

APPENDIX C

NJ Drinking Water Quality Institute  
Treatment Subcommittee

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Recommendation on 1,4-Dioxane  
Treatment Options for Drinking Water

New Jersey Drinking Water Quality Institute

Treatment Subcommittee

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## Background

The Treatment Subcommittee of the New Jersey Drinking Water Quality Institute (DWQI) is responsible for identifying available treatment technologies or methods for removal of hazardous contaminants from drinking water. The subcommittee has met several times over the last year beginning in December 2018 to discuss and investigate best available treatment options for 1,4-dioxane. The subcommittee has gathered and reviewed data from several sources, including the literature and direct contact with public drinking water systems, in order to identify widely-accepted and well-performing strategies for removal of 1,4-dioxane, including use of alternate water sources. This report is intended to present the subcommittee's findings.

At this time, there are no enforceable Federal drinking water standards for 1,4-dioxane. Several states have established standards or action levels for 1,4-dioxane in drinking water. A full list of these states is presented in the DWQI Health Effects Subcommittee's Health-Based Maximum Contaminant Level Support Document: 1,4-Dioxane. As such, there are several examples of systems nationally that are endeavoring to remove 1,4-dioxane from drinking water. In addition to drinking water standards, many states have groundwater cleanup levels or screening levels. In January 2018, New Jersey adopted amendments to the Ground Water Quality Standards (GWQS) establishing a specific Ground Water Quality Standard for 1,4-dioxane of 0.4 µg/L (NJDEP, 2018).

In 2013-2015, USEPA required monitoring of 1,4-dioxane at public water systems under the Third Unregulated Contaminant Rule (UCMR3). This requirement was for all public drinking water systems serving a population greater than 10,000 people and 800 representative smaller systems. Samples were analyzed using USEPA Method 522, with a reporting level of 0.07 µg/L. Of the systems required to sample under UCMR3, 1,4-dioxane was detected in 21% of water systems nationally and was detected in 46% (80 out of 174) systems in New Jersey. The concentration of 1,4-dioxane that was reported ranged from 0.07 µg/L to 5.83 µg/L in New Jersey.

According to published literature 1,4-dioxane can be successfully removed from water using treatment technologies discussed in the section below. Removal ratios vary depending on a number of factors (such as initial concentration and presence of other contaminants). Given this information, the ability of treatment options to remove these contaminants is not anticipated to be a limiting factor in the development of a recommended MCL for 1,4-dioxane.

## Treatment Options

Water systems that face 1,4-dioxane contamination should thoroughly evaluate all possible treatment approaches. This should include the incorporation of treatment methods that can be combined with existing infrastructure. While engineering a solution that includes blending is not “treatment,” and may not be the preferred solution, it may be a cost-effective and viable option for some water systems. The cost of this option will vary depending on the availability and proximity of alternate sources. In order to make an informed and cost-effective decision, the use of an alternate source should be evaluated in addition to all available, effective treatment options.

Based on currently available information, the members of the Treatment Subcommittee recommend that Advanced Oxidation Processes (AOPs) be considered for treatment of 1,4-dioxane detected above the DWQI recommended MCL, subject to the on-site pilot testing performance results.

When selecting an appropriate treatment option(s) there are many factors to be considered. According the USEPA (2006) document, 1,4-Dioxane & Treatment Technologies for 1,4-Dioxane: Fundamentals and Field Applications, these include initial concentrations of 1,4-dioxane, operation and maintenance costs, wastes and residual disposal, and ability to address more than one contaminant with the same treatment option. Additional considerations are the difficulties in detection and treatment due to the unique characteristics of 1,4-dioxane, such as its high aqueous miscibility and mobility. This compound has limited effectiveness with convention treatment techniques, such as air stripping and granular activated carbon (USEPA 2006; USPEPA 2017). While technology continues to evolve and new methods continue to emerge, this report discusses technologies demonstrated in the literature and in practice to be effective for removal of 1,4-dioxane.

The following discussion of treatment options evaluates the advantages and limitations as well as cost considerations for each method. This information presented is general and selection of the most cost-effective treatment process(es) requires case-by-case evaluation (both bench and pilot-scale studies) of system needs, including the use of alternate sources that are not contaminated as a replacement for, or in combination with existing sources. There may be a need for use of more than one of the identified options in a treatment train. Both bench and pilot studies should be designed to aid in the establishment of the required design parameters specific to the treatment processes being evaluated. It should be noted that most of the case studies mentioned below included bench and pilot studies for this reason. Conceptual level design should then be used to develop reasonable cost estimates for a full life-cycle cost analysis to include capital, operation and maintenance costs. The full

life-cycle cost analysis can be utilized to define the best option specific to an individual water system.

