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OCCURRENCE OF 1,4-DIOXANE IN THE CAPE FEAR RIVER WATERSHED AND  
EFFECTIVENESS OF WATER TREATMENT OPTIONS FOR 1,4-DIOXANE CONTROL

By

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## ABSTRACT

1,4-Dioxane is a cyclic diether that is used in paint strippers, dyes, greases and varnishes; serves as a purifying agent in the production of pharmaceuticals and specialty chemicals; and is a by-product of manufacturing processes involving ethylene oxide such as the production of polyethylene terephthalate (PET), polyester, and detergents. 1,4-Dioxane is classified as a likely human carcinogen by the United States Environmental Protection Agency (USEPA), and an excess  $10^{-6}$  cancer risk is associated with the lifetime consumption of drinking water containing 0.35  $\mu\text{g/L}$  1,4-dioxane. Data collected between 2013 and 2015 as part of USEPA's third unregulated contaminant monitoring rule (UCMR3) show that seven of the twenty highest 1,4-dioxane concentrations in US drinking water occur in the Cape Fear River (CFR) watershed of North Carolina. The overarching goal of this research was to gain insights into the occurrence of 1,4-dioxane in surface water and drinking water in the CFR watershed. Specific objectives included to (1) identify sources of 1,4-dioxane, (2) establish temporal and spatial variability of 1,4-dioxane concentrations and mass flows, (3) determine the fate of 1,4-dioxane in three surface water treatment plants, (4) determine the effectiveness of ozonation and advanced oxidation processes for 1,4-dioxane transformation in surface water, and (5) assess the effectiveness of point-of-use (POU) treatment devices for 1,4-dioxane removal.

Forty-seven sampling points were strategically selected across the CFR watershed to bracket wastewater treatment plant (WWTP) discharges. Monthly samples were collected from October 2014 to October 2015 and analyzed by gas chromatography/mass spectrometry (GC/MS). Results showed that discharges of three municipal WWTPs located in the headwater region are primarily responsible for elevated instream 1,4-dioxane concentrations. The highest 1,4-dioxane concentrations (up to 1,700  $\mu\text{g/L}$ ) were observed in the headwaters just downstream of the WWTP discharges. Median 1,4-dioxane concentrations decreased in a downstream direction with increasing distance from the identified sources. This phenomenon was primarily attributed to dilution from tributaries that did not contain measurable 1,4-dioxane levels. 1,4-Dioxane concentrations and mass flows were highly variable in space and time, with concentrations ranging from sub-microgram to milligram per liter levels, and mass flows ranging from a few kilograms to more than one hundred kilograms per day. Large temporal fluctuations in 1,4-dioxane mass flows were observed at all sampling locations downstream of the identified point sources, suggesting that 1,4-dioxane discharges into the sewer system of source communities were highly episodic in nature. The variability in 1,4-dioxane sources combined with the variability in stream flow led to large temporal fluctuations in downstream 1,4-dioxane concentrations.

Daily composite raw and finished water samples were analyzed and collected over a period of 2 months at three drinking water utilities. For two conventional water treatment plants 1,4-dioxane concentrations were not attenuated. Average 1,4-dioxane concentrations exceeded the one in-a-million cancer risk level by a factor of  $\sim 25$  in a small community and by a factor of  $\sim 7$  in a larger community located further downstream. Results from the third utility, which employs raw and settled water ozonation, showed that 1,4-dioxane concentrations in the finished water were  $\sim 35\%$  of those measured in the raw water, but average finished water 1,4-dioxane concentrations still exceeded the one in-a-million cancer risk level by a factor of 3.4.

