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Fact Sheet

Guidance on Sampling and Analysis for 1,4-Dioxane at Disposal Sites Regulated under the Massachusetts Contingency Plan

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INTRODUCTION

This Fact Sheet, prepared by MassDEP's Bureau of Waste Site Cleanup, provides guidance regarding when it is appropriate to sample and analyze for 1,4-dioxane at disposal sites regulated under the Massachusetts Contingency Plan (MCP), focusing on 1,4-dioxane in groundwater. It also provides a summary of physical and chemical properties, environmental health impacts, state and federal standards and guidelines, and appropriate analytical methods for 1,4-dioxane.

BACKGROUND INFORMATION

What is 1,4-dioxane?

1,4-Dioxane is a volatile, flammable, colorless liquid at room temperature. The physical and chemical properties and behavior of 1,4-dioxane create challenges for its characterization and treatment in the environment as it is highly soluble in water, does not bind to soils, and readily leaches to groundwater. It is also resistant to naturally occurring biodegradation processes.

Human Exposure and Potential Health Effects

The U.S. Environmental Protection Agency (EPA) has classified 1,4-dioxane as a likely human carcinogen, with the potential to cause nasal and liver tumors. Noncarcinogenic effects include effects on the nervous system, liver and kidney. For cases of environmental contamination, the most important route of exposure with respect to dose and risk is ingestion of contaminated water.

Sources of 1,4-Dioxane at MCP Sites

1,4-Dioxane is a manufactured chemical that does not occur naturally in the environment. Commercial production of 1,4-dioxane was first reported in 1951.

Historically, 1,4-dioxane was primarily used as a stabilizer and corrosion inhibitor for chlorinated solvents, especially 1,1,1-trichloroethane (TCA). Degreasing formulations of TCA containing from approximately 1.0 to 10% by volume of 1,4-dioxane for metal cleaning operations have been documented in scientific literature. Wastewater discharges, unintended spills, leaks, and historical TCA disposal practices are the largest sources of 1,4-dioxane contamination in groundwater and drinking water sources. On January 1, 1996, under the Clean Air Act, the EPA banned TCA production, with selected exceptions for existing stocks and essential uses. As a result, 1,4-dioxane is no longer used as a stabilizer in TCA, but it is still widely manufactured and distributed in the U.S. for other purposes.

Currently identified processes and product uses/sources of 1,4-dioxane (Mohr, 2001 and USDHHS, 2002) include the following:

Processes	Product Uses/Sources
<ul style="list-style-type: none">• Stabilizer in chlorinated solvents used for degreasing, electronics manufacturing, and metal finishing• Solvent for specific applications in biological procedures (histology)• Solvent used in impregnating cellulose acetate membranes used as filters• Wetting and dispersing agent in textile processes• Solvent used in microscopy• Reaction medium solvent in organic chemical manufacturing• By-product formed during esterification of polyester	<ul style="list-style-type: none">• Solvent in paints, lacquer, and varnish remover• Solvent in stain and printing compositions• Solvent in liquid scintillation counters• Surface treating agent for artificial leather• Impurity in antifreeze, including aircraft de-icing fluid formulations• “Inert” ingredient in pesticides and fumigants• Purifying agent in pharmaceuticals• Solvent in resins, oils, rubber chemicals, sealants, adhesives, waxes and cements

The co-occurrence of 1,4-dioxane and trichloroethylene (TCE) has been the subject of debate. A 2012 study by the US Air Force aimed at determining the extent to which 1,4-dioxane co-occurs with TCE as compared to TCA examined a large data set from 49 U.S. Air Force installations (Anderson et al., 2012). It found 1,4-dioxane in 17% of groundwater monitoring wells with detections of TCA and/or TCE. Nearly 94 percent of all 1,4-dioxane detections were

co-located with TCE and/or TCA, confirming that, at U.S. Air Force installations, 1,4-dioxane is seldom found without chlorinated solvent contamination. Additionally, 64% of all 1,4-dioxane detections were associated with TCE alone. These results indicate that 1,4-dioxane is a relatively common groundwater contaminant with both TCE and TCA.

Non-MCP Sources of 1,4-Dioxane

1,4-Dioxane present in products used by both residential and commercial/industrial users can also enter the environment via the wastewater stream and septic systems. Its presence in the environment from wastewater/septic systems would typically not be regulated under the MCP.

