

Development of a Cost Effective 1,4-Dioxane Treatment System for Small Community Water Supplies



Office of Research and Development
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Development of a Cost Effective 1,4-Dioxane Treatment System for Small Community Water Supplies

RARE Project #2147

by

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List of Abbreviations

AOP	advanced oxidation process
ATSDR	Agency for Toxic Substances and Disease Registry
FID	flame ionization detector
GAC	granular activated carbon
GC/MS	gas chromatography/mass spectrometry
gpm	gallons per minute
H ₂ O ₂	hydrogen peroxide
HASP	Health and Safety Plan
IS	internal standard
ITRC	Interstate Technology & Regulatory Council
L	liter(s)
lpm	liters per minute
MCL	maximum contaminant level
mg	milligram(s)
MSD	mass selective detector
NJDEP	New Jersey Department of Environmental Protection
NOM	natural organic material
NYSDEC	New York State Department of Environmental Conservation
O ₃	Ozone
POET	point of entry treatment
ppb	parts per billion
ppt	parts per trillion
QAPP	quality assurance project plan
RARE	Regional Applied Research Effort
SPE	solid phase extraction
SPME	solid phase microextraction
TCA	1,1,1-trichloroethane
THF	tetrahydrofuran
UV	ultraviolet

Acknowledgments

The objective of this Regional Applied Research Effort (RARE) project was to develop and evaluate a cost-effective, low-maintenance 1,4-dioxane treatment technology for small-scale Point of Entry Treatment (POET) systems. The study was accomplished by conducting bench- and pilot-scale tests at the U.S. EPA Test & Evaluation (T&E) Facility in Cincinnati, Ohio, on 1,4-dioxane-spiked tap water. The tests were begun in April 2021 and continued until August 2022.

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This RARE project was supported by EPA Region 2 and ORD's Engineering Technical Support Center (ETSC) through the Technical Support Coordination Division (TSCD). The field evaluation of this technology will be conducted at the Williams Property Superfund site in New Jersey with the help of the New Jersey Department of Environmental Protection (NJDEP). Erin Husta will serve as the field test project manager for NJDEP.

Executive Summary

The chemical 1,4-dioxane is a likely human carcinogen and has been found in groundwater and drinking water supplies throughout the United States. Historically, 90% of 1,4-dioxane production was used as a stabilizer in chlorinated solvents, such as 1,1,1-trichloroethane (TCA). The physical and chemical properties and behavior of 1,4-dioxane create challenges for its characterization and treatment. It is highly mobile and does not readily biodegrade in the environment.

In EPA Region 2, 1,4-dioxane is a high-priority chemical due to its widespread occurrence throughout the region and the low regulatory limits established by the New Jersey Department of Environmental Protection (NJDEP). As of 2014, there were 544 detections of TCA (a common co-contaminant of 1,4-dioxane) in groundwater throughout New Jersey; however, these numbers likely underestimate the occurrence of 1,4-dioxane in groundwater across the state. The New York State Department of Environmental Conservation (NYSDEC) is also working with EPA Region 2 to sample for 1,4-dioxane in groundwater at 725 remedial program sites across the state of New York. The preliminary data indicate that levels exceeding the proposed Maximum Contaminant Level (MCL) of 1 µg/L occurred at 174, or 24%, of the sites. NYSDEC is currently evaluating a MCL recommendation of 1 µg/L for 1,4-dioxane from the New York Drinking Water Quality Council. If adopted, it would be the nation's most stringent drinking water standard for 1,4-dioxane.

The objective of this research was to develop and evaluate a cost-effective, low-maintenance 1,4-dioxane treatment technology for small-scale Point of Entry Treatment (POET) systems. The study was accomplished by conducting bench- and pilot-scale tests at the U.S. Environmental Protection Agency (EPA) Test & Evaluation (T&E) Facility in Cincinnati, Ohio, on 1,4-dioxane-spiked tap water. The tests began in April 2021 and continued until August 2022.

Bench-scale studies included the following systems/enhancements: particulate filters, ultraviolet (UV), electrocoagulation, hydrogen peroxide, ozone, and combinations of these. When UV or electrocoagulation was used in addition to ozone (or in combination of ozone and hydrogen peroxide), the 1,4-dioxane concentration decreased. However, using UV or electrocoagulation by itself or in combination with hydrogen peroxide was not effective in treating 1,4-dioxane. Particulate filters (0.5 µm, 1 µm, 5 µm, and alumina filter 5 µm) were not effective in removing 1,4-dioxane, either individually or in series.

Based on the bench-scale testing, the pilot-scale testing focused on mixing ozone and hydrogen

peroxide (peroxonation), which was very effective in destroying 1,4-dioxane in water. By using a combination of approximately 3.5 mg/L hydrogen peroxide and 5 mg/L ozone, water flow rates up to 10 gallons per minute (gpm) containing up to 200 µg/L 1,4-dioxane were treated. Influent 1,4-dioxane concentrations of approximately 10 µg/L, 20 µg/L, 80 µg/L, and 180 µg/L were reduced to effluent 1,4-dioxane concentrations of approximately 0.4 µg/L, 0.7 µg/L, 5 µg/L, and 10 µg/L, respectively, when treated at flow rates of approximately 10 gpm.

The future research plan includes a field evaluation of the system at a Superfund site in New Jersey to determine its effectiveness and efficiency in a real-world scenario and apply the lessons learned from the field study to modify the system performance.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The Center for Environmental Solutions and Emergency Response (CESER) within the Office of Research and Development (ORD) conducts applied, stakeholder-driven research and provides responsive technical support to help solve the Nation's environmental challenges. The Center's research focuses on innovative approaches to address environmental challenges associated with the built environment. We develop technologies and decision-support tools to help safeguard public water systems and groundwater, guide sustainable materials management, remediate sites from traditional contamination sources and emerging environmental stressors, and address potential threats from terrorism and natural disasters. CESER collaborates with both public and private sector partners to foster technologies that improve the effectiveness and reduce the cost of compliance, while anticipating emerging problems. We provide technical support to EPA regions and programs, states, tribal nations, and federal partners, and serve as the interagency liaison for EPA in homeland security research and technology. The Center is a leader in providing scientific solutions to protect human health and the environment.

The chemical 1,4-dioxane has been identified as an emerging contaminant of concern, having been detected in both EPA Superfund sites and public water supplies throughout the United States. The objective of this Regional Applied Research Effort (RARE) project research with EPA Region 2 and New Jersey Department of Environmental Protection (NJDEP) was to develop and evaluate a cost-effective, low-maintenance 1,4-dioxane treatment technology for small-scale Point of Entry Treatment (POET) systems. This report summarizes ORD's initial research efforts to develop an approach to the 1,4-dioxane treatment in water.

Gregory Sayles, Director
Center for Environmental Solutions and Emergency Response

1.0 Introduction

The chemical 1,4-dioxane is a likely human carcinogen and has been found in groundwater and drinking water supplies throughout the United States (USDHHS, 2002). Historically, 90% of 1,4-dioxane was produced for use as a stabilizer in chlorinated solvents, such as 1,1,1-trichloroethane (TCA); however, it was also an unintended contaminant of chemical ingredients used in consumer products including bubble bath, shampoo, laundry detergent, soap, skin cleanser, adhesives, and antifreeze (MDH, 2015). The physical and chemical properties and behavior of 1,4-dioxane create challenges for its characterization and treatment. It is highly mobile and does not readily biodegrade in the environment. Synonyms for 1,4-dioxane are dioxane, *p*-dioxane, diethylene ether, diethylene dioxide, and glycol ethylene ether (EPA, 2006). It has been identified as an emerging contaminant of concern, having been detected in both U.S. Environmental Protection Agency (EPA) Superfund sites and public water supplies throughout the United States (EPA, 2017).

The chemical 1,4-dioxane has been found in at least 31 of the 1,689 current or former National Priorities List (NPL) sites (ATSDR, 2012), and 1,4-dioxane is a high-priority chemical in EPA Region 2 due to its widespread occurrence throughout the region and the low regulatory limits established by the New Jersey Department of Environmental Protection (NJDEP). The New York State Department of Environmental Conservation (NYSDEC) is currently evaluating a Maximum Contaminant Level (MCL) recommendation of 1 µg/L for 1,4-dioxane from the New York Drinking Water Quality Council. If adopted, it would be the nation's most stringent drinking water standard for 1,4-dioxane.

Both the NJDEP and NYSDEC are actively evaluating the occurrence and distribution of 1,4-dioxane in groundwater and drinking water in their states. NJDEP tracks contaminants that are commonly co-located with 1,4-dioxane in their Private Well Testing Act Database. As of 2014, there were 544 detections of TCA (a common co-contaminant of 1,4-dioxane) throughout the state. Since the Private Well Testing Act requires sampling only when a house is being sold, these numbers likely underestimate the occurrence of 1,4-dioxane in groundwater across the state. NJDEP has indicated to EPA that 1,4-dioxane treatment technologies scaled to effectively treat impacted private wells is a priority research need for the state.

The NYSDEC is working with EPA Region 2 to sample for 1,4-dioxane in groundwater at 725 remedial program sites across the state of New York. The preliminary data indicate that levels

exceeding the proposed MCL of 1 µg/L occurred at 174, or 24%, of the sites (Source: email correspondence w/ Susan Edwards, NYSDEC).

