

# Reconsideration of 1,4-Dioxane as an Emerging Contaminant of Interest

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## PROBLEM

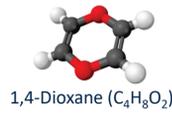
For more than two decades now, the presence of 1,4-Dioxane in the environment has had increasing focus by many regulatory agencies across the United States, based on its designation by the United States Environmental Protection Agency ("USEPA") as "likely to be carcinogenic to humans" by all routes of exposure and an excess cancer risk ( $10^{-6}$ ) is associated with a drinking water concentration of 0.35 µg/L.

### CHEMICAL PROPERTIES

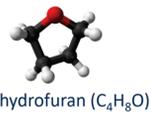
- Chemical Name and Synonyms: 1,4-dioxane, para-dioxane, dioxane, 1,4-diethylenedioxiide; 1,4-dioxacyclohexane; 1,4-dioxane (*French*); di(ethyleneoxide); diethylene dioxide; diethylene ether; dioksan (*Polish*); diossano-1,4 (*Italian*); dioxaan-1,4 (*Dutch*); dioxan; dioxan-1,4 (*German*); dioxane; dioxane-1,4; dioxane (*French*); dioxyethylene ether; glycol ethylene ether; para-dioxane; p-dioxan (*Czech*); p-dioxane; p-dioxin, tetrahydro-; tetrahydro-1,4-dioxin; tetrahydro-para-dioxin; tetrahydro-p-dioxin.
- Molecular Weight (g/mol): 88.111; Density (g/mL): 1.033;
- Melting Point: 11.8°C; Boiling Point: 101.1 °C;
- Vapor Pressure (25°C): 38.1 mmHg; Log  $K_{ow}$  -0.27; Henry's Law Constant (25°C):  $4.88 \times 10^{-6}$  atm-cm<sup>3</sup>/mole

### WHAT IS IT AND WHERE DOES IT COME FROM?

1,4-Dioxane is an ether similar to methyl-tert-butyl ether ("MTBE") and tetrahydrofuran ("THF") and has many of the same physical properties. The chemical is a cyclic ether that is highly miscible in water.



1,4-Dioxane is a volatile, colorless liquid with a mild pleasant odor and relatively low volatility. It is highly flammable and potentially explosive if not stored properly.



It is highly soluble in a wide variety of matrices including; water, alcohol, ether, most organic solvents, aromatic hydrocarbons, and oils.

Environmentally, it is very soluble and highly mobile in groundwater, but does not adsorb well to soil particles and does not readily biodegrade.

### USES

- 1,4-Dioxane has been used as a minor or major ingredient in many applications, and is also generated as an unwanted by-product of industrial processes associated with the manufacturing of polyethylene, nonionic surfactants, and many consumer products. It is one of several stabilizers historically used in industry to enhance the functional life of solvents.
- In 1995, according to USEPA nearly 90% of 1,4-Dioxane produced commercially in the US was used as a stabilizer for chlorinated solvents, in particular 1,1,1-trichloroethane ("TCA") at up to 8% by volume.
- The remaining 10% of 1,4-Dioxane is used in a wide variety of commercial applications and formulations including:
  - Degreasing agent, as a component in paint and varnish removers, as a wetting agent in the textile industry, as a solvent in chemical synthesis. Fluid for scintillation counting, as an additive in deicing fluids, and as a solvent in coatings, sealants, adhesives, and pharmaceuticals.
  - Was or is currently present in detergents, shampoos, deodorants, cosmetics, antifreeze, and is found in many landfill leachates. Surfactants containing 1,4-Dioxane are used in a wide variety of products including foods, cosmetics, and detergents.
  - Residues can be present in food packaged in 1,4-Dioxane-containing materials, or on food crops treated with pesticides containing 1,4-Dioxane. USEPA has noted 1,4-Dioxane as a component in vine-ripened tomatoes and tomato products, fresh shrimps, brewed coffee, and fried chicken.