1,4-Dioxane is found in some cosmetics, shampoos, soaps and detergents. It is a contaminant that forms as part of a secondary reaction when ethylene oxide is added during the manufacturing process to make the cleaning agents in personal care products less harsh or abrasive. Its occurrence as a by-product in cosmetics is decreasing as the result of revised manufacturing formulations.

Materials used in environmental sampling can be a source of 1,4-dioxane contamination. 1,4-Dioxane has been found in detergents used as leak detection solutions during the construction of monitoring wells. 1,4-Dioxane is also present in surfactants used to decontaminate environmental sampling equipment. Use of these surfactants, therefore, could potentially impact analytical results if sampling equipment is insufficiently rinsed during decontamination.

1,4-Dioxane residues may be present in manufactured food additives, 1,4-dioxane-containing food packaging materials, or on crops treated with pesticides that contain 1,4-dioxane (such as vine-ripened tomatoes).

Standards and Guidelines

MassDEP has promulgated the following Method 1 groundwater and soil standards for 1,4-dioxane (effective June 20, 2014):

Method 1 Groundwater Standards

GW-1: 0.3 µg/L	GW-2: 6,000 µg/L	GW-3: 50,000 µg/L
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Method 1 Soil Standards

S-1/GW-1: 0.2 mg/kg	S-1/GW-2: 6 mg/kg	S-1/GW-3: 20 mg/kg
S-2/GW-1: 0.2 mg/kg	S-2/GW-2: 6 mg/kg	S-2/GW-3: 90 mg/kg
S-3/GW-1: 0.2 mg/kg	S-3/GW-2: 6 mg/kg	S-3/GW-3: 500 mg/kg

Since 2011, Massachusetts has had a drinking water guideline (ORSG) for 1,4-dioxane of 0.3 µg/L, applicable to public water supplies under 310 CMR 22.00: The Massachusetts Drinking Water Regulations.

No federal drinking water standards have been established for 1,4-dioxane. The EPA is currently collecting drinking water frequency and occurrence data to determine if establishing a maximum contaminant level (MCL) is warranted under the Safe Drinking Water Act based on the occurrence of 1,4-dioxane in drinking water, the number of people potentially being exposed, observed exposure levels and costs for treatment to reduce levels.

1,4-DIOXANE SAMPLING AND ANALYSIS CONSIDERATIONS AT MCP SITES

When to Sample for 1,4-Dioxane in Groundwater

Groundwater sampling for 1,4-dioxane should be considered at locations where the following manufacturing activities may have occurred or where related wastes have come to be located:

- **Facilities** where chlorinated solvents have been manufactured or used and have resulted in contamination to groundwater.
- **Laboratories** where 1,4-dioxane may have been used as a reagent. (Laboratories should be disposing of excess chemicals as hazardous waste, but reagents could also end up in septic systems and leach fields of laboratories located in areas not served by sewers).
- **Landfills** where leaching of 1,4-dioxane from the disposal of products that contain it has resulted in contamination to groundwater.
- **Military sites** where the historic use of 1,4-dioxane as an additive to chlorinated solvent formulations has resulted in groundwater contamination.
- **Airports** that have used de-icing fluids.

Note: For landfills and other solid waste facilities regulated under 310 CMR 16.00: Site Assessment for Solid Waste Facilities, some of these facilities may be required to sample for 1,4-dioxane as part of their permit.

When to Sample for 1,4-Dioxane in Soil or Drinking Water

The need to sample soil or drinking water for 1,4-dioxane will depend on case-specific conditions and the Conceptual Site Model. Because 1,4-dioxane does not readily bind to soil, soil samples may be of limited utility, particularly for historic releases. The need for drinking water samples (i.e., from a public or private drinking water well or tap) would be indicated where plume delineation shows potential impacts to a drinking water well.

Field/Equipment Blanks

When sampling for 1,4-dioxane, it is recommended that additional and/or more frequent field/equipment blanks be collected prior to and during sampling to ensure no residual 1,4-dioxane remains on sampling equipment.

Considerations for Source and Plume Delineation

At some solvent release sites, 1,4-dioxane has been found to migrate considerably farther in groundwater than solvents such as TCA or its breakdown products due its complete miscibility and resistance to biodegradation. Therefore, during the assessment of the extent of chlorinated volatile organic compounds (CVOCs) in groundwater, sampling for 1,4-dioxane further downgradient of the edge of the CVOc plume should be considered.

