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May 29, 2018

MEMORANDUM

To: Solid Waste Directors, Landfill Owners/Operators, and North Carolina Certified

Laboratories

From: Ed Mussler, Section Chief

North Carolina Division of Waste Management, Solid Waste Section

Re: 1,4-Dioxane Analysis, Solid Waste Section Limits, and Laboratory Analytical

Methods

1,4-Dioxane Sampling

In accordance with 15A NCAC 13B .0601, .0544, and .1632, the Solid Waste Section (Section) is requiring that all groundwater and surface water samples collected at landfills after July 1, 2018 be analyzed for the constituent 1,4-Dioxane. It is primarily used as a stabilizer for chlorinated solvents, however also used in many products including paint strippers, dyes, greases, varnishes and waxes. Additionally, it is found in a variety of consumer products such as detergents, shampoos, deodorants, and cosmetics. **The current 15A NCAC 02L .0202 Standard for 1,4-Dioxane is 3.0 μg/l.** Due to the potential health hazards associated with 1,4-Dioxane, the Section has determined that all landfills should begin analyzing groundwater and surface water samples for 1,4-Dioxane to ensure protection of human health and the environment. A USEPA Technical Fact Sheet for 1,4-Dioxane is provided in Appendix A of this Memorandum.

Solid Waste Section Limits & Laboratory Analytical Methods

In 2006, the Solid Waste Section made a policy decision to develop and use Solid Waste Section Limits (SWSLs). The purpose for this policy decision was to ensure that low level analytical data was consistently being reported for the purpose of making the correct choices when designing site remediation strategies, alerting the public to health threats, and protecting the environment from toxic contaminants. Over the past 12 years, technologies have advanced such that the majority of the SWSLs are outdated. Given the rapid pace of technology, the need for the Section to attempt to continuously update and/or maintain the SWSLs is not warranted.

Although the use of the SWSLs will be discontinued, facilities should choose EPA approved analytical methods sufficiently sensitive to quantify the presence of a pollutant at or below applicable standards. Consistently achieving low level data is key for the continued purpose of making the correct choices when designing site remediation strategies, alerting the public to health threats, and protecting the environment from toxic contaminants. Facilities should communicate and coordinate with their analytical laboratory(s) to use sufficiently sensitive analytical methods to achieve analytical results with detection limits below the applicable groundwater standards and surface water standards. For guidance purposes, the Section recommends the use of the following analytical methods for groundwater and surface water samples.

Volatile Organic Compounds	SW 846 Method 8260
1,4-Dioxane	SW 846 Method 8260 SIM
	SW 846 Method 8270 SIM
Semi-Volatile Organic	SW 846 Method 8270
Compounds	
Metals, Pesticides, PCBs,	SW 846 Methods, USEPA
Dioxins, Cyanide,	methods, or method published
Formaldehyde, and any other	in Standard Methods for the
constituents not covered by	Examination of Water and
above methods	Wastewater having the lowest
	detection limits or having
	detection limits below
	applicable standards

Notes:

- The analytical methods should be the most recent versions of the analytical methods tabulated above. For SW- 846 Methods, the latest edition of SW-846, including any subsequent updates which have been incorporated into the edition, must be used. Sampling must be planned so that required holding times for analytical methods are met.
- Select Ion Monitoring (SIM) is recommended when analyzing for 1,4-Dioxane in order to achieve applicable detection limits. SIM may be useful for other VOCs/SVOC constituents.
- SW-846 Method 1610 does not have detection limits below the 15A NCAC 2L standards for all of the hazardous substance list metals.
- The Section considers "J" flag values valid and relevant in the decision making process and hence all "J" flag values should be reported.

If you have any questions, please contact Adam Ulishney at (919) 707-8210 or via email at adam.ulishney@ncdenr.gov. Thank you for your cooperation in this matter.