Oxidation of 1,4-dioxane was studied by ozone, ozone/H<sub>2</sub>O<sub>2</sub>, and UV/H<sub>2</sub>O<sub>2</sub> processes. For ozonation, the key variable affecting 1,4-dioxane oxidation was the ozone to total organic carbon (O<sub>3</sub>:TOC) ratio. For settled Cape Fear River water, ozonation led to >95% 1,4-dioxane oxidation at an O<sub>3</sub>:TOC ratio of 1.25, which was reached with an O<sub>3</sub> dose of 3.5 mg/L. Raw water ozonation at this O<sub>3</sub>:TOC ratio would be costly given that the TOC concentration in raw water is typically substantially higher than in settled water (here by a factor of ~2). The extent of 1,4-dioxane oxidation during ozonation was not affected by pH, but an increase in alkalinity had a small negative effect on 1,4-dioxane oxidation. The effect of H<sub>2</sub>O<sub>2</sub> addition was evaluated at H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> ratios of 1:2, 1:1, and 2:1. While the addition of H<sub>2</sub>O<sub>2</sub> during ozonation improved 1,4-dioxane oxidation, no effect of H<sub>2</sub>O<sub>2</sub> dose was observed at the tested levels. Finally, UV/H<sub>2</sub>O<sub>2</sub> treatment was studied in coagulated/settled/filtered Cape Fear River water (UV transmittance of 90.1%). To achieve ~90% 1,4-dioxane oxidation, an H<sub>2</sub>O<sub>2</sub> dose of 10 mg/L was required in conjunction with a UV dose of 1500 mJ/cm<sup>2</sup>. These results suggest that UV/H<sub>2</sub>O<sub>2</sub> treatment of 1,4-dioxane in coagulated, settled, and filtered Cape Fear River water will be costly and energy-intensive.

To evaluate POU treatment devices, two commercial pitcher filters, a custom pitcher filter containing a tailored carbonaceous resin, and two refrigerator filters were tested for their ability to remove 1,4-dioxane. Experiments were conducted in NaCl-amended tap water spiked either with constant or variable 1,4-dioxane concentrations. After treating 130 L, average removals for the two commercial pitcher filters and the custom pitcher filter were 25%, 44% and 74%, respectively. For the two refrigerator filters that were designed to treat a larger water volume, average removals were 17% and 85% after treating 300 L. Desorption of 1,4-dioxane occurred when a period of high influent 1,4-dioxane concentration was followed by a period of low influent 1,4-dioxane concentration and diminished the overall benefit of POU treatment. In the custom pitcher filter, desorption of 1,4-dioxane was less pronounced. Overall, commercially available POU treatment devices exhibited limited effectiveness for 1,4-dioxane removal from tap water, especially under variable 1,4-dioxane concentrations. A POU device containing the tailored resin was more effective, but in the tested configuration, it would not be able to lower 1,4-dioxane concentrations to 0.35 µg/L when receiving water with the 1,4-dioxane concentrations observed in finished drinking water of three communities in the CFR watershed.

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## INTRODUCTION AND OBJECTIVES

### Motivation

In the past, 1,4-dioxane was widely used as a solvent stabilizer, and it is commonly considered to be a groundwater contaminant that co-occurs with chlorinated solvents. While 1,4-dioxane usage in the context of solvent stabilization has decreased, 1,4-dioxane continues to serve as an industrial solvent (e.g. textile industry, paper industry, production of specialty chemicals), and it is a by-product of manufacturing processes involving ethylene oxide (e.g. production of surfactants used in laundry detergents and shampoos, production of certain plastics). The US Environmental Protection Agency (USEPA) included 1,4-dioxane in the third contaminant candidate list (CCL3) and classified it as a “likely human carcinogen” by all routes of exposure. An excess one-in-a-million cancer risk is associated with a lifetime consumption of drinking water containing 0.35 µg/L 1,4-dioxane. 1,4-Dioxane possesses unique characteristics that explain its industrial use and environmental fate. Its cyclic structure with two opposed ether linkages results in a very stable structure, high solubility in water and organic solvents, and high resistance to biodegradation. Moreover, its low Henry’s law constant and low octanol-water partition coefficient make it difficult to remove from water by gas transfer and adsorption processes.

