1,4-Dioxane Sampling Fact Sheet

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Contaminated Site Remediation & Redevelopment
New Jersey Department of Environmental Protection

What is 1,4-Dioxane?

1,4-Dioxane (CASRN 123-91-1) (also known as dioxane, p-dioxane, diethylene oxide, 1,4-diethylene dioxide, and glycol ethylene ether) is a synthetic organic compound used in various industrial applications as a solvent. 1,4-Dioxane has mostly been used as a stabilizer for 1,1,1-Trichloroethane. In addition, it has been used as a solvent in the production of a variety of organic chemicals found in paints, lacquers, dyes, antifreeze, deodorants, shampoos, cosmetics, as a food additive and in the formulation of pesticides and food packaging adhesives. Refer to the Interstate Technology Regulatory Council's (ITRC's) History of Use and Potential Source website for specifics. A list of 1,4-Dioxane sampling resources and information can be found below:

- ITRC's History of Use and Potential Sources
- EPA's Technical Fact Sheet - 1,4-Dioxane
- ITRC's Sampling and Analysis 1,4-Dioxane
- NJDEP's Field Sampling Procedures Manual
- ATSDR Toxicological Profile for 1,4-Dioxane

Properties of 1,4-Dioxane

Due to its miscibility in water, 1,4-Dioxane should not accumulate at the water table or exhibit Light Non-Aqueous Phase Liquid (LNAPL) properties (i.e., floating on the water table). 1,4-Dioxane has a density of 1.03 g/cm^3, similar to that of water. When discharged by itself or as a component of an aqueous wastewater, 1,4-Dioxane should not behave like a Dense Non-Aqueous Phase Liquid (DNAPL). As such, one of the principal uses of 1,4-Dioxane is as an additive for the stabilization of 1,1,1- Trichloroethane (1,1,1-TCA). 1,1,1-TCA has a density of 1.35 g/cm^3 and can exhibit DNAPL behavior when discharged in high concentrations. When associated with a discharge of 1,1,1-TCA, the depth occurrence in ground water of 1,4-Dioxane may mimic that of the associated 1,1,1-TCA. Accordingly, when sampling for 1,4-Dioxane, one should consider the nature of the 1,4-Dioxane discharge. 1,4-Dioxane is not significantly removed by conventional treatment technologies (i.e., air stripping and carbon absorption) due to its miscibility in water, and it does not have a strong affinity for soil/sediment. These actions are a function of 1,4-Dioxane's chemical properties and provide support for how 1,4-Dioxane should be handled during sampling. For general sampling information, see Chapter 6 of the FSPM.

For a summary of current drinking water treatment options for removal of 1,4-Dioxane, see below table from Appendix C of the New Jersey Drinking Water Quality Institute Treatment Subcommittee Recommendations on 1,4-Dioxane Treatment Options for Drinking Water. For additional information on remediation and treatment technologies for soil, ground water, and wastewater, see ITRC's 1,4-Dioxane Remediation and Treatment Technologies.

Treatment Option		Notes	Removal Rates
Advanced Oxidation Process (AOP)	Ultraviolet Irradiation & Hydrogen Peroxide	Ultraviolet irradiation combined with hydrogen peroxide.	Up to > 99% removal[1]
	Ozone & Hydrogen Peroxide	Ozone combined with hydrogen peroxide.	Up to > 99% removal[1]
	Ultraviolet Irradiation & Ozone	Ultraviolet irradiation combined with ozone.	Up to 98% removal[1]
	Ultraviolet Irradiation & Free Chlorine/Chloramines	Full scale study treating water reclamation effluent.	> 68% removal[3]
Membrane Separation	Reverse Osmosis (RO)	Membrane separation varied in its effectiveness for removing 1,4-dioxane, using spiral-wound type membranes.	RO in combination with other filtration methods yields a more effective result rather than using a solitary RO treatment.
	Nanofiltration (NF)	Membrane separation varied in its effectiveness for removing 1,4-dioxane.	~46% removal[1]
Activated Carbon	Granular Activated Carbon (GAC)	Pilot-scale study suggests the hydrophilic nature of the contaminant will reduce efficiency. No data pertaining to full-scale treatment was found.	18% removal in pilot-scale test.[1] 56% removal when GAC was applied downstream of a reverse osmosis (RO).[1]
Synthetic Media Sorption Units	AMBERSORB™ 560	Full scale contaminated ground water remediation system.	Up to > 99% removal[2]

[1]USEPA, 2020; [2]Woodard et al., 2014; [3]Royce et al., 2015

Analytical Methods

Selection of 1,4-Dioxane analytical methods can be complex, based on multiple factors, and should include consultation with the certified laboratory. A project specific Quality Assurance Project Plan (QAPP) should be developed, including development of Data Quality Objectives (DQOs) and preparation of a Sampling and Analysis Plan, pursuant to the NJDEP Technical Requirements for Site Remediation (N.J.A.C. 7:26E-2.2). Refer to the NJDEP Office of Quality Assurance (OQA) website for preparation of a QAPP, accessing the QAPP template developed by OQA, and accessing the QAPP checklist.