APPENDIX A





TECHNICAL FACT SHEET - 1,4-DIOXANE

At a Glance

- Flammable liquid and a fire hazard. Potentially explosive if exposed to light or air.
- Found at many federal facilities because of its widespread use as a stabilizer in certain chlorinated solvents, paint strippers, greases and waxes.
- Short-lived in the atmosphere, may leach readily from soil to groundwater, migrates rapidly in groundwater and is relatively resistant to biodegradation in the subsurface.
- Classified by the EPA as "likely to be carcinogenic to humans" by all routes of exposure.
- Short-term exposure may cause eye, nose and throat irritation; long-term exposure may cause kidney and liver damage.
- No federal maximum contaminant level (MCL) has been established for 1,4-dioxane in drinking water.
- Federal screening levels, state health-based drinking water guidance values and federal occupational exposure limits have been established.
- Modifications to existing sample preparation procedures may be required to achieve the increased sensitivity needed for detection of 1,4-dioxane.
- Common treatment technologies include advanced oxidation processes and bioremediation.

Introduction

This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Federal Facilities Restoration and Reuse Office (FFRRO), provides a summary of the contaminant 1,4-dioxane, including physical and chemical properties; environmental and health impacts; existing federal and state guidelines; detection and treatment methods; and additional sources of information. This fact sheet is intended for use by site managers who may address 1,4-dioxane at cleanup sites or in drinking water supplies and for those in a position to consider whether 1,4-dioxane should be added to the analytical suite for site investigations.

1,4-Dioxane is a likely human carcinogen and has been found in groundwater at sites throughout the United States. The physical and chemical properties and behavior of 1,4-dioxane create challenges for its characterization and treatment. It is highly mobile and has not been shown to readily biodegrade in the environment.

What is 1,4-dioxane?

- 1,4-Dioxane is a synthetic industrial chemical that is completely miscible in water (EPA 2006).
- Synonyms include dioxane, dioxan, p-dioxane, diethylene dioxide, diethylene oxide, diethylene ether and glycol ethylene ether (EPA 2006; Mohr 2001).
- 1,4-Dioxane is unstable at elevated temperatures and pressures and may form explosive mixtures with prolonged exposure to light or air (DHHS 2011; HSDB 2011).
- 1,4-Dioxane is a likely contaminant at many sites contaminated with certain chlorinated solvents (particularly 1,1,1-trichloroethane [TCA]) because of its widespread use as a stabilizer for chlorinated solvents (EPA 2013a; Mohr 2001)
- It is used as: a stabilizer for chlorinated solvents such as TCA; a solvent for impregnating cellulose acetate membrane filters; a wetting and dispersing agent in textile processes; and a laboratory cryoscopic solvent for molecular mass determinations (ATSDR 2012; DHHS 2011; EPA 2006).
- It is used in many products, including paint strippers, dyes, greases, varnishes and waxes. 1,4-Dioxane is also found as an impurity in antifreeze and aircraft deicing fluids and in some consumer products (deodorants, shampoos and cosmetics) (ATSDR 2012; EPA 2006; Mohr 2001).

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What is 1,4-dioxane? (continued)

- 1,4-Dioxane is used as a purifying agent in the manufacture of pharmaceuticals and is a byproduct in the manufacture of polyethylene terephthalate (PET) plastic (Mohr 2001).
- Traces of 1,4-dioxane may be present in some food supplements, food containing residues from packaging adhesives or on food crops treated with pesticides that contain 1,4-dioxane as a solvent or inert ingredient (ATSDR 2012; DHHS 2011).

Exhibit 1: Physical and Chemical Properties of 1,4-Dioxane

(ATSDR 2012; Howard 1990; HSDB 2011)

Property	Value
Chemical Abstracts Service (CAS) Number	123-91-1
Physical Description (physical state at room temperature)	Clear, flammable liquid with a faint, pleasant odor
Molecular weight (g/mol)	88.11
Water solubility	Miscible
Melting point (°C)	11.8
Boiling point (°C) at 760 mm Hg	101.1 °C
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 °C (atm-m³/mol)	4.80 X 10 ⁻⁶

Abbreviations: g/mol – grams per mole; °C – degrees Celsius; mm Hg – millimeters of mercury; atm-m³/mol – atmosphere-cubic meters per mole.

What are the environmental impacts of 1,4-dioxane?