The current approach for preventing exposure to homeowners with private drinking water wells contaminated with 1,4-dioxane is to provide them with bottled water, which is costly. While ex situ treatment technologies for 1,4-dioxane have been refined over the years, these technologies are better suited for large-scale drinking water systems (ITRC, 2021). Research is needed to find solutions to cost-effective, small-scale 1,4-dioxane treatment systems that can reduce concentrations to the low levels required by some state agencies.

A 1,4-dioxane Point of Entry Treatment (POET) system for residents on private drinking water wells near the Combe Fill South Superfund site in New Jersey was funded and tested by EPA Region 2 several years ago. The system performance was acceptable; however, the monitoring and maintenance requirements were too cumbersome for an average homeowner to perform. Due to its low Henry's constant, 1,4-dioxane is miscible and is difficult to treat (Mohr et al., 2010). Conventional water treatment practices (e.g., coagulation, filtration, and air stripping) have proven ineffective for water treatment (Water Research Foundation, 2014). It is also resistant to substantial biodegradation at ambient conditions (Woodard, Mohr, & Nickelsen, 2014).

Commonly used treatment technologies to remove 1,4-dioxane and other organic chemicals from water include advanced oxidation processes (AOPs), granular activated carbon (GAC), and synthetic media. AOPs are a group of technologies that use the highly reactive hydroxyl radical to destructively remove organic contaminants (ITRC, 2021). The most used AOPs are those that involve ozone (O₃), hydrogen peroxide (H₂O₂), and ultraviolet (UV) light (Broughton et al., 2019; Elkacmi et al., 2019).

The blending of O₃ and H₂O₂ is called peroxonation and is a powerful oxidation process for treating 1,4-dioxane in water. During peroxonation, O₃ and H₂O₂ react with each other and produce hydroxyl radicals (OH·):



Hydroxyl radical (2.80 eV) has higher oxidation potential than O₃ (2.08eV) and H₂O₂ (1.78eV). Hence, hydroxyl radical is a very strong oxidant in water but non-selective and reacts fast with

most organic compounds in water. Since the reaction is diffusion-limited, efficient mixing of the compound and reagents is important to transform the organic chemicals to carbon dioxide and water. Therefore, careful system design is very important to achieve high efficiency for producing hydroxyl radicals. Hydroxyl radical is also very effective for disinfection viruses. Hydroxyl radicals are formed when ozone and hydrogen peroxide are added to water simultaneously. It is also an established technology and has shown effective reduction of 1,4-dioxane concentrations to less than 2 µg/L in California (Mohr et al., 2010). The main disadvantages with these systems are bromate formation in bromide-containing waters and the need to destroy the unreacted ozone and hydrogen peroxide.

Adams et al. (1994) also examined the use of hydrogen peroxide and ozone to increase the biodegradability of 1,4-dioxane in synthetic groundwater and industrial wastewater. The oxidant combination was found to be effective at enhancing the biodegradability of 1,4-dioxane by conventional wastewater treatment plant microorganisms. However, neither hydrogen peroxide nor ozone alone readily oxidized 1,4-dioxane.

The hydroxyl radical formations are enhanced by introducing low or medium pressure UV light on ozonated water. The use of UV in the system provides an added advantage of disinfection. However, the UV transmittance could be reduced by turbidity where other materials could absorb UV light, making it unavailable for enhancing hydroxyl radicals. In addition, the unreacted ozone gas needs to be treated before venting.

The hydroxyl radical formations are also enhanced by introducing low or medium pressure UV light with hydrogen peroxide in water. This system has the advantages of disinfection, no bromate formation, and ozone gas treatment, but UV light interference due to turbidity is still a problem.

Lee et al. (2020) examined the effect of groundwater quality on advanced oxidation. They found little effect due to pH or alkalinity; however, natural organic material (NOM) significantly reduced the efficiency of 1,4-dioxane treatment. They also found that an increase in iron in groundwater enhanced oxidation by hydrogen peroxide (Fenton reaction); however, it hindered oxidation by hydrogen peroxide and UV. The decrease in performance during UV treatment might be due to lower UV transmission.

The Fenton process is a catalytic reaction based on the generation of hydroxyl radicals from hydrogen peroxide with iron ions acting as a homogeneous catalyst in acidic pH and ambient

conditions. Fenton oxidation has been demonstrated in full-scale applications as a feasible technology for the treatment of a wide diversity of industrial wastewaters. It represents a useful solution in many cases where the presence of recalcitrant and toxic pollutants eliminates the use of conventional biological treatments (Bautista et al., 2008).

Heck et al. (2019) investigated the use of solid metal oxide catalysts to assist in hydrogen peroxide oxidation of 1,4-dioxane. Like Fenton reagents, these reactions would use a solid catalyst rather than dissolved ferrous ions. Based on batch kinetics measurements, several metal oxides appeared suitable for use as a catalyst.

Chloramines may be added to water that is treated using reverse osmosis for water reuse to minimize membrane fouling. The chloramine can pass through the membrane, and Patton et al. (2017) found that the combination of UV and chloramines is also able to degrade 1,4-dioxane as the chloramine is broken into radicals that react with it.

1.2 Research Objectives

The overall objective of this research project is to find a cost-effective, low-maintenance 1,4-dioxane treatment technology for small-scale POET systems. The project will 1) test the efficacy of promising technologies in treating 1,4-dioxane levels to the NJDEP criteria of 0.4 µg/L; 2) evaluate the monitoring and maintenance requirements for the developed treatment system designs; and 3) provide recommendations for the best treatment configuration for small-scale systems.

EPA Region 2 has listed 1,4-dioxane as a high-priority chemical due to its widespread occurrence throughout the region and the low regulatory limits established by the NJDEP. However, this research is relevant to other EPA regions since 1,4-dioxane has been found in groundwater and drinking water supplies throughout the U.S. and several states have working on establishing groundwater criteria as shown in Table 1.

Table 1. State groundwater criteria

State	1,4-Dioxane Guidance (µg/L)	State	1,4-Dioxane Guidance (µg/L)
Alaska	4.6	Mississippi	6.09
California	1.0	New Hampshire	0.25
Colorado	0.35	New Jersey	0.4
Connecticut	3.0	North Carolina	3.0

Delaware	6.0	Pennsylvania	6.4
Florida	3.2	Texas	9.1
Indiana	7.8	Vermont	3.0
Maine	4.0	Washington	0.438
Massachusetts	0.3	West Virginia	6.1

This EPA Regional Applied Research Effort (RARE) project determined the treatment effectiveness of advanced UV oxidation to achieve 1,4-dioxane reduction to meet the regulatory level needs. The study 1) evaluated the 1,4-dioxane contaminated source water, 2) evaluated the cost of treatment and its efficiency, and 3) optimized operation and maintenance of the treatment process. Water quality monitoring technologies were used before and after treatment to ensure the system is effective. The project team documented the ease of use and operation and maintenance costs of each water treatment unit configuration and water quality monitoring system. The Williams Property Superfund site in New Jersey was a candidate site for this research project since it has 1) groundwater contaminated with 1,4-dioxane and 2) an existing groundwater extraction and treatment system that can be outfitted with an advanced UV oxidation system.

The project was conducted at the U.S. EPA Test & Evaluation (T&E) Facility and Andrew W. Breidenbach Environmental Research Center (AWBERC) in Cincinnati, Ohio. The experiments were conducted by APTIM Federal Services LLC (APTIM). Pegasus Technical Services, Inc. (Pegasus) was subcontracted to APTIM to perform 1,4-dioxane analysis and provide technical support.

1.3 Report Organization

This report is organized in the following sections. This section (Section 1.0) addresses the background and purpose of the study, introduces the project team, and provides an outline of the report. Section 2.0 describes the treatment system involved in treating 1,4-dioxane and the analytical methods used in the study. Section 3.0 presents the results of the treatment system testing (filter system, UV units, electro-coagulation/electro oxidizer, hydrogen peroxide, and ozone individually and in combinations), and Section 4.0 provides a list of references.

2.0 Experimental Methods

This section describes the materials, chemicals and equipments involved in this study. In addition, details of test approach, sampling, and analytical methods used in this project are also described.

2.1 Test Water

Test water for this study was made from Cincinnati, Ohio tap water mixed with 1,4-dioxane (Sigma-Aldrich, Lot No. SHBM9675).

2.2 Pilot-Scale Treatment System

The primary pilot-scale treatment system used in this study included ozone, hydrogen peroxide, and GAC. Other components, such as UV and electrocoagulation, were also tested. Table 2 lists the equipment used to assemble the treatment system. The process flow diagram for the treatment system is shown in Figure 1.

Water enters the system and passes through a flow switch. The flow switch, through a control box, activates the oxygen generator, which then activates the ozone generator and produces ozone. After passing through the flow switch, the water goes through a flowmeter, which controls the feed rate of a pump that injects hydrogen peroxide into the water at a concentration of approximately 3.5 mg/L. Following the hydrogen peroxide injection, the manufactured ozone is pulled into the water through a venturi injector. An ozone concentration of approximately 4.5 mg/L is produced in the water. The water then passes through a flash reactor and into a 25-gallon contact tank. Undissolved ozone from the water leaves the contact tank and passes through an ozone destruct unit. An ozone monitor measures the ozone in the ambient air to ensure the ozone concentration does not become hazardous. The Permissible Exposure Limit (PEL) for ozone is 0.1 ppm. After the contact tank, the water passes through a GAC filter to remove any remaining hydrogen peroxide, ozone, and organic chemicals. Initial testing used an air dryer instead of an oxygen generator and a 15-gallon contact tank in place of a 25-gallon contact tank, but these were replaced to improve the system's performance. Influent water temperature was 20-22°C and there was no noticeable change in water temperature during the treatment.