Plume delineation should be sufficient to determine the location of the source of 1,4-dioxane contamination. Because household/consumer products such as shampoos and detergents are known to contain high levels of 1,4-dioxane and can enter the environment through wastewater treatment plants and septic systems, assessment activities should ascertain where relevant, whether the source of 1,4-dioxane is from a release regulated under the MCP and M.G.L. Chapter 21E or from other sources, such as septic systems.

An accurate determination of horizontal and vertical groundwater flow and the depth of the contamination source can be critical in locating the potential occurrence of 1,4-dioxane in groundwater and distinguishing a disposal site source from a septic system source. With respect to investigations in areas with septic systems and potential/known impacts to residential wells, the depth of the initial detection of 1,4-dioxane near the source area should be evaluated relative to the depth of contamination downgradient from the source of 1,4-dioxane. Like chlorinated solvents, 1,4-dioxane may migrate underneath surface water bodies. A thorough evaluation of subsurface characteristics and development of the Conceptual Site Model is important to ensure a complete and accurate assessment of the nature and extent of 1,4-dioxane source areas and plume migration.

Analytical Methods and Reporting Limits

Conventional Analytical Techniques

When using conventional analytical techniques, the high solubility of 1,4-dioxane in water results in poor purging efficiency and high detection and Reporting Limits. Conventional analytical techniques can detect 1,4-dioxane in aqueous and solid samples, but at concentrations 100 times greater than the concentrations of other volatile organic compounds. Modifications of analytical methods and sample preparation procedures are needed, therefore, to achieve adequate Reporting Limits for evaluating 1,4-dioxane relative to MCP standards.

1,4-Dioxane is included on the Massachusetts Compendium of Analytical Method (CAM) analyte lists of WSC-CAM-II A¹ and WSC-CAM-II B² for SW-846 methods 8260B and 8270D, respectively.

- For WSC-CAM-II A (the 8260B method), the conventional (ambient temperature) purge-and-trap analytical method with full scan monitoring is able to achieve a Reporting Limit for 1,4-dioxane in aqueous samples that ranges from 200-500 µg/L. This Reporting Limit is too high for analyses of GW-1 areas or plumes that may migrate into GW-1 areas (the Method 1 GW-1 standard for 1,4-dioxane is 0.3 µg/L). For solid samples analyzed using this conventional method, the Reporting Limit for 1,4-dioxane ranges from 0.2 – 0.5 mg/kg, which is too high for the Method 1 S-1/GW-1, S-2/GW-1 and S-3/GW-1 standards, all of which are 0.2 mg/kg.

The Reporting Limit for 1,4-dioxane in aqueous samples is significantly lower (2 µg/L) using SW-846 method 8260B with heated (80 ± 5°C) purge-and-trap and GC/MS analysis in selective ion monitoring (SIM) mode, but still too high for analyses of GW-1 areas or plumes that may migrate into GW-1 areas.

- For WSC-CAM-II B (the 8270D method), the conventional method with full scan monitoring is able to achieve a Reporting Limit for 1,4-dioxane in aqueous samples ranges from 5 -10 µg/L, which is also too high for analyses of GW-1 areas or plumes that may migrate into GW-1 areas. It should be noted that the analysis of 1,4-dioxane in solid samples using the 8270D method is not allowed under the CAM protocol.

Special Analytical Techniques

In accordance with the CAM protocols, if 1,4–dioxane is a contaminant of concern for the site, special analytical techniques must be used to achieve the Reporting Limit for 1,4-dioxane in groundwater and soil in or with the potential to impact GW-1 areas. The different techniques available for each matrix are described below.

Special Analytical Techniques for Groundwater Samples

- Extraction using SW-846 methods 3510C or 3535A followed by isotope dilution GC/MS analysis in SIM mode using SW-846 method 8270D, as outlined in Appendix II B-4 of WSC-CAM-II B.