The treatment options identified in the literature are summarized in Table 1 below and are described in greater detail in the sections that follow. It should be noted that the treatment options listed in Table 1 cannot be practically implemented in all situations and are dependent on water treatment quantity, pretreatment requirements, residual disposal, and water quality.

**TABLE 1. Summary of Treatment Options for Removal of 1,4-Dioxane**

<b>Treatment Option</b>		<b>Notes</b>	<b>Removal Rates</b>
<b>Advanced Oxidation Process (AOP)</b>	Ultraviolet Irradiation & Hydrogen Peroxide	Ultraviolet irradiation combined with hydrogen peroxide.	Up to > 99% removal <sup>1</sup>
	Ozone & Hydrogen Peroxide	Ozone combined with hydrogen peroxide.	Up to > 99% removal <sup>1</sup>
	Ultraviolet Irradiation & Ozone	Ultraviolet irradiation combined with ozone.	Up to 98% removal <sup>1</sup>
	Ultraviolet Irradiation & Free Chlorine/Chloramines	Full scale study treating water reclamation effluent.	> 68% removal <sup>3</sup>
<b>Membrane Separation</b>	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 <sup>1</sup>
<b>Activated Carbon</b>	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. <sup>1</sup> 56% removal when GAC was applied downstream of a reverse osmosis (RO). <sup>1</sup>
<b>Synthetic Media Sorption Units</b>	AMBERSORB™ 560	Full scale contaminated ground water remediation system.	Up to > 99% removal <sup>2</sup>

<sup>1</sup>USEPA, 2020; <sup>2</sup>Woodard et al., 2014; <sup>3</sup>Royce et al., 2015

## Advanced Oxidation Processes (AOPs)

AOPs rely on highly reactive hydroxyl radicals ( $\cdot\text{OH}$ ) to oxidize contaminants and are a commercially available treatment option for 1,4-dioxane in drinking water. The hydroxyl radicals oxidize organic contaminants to carbon dioxide, water, and residual chloride (USEPA, 2006). AOP treatment can also be used as a pre- or post-treatment step. The hydroxyl radical has the capability of oxidizing a variety of organic and inorganic contaminants, including 1,4-dioxane.

The oxidants used in conventional oxidation processes are not strong enough to break down 1,4-dioxane. The oxidation potential of a hydroxyl radical (2.8 Volts) is much greater than other widely-used oxidizing agents, such as ozone (2.1 Volts), chlorine (1.40 Volts) and permanganate (1.7 Volts) (Sumner et al., 2010; USEPA, 2006).

The hydroxyl radicals are nonselective and interact with organic and inorganic compounds present in the water. Therefore, source water quality is an important consideration when designing AOP treatment, as organic matter, alkalinity, and other existing compounds in the water can interfere with its efficacy. Incomplete oxidation can yield high levels of byproducts from breakdown intermediates. Additionally, depending on the specific AOP treatment technology used, byproducts such as bromate, chlorate, and disinfection byproducts (DBPs) may be formed if bromide, chloride, or sulfate is present in the source water. Treatment should be designed and tested in order to minimize formation of these byproducts and best suit specific source water quality.

AOP for 1,4-dioxane treatment can have the added benefit of breaking down additional contaminants, such as perchlorate, methyl tert-butyl ether (MTBE), tetrachloroethylene (PCE), trichloroethylene (TCE), pesticides, pharmaceutical and personal care products, as well as difficult to remove compounds that cause undesirable taste and odor such as 2-methylisoborneol (MIB) and geosmin. Additionally, AOP may help control biological growth, iron and manganese, volatile organic compounds (VOCs) and other dissolved organic contaminants.

Although additional treatment technologies are described below, the Treatment Subcommittee found that AOPs were the most common treatment for 1,4-dioxane removal. Accordingly, more information, including published literature and case studies, was available for AOPs than for the other treatments.

## Ultraviolet Irradiation with Hydrogen Peroxide

The combination of ultraviolet (UV) irradiation and hydrogen peroxide ( $H_2O_2$ ) is a commonly used form of AOP treatment. Hydroxyl radicals are generated from hydrogen peroxide in the presence of UV light. The powerful oxidizing nature of hydroxyl radicals is necessary in the treatment of 1,4-dioxane, because UV light alone is not effective. Due to 1,4-dioxane's very weak absorption of UV light, direct photolysis, or the breaking down of chemical bonds by UV light, is not feasible (Stefan et al., 1998).

The UV/ $H_2O_2$  process includes two stages of oxidation. In the initial stage, UV light acts as a catalyst and creates chain reactions that produce hydroxyl radicals from hydrogen peroxide. Many contaminants in the water are also irradiated by the UV light.