Two other treatment options for treating 1,4-dioxane were evaluated: 1) the addition of UV light and 2) electrocoagulation after the ozone contact tank. These are shown in Figures 2 and 3, respectively.

Figure 4 shows the hydrogen peroxide injection system. Figure 5 shows the ozone system. Figure 6 shows the UV system, and Figure 7 shows the electro-coagulator/oxidizer.

Table 2. Treatment system equipment

Component	Model and Source	2023 Price
Hydrogen Peroxide Injection	Clean Water Store (www.cleanwaterstore.com) Hydrogen Peroxide Proportional Flow Well Water J-PRO-22 <ul style="list-style-type: none"> - Tank size: 5 gallons - Water meter size: ¾ inch - Injection tee: ¾ inch 	\$913
Flow Switch	Oxidation Technologies (www.oxidationtech.com) Control Box with Flow Switch	\$325
Oxygen Generator	Oxidation Technologies (www.oxidationtech.com) MAX-5 Oxygen Generator	\$1360
Ozone Generator	Oxidation Technologies (www.oxidationtech.com) WT-10 Ozone Water System <ul style="list-style-type: none"> - Venturi injector Model 684 - Contact tank 25 gallons - Static mixer Model 73-NK 	\$4480
Ozone Destruct Device	Oxidation Technologies (www.oxidationtech.com) CDU-30 Ozone Destruct Device <ul style="list-style-type: none"> - Wall bracket - Water trap - Heater element 	\$895
Ozone Monitor	Oxidation Technologies (www.oxidationtech.com) C-30ZX Ozone Monitor	\$536
GAC Filter	Clean Water Store (www.cleanwaterstore.com) Carbon Backwash Filter 5900-BT 1.5 CF 1054 <ul style="list-style-type: none"> - Catalytic carbon (well water, peroxide systems) - Add KDF cubes - 10 feet drain line tubing - 2 – 1 inch x ¾ inch Sharkbite fittings and 24 inch hoses 	\$1375
UV	ATS Model #ASV-13.5C	\$3000
Electro-oxidizer	Aquapulsar e300 Electro-Oxidizer	\$3000