- 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 typically found at some solvent release sites and PET manufacturing facilities (ATSDR 2012; Mohr 2001).
- 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 (ATSDR 2012; DHHS 2011). Breakdown products include aldehydes and ketones (Graedel 1986).
- It may migrate rapidly in groundwater, ahead of other contaminants and does not volatilize rapidly

- from surface water bodies (DHHS 2011; EPA 2006).
- 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 (EPA 2006; ATSDR 2012).
- It is relatively resistant to biodegradation in water and soil and does not bioconcentrate in the food chain (ATSDR 2012; Mohr 2001).
- As of 2007, 1,4-dioxane had been identified at more than 31 sites on the EPA National Priorities List (NPL); it may be present (but samples were not analyzed for it) at many other sites (HazDat 2007).

What are the routes of exposure and the health effects of 1,4-dioxane?

- Potential exposure could occur during production and use of 1,4-dioxane as a stabilizer or solvent (DHHS 2011).
- Exposure may occur through inhalation of vapors, ingestion of contaminated food and water or dermal contact (ATSDR 2012; DHHS 2011).
- Inhalation is the most common route of human exposure, and workers at industrial sites are at greatest risk of repeated inhalation exposure (ATSDR 2012; DHHS 2011).

What are the routes of exposure and the health effects of 1,4-dioxane? (continued)

- 1,4-Dioxane is readily adsorbed through the lungs and gastrointestinal tract. Some 1,4-dioxane may also pass through the skin, but studies indicate that much of it will evaporate before it is absorbed. Distribution is rapid and uniform in the lung, liver, kidney, spleen, colon and skeletal muscle tissue (ATSDR 2012).
- Short-term exposure to high levels of 1,4dioxane may result in nausea, drowsiness, headache, and irritation of the eyes, nose and throat (ATSDR 2012; EPA 2013b; NIOSH 2010).
- Chronic exposure may result in dermatitis, eczema, drying and cracking of skin and liver and kidney damage (ATSDR 2012; HSDB 2011).
- 1,4-Dioxane is weakly genotoxic and reproductive effects in humans are unknown; however, a developmental study on rats indicated that 1,4-dioxane may be slightly toxic to the developing fetus (ATSDR 2012; Giavini and others 1985).

- Animal studies showed increased incidences of nasal cavity, liver and gall bladder tumors after exposure to 1,4-dioxane (DHHS 2011; EPA IRIS 2013).
- EPA has classified 1,4-dioxane as "likely to be carcinogenic to humans" by all routes of exposure (EPA IRIS 2013).
- The U.S. Department of Health and Human Services states that 1,4-dioxane is reasonably anticipated to be a human carcinogen based on sufficient evidence of carcinogenicity from studies in experimental animals (DHHS 2011).
- The American Conference of Governmental Industrial Hygienists (ACGIH) has classified 1,4-dioxane as a Group A3 carcinogen confirmed animal carcinogen with unknown relevance to humans (ACGIH 2011).
- The National Institute for Occupational Safety and Health (NIOSH) considers 1,4-dioxane a potential occupational carcinogen (NIOSH 2010).

Are there any federal and state guidelines and health standards for 1,4-dioxane?

- Federal and State Standards and Guidelines:
 - EPA's Integrated Risk Information System (IRIS) database includes a chronic oral reference dose (RfD) of 0.03 milligrams per kilogram per day (mg/kg/day) based on liver and kidney toxicity in animals and a chronic inhalation reference dose (RfC) of 0.03 milligrams per cubic meter (mg/m³) based on atrophy and respiratory metaplasia inside the nasal cavity of animals (EPA IRIS 2013).
 - The Agency for Toxic Substances and Disease Registry (ATSDR) has established minimal risk levels (MRLs) for inhalation exposure to 1,4-dioxane: 2 parts per million (ppm) for acute-duration (14 days or less) inhalation exposure; 0.2 ppm for intermediate-duration (15 to 364 days) inhalation exposure; and 0.03 ppm for chronic-duration (365 days or more) inhalation exposure (ATSDR 2012).
 - Oral exposure MRLs have been identified as 5 mg/kg/day for acute-duration oral exposure; 0.5 mg/kg/day for intermediateduration oral exposure; and 0.1 mg/kg/day for chronic-duration oral exposure (ATSDR 2012).

