1,4-Dioxane:
Regulatory Developments, Uses, Properties, Assessment, and Remediation

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Abstract

This paper reviews literature about 1,4-dioxane. It attempts to provide information anticipated to be of interest to Licensed Site Professionals as they deal with this contaminant that has recently received increased attention. First, recent regulatory developments are discussed, followed by a description of the many processes and products that have potentially included 1,4-dioxane. Chemical and physical properties, along with fate and transport consequences, are then summarized and contrasted with those of 1,1,1-trichloroethane, a chlorinated solvent commonly associated with 1,4-dioxane. Challenges and solutions regarding laboratory analysis are reviewed, and the current state of the art of remediation is summarized. An extensive reference list, with live internet links in most cases, concludes the paper.

Regulatory Developments

1,4-Dioxane (dioxane) has received increased attention at the Federal and State levels in recent years. A Federal Maximum Contaminant Level (MCL) has not been established for this chemical, but the U.S. Environmental Protection Agency (USEPA) in February 2008 included dioxane on its list of 104 candidate chemicals for consideration for national drinking water regulation in the future. Some USEPA regions have developed guidelines; for example Regions 3, 6, and 9 all use a guideline of 6.1 micrograms per liter (ug/l) for drinking water in Risk-Based Concentrations (2007), Medium-Specific Screening Levels (2007), and Preliminary Removal Goals (2004), respectively.

Massachusetts Department of Environmental Protection (MADEP) promulgated dioxane standards in the Massachusetts Contingency Plan (MCP), which became effective as of February 14, 2008. These include a new Method 1 GW-1 standard of 3 ug/l for dioxane. (GW-1 standards apply to groundwater at sites in areas where private or public drinking water supplies could be impacted.) Standards relative to vapor intrusion and surface water (GW-2 and GW-3) are 6,000 and 50,000 ug/l, respectively. Method 1 soil standards range from 0.2 to 500 milligrams per kilogram (mg/kg). While the Reportable Quantity of 10 pounds remains unchanged, the Reportable Concentrations have been reduced to 0.003 milligrams per liter (mg/l) for RCG1, 6 mg/l for RCG2, 0.2 mg/kg for RCS1, and 6 mg/kg for RCS2. There is a Drinking Water Guideline (DWG) of 3 ug/l for dioxane in Massachusetts, which became effective in Spring 2006; a previous DWG for dioxane was 50 ug/l (Mohr, 2001). A guideline does not have the force of law. The MADEP Bureau of Resource Protection that regulates public drinking water systems (PWS) is retaining the DWG for dioxane and has not adopted it as an MCL.
Because dioxane only has a guideline and not an MCL, PWS are not required to test for dioxane in their Safe Drinking Water Act compliance sampling programs. In accordance with 2005 revisions of applicable regulations (310 CMR 19.000) landfills are required to test for dioxane with a reporting limit of 3 ug/l, at least for several monitoring rounds. A summary of dioxane standards and guidelines in other Northeast states is included in Appendix A.

**Historical Uses of Dioxane**

Dioxane is used in a wide variety of processes and products. Dioxane has been used primarily as a stabilizer in chlorinated solvents, mainly for 1,1,1-trichloroethane (TCA). Stabilizers scavenge hydrochloric acid produced by the hydrolysis of solvents and oils and prevent the degradation of the solvent. Dioxane has been added to many grades of TCA at 2 to 3 percent by volume, and in some instances, up to 8 percent (Mohr, 2001). While present in industrial grade TCA in relatively small volumes, dioxane becomes concentrated in vapor degreasing wastes due to its higher boiling point (Mohr, 2003a).