## CONCERNS

### ENVIRONMENTAL OCCURRENCE

1,4-Dioxane has been manufactured since the 1950's and has been found in surface and groundwater throughout the US and other countries. In Japan, 1,4-Dioxane was identified in 87% of samples from a survey of surface and groundwater samples at levels up to 95 µg/L.

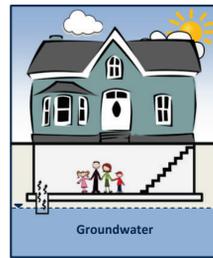
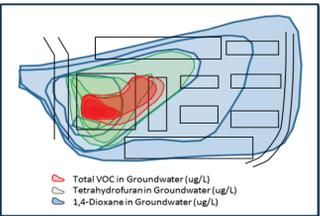
The largest reported sources of 1,4-Dioxane in drinking water sources are wastewater discharge, unintended spills, leaks, and historical disposal practices of its host solvent, TCA.

As of 2007, 1,4-Dioxane had been identified at more than 31 sites on the USEPA National Priorities List ("NPL"), though it may be present (but samples were not analyzed) at many other sites. Concentrations as high as 300 mg/L identified in groundwater at the Pall/Gelman site in Michigan.



1,4-Dioxane is released into the environment during its production, the processing of other chemicals, its use and its generation as an impurity during the manufacture of some consumer products.

- It is short-lived in the atmosphere, with an estimated 1- to 3-day half-life as a result of its reaction with photochemically produced hydroxyl radicals.
- Breakdown products include aldehydes and ketones.
- It readily mixes with water and can generally be found in groundwater plumes far in advance of any solvents with which it might have entered the subsurface originally.
- Migration to groundwater is weakly retarded by sorption of 1,4-Dioxane to soil particles; it is expected to move rapidly from soil to groundwater.
- Historically, the discovery of 1,4-Dioxane at cleanup sites often occurred well after the completion of site characterization and remedial design, complicating implementation of effective remedial measures for the compound.
- Recent USEPA data identifies frequently detected 1,4-Dioxane in U.S. drinking water derived from both groundwater and surface water.



- Exposure may occur through inhalation of vapors, ingestion of contaminated food and water or dermal contact.
- Groundwater and vapor intrusion are processes by which contaminants can partition from contaminated groundwater and into overlying buildings.
- Inhalation is the most common route of human exposure, and workers at industrial sites are at greatest risk of repeated inhalation exposure.

### TREATMENT

Conventional treatment systems have been ineffective at removing 1,4-Dioxane to site cleanup levels or drinking water advisory limits in the case of well-head treatment. The compound does not respond to air stripping or granular activated carbon treatment, nor does it biodegrade in the subsurface other than very slowly. It does not bioconcentrate in the food chain.

Researchers are developing new treatment technologies for 1,4-Dioxane. Advanced oxidation processes involving hydrogen peroxide and ultraviolet light or ozone have been applied successfully. Distillation is physically viable, but the relatively high boiling point (101°C) makes this approach generally uneconomical for most applications.

## METHOD 1624B (USEPA, 1984)

### METHOD SUMMARY

- This method determines the concentration of 1,4-Dioxane in water and wastewater using an analyte-optimized version of USEPA 1624B, which is based upon dynamic headspace purge-and-trap concentration followed by conventional GC/EI-MS detection and isotope dilution calibration.
- As currently implemented, this method is sensitive enough, and has adequate accuracy and precision, to address regulatory compliance values based upon the one-in-a-million excess cancer risk concentration associated with lifetime consumption of drinking water (0.35 ppb).