Refer to NJDEP Office of Quality Assurance (OQA) for information on the types of laboratory certification offered.

A list of NJDEP certified laboratories performing 1,4-Dioxane analysis can be accessed using NJDEP DataMiner. Search Laboratories Certified by Parameters by choosing Dioxane (1,4) as the parameter.

The selection of sample analytical methods for a project includes consideration of several factors, such as sample matrix, target analyte report list, sample preparation protocols, analytical instrumentation, analytical method options, analytical method sensitivity, laboratory certification, project application (or purpose), and data quality objectives. Certified commercial laboratories provide pre-cleaned sampling containers for the analytical method selected for the project. Note: sample container sizes and volumes may vary by laboratory for select analytical methods. The laboratory should be contacted for details. Refer to the table below for a summary of some of the 1,4-Dioxane analytical method options. Refer to Chapter 2 -

Quality Assurance and Chapter 3- Contaminants of Emerging Concern of the Field Sampling Procedures Manual (FSPM), as well as Chapter 2 of the FSPM training materials for additional information.

Method #	**522**	**8260**	**8260-SIM**	**8270-SIM**	**8270-SIM ID**
Issued By	USEPA	USEPA	USEPA	USEPA	USEPA
Date Published	2008	2006, rev. 2018	2006, rev. 2018	2014, rev. 2018	2014; rev. 2018
Applicable Media	drinking water (potable water)	aqueous, non-potable (NPW, GW, SW, WW); solids	aqueous, non-potable (NPW, GW, SW, WW); solids	aqueous, non-potable (NPW, GW, SW, WW); solids	aqueous, non-potable (NPW, GW, SW, WW)
Sample Preparation	Solid Phase Extraction (SPE)	5030, 5035	5030, 5035	Liquid-Liquid Extraction (NPW); SPE (solids)	Liquid-Liquid Extraction (NPW)
Analytical Instrumentation	GC/MS-SIM – with Isotope Dilution	GC/MS full scan	GC/MS-SIM – Isotope Dilution may be an option	GC/MS-SIM	GC/MS-SIM with Isotope Dilution
Preservative	Na2O3S (sodium sulfite, dechlorinating agent) / NaHSO4 (sodium bisulfate, antimicrobial agent), < pH 4, </= 10 °C (for DW)	HCL, pH<2, 0-6 ° C (for NPW); DI water & MeOH, 0-6 °C (for solids).	HCl, pH<2, 0-6 °C (for NPW); DI water & MeOH, 0-6 °C (for solids).	0-6 °C (for NPW and Solids)	0-6 °C (for NPW)
Volume/Mass	2 x 500 mL Amber Glass, Teflon Lined (potable water)	3 x 40 mL VOA vials Amber Glass, Teflon Lined (NPW); 3-vial 5-gram Terracore kits or 3 x 5-gram Encores (solids)	3 x 40 mL VOA vials Amber Glass, Teflon Lined (NPW); 3-vial 5-gram Terracore kits or 3 x 5-gram Encores (solids)	2 x 250 mL (or 2 x 500 mL) (or 2 x 1000 mL) Amber (for NPW); 4 oz jar (solids)	2 x 250 mL (or 2 x 500 ml) (or 2 x 1000 mL) Amber (for NPW)
Hold time Extract / Analyze	28 days	14 days (NPW); 48 Hours (extrude/freeze), 14 Days (Analysis) (Solids)	14 days (NPW); 48 Hours (extrude/freeze), 14 Days (Analysis) (Solids)	7 days (NPW); 14 days (solids)	7 days (NPW)