Currently, no federal drinking water standard exists for 1,4-dioxane, but some states have implemented notification or guidance levels. For example, the notification level in California is 1 µg/L, and wells have to be taken out of service when the 1,4-dioxane concentration exceeds 35 µg/L, (CDPH, 2010). Massachusetts has a guidance level of 0.3 µg/L in drinking water (Standards & Guidelines for Drinking Water Contaminants, 2014). In NC, an instream water quality standard of 0.35 µg/L applies for streams classified as drinking water supplies (DEQ, 2015).

Even though the first detection of 1,4-dioxane in US drinking water was in 1975 (Kraybill, 1975), reports about its prevalence in wastewater treatment plant (WWTP) effluents, surface water, and drinking water are limited. Recently the possible impact of WWTP discharges on 1,4-dioxane concentrations at downstream drinking water intakes was estimated by Simonich et al. (2013). 1,4-Dioxane concentrations in 40 WWTP effluents were measured and dilution factors of 1,323 drinking water intakes were calculated. 1,4-Dioxane concentrations in the WWTP effluents ranged from <0.3 to 3.30 µg/L, and dilution factors were between 2.6 and 48,113. Simonich et al. (2013) concluded that the probability of 1,4-dioxane concentrations exceeding 0.35 µg/L at downstream drinking water intakes is negligible. However, data collected between 2013 and 2015 as part of USEPA’s third unregulated contaminant monitoring rule (UCMR3) show 1,4-dioxane detections in 11.5% of the 36,479 drinking water samples analyzed nationwide. Furthermore, 1,4-dioxane concentrations  $\geq 0.35$  µg/L occurred in 3.0% of the analyzed samples. Of the 1,097 drinking water samples with 1,4-dioxane concentration  $\geq 0.35$  µg/L, 23% were of surface water origin, and seven of the twenty highest 1,4-dioxane concentrations occurred in drinking water derived from the CFR watershed in NC.

No information is available on the effectiveness of household filters for 1,4-dioxane removal. Given the high prevalence of 1,4-dioxane occurrence in US drinking water, the effectiveness of household filtration devices should be explored to assess whether they can serve as an immediate solution for reducing human exposure to 1,4-dioxane via drinking water.

To our knowledge, this is the first US study that focuses on (1) the occurrence of 1,4-dioxane in surface water, (2) the fate of 1,4-dioxane in surface water treatment plants, (3) the treatment of 1,4-dioxane by ozone and advanced oxidation in a surface water treatment context, and (4) the removal of 1,4-dioxane by point-of-use treatment devices.

## **Objectives**

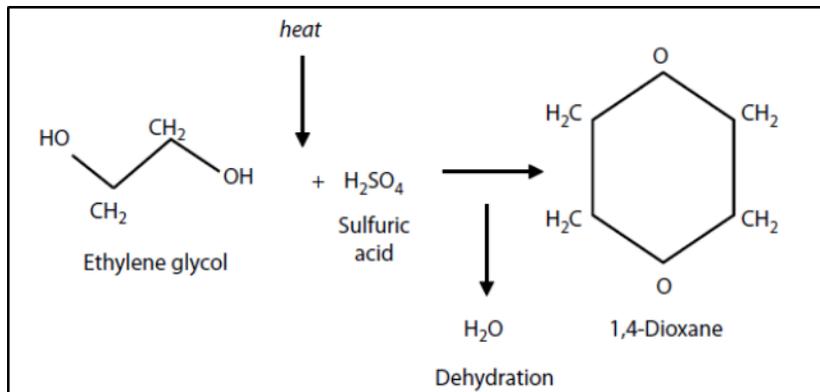
The overarching goal of this research was to gain insights into the occurrence of 1,4-dioxane in surface water and drinking water in the CFR watershed. Specific objectives included to

1. identify sources of 1,4-dioxane in the CFR watershed
2. establish temporal and spatial variability of 1,4-dioxane concentrations and mass flows in the CFR watershed
3. determine the fate of 1,4-dioxane in three surface water treatment plants,
4. determine the feasibility of oxidizing 1,4-dioxane by ozone and advanced oxidation processes in a surface water treatment context, and
5. assess the effectiveness of point-of-use (POU) treatment devices for 1,4-dioxane removal.