USEPA (1995) states that in 1985, 90% of the dioxane produced in the U.S. was used as a chlorinated solvent stabilizer, and that although this application continues to be the primary one, it is quickly being phased out. “In the future, the primary use of dioxane will be as a solvent for various applications, primarily in the manufacturing sector. Other solvent applications include those for cellulose acetates, dyes, fats, greases, lacquers, mineral oil, paints, resins, varnishes, and waxes. Dioxane is also used in paint and varnish strippers, as a wetting agent and dispersing agent in textile processing, dye baths, stain and printing compositions, and in the preparation of histological slides...in cosmetics, deodorants, fumigants, automotive coolant liquid, and scintillation counters.” Other uses noted by USEPA (2006) include as: a surface treating agent for artificial leather, an “inert” ingredient in pesticides and fumigants, a purifying agent in pharmaceuticals, a reaction medium solvent in organic chemical manufacturing, and a solvent in oils, rubber chemicals, sealants, adhesives, and cements. It is also an impurity in antifreeze, including aircraft de-icing fluid formulations.

USEPA in the Contaminant Candidate List (2008) states that dioxane is used as a solvent or solvent stabilizer in the manufacture and processing of paper, cotton, textile products, automotive coolant, cosmetics, and shampoos. The U.S. Centers for Disease Control and Prevention (CDC) Agency for Toxic Substances and Disease Registry (ATSDR) draft toxicological profile for dioxane (CDC, 2004) says the current use of dioxane as a stabilizer of TCA will not be significant.

1,1,1-Trichloroethane. Since dioxane was added to TCA, it is important to review TCA uses for a better understanding about where dioxane may be expected to occur. According to Mohr (2001), “TCE [trichloroethylene] was the preferred solvent used in many industrial applications throughout the fifties and sixties. In the late 1960s, TCE came under increasing scrutiny for occupational exposure because it was identified as an animal carcinogen. As a result, many firms switched to TCA. During the late 1980s and early 1990s, many firms using Freon-113 as a solvent converted to TCA as it is a less potent ozone depleter. Because of the current production
ban on TCA,¹ some firms are now converting back to TCE.” CDC ATSDR (2006) states that TCA was still allowed to be used for essential applications such as medical devices and aviation safety until January 1, 2005, and that in 2002, TCA was still being manufactured in the U.S. in a production volume range of 100 to 500 million pounds. According to an undated USEPA Technical Fact Sheet on TCA, proportions consumed for various uses in 1989 were: vapor degreasing 34%, cold cleaning 12%, aerosols 10%, adhesives 8%, intermediate 7%, coatings 5%, electronics 4%, other 5%, and exports 15%; and major industries reporting Toxic Release Inventory releases to water and land from 1987 to 1993 were: gray iron foundries, aircraft, manufacturing industries, wood furniture, fabricated structural metal, plating and polishing, and turbines and generators.

As an indication of the types of TCA sites that may exist, CDC (2006) states that the largest number of workers is exposed in the following types of industries/services: sewing machine operators in apparel industry; registered nurses, maids, janitors and cleaners in hospitals; electricians; technicians, assemblers, installers, machinists and repairers in electrical and electronic industry; and janitors and cleaners in building maintenance service. Specific industrial applications listed by CDC were: degreasing and cleaning of fabricated metal parts, manufacture of electronic components, mixing and application of commercial resins, and spray painting and spray gluing. TCA is found at 823 of the 1,662 hazardous waste sites nationwide that have been proposed for inclusion on the USEPA National Priorities List (CDC, 2006).

1,1-Dichloroethylene and Trichloroethylene. At some sites, dioxane is also found with 1,1-dichloroethylene (11DCE), because 11DCE is an abiotic degradation product of TCA (Mohr, 2003b). At other sites, dioxane is found with TCE, for example at the Air Force Plant 44 facility in Arizona (National Ground Water Association, 2007). The literature contains conflicting information as to whether dioxane was added to TCE as a stabilizer. Jackson and Dwarakanath (1999) state that it was. By contrast, Mohr (2003a) says that at several locations, the presence of dioxane in TCE-dominated plumes led to the assumption that dioxane was added to TCE. However, closer examination usually indicates that TCE is not the source of dioxane in any appreciable quantities. TCE usually has a stabilizer package made of small quantities of four or more compounds, with most combinations drawn from a list of more than 50 stabilizers. Mohr (2001) states that stabilizers generally comprise less than 1% of TCE and that although numerous articles list dioxane as an additive to TCE, he could not find primary evidence of this.