### INSTRUMENT SYSTEMS and ANALYTICAL CONDITIONS

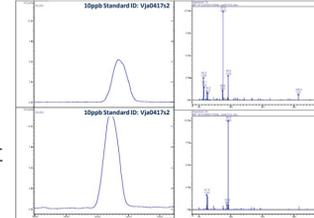
#### Xylem/OI Analytical 4660 Dynamic Purge & Trap Concentrator w/ Heater Module

- Sample volume: 5.0 mL
- Purge temperature: 50 °C
- Trap: Tenax
- Purge flow and time: 60 mL/min helium for 18 minutes
- Dry purge flow and time: 60 mL/min helium for 6 minutes
- Trap desorb temperature: 200 °C
- Trap bake temperature: 220 °C

#### Varian 3900 Gas Chromatograph

- Column: Restek RTX-624 (60m x 0.32 mm id, 1.8 micron film)
- Carrier gas: helium at 1.2 mL/min
- Injector split ratio:
  - Initial 2.0 minutes: 1:6
  - Balance of run: 1:20
- Transfer line temperature: 110 °C
- Injector temperature: 150 °C
- Temperature program:
  - Initial: 4.0 minutes at 32 °C
  - Ramp: 32 °C to 180 °C at 10 °C/minute
  - Final: 3.5 minutes at 180 °C

#### GC/MS Chromatogram and Mass Spectra



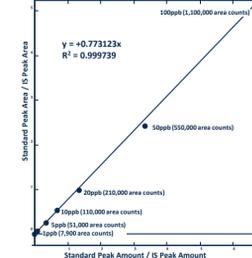
#### Varian 2100T Ion Trap Mass Spectrometer

- Mode: Full scan EI/MS
- Scan range: 50-250 amu
- Scan time: 0.5 second
- Filament delay: 12 minutes
- Total acquisition time: 16.5 minutes
- Tune verification: FC43

### CALIBRATION WORKING RANGE AND MDL

- The instrument system is calibrated over an analyte working range of 1 to 100 ppb.
  - Curve Fit: Linear
  - Origin: Forced
  - Curve Weighting: 1/x<sup>2</sup>
  - Response Factor RSD: 8.481%
  - Coefficient of Determination (R<sup>2</sup>): 0.9999739

#### Calibration Curve



- The performance validated Method Detection Limit (MDL) is 0.3 ppb.

Method Detection Limit (MDL) Study	QA/QC Acceptance Criteria
Replicate #1 (ug/L)	2.141
Replicate #2 (ug/L)	2.144
Replicate #3 (ug/L)	2.136
Replicate #4 (ug/L)	2.316
Replicate #5 (ug/L)	2.371
Replicate #6 (ug/L)	2.151
Replicate #7 (ug/L)	2.368
Standard Concentration (ug/L)	2.000
Average (ug/L)	2.232
Standard Deviation	0.1130
Percent Difference	10.5
Calculated MDL (ug/L)	0.3553
Continuing Calibration Verification (CCV)	90 - 110%
CCV Internal Standard (area)	50 - 150%
Laboratory Fortified Blank (10ppb)	80 - 120%
Matrix Spike / Matrix Spike Duplicate (10ppb)	80 - 120%
Precision	<20% RPD

## CONCLUSIONS

- ATS has performance validated analysis of 1,4-Dioxane using USEPA Method 1624B as a method framework.
- The Method Detection Limit (MDL) for 1,4-Dioxane is reduced by a factor of 30x from that given in 1624B by optimizing the analytical conditions for recovery and quantitation of an analyte that has a boiling point of 101°C, and is miscible with water. This analyte-specific method optimization is applicable to other water soluble analytes listed in USEPA 1624B.
- As currently implemented the statistically-derived MDL of 0.35 ppb.
- Precision for the method as currently implemented at the 2.0 ppb level is +/- 10%.
- Advantages of the method over USEPA Method 8270 are:
  - Lower complexity
  - Better sensitivity
  - Better precision
  - May be run in the same laboratory and on the same equipment as conventional VOCs
  - Reduced worker exposure to methylene chloride
- Advantages of the method over USEPA Method 522 are:
  - Lower complexity
  - Lower cost
  - Suitable to a wider range of water and wastewater matrices
  - May be run in the same laboratory and on the same equipment as conventional VOCs
  - Reduced worker exposure to methylene chloride
- Opportunities exist to push the MDL for 1,4-Dioxane even lower through the use of the following:
  - Selective Ion Storage (SIS) mode of operation
  - EI/MS/MS mode of operation
  - Higher purge temperatures
  - "Salting out" to increase purge efficiency

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