## LITERATURE REVIEW

### Production of 1,4-Dioxane

1,4-Dioxane is produced from ethylene glycol in the presence of concentrated sulfuric acid at elevated temperature (~160 °C). The strong acid displaces one molecule of water from the ethylene glycol and leads to a reconfiguration into a ring structure (Mohr, 2010). A conceptual representation of the 1,4-dioxane production method is described in Figure 1.



**Figure 1. Conceptual representation of a common 1,4-dioxane production method involving the dehydration and ring closure of ethylene glycol with a strong acid catalyst (sulfuric acid). Source: Mohr (2010).**

Commercial production of 1,4-dioxane in the United States was first reported in 1951 (ATSDR, 2012). Because of its solvent-stabilizing properties, 1,4-dioxane production was strongly influenced by the production volume of 1,1,1-trichloroethane (TCA) until 1995 (Mohr, 2010), when TCA was phased out under the Montreal Protocol due to its ozone depletion potential. Currently, 1,4-dioxane is produced by Ferro Corporation in Baton Rouge, Louisiana, BASF AG in Ludwigshafen, Germany and Osaka Yuki and Toho Chem, in Japan (ATSDR, 2012).

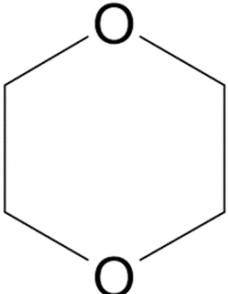
Current 1,4-dioxane production volumes in the United States are not available. In 1990 production volume was between 4,763 and 8,300 metric tons (ATSDR, 2012). According to Chemsources (2012), there are 24 companies in the US that sell 1,4-dioxane, but no sales volume was reported. In Europe, production volume was estimated between 2,000 and 2,500 metric tons in the year 2000 (ATSDR, 2012).

### Physicochemical Properties of 1,4-Dioxane

1,4-Dioxane is a cyclic organic compound with two ether linkages located at the 1 and 4 positions of the six-member aliphatic ring. This structure makes 1,4-dioxane stable and relatively immune to reaction with acids, oxides, and oxidizing agents (Mohr, 2010). The two oxygen atoms give 1,4-dioxane a high dipole moment, which makes it hydrophilic (Table 1) and gives 1,4-dioxane a high aqueous solubility (Mohr, 2010). Its low Henry's Law constant indicates minimal volatilization and its low octanol-water partition coefficient (Table 1) explains its high

mobility in soil. It is well documented that plumes of 1,4-dioxane measured twice the length of its associated solvent plumes (TCA) and area extent can be up to six times larger than areas affected by TCA (Otto et al., 2007).

**Table 1. Physico-chemical properties and structure of 1,4-dioxane**

Physico-chemical properties and structure of 1,4-dioxane			
Property	Value	Reference	Structure
Molecular Formula	C <sub>4</sub> H <sub>8</sub> O <sub>2</sub>	(Moyer, 2008)	
Molecular weight (g/mol)	88.106	(Mohr, 2010)	
Density (g/cm <sup>3</sup> )	1.028	(Mohr, 2010)	
Boiling point (°C at 760 mmHg)	101.2	(Mohr, 2010)	
Water solubility (At 25°C, g/L)	Miscible	(Stepien et al., 2014)	
Henry's law constant (atm x m <sup>3</sup> / mol)	4.88x10 <sup>-6</sup>	(Stepien et al., 2014)	
Vapor density air=1	3.03	(Moyer, 2008)	
Octanol- Water Partition Coefficient (Log K <sub>ow</sub> )	-0.27	(Stepien et al., 2014)	

### Uses of 1,4-Dioxane

Because of its extensive solvent properties, 1,4-dioxane has been used in a variety of applications. Direct uses of 1,4-dioxane include (1) stabilizer for chlorinated solvents such as TCA, (2) wetting and dispersing agent in textile processing, (3) solvent in reverse osmosis membranes manufacture, and (4) purifying agent in the manufacture of pharmaceuticals (Mohr, 2010)(EPA, 2014). 1,4-Dioxane can result as a by-product in processes involving ethylene oxide such as production of polyethylene terephthalate (PET), polyester, detergents and cosmetics.