Properties and Environmental Fate

According to the USEPA (2006), “dioxane is a probable carcinogen and is found as a contaminant in water at sites throughout the United States. The physical properties and behavior of dioxane, including its high mobility and persistence in the environment, make characterization and treatment of this chemical challenging. Its potential risks as a contaminant in groundwater have not been fully identified; the USEPA and most states have not promulgated cleanup levels for dioxane. USEPA and the International Agency for Research on Cancer classify dioxane as a Group B2 (probable human) carcinogen.” For additional information on the toxicology of dioxane, see CDC (2004) and CDC (2007).

¹ TCA was banned by the Montreal Protocol in the 1990s.
Several key chemical and physical properties are summarized in Table 1, along with the properties of TCA for comparison. Compared to TCA, dioxane has a higher boiling point, much higher (infinite) solubility, lower tendency to adsorb (lower organic carbon partitioning coefficient $[K_{oc}]$ and octanol-water partitioning coefficient $[K_{ow}]$, and lower volatility (lower vapor pressure and Henry’s Law Constant).

<table>
<thead>
<tr>
<th>Characteristic/Property</th>
<th>Units</th>
<th>1,4-Dioxane</th>
<th>1,1,1-Trichloroethane</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAS Number</td>
<td>None</td>
<td>123-91-1</td>
<td>71-55-6</td>
</tr>
<tr>
<td>Common Synonyms</td>
<td>None</td>
<td>1,4-diethylene oxide</td>
<td>methylchloroform, chloroethene</td>
</tr>
<tr>
<td>Molecular Formula</td>
<td>None</td>
<td>C_4H_8O_2</td>
<td>C_2H_3Cl_3</td>
</tr>
<tr>
<td>Molecular Weight</td>
<td>amu</td>
<td>88.1</td>
<td>133.4</td>
</tr>
<tr>
<td>Melting Point</td>
<td>ºC at 760 mmHg</td>
<td>11.8</td>
<td>-30.4</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>ºC at 760 mmHg</td>
<td>101.1</td>
<td>74.1</td>
</tr>
<tr>
<td>Water Solubility</td>
<td>mg/l</td>
<td>miscible</td>
<td>950</td>
</tr>
<tr>
<td>Density</td>
<td>g/ml at 20 ºC</td>
<td>1.0329</td>
<td>1.3</td>
</tr>
<tr>
<td>Vapor Density</td>
<td>air=1</td>
<td>3.03</td>
<td>4.54</td>
</tr>
<tr>
<td>$K_{oc}$</td>
<td>Dimensionless</td>
<td>1.23</td>
<td>152</td>
</tr>
<tr>
<td>Log $K_{ow}$</td>
<td>Dimensionless</td>
<td>-0.27</td>
<td>2.49</td>
</tr>
<tr>
<td>Vapor Pressure</td>
<td>mm Hg at 20 ºC</td>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>Flash Point</td>
<td>ºC</td>
<td>5 to 8</td>
<td>none</td>
</tr>
<tr>
<td>Henry’s Law Constant</td>
<td>atm-m³/mol</td>
<td>4.88 x 10⁻⁶</td>
<td>1.72 x 10⁻²</td>
</tr>
</tbody>
</table>


Due to its physical and chemical properties, dioxane is usually one of the most mobile contaminants at solvent release sites, and the footprint of the dioxane plume may be many times larger than the plume of TCA and its breakdown products (Mohr, 2003a). Dioxane plumes have been documented to measure twice the length of the associated solvent plumes and to affect an area up to six times greater (Walsom and Tunnicliffe, 2002).