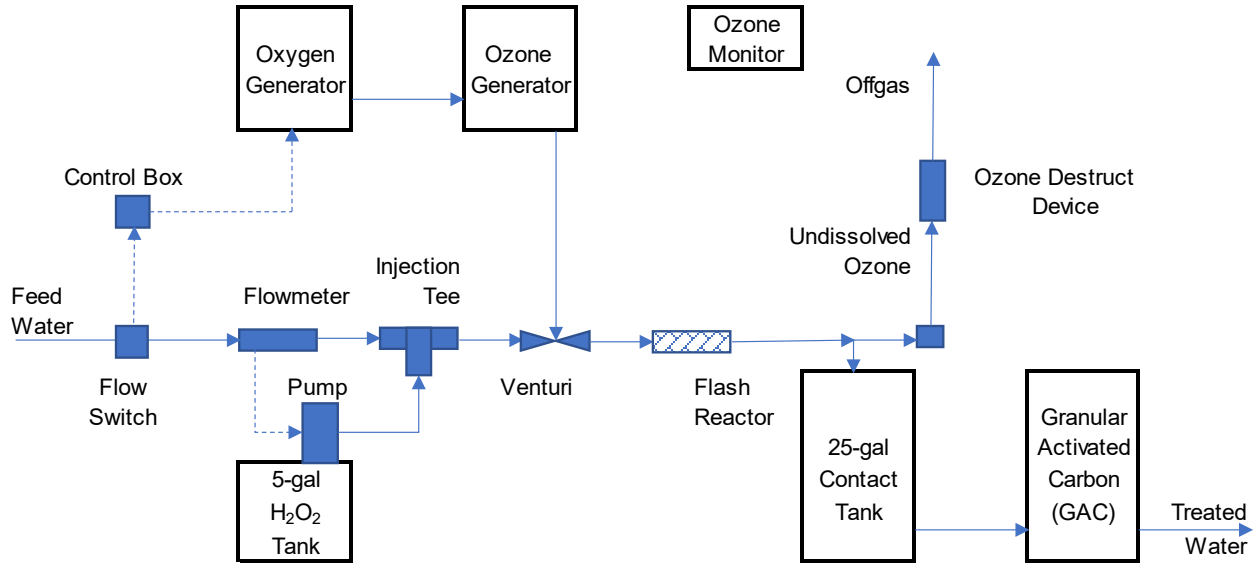


Figure 1. 1,4-dioxane treatment process flow diagram

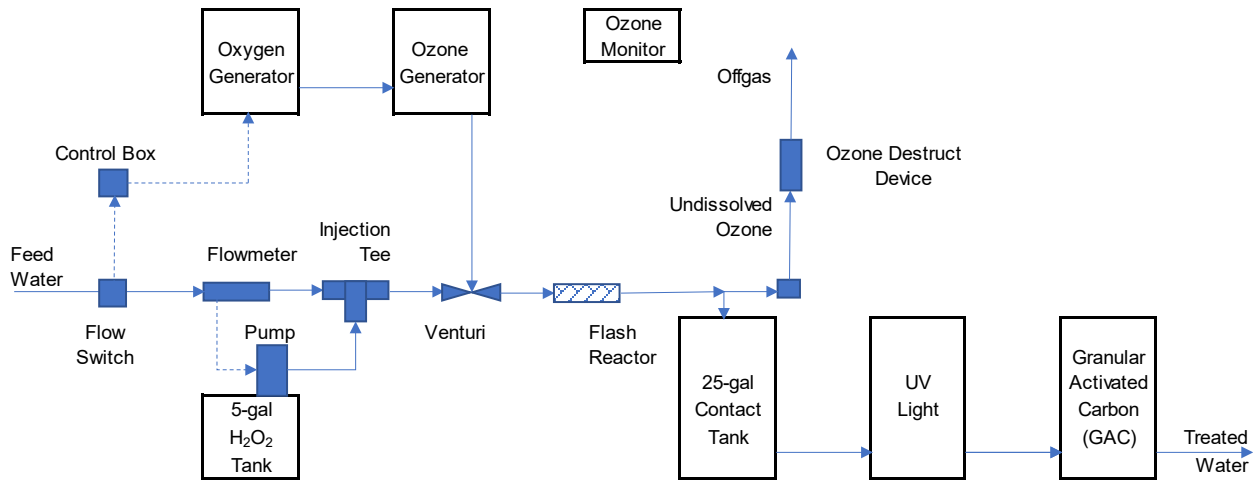


Figure 2. 1,4-dioxane treatment process flow diagram with UV light

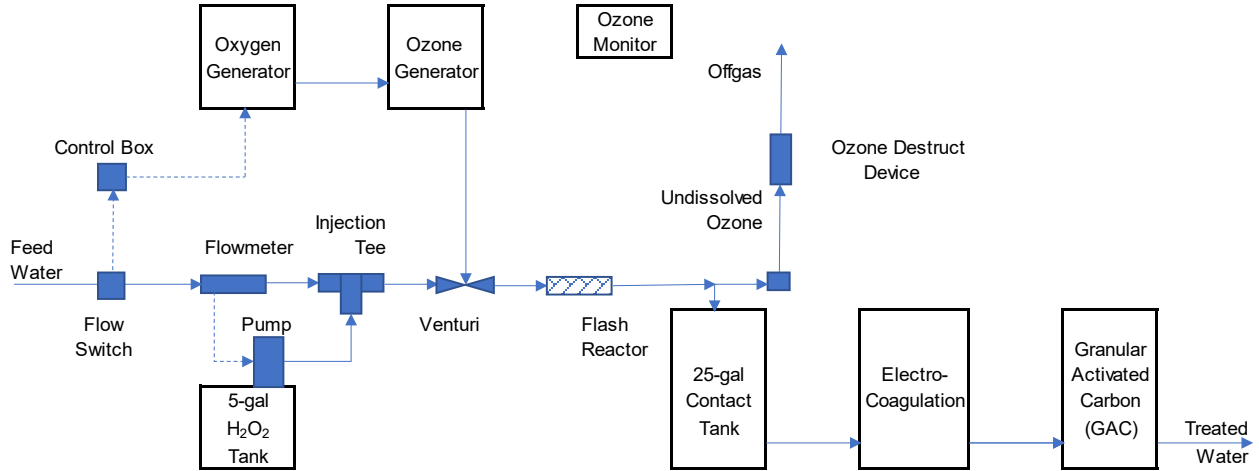


Figure 3. 1,4-dioxane treatment process flow diagram with electrocoagulation



Figure 4. Hydrogen peroxide injection system

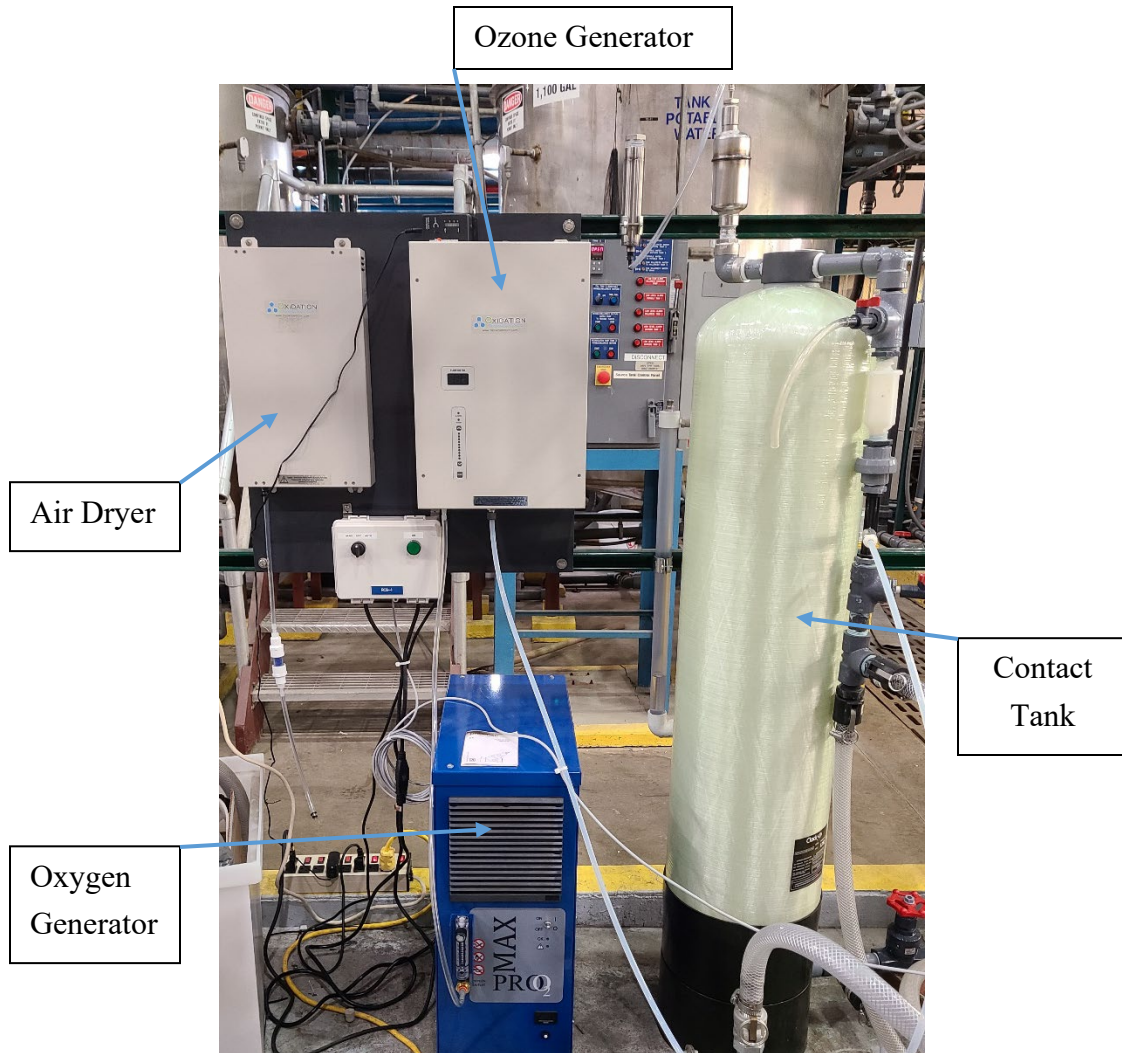


Figure 5. Ozone system (air dryer, oxygen generator, ozone generator, contact tank)

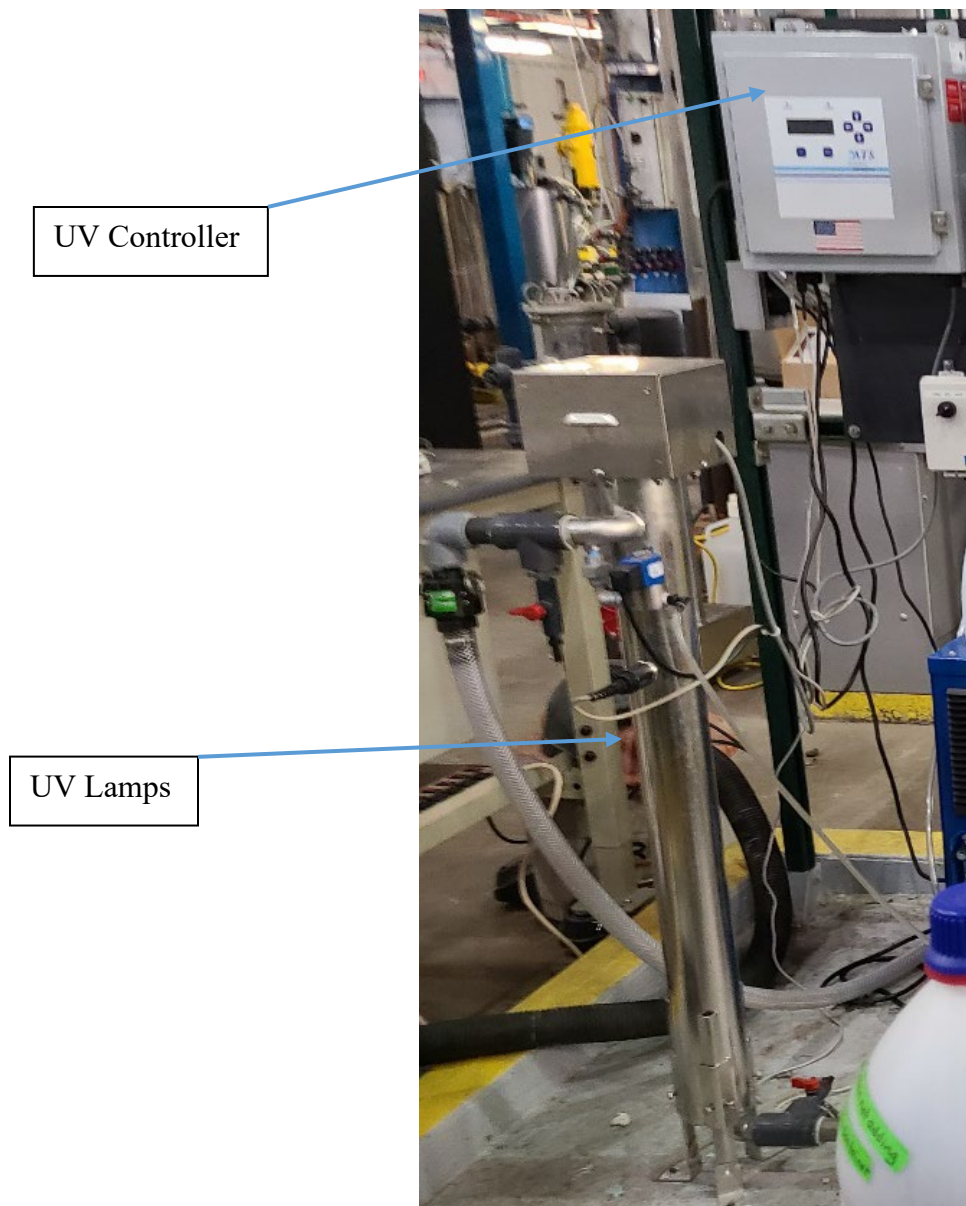


Figure 6. UV system



Figure 7. Electro-coagulator/oxidizer

2.3 Analytical Methods

Grab samples were collected from various points in the system: influent and effluent after each treatment. Hydrogen peroxide and ozone were monitored periodically when the system was tested. Table 3 presents the measurements and analytical methods for the various parameters that were monitored during the testing program.

1,4-dioxane samples were transported to the AWBERC building and were extracted and analyzed by Pegasus. All collected samples were analyzed for 1,4-dioxane. Samples were

collected headspace-free in 40 mL amber vials or 1 L amber bottles and stored at 4±2 °C until analysis.

Table 3. Measurements and analytical methods

Measurement	Analytical Method/ SOP
1,4-Dioxane	EPA Method 524.3 (modified)
1,4-Dioxane	EPA Method 522
Hydrogen Peroxide	CHEMetrics K-5543
Ozone	CHEMetrics K-7433

Samples collected in 40 mL amber vials were analyzed for 1,4-dioxane by adding approximately 10 mL of the aqueous sample to a 20 mL autosampler vial and spiking with a surrogate mix and internal standard (IS). Initial analysis was carried out using d₈-tetrahydrofuran as the internal standard, and d₈-1,4-dioxane, d₃-methyl tert-butyl ether, 4-bromofluorbenzene, and d₄-1,2-dichlorobenzene as the surrogate standards (Spex Certiprep, Metuchen, NJ). Based on the matrix effects encountered, d₈-1,4-dioxane (spex Certiprep, Metuchen NJ) was used instead as the internal standard, and d₈-tetrahydrofuran was added as a fourth surrogate, and the final concentration was determined using isotopic dilution. The samples were then quantified using an Agilent 7890A Gas Chromatograph (GC) with a 5975C mass selective detector (MSD) with Triple Axis Detector (Agilent Technologies, Santa Clara, CA) and CombiPal autosampler (CTC Analytics, Zwingen Switzerland) following EPA Method 524.3 modified to perform headspace analysis instead of purge and trap. With the modified method, the autosampler heats the sample-containing vials to 90 °C for 30 minutes prior to analysis, and an aliquot of air (adjustable from 250 µl to 2500 µl) drawn from the headspace or a solid phase microextraction (SPME) microfiber that is equilibrated with the water in the autosampler vial was injected into the GC/MS.