<u>Aqueous Sample Analytical Options:</u>

Potable water (drinking water or DW) sample analysis for 1,4-Dioxane uses EPA 522 with Isotope Dilution (ID) and Selected Ion Monitoring (SIM) with Solid Phase Extraction (SPE). USEPA drinking water methods are prescriptive and cannot be modified. However, USEPA SW846 Compendium Methods can be modified for specific applications. Selection of analytical options for 1,4-Dioxane in non-potable water (NPW) such as ground water (GW) samples that need to meet the NJDEP Ground Water Quality Standard (N.J.A.C 7:9C) of 0.4 micrograms per liter (µg/l) or the GW Practical Quantitation Level (PQL) of 0.1 µg/l will need to consider the method sensitivity (reporting limit), the analyte recovery potential of the selected approach, and the ability of the approach to achieve the method defined quality control (QC) criteria. Analysis of 1,4-Dioxane in NPW includes method options (i.e., EPA Method 8260 with SIM and USEPA 8270 with SIM). Since 1,4-Dioxane is completely miscible in water, this compound presents challenges for achieving sensitivity, analyte recovery, and ability to meet method defined QC criteria. Volatile organic analysis (VOA) approach of USEPA

Method 8260 using the purge and trap technique with gas chromatograph and mass spectrometer (GCMS) analytical approach with ID and SIM may be a method modification option. The semi-volatile organic compounds (SVOC) extraction with GCMS analysis approach by USEPA 8270-SIM with ID (method modification options) provides for analyte recovery correction and ability to meet method defined QC criteria plus the sensitivity level needed to meet applicable regulatory criteria. These analytical approaches – USEPA 522, VOA 8260-SIM, with ID and SVOC-SIM with ID – are limited to the determination of a single target analyte (1,4-Dioxane) in aqueous sample matrixes.

Soil and Sediment Sample Analytical Options:

Selection of analytical options for 1,4-Dioxane in soils (with low percent moisture levels) is typically more direct. The Soil VOA collection approach by EPA 5035 coupled with VOA 8260 full scan analysis by purge and trap, or the SVOC 8270 full scan analysis approach, both typically yield a reporting limit suitable to meet the NJDEP Soil Remediation Standards (N.J.A.C. 7:26D) for the Ingestion-Dermal Exposure Pathway (7 milligrams per kilograms [mg/kg]), the Inhalation Exposure Pathway (45 mg/kg), the Migration to Ground Water Exposure Pathway Soil Remediation Standard (0.067 mg/kg) and Soil Leachate Remediation Standard (8.0 µg/L).

Air Sample Analytical Options:

The TO-15 VOA analytical approach with canister sample collection media is used to determine 1,4-Dioxane in indoor air, ambient air, and soil gas samples for vapor intrusion applications. The TO-15 method, which includes determination and reporting of this target analyte, results in a sensitivity level (reporting limit) needed to meet the NJDEP Indoor Air Remediation Standards for the Vapor Intrusion Exposure Pathway Residential (0.72 micrograms per cubic meter [µg /m^3]).

For more information on laboratory certification for 1,4-Dioxane analytical methods refer to the NJDEP| Division of Science and Research | Office of Quality Assurance Laboratory Certification Programs website. For a list of certified laboratories offering analytical methods use DataMiner to search the “Laboratories Certified by Analytical Method” listing under the Certified Laboratories Category.

Field QC Samples:

Collection of field quality control (QC) samples is based on several factors including the purpose of the sampling event, the project data quality objectives, and the sample matrix. USEPA drinking water analytical methods specify collection of a field reagent blank (FRB) with the field sample. This includes EPA Method 522 for 1,4-Dioxane analysis of potable water samples. Certified commercial laboratories provide sample containers for both the potable water field sample and the field reagent blank. Collection of field blank samples for non-potable water and soil, sediment, solid sample matrices for 1,4-Dioxane analysis is based on the project data quality objectives and the need to document potential cross contamination introduced during the sample collection process. Analyte-free water should be used for collection of project field blank samples for 1,4-Dioxane analysis and the water source should be documented. Project field QC samples may also include collection of project specific matrix spike (MS) and MS duplicate (MSD) samples using project specific samples.

Refer to Chapter 2 of the FSPM for field QC frequency. Refer to Sampling and Analysis 1,4-Dioxane of the ITRC Document for specific information. Field QC frequency is discussed in the NJDEP Analytical QA/QC Technical Guidance, QAPP Guidance (2014).

General Sampling Considerations

Materials used in environmental sampling can be a source of 1,4-Dioxane contamination. 1,4-Dioxane may be present in detergents used to decontaminate environmental sampling equipment (see Decontamination Considerations below). Use of those detergents, therefore, could potentially affect analytical results if sampling equipment is insufficiently rinsed during decontamination. Therefore, detergents should be mixed according to the manufacturer’s instructions and equipment should be thoroughly rinsed after decontamination. When sampling for 1,4-Dioxane, collection of additional or more frequent field/equipment blanks is recommended prior to and during sampling to ensure no residual 1,4-Dioxane remains on the sampling equipment.