The second stage of oxidation occurs when the hydroxyl radicals created in the initial stage react with 1,4-dioxane. Stefan et al. (1998) found that 1,4-dioxane is initially degraded into the primary reaction intermediates 1,2-ethanediol mono- and di-formate esters, formic acid, and methoxyacetic acids. This initial degradation of 1,4-dioxane happens very rapidly, with a 90% depletion of 1,4-dioxane occurring within the first five minutes of treatment (Stefan et al., 1998). The hydroxyl radicals created in the initial stage continue to react with these newly formed intermediates, oxidizing and degrading into several aldehydes, such as formaldehyde, acetaldehyde, and glyoxal, as well as glycolic and acetic acids. The final and most degraded intermediate of 1,4-dioxane is oxalic acid, which further reacts with hydrogen radicals to form carbon dioxide and water (Stefan et al., 1998).

There are several important design considerations when using UV/ $H_2O_2$  systems, including hydrogen peroxide dosage, the type and intensity of the UV lamp, and the amount of time the contaminated water is in the UV reactor. Additionally, pH and temperature monitoring and control should be considered.

Two types of UV lamps may be used in UV/ $H_2O_2$  processes. One utilizes low pressure (LP) UV light, and the other utilizes medium pressure (MP) UV light. A low pressure, high output (LP-HO) lamp is more effective when dealing with continuous contaminant removal, as would be expected when treating for 1,4-dioxane. MP is better suited towards periodic events, and is therefore likely to be less effective for the continuous removal of 1,4-dioxane. Additionally, LP-HO lamps consume less energy and may require less maintenance for scaling of sleeves than the MP equivalents. (USEPA, 2006)

Most commonly, the point of application for a UV/ $H_2O_2$  system is the end of a conventional treatment process. At this stage, water has already undergone most chemical treatment and filtration, and has a lower turbidity, allowing for better intensity and saturation of UV light.

Dosing of hydrogen peroxide is also important to determine during testing. If insufficient hydroxyl radicals are produced, intermediates may accumulate in the water. Excess peroxide can interact with hydroxyl radicals and reduce their efficiency (USEPA, 2006). However, a study showed that the initial concentration of hydrogen peroxide was depleted less than 10% after treatment of 1,4-dioxane (Maurino et al., 1997). With UV/H<sub>2</sub>O<sub>2</sub>, quenching of excess hydrogen peroxide with additional treatment such as GAC may be required.

A review of the literature and several case studies indicated that the UV/H<sub>2</sub>O<sub>2</sub> method of treatment was effective (>99% removal) treatment for 1,4-dioxane.

Costs will vary depending on the size of operation, level of contaminant in the source water, as well as the presence and concentration of other contaminants that compete for oxidation. See the case studies below, which include examples of costs.

### Case Studies

**New Jersey American Water – Hummocks Wellfield** – A full scale UV/ H<sub>2</sub>O<sub>2</sub> system was tested for removal of 1,4-dioxane at the Hummocks Wellfield starting in January 2018. Raw water concentrations of 1,4-dioxane were between approximately 1.4 µg/L and 0.4 µg/L. The treatment was shown to effectively remove 1,4-dioxane down to 0.15 µg/L on average, as measured using EPA Method 522. The treatment consists of an AOP mobile unit with 1.7 MGD capacity. UV treatment consists of double reactor chambers with 144 high-output lamps and 35% strength hydrogen peroxide. GAC filters after the mobile unit are used to quench hydrogen peroxide residual. The capital cost of the mobile system was \$1.7 million and included all expenses including chemical delivery. Operational costs of running the system were estimated to be \$120,000 per year. Upgrades to the UV/H<sub>2</sub>O<sub>2</sub> and GAC treatment systems to increase capacity to 5.2 MGD are estimated to have a capital cost of \$19 million dollars, including building construction costs. Annual operation and maintenance cost with this increased capacity are estimated to be \$450,000. (Monaco, 2020).

**Tucson Water, Arizona** – The City of Tucson in Arizona finished construction on a UV/H<sub>2</sub>O<sub>2</sub> facility in January 2014. The facility included 3 UV reactors, 8 GAC contactors for quenching hydrogen peroxide, a blending station, booster pumps, GAC backwash tanks, and a 4,500 square-foot building. The facility cost \$18 million to construct and treats around 7 MGD, serving approximately 60,000 customers. The facility was able to reduce 1,4-dioxane from an initial concentration of 1.5 µg/L to non-detectable levels, with a detection limit of 0.1 µg/L. (Tucson Water, 2017; Tucson Water, 2020a; Tucson Water, 2020b).



**Monterey Park, California** – The City of Monterey Park water utility has constructed a treatment plant designed for the removal of 1,4-dioxane through use of UV/ H<sub>2</sub>O<sub>2</sub>. Full scale testing of the plant shows that 1,4-dioxane has been reduced from an initial concentration of 2.0 µg/L to non-detect. EPA Method 522 with a Method Detection Limit (MDL) of 0.5 µg/L was used for analysis. Sampling costs were \$75 per sample, with multi-year contractual pricing. The system also employs catalytic GAC for hydrogen peroxide quenching. Capital costs were \$8.3 million for a 10 MGD plant. (Gonzales and Martinez, 2019).