The samples collected in 1 L amber bottles were analyzed using EPA Method 522. In this method, a water sample (400-500 mL) that has been dechlorinated using sodium sulfite and preserved with a microbial inhibitor (sodium bisulfate) was fortified with the isotopically labeled surrogate, 1,4-dioxane-d₈. The sample with surrogate was then extracted by passing through a solid phase extraction (SPE) cartridge containing 2 g of coconut charcoal. The compounds were eluted from the solid phase with a small amount of dichloromethane (DCM), approximately 9 mL or 1.5 mL. The extract volume was adjusted, and the IS, tetrahydrofuran-d₈ (THF-d₈), was added. Finally, the extract was dried with anhydrous sodium sulfate. Analysis of the extract was performed by GC/MS/MS. In this study, these methods were compared to select a robust method that can be used to determine 1,4-dioxane concentrations at low levels (low ppt), while

minimizing sample processing (e.g., concentrating samples using SPE can potentially lead to lower detection limits, but there could be losses associated with sample processing).

3.0 Results

This section describes the results from the preliminary bench-scale experiments and the pilot-scale experiments. The pilot-scale experiments are broken down into the results from each of the different treatment process designs.

3.1 Preliminary Bench-Scale Experiments

Preliminary bench-scale tests were conducted on several units to determine their effectiveness on removing 1,4-dioxane prior to beginning the pilot-scale tests. These units included the following: particulate filters, UV, electrooxidation, hydrogen peroxide, ozone, and combinations of these.

When UV or electrooxidation was used in addition to ozone (or to a combination of ozone and hydrogen peroxide), the 1,4-dioxane concentration decreased. However, using UV or electrocoagulation by itself or in combination with hydrogen peroxide was not effective in treating 1,4-dioxane.

Particulate filters (0.5 μm , 1 μm , 5 μm , and alumina filters) were not effective in removing 1,4-dioxane, either individually or in series. The particulate filters were Waterline Technology AlwaysFresh RC-HFC-1000, RC-HF-SED-5, and RC-HF-20000.

3.2 Pilot-Scale Experiments

The hydrogen peroxide system and the ozone system were tested individually at a 10 gallons per minute (gpm) flowrate to measure the hydrogen peroxide concentration injected and ozone concentration generated in the test water. This system used a dry air generator (as opposed to an oxygen generator) and had a 15-gallon contact tank after the ozone generator. The systems were operated for two hours, and the hydrogen peroxide and ozone levels were measured using CHEMetrics test kits every 30 minutes.

The system had three sample ports: Port 1 was located after the hydrogen peroxide injection point, Port 2 was located after the ozone injection, and Port 3 was the effluent sample that was discharged from the contact tank. The samples from Port 1 were tested only for hydrogen peroxide, the samples from Port 2 were tested only for ozone, and the samples from Port 3 were tested for both hydrogen peroxide and ozone. The desired hydrogen peroxide concentration to be injected in the system was 3.5 mg/L. Table 4 shows the measured concentrations of hydrogen peroxide and ozone when only one of the systems, ozone or hydrogen peroxide, was operated, and when both systems were operated simultaneously. The ozone concentrations were tested before starting the hydrogen peroxide system to get the exact ozone concentration entering the

contact tank. As can be seen, the ozone concentrations that were measured while hydrogen peroxide was being added were much lower, as the hydrogen peroxide reacted immediately with the ozone.

Table 4. Ozone and hydrogen peroxide monitoring for combined treatment

Time (minutes)	Flow rate (gpm)	O ₃ generator flow rate (lpm)	Port	Peroxide (mg/L)	Ozone (mg/L)
Ozone Only					
0	9.75	3.1	3	NA	1.66
30	9.75	3.3	3	NA	1.58
Ozone and H ₂ O ₂					
0	9.75	3.4	1	3.51	0.05
			2	3.7	0.01
			3	3.21	0.02
30	9.75	3.4	1	3.32	B.D.
			2	3.12	0.09
			3	3.41	0.1

B.D. = Below detection

Since the ozone concentration was not at the desired level (approximately 4 mg/L), a recirculation pump was added after the contact tank to pressurize the system and enhance ozone generation, per the manufacturer's suggestion. The recirculation pump also allowed the system to be operated at a lower flow rate while producing ozone.

For later experiments, the air dryer was replaced with an oxygen generator, and the 15-gallon contact tank was replaced with a 25-gallon contact tank. After installing the oxygen generator, the ozone concentration in the water was approximately 5 mg/L before H₂O₂ injection.

3.2.1 Destruction of 10 ppb 1,4-Dioxane using Air Dryer for Ozone

The 1,4-dioxane spiked tap water (10 µg/L, 1,000 gallons) were pumped through the treatment system at flowrates of 2.5, 5, 7.5, and 10 gpm while the recirculation pump was operating and at flowrates of 8.5 and 10 gpm without the recirculation pump being used. The treatment samples were collected after 10 minutes and 20 minutes of each flow rate to check the treatment reproducibility.

The pilot-scale system was tested with and without the recirculation pump to measure 1,4-dioxane removal. The recirculation pump helps to increase the ozone concentration in the test water. When the recirculation pump was not used, the ozone generator required a minimum of

8.5 gpm of flowrate to generate ozone (or the ozone generator turned itself off). This flow rate limitation was not an issue while using the recirculation pump.

The 1,4-dioxane concentrations decreased from approximately 13 µg/L to between 1 – 8 µg/L depending on the water flow rate and recirculation pump. Operating the system without the recirculation pump decreased the system's 1,4-dioxane destruction. The ozone concentrations were low due to the hydrogen peroxide reacting with the ozone. The ozone flow is controlled by the water flow rate passing through the venturi and pulling the ozone into the water. Tables 5 and 6 show the 1,4-dioxane concentrations measured by Pegasus using EPA Method 522 and modified EPA Method 524.3, when using the pilot-scale system with and without the recirculation pump, respectively.

Table 5. Pilot study data with recirculation pump

Flow rate (gpm)	Time (min)	O ₃ injection (mg/L)	H ₂ O ₂ injection (mg/L)	O ₃ discharge (mg/L)	H ₂ O ₂ discharge (mg/L)	Ozone flow (lpm)	Concentration of 1,4-dioxane (µg/L)			
							EPA Method 524.3		EPA Method 522	
							Influent	Effluent	Influent	Effluent
2.5	10	0.2	2.44	B.D.	1.78	3.5	14.9	1.77	14.5	1.15
	20	0.16	2.11	0.02	1.66	3.5	16.8	0.701	16.2	0.807
5	10	0.01	3.01	0.01	2.69	3.5	14.3	2.17	15.8	2.05
	20	B.D.	2.81	0.01	3.26	3.6	11.7	1.61	20.2	1.93
7.5	10	0.03	3.49	0.06	3.28	3.5	10.6	2.52	14.7	4.06
	20	0.08	3.2	0.04	3.55	3.6	13.0	2.42	14.0	2.95
10	10	0.01	3.91	0.01	3.14	3.6	11.7	3.31	12.9	5.06
	20	0.08	3.59	0.04	2.85	3.5	15.0	3.28	13.7	4.57

B.D.: below the detection level

Table 6. Pilot study data without recirculation pump

Flow rate (gpm)	Time (min)	O ₃ injection (mg/L)	H ₂ O ₂ injection (mg/L)	O ₃ discharge (mg/L)	H ₂ O ₂ discharge (mg/L)	Ozone flow (lpm)	Concentration of 1,4-dioxane (µg/L)			
							EPA Method 524.3		EPA Method 522	
							Influent	Effluent	Influent	Effluent
8.5	10	0.47	3.07	0.05	3.13	2	12.2	5.85	15.9	7.57
	20	0.35	2.68	0.04	3.47	2	14.2	7.29	12.7	8.34
10	10	0.09	3.24	B.D.	3.03	3.6	15.0	4.36	15.7	6.14
	20	0.1	2.96	0.02	2.65	3.7	13.0	5.14	13.7	6.18

B.D.: below the detection level

3.2.2 Destruction of 10 ppb 1,4-Dioxane with Oxygen Generator

Because the baseline ozone concentration in the water was approximately 1.5 mg/L, the pilot-scale system was then modified by replacing the air dryer with an oxygen generator to increase the ozone concentration in the water. Using oxygen rather than air to generate ozone increases the ozone concentration that is generated, and the higher ozone concentration in air increases the concentration of dissolved ozone in water. Therefore, the recirculation pump was not necessary for this configuration. The oxygen generator was used for all additional tests.

The modified system was then tested for 1,4-dioxane removal. For the treatment process with the oxygen generator, 1,000 gallons of 1,4-dioxane spiked tap water (10 µg/L) were pumped through the system at two flowrates: 2.5 and 10 gpm. Table 7 shows the 1,4-dioxane concentrations at 2.5 and 10 gpm with the modified pilot system, analyzed using the EPA Method 522 by Pegasus. As can be seen, the 1,4-dioxane concentration decreased from approximately 19 µg/L to less than 0.7 µg/L. The increased ozone in the water improved the 1,4-dioxane destruction.