¹ Massachusetts WSC-CAM-II A method protocol is titled *Quality Control Requirements and Performance Standards for the Analysis of Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*

² Massachusetts WSC-CAM-II B method protocol method is titled *Quality Control Requirements and Performance Standards for the Analysis of Semivolatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS) in Support of Response Actions under the Massachusetts Contingency Plan (MCP)*

- Some laboratories have modified EPA Method 522 for the analysis of groundwater (instead of drinking water). EPA Method 522 requires specific chemical preservation techniques that include the use of sodium sulfite for dechlorination followed by the addition of sodium bisulfate as a microbial inhibitor. When this method is used for groundwater, modifications are performed only to accommodate routine groundwater sampling and chemical preservation techniques (hydrochloric acid to pH <2) while still adhering to analytical and quality control requirements of EPA Method 522. If EPA Method 522 is modified in this manner, **it cannot be used for the analysis of public water systems**. If the modified EPA Method 522 is used for groundwater (non-public water systems), the laboratory should be consulted on their ability to achieve project-required Reporting Limits as well as any possible modifications to the method to overcome matrix interferences. Since EPA Method 522 is not included in the CAM, a detailed QA/QC evaluation and a separate Initial Demonstration of Capability, as described in the method, are necessary to document data usability in accordance with 310 CMR 40.1056(2)(k). Additional guidance on documenting usability for "non-CAM" analytical data is also provided in Section 7.1.2 and Appendix II of the *MCP Representativeness Evaluations and Data Usability Assessments Policy #WSC-07-350*.

Special Analytical Techniques for Soil/Sediment Samples

- Heated ($80 \pm 5^{\circ}\text{C}$) purge-and-trap with GC/MS analysis in SIM mode by SW-846 Method 8260B. The quality control requirements and performance standards for this technique are covered under WSC-CAM-II A. However, if elevated concentrations of CVOCs are present in the sample, this may not be a preferable approach due to the likely contamination/saturation of the trap during analysis. The use of this technique for soil/sediment samples should be considered when trying to achieve S-1/GW-1, S-2/GW-1 and S-3/GW-1 standards as the moisture content of the samples will cause the Reporting Limits to exceed the standards in most cases if the standard 8260B technique is employed.

Drinking Water Samples

- For drinking water samples **from a public drinking water supply**, EPA Method 522 must be used as this is the only analytical method approved by the EPA for the analysis of 1,4-dioxane in public water supplies. This method employs solid-phase extraction followed by GC/MS analysis in SIM mode. EPA Method 522 is the most sensitive of the 1,4-dioxane analytical methods.
- For drinking water samples from a private water supply well or tap connected to a private water supply well, either SW-846 Method 8270D with SIM/isotope dilution, as outlined in Appendix II B-4 of WSC-CAM-II B, or EPA Method 522 may be used to achieve a Reporting Limit low enough to assess compliance with the GW-1 standard. Because the 8270D with SIM/isotope dilution method has a CAM protocol, it has the benefit of

established QA/QC for the purpose of evaluating data usability in accordance with 310 CMR 40.1056(2)(k). Where EPA Method 522 is used, a separate Initial Demonstration of Capability, as described in the method, is necessary to document data usability under the MCP.

Summary of 1,4-Dioxane Reporting Limits		
Analytical Technique	Typical Aqueous Reporting Limits	Typical Solid Reporting Limits
SW-846 8260B (ambient purge-and-trap with full scan GC/MS)	200 - 500 µg/L	0.2 - 0.5 mg/kg
SW-846 8260B (heated purge-and-trap with SIM)*	2 µg/L	0.002 - 0.005 mg/kg
SW-846 8270D (with full scan GC/MS)	5 - 10 µg/L	NA
SW-846 8270D (with SIM/isotope dilution)*	0.15 - 0.2 µg/L	NA
EPA Method 522*	0.05 µg/L	NA
NA – Not applicable; not allowed under the CAM or applicable only to drinking water * Special Analytical Techniques		

References

Anderson RH, Anderson JK, Bower PA, (2012, October). "Co-occurrence of 1,4-dioxane with trichloroethylene in chlorinated solvent groundwater plumes at US Air Force installations: Fact or fiction." *Integrated Environmental Assessment and Management*, 8(4):731-7.

Mohr, T.K.G. (2001, June 14). "Solvent Stabilizers White Paper." Santa Clara Valley Water District of California. San Jose, California.

USDHHS. (2002, December). "Report on Carcinogens." Public Health Service, National Toxicology Program. Tenth Edition.