### Sources of 1,4-Dioxane

Because of the wide range of 1,4-dioxane uses, it can be found in domestic and industrial wastewater. Upon treatment, these wastewaters are discharged into surface water and affect downstream drinking water supplies. In groundwater, 1,4-dioxane contamination is principally associated with TCA spills. Elevated 1,4-dioxane levels have also been found in landfill leachates as a result of landfilling of materials that contain 1,4-dioxane. Common industries that could be sources 1,4-dioxane are (FerroCorp, 2006):

- Textile industry
- Plastic industry
- Specialty chemical manufacturers
- Plastic Recycling
- Pharmaceuticals

- Paint and varnish industry
- Medical filter manufacturers
- Membranes manufacturers (reverse osmosis and dialysis membranes)

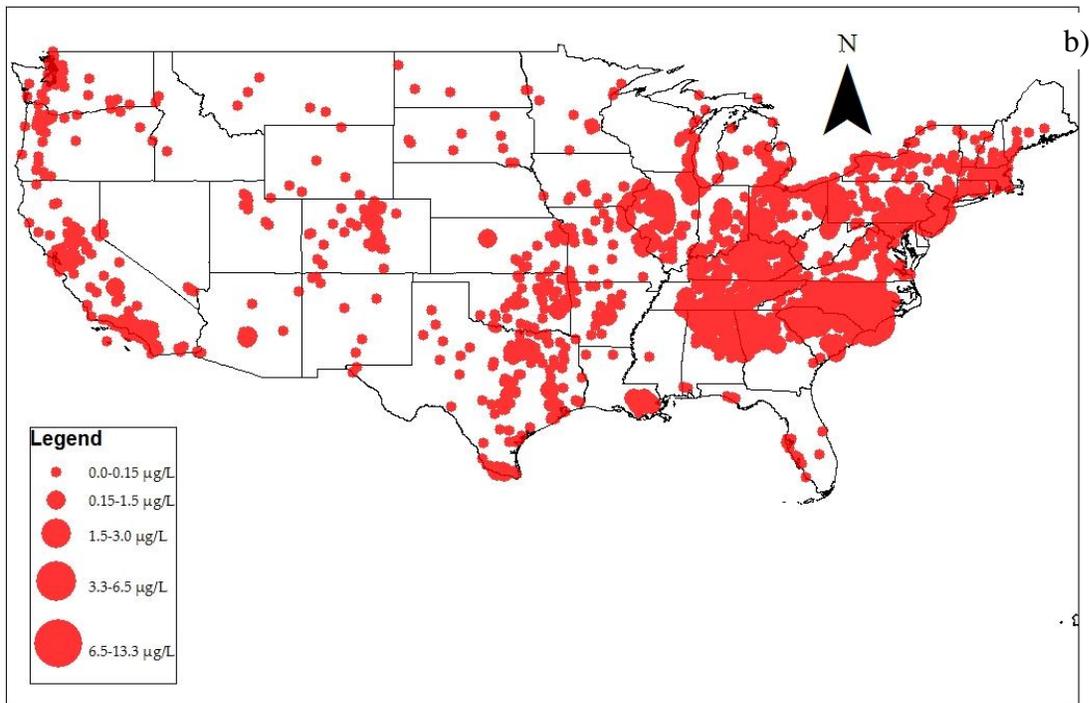
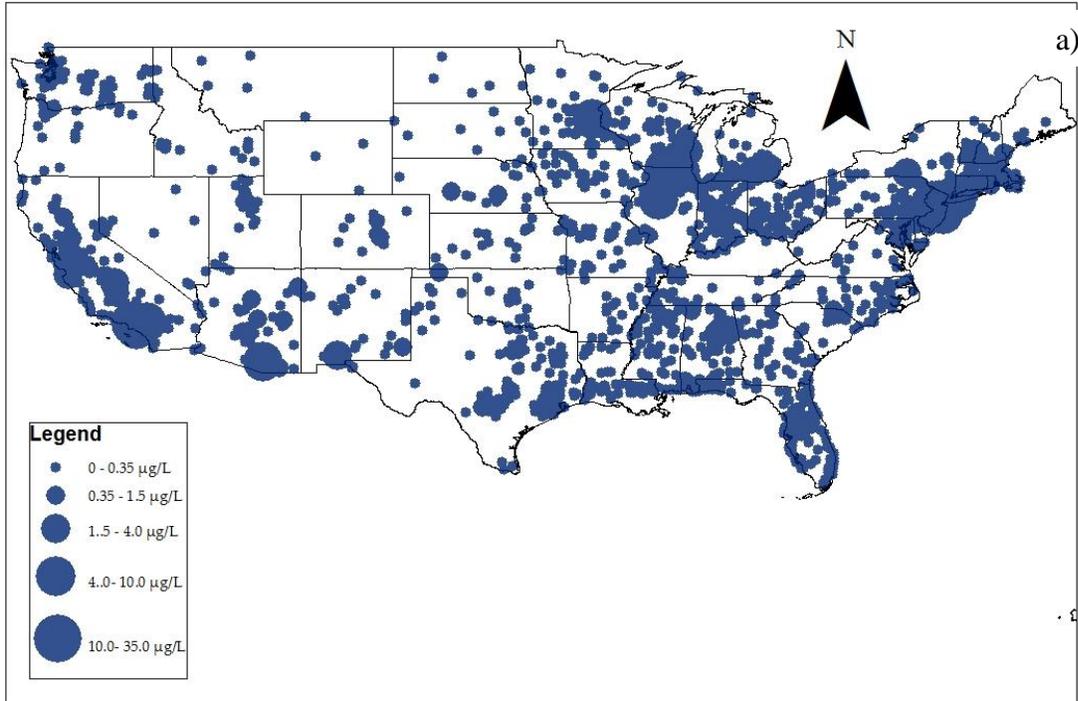
## **1,4-Dioxane Occurrence**