Table 7. Pilot study data with oxygen generator

Flow rate (gpm)	Time (min)	O ₃ injection (mg/L)	H ₂ O ₂ injection (mg/L)	O ₃ discharge (mg/L)	H ₂ O ₂ discharge (mg/L)	Airflow (lpm)	Concentration of 1,4-dioxane (µg/L)	
							EPA Method 522	
							Influent	Effluent
2.5	10	B.D.	2.56	0.4	0.04	3.5	17.8	0.16
	20	0.04	2.65	0.49	0.04	3.4	20.7	0.34
10	10	0.02	3.33	0	1.55	3.7	18.0	0.65
	20	0.28	2.92	0.23	1.45	3.9	20.4	0.50

B.D.: below the detection level

3.2.3 Destruction of 10 ppb 1,4-Dioxane with Oxygen Generator and 25-Gallon Contact Tank

Initially, a 25-gallon contact tank after the injection point was not available when the treatment system was installed, and the system was tested with a 15-gallon contact tank. When the 25-gallon contact tank became available, the 15-gallon contact tank was replaced with a 25-gallon contact tank to increase the residence time of the system.

Table 8 shows the 1,4-dioxane concentrations at 2.5, 5, 7.5, and 10 gpm with the modified pilot system that uses both the oxygen generator and the 25-gallon contact tank, analyzed using the

EPA Method 522 by Pegasus. The average 1,4-dioxane concentration was decreased from over 10 µg/L to less than 0.4 µg/L.

Table 8. Pilot study data with 25-gallon contact tank

Flow rate (gpm)	Time (min)	O ₃ injection (mg/L)	H ₂ O ₂ injection (mg/L)	O ₃ discharge (mg/L)	H ₂ O ₂ discharge (mg/L)	Airflow (lpm)	Concentration of 1,4-dioxane (µg/L)	
							EPA Method 522	
							Influent	Effluent
2.5	10	3.44	NA*	0.28	NA	2.8	10.3	0.029
	20	4.31	NA	0.26	NA	2.8	11.5	0.026
5	10	0.36	NA	0.01	NA	3.1	11.1	0.16
	20	0.09	NA	0.05	NA	3.0	11.0	0.15
7.5	10	0.12	NA	0	NA	3.8	13.5	0.16
	20	0.18	NA	0.02	NA	3.7	12.3	0.20
10	10	0.09	NA	0.04	NA	4.1	12.2	0.39
	20	0.66	NA	0.06	NA	4.2	11.9	0.38

*NA – hydrogen peroxide concentration was not monitored. The peroxide injector was set to deliver 3mg/L H₂O₂.

3.2.4 Destruction of 10 ppb 1,4-Dioxane using Ozone and UV

The hydrogen peroxide system was then turned off, and the system was operated using ozone and UV light. Table 9 shows the 1,4-dioxane concentrations at 5, 7.5, and 9.5 gpm with the modified pilot system, analyzed using the EPA Method 522 by Pegasus. The 1,4-dioxane concentration decreased from approximately 9 µg/L to 2.5 – 5 µg/L depending on the water flow rate. This was not as effective as the combination of ozone and hydrogen peroxide.

Table 9. Pilot study data with ozone and UV light

Flow rate (gpm)	Time (min)	O ₃ injection (mg/L)	O ₃ discharge (mg/L)	Airflow (lpm)	Concentration of 1,4-dioxane (µg/L)	
					EPA Method 522	
					Influent	Effluent
5	10	2.5	NA*	2.5	8.63	2.60
	20	2.48	NA	2.5	8.72	2.71
7.5	10	2.6	NA	2.5	8.46	3.99
	20	2.58	NA	2.5	8.64	3.64
9.5	10	2.51	NA	2.5	9.96	4.46
	20	2.62	NA	2.5	8.70	4.73

*NA – ozone discharge concentration was not monitored

3.2.5 Destruction of 10 ppb 1,4-Dioxane using Ozone and Electrocoagulation

The treatment system was operated using ozone and electrocoagulation. Table 10 shows the 1,4-dioxane concentrations at 2.5, 5, 7.5, and 9.5 gpm with the modified pilot system, analyzed using the EPA Method 522 by Pegasus. The 1,4-dioxane concentration decreased from approximately 12 µg/L to 3.5 – 10 µg/L depending on the water flow rate. This was not as effective as the either the combination of ozone and hydrogen peroxide or ozone and UV.

Table 10. Pilot study data with ozone and electrocoagulation

Flow rate (gpm)	Time (min)	O ₃ injection (mg/L)	O ₃ discharge (mg/L)	Airflow (lpm)	Concentration of 1,4-dioxane (µg/L)	
					EPA Method 522	
					Influent	Effluent
2.5	10	2.71	NA*	2.5	12.0	3.78
	20	2.4	NA	2.5	12.4	4.00
5.0	10	2.48	NA	2.5	13.3	6.64
	20	2.51	NA	2.5	12.6	6.98
7.5	10	2.52	NA	2.5	11.9	8.56
	20	2.47	NA	2.5	11.4	8.66
9.5	10	2.02	NA	2.5	11.2	9.79
	20	0.51	NA	2.5	12.4	9.82

*NA – ozone discharge concentration was not monitored

3.2.6 Destruction of 80 ppb 1,4-Dioxane using Hydrogen Peroxide and Ozone

The ozone and hydrogen peroxide-based treatment system with 25-gallon contact tank was then challenged with an influent water containing approximately 80 µg/L of 1,4-dioxane. Table 11 shows the 1,4-dioxane concentrations at 2.5, 5, 7.5, and 9 gpm with the modified pilot system, analyzed using the EPA Method 522 by Pegasus. The 1,4-dioxane concentration decreased from approximately 80 µg/L to 0.4 – 4.7 µg/L depending on the water flow rate.

Table 11. Pilot study data with 80 ppb 1,4-dioxane

Flow rate (gpm)	O ₃ injection (mg/L)	H ₂ O ₂ injection (mg/L)	O ₃ discharge (mg/L)	H ₂ O ₂ discharge (mg/L)	Concentration of 1,4-dioxane (µg/L)	
					EPA Method 522	
					Influent	Effluent
2.5	0.00	0.00	B.D.	B.D.	NA*	0.518
5	B.D.	0.64	B.D.	0.52	NA	0.393
7.5	B.D.	2.26	B.D.	0.46	NA	4.70
9	B.D.	2.49	B.D.	0.58	80.4	4.25

*NA – All influent concentrations were not monitored. Only bulk concentration was monitored due to Covid situations and staff availability.

B.D.: below the detection level

3.2.7 Destruction of 188 ppb 1,4-Dioxane using Hydrogen Peroxide and Ozone

The treatment system was then run with ozone and hydrogen peroxide with an influent containing approximately 188 µg/L of 1,4-dioxane. Table 12 shows the 1,4-dioxane concentrations at 2.5, 5, 7.5, and 9 gpm with the modified pilot system, analyzed using the EPA Method 522 by Pegasus. The 1,4-dioxane concentration decreased from approximately 188 µg/L to 5.4 – 9.8 µg/L depending on the water flow rate. More studies need to be conducted for optimizing the treatment.

Table 12. Pilot study data with 188 ppb 1,4-dioxane

Flow rate (gpm)	H ₂ O ₂ injection (mg/L)	O ₃ discharge (mg/L)	H ₂ O ₂ discharge (mg/L)	Concentration of 1,4-dioxane (µg/L)	
				EPA Method 522	
				Influent	Effluent
2.5	B.D.	NA*	NA	188	5.48
5	1.63	0.09	0.87	NA	7.74
7.5	1.85	0.08	1.65	NA	9.73
9	6.36	0.03	2.76	184	8.76

*NA – concentrations were not monitored

B.D.: below the detection level

4.0 Conclusions

The objective of this project was to develop and evaluate a cost-effective, low-maintenance 1,4-dioxane treatment technology for small-scale Point of Entry Treatment (POET) systems. The study was accomplished by conducting bench- and pilot-scale tests at the U.S. EPA T&E Facility in Cincinnati, Ohio, on 1,4-dioxane-spiked tap water. The tests began in April 2021 and continued until August 2022.

Bench-scale studies included the following: particulate filters, UV, electrocoagulation, hydrogen peroxide, ozone, and combinations of these. While the use of UV or electrocoagulation in addition to ozone (or with a combination of ozone and hydrogen peroxide) was effective in decreasing the 1,4-dioxane concentration, using UV or electrocoagulation by itself or in combination with hydrogen peroxide was not effective in treating 1,4-dioxane. Particulate filters (0.5 μm , 1 μm , 5 μm , and alumina filters) were not effective in removing 1,4-dioxane, either individually or in series.

Building on the bench-scale testing, the pilot-scale testing was focused on combining ozone and hydrogen peroxide to destroy 1,4-dioxane. By using a combination of approximately 3.5 mg/L hydrogen peroxide and 5 mg/L of ozone, water flow rates up to 10 gpm containing up to 200 $\mu\text{g/L}$ of 1,4-dioxane were treated. Influent 1,4-dioxane concentrations of approximately 10 $\mu\text{g/L}$, 20 $\mu\text{g/L}$, 80 $\mu\text{g/L}$, and 180 $\mu\text{g/L}$ were reduced to effluent 1,4-dioxane concentrations of approximately 0.4 $\mu\text{g/L}$, 0.7 $\mu\text{g/L}$, 5 $\mu\text{g/L}$, and 10 $\mu\text{g/L}$, respectively, when treated at almost 10 gpm.

In this study, two analytical methods were compared: Method 522 and modified EPA Method 524.3. These methods were compared to find the most practical and cost-effective way to determine 1,4-dioxane concentrations at low levels (low ppt), while minimizing sample processing (e.g., concentrating samples using SPE can potentially lead to lower detection limits, but there could be losses associated with sample processing). Modified EPA Method 524.3 requires only minimum sample processing and processing time and provides better recovery.