Dioxane’s properties favor its occurrence in water rather than soil, and in water rather than air. Volatilization from water is a very slow process; when dioxane does enter the atmosphere, it rapidly degrades photolytically, with half-lives of less than 7 hours (NICNAS, 1998). It is resistant to anaerobic and aerobic biodegradation and is chemically stable and will not hydrolyze. The only attenuation processes that apply to dioxane are dilution, dispersion, and to a limited degree, volatilization (Brown and Robinson, 2004). CDC (2004) notes that dioxane does not undergo significant biodegradation in wastewater treatment plants.
Laboratory Analysis

Because of dioxane’s physical and chemical properties, the reporting limit is elevated for this compound if conventional volatile organic compound (VOC) or semi-VOC analytical methods (Methods 8260 or 8270) are used. Typical reporting limits using conventional analysis are in the 10s or 100s of ug/l. An additional challenge is presented in many samples in which other compounds (such as TCA) are present at much higher concentrations, necessitating sample dilution and thus further elevating dioxane reporting limits. Laboratories have developed special techniques modifying Methods 8260 or 8270 to lower the reporting limit to low levels around 1 ug/l. Modifications to Method 8260 may consist of including a moisture control module, adding sodium sulfate to the sample to increase purge efficiency, and heated sparging. Modifications to Method 8270 may include using an isotope dilution standard added to the sample before extraction, followed by liquid-liquid extraction with methylene chloride, and concentration of the extract (Brown and Robinson, 2004). These modifications increase the analytical cost per sample. Historically, dioxane has not been widely detected in environmental samples because of the high reporting limits using conventional methods and the need to modify analytical methods, at higher cost, to detect low concentrations of interest. MADEP’s Compendium of Analytical Methods (2007) includes guidance on 1,4-dioxane analysis.

Remediation

Soil Remediation. USEPA (2006) did not identify any full- or pilot-scale in situ or ex situ soil remediation projects, but indicated that co-solvent extraction with water as a solvent should be effective for in situ or ex situ treatment of soil. Dioxane is theoretically volatile enough to be removed using soil vapor extraction even though its vapor pressure is lower than that of many VOCs; however, dioxane will tend to partition into the soil pore water in the vadose zone, so the system would need to be able to eliminate soil moisture to be effective. With thermal treatment, Brown and Robinson (2004) similarly expect dioxane to volatilize but then readily dissolve into the aqueous phase (soil moisture) once volatilized due to its miscibility and low Henry’s Law Constant. The soil would have to be maintained at elevated temperature much longer for dioxane than for chlorinated VOCs (CVOCs). Steam treatment would also be technically feasible, but dioxane would require higher temperatures and longer treatment times than CVOCs. Phytoremediation theoretically could be used for soil remediation.

Ex Situ Groundwater Remediation. Dioxane is well suited to groundwater extraction due to its high solubility and low tendency to adsorb. However, ex situ treatment options are limited and may be different than for associated compounds such as CVOCs. Its low tendency to adsorb makes granular activated carbon (GAC) adsorption inappropriate, although one full-scale GAC application was identified by USEPA (2006); it was thought that the unexpected success could be attributed to low influent concentrations, low flow rate, and/or possible biodegradation on GAC surfaces in the presence of tetrahydrofuran. Air stripping is inappropriate due to dioxane’s low Henry’s Law Constant. Reverse osmosis is expected to be ineffective due to the dioxane’s small physical size (Bowman, 2008). A fixed-film bioreactor was used at a site in Colorado; testing indicated that dioxane was biodegraded as a co-metabolite in the presence of tetrahydrofuran to effluent concentrations less than 200 ug/l in a pilot test; performance data for
the full-scale system were not available (USEPA, 2006). Papers about bioreactor treatment at
two dioxane sites are planned for the upcoming Battelle Sixth International Conference on
Remediation of Chlorinated and Recalcitrant Compounds (Evans et al., 2008; Plaehn et al.,
2008). Phytoremediation in aboveground hydroponic treatment systems is another possible
option (USEPA, 2006).

Advanced oxidation appears to be the most commonly employed full-scale ex situ dioxane
treatment technology, particularly using hydrogen peroxide with ozone or hydrogen peroxide
with ultraviolet (UV) light. Full-scale treatment at five sites using hydrogen peroxide with ozone
and four sites using hydrogen peroxide with UV light was reviewed; effluent data that were
available for all but one site were all below 10 ug/l (USEPA, 2006). Ozone with UV light,
photocatalysis employing titanium dioxide and UV light, and Fenton’s reagent (USEPA, 2006)
are other possibilities, although USEPA did not identify any sites where these methods were
used. High energy electron beam and ultrasonic cavitation have also been mentioned as options.