**Suffolk County Water Authority, New York** – In 2017, the Suffolk County Water Authority constructed a UV/ H<sub>2</sub>O<sub>2</sub> facility for treatment of 1,4-dioxane. Removal rates of 1,4-dioxane were found to be 99% during full scale testing. Overall cost of the project was \$1.5 million. The system has been designing AOPs for additional wells and estimates that capital costs will range between \$1.5-6 million, depending on the size of the system. (SCWA, 2020a; SCWA 2020b)

### Ozone with Hydrogen Peroxide

The combination of ozone (O<sub>3</sub>) with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) has been shown to be an effective technique for the treatment of 1,4-dioxane. The O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> process works similarly to other AOPs by creating powerful oxidizers that break down contaminants. Ozone alone is a powerful oxidant; however, it is a selective oxidant and does not readily oxidize certain compounds. Ozone is ineffective and is slow acting for the treatment of 1,4-dioxane. However, when paired with hydrogen peroxide, ozone can produce hydroxyl radicals, which are nonselective as mentioned above. This nonselective nature makes the reaction rates of O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> nine orders of magnitude greater than ozone on its own. (Adams et al., 1994)

Once the ozone and hydroxyl radicals begin to oxidize and break down the 1,4-dioxane molecules found in the water, the solution will become more acidic (lowering the pH). Similar to the process with UV/ H<sub>2</sub>O<sub>2</sub>, the degradation of 1,4-dioxane with O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment forms intermediate compounds, such as methoxyacetic acid, 1,2-ethanediol mono(di)formate, formic acid, aldehydes including acetaldehyde and formaldehyde, and acetic acid, glycolic acid, and oxalic acid (Suh and Mohseni, 2004).

The removal efficiency of an O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system depends on the dosage of ozone and hydrogen peroxide, the contact time, the concentrations of 1,4-dioxane and other competing compounds such as bicarbonate alkalinity and organic chemicals.

The O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system can provide a degree of flexibility regarding the required molar ratios for 1,4-dioxane removal. A study conducted by Adams et al. (1994) found that while both a 0.5 O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> molar ratio and a 1.0 O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> molar ratio effectively oxidized 1,4-dioxane, the

1.0 O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> ratio required more hydrogen peroxide and less ozone. The optimal molar ratio will be system specific and should be determined by considering raw material and operational costs and allowable concentration of peroxide residuals. (Adams et al., 1994)

Co-occurring contaminants can affect the oxidation of 1,4-dioxane. If there is bromide present in source water, bromate is generated. Bromate has a drinking water MCL regulated at 10 µg/L. Increased bromide concentration can inhibit 1,4-dioxane breakdown and increase bromate concentrations in the finished water. However, increasing the dosage of hydrogen peroxide can counteract bromate formation and improve 1,4-dioxane oxidation. (AWWA, 2018)

The O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system would be preferable for utility systems that need or want to avoid peroxide quenching. Additionally, when compared to UV/ H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> treatment is not as sensitive to lower source water quality and has an overall lower power consumption.

### Case Studies

**Orange County, California** - An industrial site in Orange County, California installed a HiPOx unit which is reducing the concentration of dioxane to below 3 µg/L. Additional benefits include reduction of 1,1 dichloroethylene (DCE) at 8 µg/L and trichloroethene (TCE) at 3 µg/L each to below 1 µg/L. The GAC system was retained at the effluent of the HiPOx system to remove other VOCs, such as TCA. (USEPA, 2006)

**Unspecified location, California** - A confidential site in an industrial city in California conducted pilot tests which showed that the HiPOx system could reduce the concentration of dioxane from 610 µg/L in the influent to 9.5 µg/L in the effluent. The commercial unit was installed in February 2002 and operates at a flow rate of 45 gpm. (USEPA, 2006)

### Ozone with Ultraviolet Irradiation

The combination of ozone (O<sub>3</sub>) with Ultraviolet Irradiation (UV) has been shown to be an effective technique for the treatment of 1,4-dioxane (up to 99%) (Asano et al., 2012). As mentioned above, both ozone and UV irradiation on their own are not very effective in degrading 1,4-dioxane. However, the combination of these two processes results in a much more rapid and effective degradation (Kishimoto and Nakamura, 2011). The removal efficiency of a O<sub>3</sub>/UV treatment system depends on the size of the ozone bubbles generated and the level of pH.

Kishimoto and Nakamura (2011) found that increasing the size of the ozone bubbles and decreasing the pH increased the efficiency of ozone utilization but simultaneously decreased its dissolution efficiency. Alternatively, when the pH was increased, the ozone generated

more hydroxyl radicals through decomposition and thus aided in the degradation of 1,4-dioxane.