As noted in the above table, 1,4-Dioxane can be sampled as a volatile compound, a semi-volatile compound, or individually. When sampled and analyzed as a volatile compound, sampling should be conducted following the guidance for volatile compounds (i.e., the sample should not be collected by use of a negative pressure pump). However, when sampled individually as a SVOC, 1,4-Dioxane can be sampled by use of a negative pressure pump.

Since 1,4-Dioxane is miscible in water, is nonionic, and has a low sorption potential (i.e., low organic carbon partitioning coefficient), 1,4-Dioxane should not strongly bind to soil and sediment. As such, the collection and analysis of 1,4-Dioxane samples should not be significantly biased by the presence of turbidity in the ground water sample. With respect to ground water sampling policy in Chapter 6 of the FSPM, 1,4-Dioxane should not be considered a turbidity sensitive compound and does not qualify for the exclusions afforded to that designation. See the section below, Media Specific Sampling Considerations for additional turbidity discussion.

Due to its miscibility in water, field treating investigative derived waste generated water that contains 1,4-Dioxane for a discharge to the ground may be problematic, as 1,4-Dioxane is not significantly removed by air stripping or activated carbon. As noted above, for additional information on remediation and treatment technologies for soil, ground water, and wastewater, see ITRCs document 1,4-Dioxane Remediation and Treatment Technologies.

Given 1,4-Dioxane's high vapor pressure and low Henry's Law constant, the potential for 1,4-Dioxane to trigger a VI concern is low where 1,4-Dioxane is dissolved in water but may warrant a Vapor Intrusion (VI) investigation where the 1,4-Dioxane is present in unsaturated or dry conditions.

Media Specific Sampling Considerations

Aqueous (Ground Water, Potable Water, and Surface Water):

Because 1,4-Dioxane is not a turbidity sensitive compound, appropriate sampling procedures should be followed as per Chapter 6.9.1.4 of the FSPM. Samples collected after the first two sampling events and not including the last two sampling events can generally be collected by any of the principal sampling methods: volume average, low flow, grab, or passive. Adequate justification should be provided regarding any deviation from the FSPM.

The miscibility of 1,4-Dioxane in water allows samples to be collected using most ground water sampling equipment: positive displacement pumps, tubing with a downhole check valve, bailers, HydraSleeve (various models), Snap Sampler, Dual Membrane PDBs and Rigid Porous Polyethylene (RPP) passive diffusion samplers. When sampled individually, 1,4-Dioxane can be sampled by use of a negative pressure pump. Refer to Chapter 5 of the FSPM for sampler information. Refer to Sampling and Analysis 1,4-Dioxane of the ITRC Document for specific sampling information.

"Because of 1,4-Dioxane's low Henry's law constant, following typical ground water sampling procedures for SVOCs is appropriate for 1,4-Dioxane. No precautions to prevent volatilization would be needed beyond those that would be used for other chemicals analyzed by a SVOC analytical method. While not required, sampling procedures for VOCs may be equally acceptable." See ITRCs Document 1,4-Dioxane Sampling and Analysis for additional information.

Soil and sediment:

Sampling of solid materials often requires the use of non-dedicated equipment (i.e. scoops, shovels, augers, grab samplers, coring devices). Non-dedicated sampling equipment should be decontaminated prior to use and between samples following the procedures described in the *Decontamination Considerations* section below.

1,4-Dioxane adsorbs weakly to soil and will quickly migrate to ground water. As stated in the ITRC guidance document, Sampling and Analysis for 1,4-Dioxane, if soil moisture is present in soil, volatilization from the soil moisture would likely be controlled based on its Henry's Law Constant and sampling techniques for SVOCs (i.e., homogenization and collection in 4-8 oz. glass jars) would be appropriate. In soils with little to no soil moisture that contains non-aqueous 1,4-Dioxane, volatilization of the 1,4-Dioxane is more likely to occur. Therefore, homogenization or mixing of the soil could result in volatilization of the compound. In these cases, volatilization potential would be a function of the vapor pressure, and VOC soil sampling procedures should be followed consistent with section 6.2.7 of the NJDEP's FSPM. No specific soil moisture levels have been identified as a cut-off for this consideration, so when in doubt, VOC sampling procedures should be considered.