A field study at the Williams property Superfund site in New Jersey will 1) evaluate the 1,4-dioxane contaminated groundwater source water, 2) evaluate the cost of treatment and its efficiency, and 3) optimize operation and maintenance of the treatment process. A summary report will be prepared at the end of the evaluation to describe all findings.

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Appendix A – Summary of the Quality Assurance/Quality Control (QA/QC) Measures

A.1 Introduction

An important aspect of technology testing is the QA/QC procedures and requirements developed. Careful adherence to the procedures detailed in the Quality Assurance Project Plan (QAPP) enables researchers to evaluate the performance of 1,4-dioxane destruction. The primary measures of evaluation for data quality were accuracy, precision, completeness, and representativeness.

Water samples for the bench- and pilot-scale tests were collected from the EPA T&E Facility. Analysis of the samples for 1,4-dioxane was performed at the EPA AWBERC. System performance evaluation testing and laboratory activities were conducted by APTIM and Pegasus in accordance with the provisions of the EPA *Quality Requirements for Measurement Projects* (U.S. EPA, 2008).

A.2 Analytical Procedures

APTIM and Pegasus staff conducted the performance evaluation tests following an EPA-approved QAPP (APTIM, 2020) that was created specifically for these evaluations. Pegasus staff conducted the 1,4-dioxane analyses. Analytical methods for 1,4-dioxane analyses are presented in Table A-1.

Table A-1. Measurements and analytical methods

Measurement	Analytical Method (SOP)
1,4-Dioxane (Headspace)	EPA Method 524.3 (modified)
1,4-Dioxane	EPA Method 522

A.3 Sample Handling

Samples collected by APTIM were labeled with unique identification numbers in the format specified in the EPA-approved QAPPs. Samples transferred by APTIM from the T&E Facility to AWBERC for 1,4-dioxane analyses were transferred after sample collection in hard-sided coolers with ice. All samples were analyzed within sample holding times identified in the QAPPs.

A.4 Sample QA/QC

The calibration of analytical instruments and the analyses of parameters complied with the QA/QC provisions of the EPA-approved QAPP used in this evaluation. Sample volumes, preservation, and holding times are shown in Table A-2. Laboratory QA/QC checks for 1,4-dioxane analyses are shown in Table A-3.

The APTIM QA/QC requirements specified in the referenced methods (Table A-1) are compliant with those stated in the EPA-approved QAPPs and based on EPA published methods for 1,4-dioxane.

Table A-2. Sample volumes, preservation, and holding times

Measurement	Sample Container	Volume of Sample	Preservation	Holding Time
1,4-Dioxane (Headspace)	VOA	40 mL	pH<2; <6°C	14 days
1,4-Dioxane	Glass jar	500 mL	50 mg/L sodium sulfite; 1 g/L sodium bisulfate; pH<4; <6°C	14 days

Table A-3. QA/QC checks

Measurement	QA/QC Check	Frequency	Acceptance Criteria	Corrective Action
1,4-Dioxane [EPA Method 524.3 (modified)]	Calibration	At the beginning of sequence or after CCC failure	$R^2 \geq 0.99$	Investigate problem. Prepare new calibration standards.
	Lab control sample (LCS)	Following calibration	$\pm 25\%$ of the true value	Recalibrate.
	Continuing calibration check (CCC)	Beginning/end of each batch and after every 10 samples	$\pm 25\%$ of the true value	Evaluate data for usability. Recalibrate, reanalyze affected samples.
	Sample matrix blank	One per batch	< the lowest sample concentration for each analyte	Reanalyze. Evaluate data for usability.
	Sample duplicates	One per batch	$\pm 25\%$ RPD	Reanalyze. Evaluate data for usability.
	Lab fortified sample matrix (LFM/LFMD)	One per batch	$\pm 50\%$ of the true value	Reanalyze. Evaluate data for usability.
	Surrogate	Add to each sample	$\pm 30\%$ of the true value	Reanalyze. Evaluate data for usability.

Measurement	QA/QC Check	Frequency	Acceptance Criteria	Corrective Action
	Internal standard	Add known quantity to each sample prior to reconstituting	Area must be within $\pm 50\%$ of the average peak area in the initial calibration	Reanalyze. Evaluate data for usability.
	Standard reference material (SRM, if available)	One per sequence	$\pm 35\%$ of the certified value for 70% of the analytes	Reanalyze. Evaluate data for usability.
1,4-Dioxane (EPA Method 522)	Initial Calibration	Prior to the start of experiments	5 different concentrations; $r^2 > 0.99$	Rerun standard curve, change standards.
	Continuing calibration check (CCC)	Daily before and after each set of 20 samples	70-130% recovery	Rerun standard curve, change standards.
	Laboratory reagent blank	Each extraction batch	$< 1/3$ MRL	Check for benzene contamination.
	Lab fortified blank (low)	Each extraction batch	50-150% recovery	Check for benzene contamination.
	Lab fortified blank (medium or high)	Each extraction batch	70-130% recovery	Check for benzene contamination.
	Surrogate	Add to each sample	$\pm 30\%$ of the true value	Reanalyze. Evaluate data for usability.
	Lab fortified sample matrix	Once per set of 20 samples	50-150% recovery	Resample and repeat analysis.
Duplicate	Once per set of 20 samples	$\pm 30\%$ RPD	Resample and repeat analysis.	

CCC – Continuing calibration check

LCS – Lab control standard

LFM – Lab fortified matrix

LFMD – Lab fortified matrix duplicate

RPD – Relative percent difference

SRM – Standard reference material

DL – Detection limit

MRL – Method reporting limit

A.5 Test System QA/QC

Samples were collected according to the schedule provided in the EPA-approved QAPP. Field duplicate samples were collected to verify the homogeneity of test water concentrations. No significant variations were observed for the field duplicate samples based on accuracy and precision. Duplicate sample analyses are included in Tables A-4. Standard recoveries are included in Tables A-5. Surrogate recoveries are included in Table A-6, and lab fortified blank/lab fortified matrix spike recoveries are included in Table A-7.

Table A-4. Duplicate sample analysis for 1,4-dioxane

Date	Method	Units	Sample 1	Sample 2	Sample 3	RSD/RPD ¹ (%)
03/05/2021	In-house Headspace	ppt	1066.67	852.53	881.56	12.44
03/05/2021	In-house Headspace	ppt	10782.23	10336.4		4.22
05/11/2021	In-house Headspace	ppt	7386.81	7735.17		4.61
06/09/2021	In-house Headspace	ppt	1808.18	2278.46		23.01
06/09/2021	In-house Headspace	ppt	2729.70	3432.34		22.81
06/11/2021	EPA 522	ppb	11.59	9.63		18.41
06/11/2021	In-house Headspace	ppt	11032.0	10698.8		3.06
06/11/2021	In-house Headspace	ppt	10139.4	10154.5		0.15
07/07/2021	In-house Headspace	ppt	12523.29	11797.13		5.97
08/11/2021	In-house Headspace	ppt	380.81	323.14		16.38
10/23/2021	In-house Headspace	ppt	1838.97	1825.28		0.75
10/23/2021	In-house Headspace	ppt	4212.15	3901.48		7.66
11/08/2021	In-house Headspace	ppt	7699.13	8196.96		6.26
11/08/2021	In-house Headspace	ppt	531.69	553.74		4.06
11/20/2021	In-house Headspace	ppt	9663.43	9600.89		0.65
11/20/2021	In-house Headspace	ppt	154.75	154.25		0.32
12/08/2021	In-house Headspace	ppt	11383.7	11841.8		3.94
12/08/2021	In-house Headspace	ppt	101.18	115.27		13.02
02/27/2022	In-house Headspace	ppt	4375.46	4359.63		0.36
02/27/2022	In-house Headspace	ppt	7044.27	8076.31		17.71
04/04/2022	EPA 522	ppt	406.17	388.31		4.49
05/18/2022	In-house Headspace	ppt	160.1	161.04		0.59
05/18/2022	In-house Headspace	ppt	2793.02	2810.93		0.64
06/10/2022	In-house Headspace	ppt	8657.55	8503.21		1.80
07/08/2022	In-house Headspace	ppt	2595.41	2577.72		0.68
07/16/2022	In-house Headspace	ppt	4251.13	4381.14		3.01
07/16/2022	In-house Headspace	ppt	80380.5	84839.4		5.40
07/31/2022	In-house Headspace	ppt	188230	190784		1.35
07/31/2022	In-house Headspace	ppt	1009.61	979.82		2.99

RPD calculated as described in Section A.8.2.