- The cancer risk assessment for 1,4-dioxane is based on an oral slope factor of 0.1 mg/kg/day and the drinking water unit risk is 2.9 x 10⁻⁶ micrograms per liter (μg/L) (EPA IRIS 2013).
- EPA risk assessments indicate that the drinking water concentration representing a 1 x 10⁻⁶ cancer risk level for 1,4-dioxane is 0.35 μg/L (EPA IRIS 2013).
- 1,4-Dioxane may be regulated as hazardous waste when waste is generated through use as a solvent stabilizer (EPA 1996b).
- No federal maximum contaminant level (MCL) for drinking water has been established; however, an MCL is not necessary to determine a cleanup level (EPA 2012).
- 1,4-Dioxane was included on the third drinking water contaminant candidate list, which is a list of unregulated contaminants that are known to, or anticipated to, occur in public water systems and may require regulation under the Safe Drinking Water Act (EPA 2009).

Are there any federal and state guidelines and health standards for 1,4-dioxane? (continued)

- Federal and State Standards and Guidelines (continued):
 - The EPA has established drinking water health advisories for 1,4-dioxane, which are drinking water-specific risk level concentrations for cancer (10⁻⁴ cancer risk) and concentrations of drinking water contaminants at which noncancer adverse health effects are not anticipated to occur over specific exposure durations. The EPA established a 1-day health advisory of 4.0 milligrams per liter (mg/L) and a 10-day health advisory of 0.4 mg/L for 1,4-dioxane in drinking water for a 10-kilogram child. EPA also established a lifetime health advisory of 0.2 mg/L for 1,4-dioxane in drinking water (EPA 2012).
 - The EPA's drinking water equivalent level for 1,4-dioxane is 1 mg/L (EPA 2012).
 - EPA has calculated a screening level of 0.67 μg/L for 1,4-dioxane in tap water, based on a 1 in 10⁻⁶ lifetime excess cancer risk (EPA 2013c).
 - EPA has calculated a residential soil screening level (SSL) of 4.9 milligrams per kilogram (mg/kg) and an industrial SSL of 17 mg/kg. The soil-to-groundwater risk-based SSL is 1.4 x10⁻⁴ mg/kg (EPA 2013c).
 - EPA has also calculated a residential air screening level of 0.49 micrograms per cubic meter (μg/m³) and an industrial air screening level of 2.5 μg/m³ (EPA 2013c).

- Workplace Exposure Limits:
 - The Occupational Safety and Health Administration set a general industry permissible exposure limit of 360 mg/m³ or 100 ppm based on a time-weighted average (TWA) over an 8-hour workday for airborne exposure to 1,4-dioxane (OSHA 2013).
 - The ACGIH set a threshold limit value of 72 mg/m³ or 20 ppm based on a TWA over an 8-hour workday for airborne exposure to 1,4-dioxane (ACGIH 2011).
 - The NIOSH has set a ceiling recommended exposure limit of 3.6 mg/m³ or 1 ppm based on a 30-minute airborne exposure to 1,4-dioxane (NIOSH 2010).
 - NIOSH also has established an immediately dangerous to life or health concentration of 500 ppm for 1,4-dioxane (NIOSH 2010).
- Other State and Federal Standards and Guidelines:
 - Various states have established drinking water and groundwater guidelines, including the following:
 - Colorado has established an interim groundwater quality cleanup standard of 0.35 µg/L (CDPHE 2012);
 - California has established a notification level of 1 μg/L for drinking water (CDPH 2011);
 - New Hampshire has established a reporting limit of 0.25 μg/L for all public water supplies (NH DES 2011); and
 - Massachusetts has established a drinking water guideline level of 0.3 μg/L (Mass DEP 2012).
 - The Food and Drug Administration set 10 mg/kg as the limit for 1-4-dioxane in glycerides and polyglycerides for use in products such as dietary supplements. FDA also surveys raw material and products contaminated with 1,4-dioxane (FDA 2006).
 - 1,4-Dioxane is listed as a hazardous air pollutant under the Clean Air Act (CAA) (CAA 1990).
 - A reportable quantity of 100 pounds has been established under the Comprehensive Environmental Response, Compensation, and Liability Act (EPA 2011).