Air:

As discussed above, given the fact that 1,4-Dioxane is fully miscible in water and has a low Henry's law constant, the chances of volatilization from ground water into overlying buildings is low when assessing whether a vapor intrusion pathway is present. As 1,4-Dioxane is considered volatile and is highly mobile in groundwater, the vapor intrusion pathway should be investigated if there is the potential for 1,4-Dioxane to migrate from the subsurface into overlying buildings. When developing a sampling and analysis plan, it is important to understand the reporting limits that are required to meet remedial objectives as the residential indoor air remediation standard for 1,4-Dioxane is set at the reporting limit. The certified laboratory should be selected to run the analysis that can meet the necessary reporting limits.

Wastewater Discharge:

As noted above in the Properties Section, 1,4-Dioxane is fully miscible in water, as such, it may be knowingly or inadvertently encountered in various wastewater discharges from commercial/industrial and/or remediation-related activities, The NJDEP Division of Water Quality regulates wastewater discharges through the implementation of the New Jersey Discharge Elimination System (NJPDES) permitting program. Therefore, sampling and analysis for planned wastewater discharges should include 1,4-Dioxane if it is known or anticipated in the effluent such as, but not limited to, industrial/commercial discharges (e.g., residuals, sludges, liquid wastes, etc.), and remediation discharges (e.g., excavation dewatering, pump & treat, etc.). Depending on the wastewater discharge pathway/process, an evaluation may be required to determine permit compliance with NJDEP NJPDES for wastewater discharges to stormwater, surface water, or publicly owned treatment works (POTW) approval prior to performing wastewater discharge. A pretreatment program may be required to address contaminants prior to performing wastewater discharge from a site and/or facility.

Sampling Sequence

Sampling sequence should be planned in advance of the field sampling event for all media; sample matrix (potable water, non-potable water, soil/sediment), and contamination level.

Sample collection should in general proceed from areas of concern that are known or suspected to be less impacted, and progress through from these low impact areas to medium impact areas to higher impact areas. In addition, potable water samples are typically collected first, before other environmental media are sampled. It is recommended potable water samples be collected first followed by non-potable water, soil, sediment, sludge/biosolids, and waste sample media.

Decontamination Considerations

As stated in the ITRC document, Sampling and Analysis 1,4-Dioxane Fact Sheet from March 2020:

> 1,4-Dioxane is a common impurity in detergents (see the ITRC's History of Use and Potential Sources). In early 2014, 1,4-Dioxane was detected at elevated concentrations in leachate from a widely used decontamination detergent. Because manufacturing processes can introduce 1,4-Dioxane into cleaning products through ethoxylation, individuals should take care to prevent residual detergents or surfactants from remaining on sampling equipment. In studying the potential presence of 1,4-Dioxane in detergents used for decontamination of sampling equipment, researchers demonstrated that some common products were free of 1,4-Dioxane when used according to the manufacturer's instructions (DiGuiseppi et al. 2015). The collection of equipment blanks is useful for the detection of any residual 1,4-Dioxane on sampling equipment. Disposable equipment reduces the likelihood of cross-contamination and eliminates the need for equipment decontamination. In addition, the extended residence time of passive samplers allows sampler materials to reach chemical equilibrium with the surrounding ground water, minimizing the potential effects of leaching or adsorption related to equipment materials.

Investigation Derived Waste Disposal

Project planning should include consideration of disposal options for investigation derived waste (IDW). Typically, these wastes are containerized and stored on site until sampling results can be used to develop a waste profile for disposal facility approval. Per the Resource Conservation and Recovery Act (RCRA), 1,4-Dioxane, as an unused chemical or as the sole active ingredient in an unused product, is a listed hazardous waste when it is discarded or spilled (See 40 CFR 261.33). Thus, in certain circumstances, special consideration should be made for 1,4-Dioxane-impacted IDW as it may need to be handled and disposed as a hazardous waste. Waste classification sampling of the IDW may also be needed to determine the appropriate handling and disposal options.

IDW may also contain other contaminants which may complicate and/or limit disposal options. Some disposal facilities, treatment and/or recycling options may have limitations and/or restrictions for such waste. Therefore, the investigator and/or waste generator should discuss disposal options with a licensed waste hauler/facility to understand acceptance limitations and considerations.

Supporting guidance and recommendations for 1,4-Dioxane IDW are included in the following:

- USEPA – Learn the Basics of Hazardous Waste - https://www.epa.gov/hw/learn-basics-hazardous-waste#regulations
- RCRA – Resource Conservation and Recovery Act (RCRA) Tools and Resources - https://www.epa.gov/rcra/resource-conservation-and-recovery-act-rcra-tools-and-resources
- TSCA – Risk Management for 1,4-Dioxane - https://www.epa.gov/assessing-and-managing-chemicals-under-tsca/risk-management-14-dioxane