Table A-5. Standard recoveries for 1,4-dioxane

Date	Method	Units	Standard	Measured	Recovery (%)
03/05/2021	In-house Headspace	ppt	10000	9519.73	95.2
03/05/2021	In-house Headspace	ppt	10000	9205.93	92.1
05/11/2021	In-house Headspace	ppt	10000	9001.38	90.0
05/11/2021	In-house Headspace	ppt	10000	8048.12	80.5
05/28/2021	In-house Headspace	ppt	2500	2610.94	104.4
05/28/2021	In-house Headspace	ppt	2500	2906.94	116.3
06/09/2021	In-house Headspace	ppt	1250	1261.23	100.9
06/09/2021	In-house Headspace	ppt	1250	1259.37	100.8
06/11/2021	EPA 522	ppt	100	116.25	116.3
06/11/2021	EPA 522	ppt	100	87.88	87.9
06/11/2021	In-house Headspace	ppt	2500	2352.78	94.1
06/11/2021	In-house Headspace	ppt	2500	2024.27	81.0
07/07/2021	In-house Headspace	ppt	5000	4295.71	85.9
07/07/2021	In-house Headspace	ppt	5000	4819.3	96.4
08/11/2021	In-house Headspace	ppt	5000	5876.46	117.5
08/11/2021	In-house Headspace	ppt	5000	5839.83	116.8
10/23/2021	In-house Headspace	ppt	10000	11769.5	117.7
10/23/2021	In-house Headspace	ppt	10000	8976.68	89.8
11/08/2021	In-house Headspace	ppt	5000	4516.87	90.3
11/08/2021	In-house Headspace	ppt	3000	3386.22	112.9
11/20/2021	In-house Headspace	ppt	5000	4259.24	85.2
11/20/2021	In-house Headspace	ppt	5000	5158.88	103.2
12/08/2021	In-house Headspace	ppt	5000	5017.5	100.4
12/08/2021	In-house Headspace	ppt	5000	5999.25	120.0
02/27/2022	In-house Headspace	ppt	10000	9890.93	98.9
02/27/2022	In-house Headspace	ppt	10000	9382.22	93.8
04/04/2022	EPA 522	ppt	250	238.43	95.4
04/04/2022	EPA522	ppt	1000	1068.32	106.8
05/18/2022	In-house Headspace	ppt	2500	2471.29	98.9
05/18/2022	In-house Headspace	ppt	2500	2397.05	95.9
06/10/2022	In-house Headspace	ppt	2500	2607.93	104.3
06/10/2022	In-house Headspace	ppt	2500	2539.84	101.6
07/08/2022	In-house Headspace	ppt	1000	979.25	97.9
07/08/2022	In-house Headspace	ppt	750	715.91	95.4
07/16/2022	In-house Headspace	ppt	1000	1137.52	113.8
07/16/2022	In-house Headspace	ppt	1000	1007.44	100.7
07/31/2022	In-house Headspace	ppt	5000	5660.11	113.2
07/31/2022	In-house Headspace	ppt	5000	5074.03	101.5

RPD calculated as described in Section A.8.1.

Table A-6. Surrogate recoveries for 1,4-dioxane

Date	Method	Units	Spike	Measured	Recovery (%)
03/05/2021	In-house Headspace	ppt	10000	9050.4	90.5
03/05/2021	In-house Headspace	ppt	10000	9489.74	94.9
05/11/2021	In-house Headspace	ppt	10000	9731.95	97.3
05/11/2021	In-house Headspace	ppt	10000	9258.7	92.6
05/28/2021	In-house Headspace	ppt	2500	2447.6	97.9
05/28/2021	In-house Headspace	ppt	2500	2512.11	100.5
06/09/2021	In-house Headspace	ppt	2000	2035.77	101.8
06/09/2021	In-house Headspace	ppt	2000	2124.55	106.2
06/11/2021	EPA 522	ppt	500	541.95	108.4
06/11/2021	EPA 522	ppt	500	455.85	91.2
06/11/2021	In-house Headspace	ppt	2500	2119.28	84.8
06/11/2021	In-house Headspace	ppt	2500	2370.96	94.8
07/07/2021	In-house Headspace	ppt	5000	5483.86	109.7
07/07/2021	In-house Headspace	ppt	5000	5375.31	107.5
08/11/2021	In-house Headspace	ppt	20000	18472.1	92.4
08/11/2021	In-house Headspace	ppt	20000	20211	101.1
10/23/2021	In-house Headspace	ppt	5000	5260.05	105.2
10/23/2021	In-house Headspace	ppt	5000	5448.71	109.0
11/08/2021	In-house Headspace	ppt	3000	2836.17	94.5
11/08/2021	In-house Headspace	ppt	3000	3469.63	115.6
11/20/2021	In-house Headspace	ppt	2500	2672.27	106.9
11/20/2021	In-house Headspace	ppt	2500	2962.54	118.5
12/08/2021	In-house Headspace	ppt	3000	3592.66	119.8
12/08/2021	In-house Headspace	ppt	3000	2934.06	97.8
02/27/2022	In-house Headspace	ppt	2500	2459.08	98.4
02/27/2022	In-house Headspace	ppt	2500	2708.52	108.3
04/04/2022	EPA 522	ppt	500	493.98	98.8
04/04/2022	EPA522	ppt	500	527.34	105.5
05/18/2022	In-house Headspace	ppt	2500	2912.2	116.5
05/18/2022	In-house Headspace	ppt	1000	949.81	95.0
06/10/2022	In-house Headspace	ppt	500	489.3	97.9
06/10/2022	In-house Headspace	ppt	500	414.38	82.9
07/08/2022	In-house Headspace	ppt	1000	859.64	86.0
07/08/2022	In-house Headspace	ppt	1000	802.27	80.2
07/16/2022	In-house Headspace	ppt	1000	807.15	80.7
07/16/2022	In-house Headspace	ppt	1000	853.04	85.3
07/31/2022	In-house Headspace	ppt	1000	1177.2	117.7
07/31/2022	In-house Headspace	ppt	1000	1180.04	118.0

RPD calculated as described in Section A.8.1.

Table A-7. LFB/Matrix spike recoveries for 1,4-dioxane

Date	Method	Units	Spike	LFB/LFM	Sample	Recovery (%)
05/08/2021	EPA 522	ppt	500	552.21		110.4
06/11/2021	EPA 522	ppt	500	309.29		61.8
06/11/2021	EPA 522	ppt	500	381.27		76.3
06/11/2021	EPA 522	ppt	500	340.10		68.0
06/11/2021	EPA 522	ppt	500	425.97		85.2
04/04/2022	EPA 522	ppt	500	428.29		85.7
04/04/2022	EPA 522	ppt	50	43.63		87.3
04/04/2022	EPA 522	ppt	500	449.81		90.0
04/04/2022	EPA 522	ppt	500	397.49		79.5
04/04/2022	EPA 522	ppt	500	389.70		77.9
04/04/2022	EPA 522	ppt	500	286.56	0.00	57.3
04/04/2022	EPA 522	ppt	500	642.39	122.27	104.0
05/18/2022	In-house Headspace	ppt	2500	2793.02	85.99	108.3
05/18/2022	In-house Headspace	ppt	2500	2810.93	85.99	109.0

RPD calculated as described in Section A.8.1.

A.6 Documentation

Laboratory activities were documented using standardized datasheets, logbooks, and laboratory notebooks. Laboratory data reports were entered into Microsoft™ Excel® spreadsheets. These spreadsheets were used to calculate the mean, standard deviation, and ranges, as applicable.

A.7 Data Review

Calculations performed on a computer were checked initially by the analyst for gross error and miscalculation. The calculations and data entered into computer spreadsheets were checked by a peer reviewer for accuracy by printing out the calculation or data spreadsheet and checking the calculation by hand or comparing each entry of data with the original.

A.8 Data Quality Indicators

The quality of data generated for this system performance evaluation was established through four indicators of data quality: accuracy, precision, completeness, and representativeness.

A.8.1 Accuracy

Accuracy was quantified as the percent recovery of the parameter in a sample of known quantity. Accuracy was measured through use of certified standards during calibration of an instrument.

Percent Recovery was calculated using the following equation:

For controls:

$$\%R = (M/K)*100\%$$

For matrix spike:

$$\%R = [(Xs-Xu)/K]*100\%$$

where

R = percent recovery

M = Measured analyte concentration

K = Known analyte/spike concentration

Xs = Measured concentration of analyte in spiked sample

Xu = Measured concentration of analyte in un-spiked sample

A.8.2 Precision

Precision refers to the degree of mutual agreement among individual measurements and provides an estimate of random error. Precision of duplicate analyses was measured using the following equation to calculate RPD:

$$RPD = \frac{|S_1 - S_2|}{|S_1 + S_2|} \times 200$$

Where:

S_1 = sample analysis result; and

S_2 = sample duplicate analysis result.

If calculated from three or more replicates, the relative standard deviation (RSD) was used according to the following equation:

$$RSD = (s/y_{ave}) \times 100\%$$

where:

RSD = relative standard deviation (%)

s = standard deviation

y_{ave} = mean of the replicate analyses

Standard deviation is defined as follows:

$$s = \sqrt{\sum_{i=1}^n \frac{(y_i - y_{ave})^2}{n - 1}}$$

where:

s = standard deviation

y_i = measured value of the i th replicate

y_{ave} = mean of the replicate measurements

n = number of replicates

A.8.3 Completeness

Completeness is a measure of the relative number of analytical data points that meet all the acceptance criteria for accuracy, precision, and additional criteria required by the specific analytical methods used. The goal is that sufficient amounts of valid data will be generated to satisfy the quality assurance conditions. Completeness was expressed as a percentage, as follows:

$$\text{Percent Completeness} = (\text{number of valid data}) / (\text{expected number of data points}) \times 100\%$$

The completeness goal for this study was 100%.

A.8.4 Representativeness

Representativeness describes the degree to which sample data accurately and precisely represent a characteristic of the material being measured. Representativeness is a qualitative term that is evaluated to determine whether field measurements were made, and physical samples were collected, in such a manner that the resulting data appropriately reflect the media and phenomena measured or studied.

Representativeness was determined by the following procedures:

- Comparison of actual testing procedures to those specified in the QAPP.
- Comparison of analytical results of field duplicates to determine the spread in the analytical results.
- Examination of the analytical results of the QC blanks for evidence of contamination.

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