Due to the wide use of 1,4-dioxane in industrial applications and its recalcitrant nature, 1,4-dioxane can be found in drinking water, groundwater, surface water, wastewater, and landfill leachate. A brief survey of published 1,4-dioxane data in different aqueous media is presented below.

### ***Drinking Water***

Already, four decades ago, 1,4-dioxane was found as a drinking water contaminant in the US. Kraybill (1975) first reported the detection of 1,4-dioxane in drinking water at  $\sim 1$   $\mu\text{g/L}$ . A comprehensive look at 1,4-dioxane occurrence in US drinking water can be obtained from 2013-2015 data collected during USEPA's third unregulated contaminant monitoring rule (UCMR3). Results illustrate that 1,4-dioxane was detected ( $\geq 0.07$   $\mu\text{g/L}$ ) in 11.5% of 36,479 analyzed samples, and concentrations  $\geq 0.35$   $\mu\text{g/L}$  were measured in 3.0% of analyzed samples (USEPA, 2016). Of the 1,097 drinking water samples with 1,4-dioxane concentrations  $\geq 0.35$   $\mu\text{g/L}$ , 23% were of surface water origin, a perhaps surprising result given that 1,4-dioxane is typically considered to be a groundwater contaminant. For example, in North Carolina (NC), 125 out of 216 UCMR3 samples with detectable 1,4-dioxane concentrations were derived from surface water. Furthermore, 7 of the 20 highest 1,4-dioxane concentrations in the UCMR3 database were measured in drinking water produced from the Cape Fear River (CFR) in NC (up to 13.3  $\mu\text{g/L}$ ).