In Situ Groundwater Remediation. Brown and Robinson (2004) review the effectiveness of in
situ groundwater treatment technologies that are commonly used for treating CVOC
contamination for treating dioxane contamination as well. Like air stripping, air sparging is
ineffective for dioxane. Microcosm studies indicate that aerobic co-metabolic bioremediation is
promising; anaerobic bioremediation has not been effective. Experimental data indicate that
zero-valent iron walls will be ineffective for dioxane.

In situ chemical oxidation (ISCO) is effective for dioxane remediation. Hydrogen peroxide with
ozone has been used at a number of sites (USEPA Region 9, 2007; Sadeghi et al., 2006; Haley &
Adlrich, 2005). Fenton’s reagent (ferrous sulfate and hydrogen peroxide), permanganate,
persulfate, and ozone have been demonstrated successfully in bench testing (Brown and
Robinson, 2004), if not at full scale.

An in-well technology combining in situ air stripping, air sparging, soil vapor extraction,
bioremediation, and groundwater circulation has been pilot-tested at a field site.
Phytoremediation is also being investigated for dioxane removal. Processes potentially at work
in phytoremediation of dioxane include uptake of water, followed by metabolism or
volatilization of dioxane from leaves, as well as biodegradation of dioxane in the rhizosphere
(root zone of the plants) (USEPA, 2006).

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References


APPENDIX A
1,4-DIOXANE STANDARDS AND GUIDELINES IN OTHER NORTHEAST STATES

New Hampshire has had an Ambient Groundwater Quality Standard (AGQS) for 1,4-dioxane (dioxane) of 3 micrograms per liter (ug/l) since 2005. Although all groundwater in the state is considered drinking water, a Maximum Contaminant Level (MCL) has not been developed for dioxane; therefore, public water systems are not required to test for it as part of their Safe Drinking Water Act compliance sampling. Despite the AGQS, people assessing sites have often not analyzed groundwater samples for dioxane using appropriately sensitive methods. To rectify this problem, the New Hampshire Department of Environmental Services (NHDES) issued a letter on January 30, 2008, and updated February 28, 2008, requiring volatile organic compound (VOC) analyses for hazardous waste sites, salvage yards, and landfills to include low-level analysis for dioxane. In addition, dioxane analysis is required at some petroleum sites with potential discharges of waste oil, industrial solvents, automotive antifreeze, paints, lacquers, or varnishes; analysis at petroleum sites is also required if dioxane was identified as a Tentatively Identified Compound (TIC) in a VOC analysis. The required quantitation limit is 3 ug/l for groundwater and 0.5 ug/l for drinking water.

New Jersey uses an Interim Specific Groundwater Criterion of 3 ug/l for dioxane, which is based on the $10^{-6}$ cancer risk level and the USEPA IRIS carcinogen weight of evidence and slope factor (Post, 2008).

Rhode Island Department of Environmental Management (RIDEM) does not have standards for dioxane. In the absence of RIDEM standards, USEPA Region 3, 6, or 9 guidelines are used (Kulpa, 2008). Region 3 Risk-Based Concentrations, Region 6 Medium-Specific Screening Levels, and Region 9 Preliminary Removal Goals (PRGs) all list 6.1 ug/l as a guideline for dioxane in drinking water.

Connecticut has a drinking water guideline of 20 ug/l, and the Connecticut Regulated Criteria Table, which is an update of the Remediation Standard Regulations of 1996, also lists 20 ug/l for dioxane as a site-specific standard.

Vermont has an Enforcement Standard of 20 ug/l (VTDEC, 2005).

Maine uses a cleanup level of 32 ug/l as a Maine Exposure Guideline (Jones, 2008).

New York considers dioxane an Unspecified Organic Contaminant, for which a standard of 50 ug/l applies (Rivara, 2008).
References


Jones, Joan. 2008. Maine Department of Environmental Protection. Personal communication.

Kulpa, Paul. 2008. RIDEM. Personal communication.


Post, Gloria. 2008. New Jersey Department of Environmental Protection. Personal communication.