¹ Screening Levels are developed using risk assessment guidance from the EPA Superfund program. These risk-based concentrations are derived from standardized equations combining exposure information assumptions with EPA toxicity data. These calculated screening levels are generic and not enforceable cleanup standards but provide a useful gauge of relative toxicity.

² Tap water screening levels differ from the IRIS drinking water concentrations because the tap water screening levels account for dermal, inhalation and ingestion exposure routes; age-adjust the intake rates for children and adults based on body weight; and time-adjust for exposure duration or days per year. The IRIS drinking water concentrations consider only the ingestion route, account only for adult-intake rates and do not time-adjust for exposure duration or days per year.

What detection and site characterization methods are available for 1,4-dioxane?

- As a result of the limitations in the analytical methods to detect 1,4-dioxane, it has been difficult to identify its occurrence in the environment. The miscibility of 1,4-dioxane in water causes poor purging efficiency and results in high detection limits (ATSDR 2012; EPA 2006).
- Conventional analytical methods can detect 1,4-dioxane only at concentrations 100 times greater than the concentrations of volatile organic compounds (EPA 2006; Mohr 2001).
- Modifications of existing analytical methods and their sample preparation procedures may be needed to achieve lower detection limits for 1,4-dioxane (EPA 2006; Mohr 2001).
- High-temperature sample preparation techniques improve the recovery of 1,4-dioxane. These techniques include purging at elevated temperature (EPA SW-846 Method 5030); equilibrium headspace analysis (EPA SW-846 Method 5021); vacuum distillation (EPA SW-846 Method 8261); and azeotrophic distillation (EPA SW-846 Method 5031) (EPA 2006).
- The presence of 1,4-dioxane may be expected at sites with extensive TCA contamination; therefore, some experts recommend that groundwater samples be analyzed for 1,4-dioxane where TCA is a known contaminant (Mohr 2001).
- NIOSH Method 1602 uses gas chromatography flame ionization detection (GC-FID) to determine the concentration of 1,4-dioxane in air. The detection limit is 0.01 milligram per sample (ATSDR 2012; NIOSH 2010).
- EPA SW-846 Method 8015D uses gas chromatography (GC) to determine the concentration of 1,4-dioxane in environmental samples. Samples may be introduced into the GC column by a variety of techniques including the injection of the concentrate from azeotropic distillation (EPA SW-846 Method 5031). The detection limits for 1,4-dioxane in aqueous

- matrices by azeotropic microdistillation are 12 μ g/L (reagent water), 15 μ g/L (groundwater) and 16 μ g/L (leachate) (EPA 2003).
- EPA SW-846 Method 8260B detects 1,4-dioxane in a variety of solid waste matrices using GC and mass spectrometry (MS). The detection limit depends on the instrument and choice of sample preparation method (ATSDR 2012; EPA 1996a).
- A laboratory study is underway to develop a passive flux meter (PFM) approach to enhance the capture of 1,4-dioxane in the PFM sorbent to improve accuracy. The selected PFM approach will be field tested at 1,4-dioxane contaminated sites. The anticipated projection completion date is 2014 (DoD SERDP 2013b).
- EPA Method 1624 uses isotopic dilution gas chromatography – mass spectrometry (GC-MS) to detect 1,4-dioxane in water, soil and municipal sludges. The detection limit for this method is 10 μg/L (ATSDR 2012; EPA 2001b).
- EPA SW-846 Method 8270 uses liquid-liquid extraction and isotope dilution by capillary column GC-MS. This method is often modified for the detection of low levels of 1,4-dioxane in water (EPA 2007, 2013a)
- GC-MS detection methods using solid phase extraction followed by desorption with an organic solvent have been developed to remove 1,4-dioxane from the aqueous phase. Detection limits as low as 0.024 μg/L have been achieved by passing the aqueous sample through an activated carbon column, following by elution with acetonedichlormethane (ATSDR 2012; Kadokami and others 1990).
- EPA Method 522 uses solid phase extraction and GC/MS with selected ion monitoring for the detection of 1,4-dioxane in drinking water with detection limits ranging from 0.02 to 0.026 μg/L (EPA 2008).

