRIS), http://www.epa.gov/iris/subst/0326.htm

EPA Technical Factsheet, http://www2.epa.gov/sites/production/files/2014-03/documents/ffrro_factsheet_contaminant_14-dioxane_january2014_final.pdf

EPA Toxicological Review of 1,4-Dioxane, http://www.epa.gov/iris/toxreviews/0326tr.pdf

EPA UCMR3 Occurrence Database, http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/data.cfm#ucmr2013

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EPA Technical Factsheet (2014), http://www2.epa.gov/sites/production/files/2014-03/documents/ffrro_factsheet_contaminant_14-dioxane_january2014_final.pdf, Accessed on April 2014.

EPA UCMR3 Occurrence Database (2014) http://water.epa.gov/lawsregs/rulesregs/sdwa/ucmr/data.cfm#ucmr2013

Mohr, T. K. (2010). *Environmental Investigation and Remediation: 1,4-Dioxane and Other Solvent Stabilizers*. CRC Press.