### Ultraviolet Irradiation with Free Chlorine/Chloramine

Two additional forms of AOP are the ultraviolet irradiation and free chlorine (UV/Cl<sub>2</sub>) process and the ultraviolet irradiation and chloramine (UV/NH<sub>2</sub>Cl) process. Often, a UV/Cl<sub>2</sub> system is situated following a form of treatment such as reverse osmosis (RO) that requires pretreatment with chlorine, for reasons such as pH adjustment. The chlorine present in the water entering the UV/Cl<sub>2</sub> system becomes photolyzed and generates chlorine radicals and hydroxyl radicals that work in tandem with each other (Royce et al., 2015).

The process is similar for the chloramine equivalent (UV/NH<sub>2</sub>Cl), in which chloramines are added to a system's water before membrane separation or filtration in order to diminish the fouling or biofouling of the membrane (Li et al., 2018). The chloramines pass through the membrane alongside other similarly small molecular size compounds such as 1,4-dioxane, and move downstream to the AOP (Li et al., 2018). Once there, the chloramines are photolyzed and create hydroxyl and chlorine radicals that both aid in the degradation of 1,4-dioxane (Li et al., 2018).

The efficiency of these two chlorinated AOPs are dependent on several factors, such as the pH of the source water, the temperature of the source water, the contact time, and the ratios between chlorine (Cl<sub>2</sub>) and/or chloramines (NH<sub>2</sub>Cl) and ammonia (NH<sub>3</sub>) (Royce et al., 2015). Zang et al. (2019) showed that when treating for 1,4-dioxane, UV/Cl<sub>2</sub> was the most efficient technology in terms of minimizing UV dose, followed by UV/H<sub>2</sub>O<sub>2</sub> and UV/NH<sub>2</sub>Cl.

Some additional testing showed that a UV/H<sub>2</sub>O<sub>2</sub> system that did not quench its chloramines resulted in 50% less degradation of 1,4-dioxane than a UV/H<sub>2</sub>O<sub>2</sub> system that did remove its chloramines. However, the UV/H<sub>2</sub>O<sub>2</sub> system that did not quench its chloramines was still 30-50% more effective at treating 1,4-dioxane than a pure UV/chloramine (NH<sub>2</sub>Cl) system (Zhang et al., 2019). This is most likely due to the scavenging effect of NH<sub>2</sub>Cl, which can reduce the number of major radicals, degrading them into less reactive compounds and thus inhibiting availability and oxidation efficiency (Li et al., 2018).

Cost estimates to achieve 65% removal of 1,4-dioxane indicated that UV/NH<sub>2</sub>Cl and UV/H<sub>2</sub>O<sub>2</sub> systems could have a similar cost effectiveness due to the lower reagent costs for the UV/NH<sub>2</sub>Cl system, assuming that the system's chlorine dose does not need to be increased (Zhang et al., 2019). The cost of a UV/Cl<sub>2</sub> (free chlorine) system would be around half of the cost of a UV/H<sub>2</sub>O<sub>2</sub> AOP, also due to costs saved in reagents, assuming the system already provides chlorine treatment.

Several byproducts that are generated by both the UV/NH<sub>2</sub>Cl and UV/Cl<sub>2</sub> AOPs require consideration. If the feedwater contains bromide, the bromate ion (BrO<sub>3</sub><sup>-</sup>) is generated. A pilot scale study found that when 5 mg/L of chlorine is added to water with a pH of 7.2, around 15 µg/L of bromate is present in the effluent after a UV/Cl<sub>2</sub> AOP (Royce et al., 2015). Another byproduct is chlorite (ClO<sub>2</sub><sup>-</sup>), generated from the photolysis of hypochlorite. Chlorite is a federally regulated contaminant, with an MCL of 1 mg/L. The third byproduct is chlorate (ClO<sub>3</sub><sup>-</sup>), which is produced from the photolysis of the free chlorine. Chlorate is not currently regulated for drinking water, but it was monitored for in USEPA's UCMR3 using EPA Method 300.1 and a reporting level of 20 µg/L. The UCMR3 Health Reference Concentration for chlorate was 210 µg/L. The pilot-scale study found that with the addition of 5 mg/L of chlorine to water with a pH of 7.2, 1,400 µg/L of chlorate was generated in the effluent (Royce et al., 2015). Additional byproducts which should be considered are chlorinated organics, which include disinfection byproducts (DBPs). A study performed by Zhang et al. found that the use of chlorine-based oxidants within both the UV/NH<sub>2</sub>Cl and UV/Cl<sub>2</sub> AOPs did increase the production of DBPs, but the total halogenated DBP formations remained relatively low, under 15 mg/L for both forms of chlorinated AOPs. DBPs that were formed included haloacetic acids, haloketones, haloacetonitriles and halonitromethanes (Zhang et al., 2019)