What technologies are being used to treat 1,4-dioxane?

- Pump-and-treat remediation can treat dissolved 1,4-dioxane in groundwater and control groundwater plume migration, but requires ex situ treatment tailored for the unique properties of 1,4-dioxane (such as, a low octanol-water partition coefficient that makes 1,4-dioxane hydrophilic) (EPA 2006; Kiker and others 2010).
- Commercially available advanced oxidation processes using hydrogen peroxide with ultraviolet
- light or ozone is used to treat 1,4-dioxane in wastewater (Asano and others 2012; EPA 2006).
- A study is under way to investigate facilitatedtransport enabled in situ chemical oxidation to treat 1,4-dioxane-contamined source zones and groundwater plumes effectively. The technical approach consists of the co-injection of strong oxidants (such as ozone) with chemical agents that facilitate the transport of the oxidant (DoD SERDP 2013d).

What technologies are being used to treat 1,4-dioxane? (continued)

- Ex situ bioremediation using a fixed-film, movingbed biological treatment system is also used to treat 1,4-dioxane in groundwater (EPA 2006).
- Phytoremediation is being explored as a means to remove the compound from shallow groundwater. Pilot-scale studies have demonstrated the ability of hybrid poplars to take up and effectively degrade or deactivate 1,4-dioxane (EPA 2001a, 2013a; Ferro and others 2013).
- Microbial degradation in engineered bioreactors has been documented under enhanced conditions or where selected strains of bacteria capable of degrading 1,4-dioxane are cultured, but the impact of the presence of chlorinated solvent cocontaminants on biodegradation of 1,4-dioxane needs to be further investigated (EPA 2006, 2013a; Mahendra and others 2013).
- Results from a 2012 laboratory study found 1,4-dioxane-transforming activity to be relatively common among monooxygenase-expressing bacteria; however, both TCA and 1,1-dichloroethene inhibited 1,4-dioxane degradation by bacterial isolates (DoD SERDP 2012).
- Several Department of Defense Strategic Environmental Research and Development Program (DoD SERDP) projects are under way to investigate 1,4-dioxane biodegradation in the presence of chlorinated solvents or metals. Laboratory studies will (1) identify microbial cultures as well as biogeochemistry, which

- generate desirable enzymatic activity for 1,4-dioxane biodegradation; (2) assess biodegradation by methane oxidizing bacteria in coupled anaerobic-aerobic zones; (3) and evaluate branched hydrocarbons as stimulants for the in situ cometabolic biodegradation of 1,4-dioxane and its associated co-contaminants (DoD SERDP 2013c, e and f).
- Photocatalysis has been shown to remove 1,4-dioxane in aqueous solutions. Laboratory studies documented that the surface plasmon resonance of gold nanoparticles on titanium dioxide (Au – TiO₂) promotes the photocatalytic degradation of 1,4-dioxane (Min and others 2009; Vescovi and others 2010).
- Other in-well combined treatment technologies being assessed include air sparging; soil vapor extraction (SVE); and dynamic subsurface groundwater circulation (Odah and others 2005).
- SVE is known to remove some 1,4-dioxane, but substantial residual contamination is usually left behind because of 1,4-dioxane's high solubility, which leads to preferential partitioning into pore water rather than vapor. The DoD SERDP is conducting a project to evaluate and demonstrate the efficacy of enhanced or extreme SVE, which uses a combination of increased air flow, sweeping with drier air, increased temperature, decreased infiltration and more focused vapor extraction to enhance 1,4-dioxane remediation in soils (DoD SERDP 2013a).

Where can I find more information about 1,4-dioxane?

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Where can I find more information about 1,4-dioxane? (continued)

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- Massachusetts Department of Environmental Protection (Mass DEP). 2012. "Standards and Guidelines for Contaminants in Massachusetts Drinking Waters." www.mass.gov/dep/water/dwstand.pdf
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Where can I find more information about 1,4-dioxane? (continued)

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Additional information on 1,4-dioxane can be found at www.cluin.org/contaminantfocus/default.focus/sec/1,4-Dioxane/cat/Overview

Contact Information

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