### Case Study

**Long Beach, California** - The Leo J. Vander Lans Advanced Water Treatment Facility (LJVWTF) treats effluent water from a water reclamation plant. LJVWTF performed a full scale study in 2014 to test for the effectiveness of UV/Cl<sub>2</sub> and UV/ H<sub>2</sub>O<sub>2</sub> for removal of 1,4-dioxane. The UV/Cl<sub>2</sub> and UV/H<sub>2</sub>O<sub>2</sub> systems were placed after the system's existing RO treatment. Several byproducts were found in the UV/Cl<sub>2</sub> AOP treatment including bromate ions, chlorite and chlorate ions, and chlorinated organics, including DBPs. The study results showed reduction rates of 1,4-dioxane of greater than approximately 68% for both UV/Cl<sub>2</sub> and UV/ H<sub>2</sub>O<sub>2</sub>. (Royce et al., 2015)

### Membrane Separation

There are various methods of membrane separation treatment, but RO and nanofiltration (NF) are the methods that are commonly found in drinking water systems. RO and NF are pressure-driven processes that rely on the use of semipermeable membranes to remove dissolved contaminants from drinking water. Although RO and NF involve similar equipment and processes, the two treatments differ in their ability to remove 1,4-dioxane from drinking water. The efficiency of RO and NF methods in removing a contaminant is determined by the physicochemical properties of the contaminant such as hydrophobicity, charge, and molecule size. 1,4-Dioxane is a hydrophilic compound with a molar mass of 88.11 g/mol.

Compared to other common contaminants, 1,4-dioxane has a low molecular weight and a low molecular volume. Recent studies have shown that the physicochemical properties of 1,4-dioxane make it particularly difficult to remove from drinking water through the use of membrane separation treatments.

### Reverse Osmosis

Reverse osmosis (RO) can remove many types of molecules and ions from solutions and is used in both industrial processes and the production of potable water. In the RO method, water is pumped into a pressure vessel and flows through multiple elements, often spiral-wound. Each element consists of multiple layers of material, such as polyamide, that make up the semipermeable membrane. As water flows through the pressure vessel, smaller molecules, such as water, are able to pass through the membrane while larger particles become trapped. The resulting water, or permeate, passes onto the next phase of the water system while the concentrate is passed onto another set of membranes or for waste treatment.

Due to its hydrophilic nature and small size, 1,4-dioxane is usually able to pass through the semipermeable membrane. The application of RO in combination with other filtration methods is more effective than RO treatment alone. Although rejection rates do not seem to be extremely high for 1,4-dioxane with RO treatment, there is still evidence that RO treatment reduces the amount of 1,4-dioxane that is able to pass through as permeate. (Kegel et al., 2010)

The advantages of RO treatment include its ability to filter out additional contaminants of concern that may be present in the source water. However, this means that minerals and nutrients which are desirable in finished drinking water are also removed and therefore must be re-added.

Pretreatment is important when working with RO membranes due to the nature of their spiral-wound design. RO membranes are highly susceptible to fouling due to accumulation of material on the membrane surface (loss of production capacity). Therefore, effective pretreatment is a necessity for any RO system. Recovery rates, or the ratio of an RO system's permeate to its feed water flow rate, in standard RO elements are typically between 80-85%. However, a high concentration of dissolved contaminants in the concentrate stream can limit the recovery rates.

RO does have additional limitations that must be considered. A typical RO system will generate about 20 to 25% of reject streams. Rejected water from RO must be managed properly to avoid further contamination of surrounding water and in accordance with applicable regulations. Further reduction of reject to approximately 5% could be achieved

through High Recovery RO systems. Systems must account for the disposal of the waste by-products, one of which is a high level of total dissolved solids.

### Case Studies

**Brunswick County, North Carolina** - The Brunswick County Public Utilities water system in North Carolina has been pilot testing the use of low-pressure reverse osmosis (LPRO) for treatment of per- and polyfluoroalkyl substances (PFAS) in their source water. The system also monitored for 1,4-dioxane as part of this testing. Between February 26, 2018 and May 31, 2019, the system saw raw water concentrations of 1,4-dioxane between 0.42 and 3.6 µg/L. The levels of 1,4-dioxane in the RO permeate during this time ranged between 0.027 and 0.71 µg/L. Removal rates of 1,4-dioxane by the LPRO ranged between 68% and 96%. The difference in removal rates was attributed to fluctuations in water temperature along with use of membranes from various manufacturers. (Walker and Nichols, 2019)

The projected cost estimate for this project is capped at \$138 million and includes addition of a LPRO system capable of handling 36 MGD volume. In addition, these estimated costs include expansion of the treatment plant, new chlorine facilities, additional solids waste treatment, and engineering and construction management fees. Estimated operating costs are \$2.9 million per year, including replacement of membrane element and additional staff. Sample costs are expected to be \$60 per sample using EPA Method 522. (Walker and Nichols, 2019)

**Zwolle, Netherlands** - The drinking water treatment plant, Engelse Werk, near the town of Zwolle in the Netherlands conducted a study on the effectiveness of typical RO treatment in combination with activated carbon filtration. When applied in combination with activated carbon, the average removal of neutral compounds by RO, including 1,4-dioxane was around 85%. The study concluded that the smallest hydrophilic solutes, 1,4-dioxane and N-nitrosodimethylamine (NDMA), were most difficult to remove with this process. All other micropollutants had very high rejection rates. (Kegel et al., 2010)

### Nanofiltration

Nanofiltration (NF) is similar to RO, but allows for larger particles to pass through the membrane, while colloidal particles (1 nm to 1000 nm range) are filtered out. NF was developed as an alternative to RO and was specifically designed with a reduced rejection rate for smaller, less charged ions. The NF process allows nutrients such as salt, magnesium, potassium, and calcium to pass through the filtration process. Compared to RO, studies suggest that NF is a more cost-effective and technologically suitable method for the removal of organic compounds.

The advantages of NF include its cost effectiveness in comparison with RO. It also requires less operating feed pressure than RO and does not remove all desirable minerals and nutrients. Conversely, nanofiltration does not remove the other undesirable contaminants that RO is capable of removing.

However, as with RO, pretreatment is an important consideration as membranes are highly susceptible to fouling (loss of production capacity). Therefore, effective pretreatment is a necessity for any NF system. Additionally, rejected water from NF must be managed properly to avoid further contamination of surrounding water and in accordance with applicable regulations. Reducing the quantity of rejected water and the removal of other undesirable contaminants will determine the selection of either RO or NF.

### Granular Activated Carbon (GAC)

GAC is a commonly used media for filtration that can absorb natural and synthetic organic compounds. GAC is highly porous, consisting of both macropores and mesopores that greatly increase the surface area and can trap contaminants through both physical and chemical processes.

GAC can be made from many different materials that contain very high concentrations of carbon. Some examples are wood, coconut shells, and bituminous coal (Kegel et al., 2010). GAC treatment is often designed for post-filtration, ensuring better influent water quality into the GAC unit. This is beneficial when designing treatment for removal of specific contaminants that are not removed by existing processes. GAC can also be incorporated into an existing filter by replacing some of the filter media with GAC. This may significantly lower capital costs as no additional space is needed for additional filters.

However, while GAC is a commonly used method of filtration, there are several compounds that are not filtered or captured as readily as others. GAC is a relatively ineffective treatment for removal of 1,4-dioxane. Due to the high miscibility and hydrophilic nature of 1,4-dioxane, it is prone to simply pass through the carbon medium (Kegel et al., 2010).

A study performed by Kegel et al. (2010) found that on its own, GAC was relatively ineffective at adsorbing 1,4-dioxane and only removed 18% of it from the feedwater. However, when GAC is implemented downstream from other, more effective methods of treatment, such as an RO system or AOP, its capability for removal increases due to the increase in concentration (Kegel et al., 2010; Woodard et al., 2014). The study found that when placed downstream from a RO unit, the removal of 1,4-dioxane by GAC increased to 56%. The same study performed a pilot-scale batch isotherm test and the removal was increased to 67%.

GAC also requires a regeneration or replacement of the carbon medium in order to retain its capacity for filtration. A study performed rapid column testing to determine GAC's efficiency for 1,4-dioxane removal and found that less than 1,000 bed volumes of water could be treated under operating conditions before the GAC was fouled and 1,4-dioxane was able to break through (Summers et al., 2014). This would in turn make the costs of GAC treatment incredibly high and overall, unfeasible for treatment of 1,4-dioxane.

### Case Study

**Menlo Park, California** - GAC was used to treat solvents in groundwater at the Stanford Linear Accelerator Center (SLAC) site in Menlo Park, California, before 1,4-dioxane was discovered. It was later found that dioxane was present in the groundwater at concentrations ranging from a few  $\mu\text{g/L}$  to 1,000s of  $\mu\text{g/L}$ . The concentration of 1,4-dioxane was the highest at the location of a former underground storage tank (reported as high as 7,300  $\mu\text{g/L}$ ). Adsorption using GAC was found to remove the 1,4-dioxane despite poor expectations based on the properties of the contaminant. Analytical results of influent and effluent water samples collected from the treatment system showed that although the influent water has historically contained 1,4-dioxane at concentrations as high as 1,500  $\mu\text{g/L}$ , the compound was not detected in the effluent water samples that were analyzed. This unexpected result could be attributed to low influent concentrations to the treatment system, very low flow rates (0.5 gpm), or possible biodegradation of 1,4-dioxane on carbon surfaces in the presence of tetrahydrofuran, another constituent in the influent water. (USEPA, 2006)

### Synthetic Media Sorption Units

Another emerging treatment technology to be considered is a synthetic media system. These consist of engineered material that can vary in its specificity of treatment. An example of a synthetic media system that can be used to treat 1,4-dioxane is AMBERSORB™ 560, manufactured by The Dow Chemical Company. AMBERSORB™ is a carbon-based absorbent material, generated from the partial pyrolysis of sulfonated styrene-divinylbenzene copolymer (Woodard et al., 2014; Mohr et al., 2014). This process creates spherical material with large porous surface areas, in which the size and distribution of the pores can be controlled. This in turn allows for an increased selectivity for certain compounds that would otherwise be untreatable or less treatable by conventional filtration methods, more stable adsorption rates, and lowers batch-to-batch variability (Woodard et al. 2014; Mohr et al., 2014).

AMBERSORB™ 560 also differs from other conventional treatments, such as GAC, by having a greater sorptive capacity for hydrophobic organic compounds such as 1,4-dioxane



(Woodard et al., 2014; Mohr et al., 2014). By adsorbing less water, it allows for a higher adsorption rate of other compounds, including 1,4-dioxane and other volatile organic compounds. The adsorption rates of non-polar organic contaminants have also been reported by vendors to range from 5 times to an order of magnitude greater than GAC (Woodard et al., 2014; Mohr et al., 2014). Synthetic media treatment also has less energy demands than other treatment options, such as AOPs or RO.

AMBERSORB™ 560 treatment works by passing contaminated water through the synthetic media, where it is reversibly adsorbed. Typically, treatment is designed with several vessels in a lead lag configuration, so that if breakthrough due to complete saturation occurs, the lead vessel or vessels can be taken offline for regeneration and the lag vessel previously on standby becomes the primary vessel (Mohr et al., 2014). AMBERSORB™ 560 can be regenerated repeatedly with minimal reduction in capacity to remove 1,4-dioxane. (Woodard et al., 2014). Regeneration bolsters and increases the effective bed volume throughput of the material. Regeneration is typically achieved by running steam through the synthetic media and “superloading” the concentrated condensate into a GAC treatment vessel. GAC’s adsorption rates increase as the concentrations of 1,4-dioxane are increased, so the highly concentrated condensate will be more readily captured than at low concentrations. As treatment using synthetic medias does not break down 1,4-dioxane, the waste stream will need further management. The processed water after GAC filtration can be sent back to the head of the treatment train. However, the GAC media will need to be reactivated off site (Woodard et al., 2014).

### Case Study

**Waltham, Massachusetts** – A contaminated groundwater site in Waltham, Massachusetts installed synthetic media to treat for 1,4-dioxane. Influent levels of 1,4-dioxane ranged from 8 µg/L to 60 µg/L, averaging around 20 µg/L in 2011. Vessels were operated in series in a lead-lag-standby operation. In the effluent, 1,4-dioxane was non-detectable using EPA Method 522 and a detection limit of 0.04 µg/L. An additional operation was installed at this site in 2014 to treat for contaminated ground water at a rate of 100 gpm. Influent concentrations ranged from non-detectable to 12 µg/L, averaging 5.9 µg/L. Effluent concentrations of 1,4-dioxane have been non-detectable at this second operation, with a detection limit of 0.04 µg/L. Pretreatment was included to control iron residuals. (Woodard et al., 2014).

### Point of Use Treatment

There are no certified residential treatment devices for the reduction of 1,4-dioxane from drinking water. Further research is needed to better understand treatment for 1,4-dioxane at the residential level. A certification process to ensure that point of use (POU) treatment

and point-of-entry treatment (POET) units meet the recommended Health-based MCL of 0.33 µg/L needs to be developed.

## Conclusion

Given the effective treatment of 1,4-dioxane from raw water using AOPs at water systems described above, the Treatment Subcommittee concludes that it has been demonstrated that 1,4-dioxane can be reliably and feasibly removed in public water systems by carefully designed AOP treatment to levels below the recommended Health-based MCL of 0.33 µg/L.

The Treatment Subcommittee advises that AOPs and/or an equally efficient technology should be considered for treatment of 1,4-dioxane if detected above the DWQI-recommended MCL subject to the on-site pilot testing performance results.

Furthermore, the Treatment Subcommittee recommends that owners of private well with 1,4-dioxane contamination exceeding the recommended MCL consider the installation of treatment to reduce exposure. Additionally, the subcommittee recommends that research be undertaken as soon as possible for a cost effective residential treatment solution.

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