As shown in Figure 2, 1,4-dioxane detections are widespread throughout the entire US. Clusters of groundwater-derived 1,4-dioxane are prevalent in the Northeastern US, in the Illinois/Wisconsin border region, and in California. Clusters of surface water-derived 1,4-dioxane are prevalent from New Jersey, Pennsylvania, Ohio, Kentucky and Tennessee through northern Alabama and Georgia to South and North Carolina.



**Figure 2. 1,4-Dioxane concentrations in US drinking water derived from a) groundwater and b) surface water. Source: USEPA (2016).**

## ***Groundwater***

Many recent studies have focused on the occurrence of 1,4-dioxane in groundwater (e.g., Adamson et al., 2014; Anderson et al., 2012; Mahendra and Alvarez-Cohen, 2006; Mohr, 2010; Sales, 2012; Zenker et al., 2003). In Bedford, MA, four municipal supply wells were closed when TCA and 1,4-dioxane (2,100 µg/L) were detected in the water. In Washtenaw, Michigan, where Pall-Gelman Sciences Corporation manufactured medical filters, 1,4-dioxane was found in the groundwater at concentrations of up to 212,000 µg/L (Sales, 2012). In five wells near Circleville, Ohio, the concentration of 1,4-dioxane ranged from <1 to 360 µg/L after industrial wastewater infiltration ponds contaminated the groundwater (ATSDR, 2012). In Durham, Connecticut, drinking water samples from homes near the Durham Meadows Superfund site had maximum 1,4-dioxane concentrations of 26 µg/L (ATSDR, 2012). In California 1,4-dioxane concentrations ranged between 1.1 and 109 µg/L in contaminated groundwater (Mohr, 2010). Co-occurrence of 1,4-dioxane with TCA and TCE was studied by Anderson et al. (2012), 1,4-dioxane was found in 17.4% of the groundwater monitoring wells with detections of TCE and/or TCA, which accounted for 93.7% of all 1,4-dioxane detections. 1,4-dioxane frequently co-occurs with (1) TCA because it was added to TCA as a solvent stabilizer and (2) TCE because TCE use often predated the use of TCA (Adamson et al. 2014).

In Japan, Abe (1999) studied 1,4-dioxane occurrence in Kanagawa prefecture from 1995 to 1998. 1,4-Dioxane was detected in 90% of the wells, with two-thirds of the detections falling below 1 µg/L, 20% between 1 and 10 µg/L, and 10% above 10 µg/L; the highest detections ranged from 50 to 95 µg/L

In a study conducted between 1983 and 1986, 1,4-dioxane was detected in groundwater near three landfills in Canada at concentrations <1 µg/L (ATSDR, 2012); concentrations between ~300-2000 µg/L were detected in a groundwater at the Gloucester landfill in Canada in 1988 (Lesage et al., 1990).

## ***Wastewater and Wastewater Impacts on Drinking Water Sources***

Only limited information about 1,4-dioxane occurrence is available for US wastewater and wastewater-impacted surface water. In 1982, 1,4-dioxane was detected in samples from the Haw River in North Carolina, but no information on the levels of 1,4-dioxane were reported (Dietrich et al., 1988; ATSDR, 2012). Determination of 1,4-dioxane in wastewater was performed at the City of Ann Arbor, Michigan. Raw wastewater and treated wastewater effluent were tested for 1,4-dioxane. In each of three sampling events, 1,4-dioxane was present in the influent at an average concentration of 3 µg/L; 1,4-dioxane remained present in all the three corresponding treated wastewater effluent samples at an average concentration of 2 µg/L. The source of 1,4-dioxane in raw wastewater was not identified in the study (Mohr, 2010).

The impact of wastewater treatment plant (WWTP) discharges on 1,4-dioxane concentrations at downstream drinking water intakes was recently estimated by Simonich et al. (2013). On the basis of measured 1,4-dioxane concentrations in the effluents of 40 U.S. WWTPs (median: 1.13 µg/L, maximum: 3.30 µg/L) and dilution factors associated with receiving waters, Simonich et al. (2013) concluded that the probability of 1,4-dioxane concentrations exceeding 0.35 µg/L at

downstream drinking water intakes is negligible. However, 1,4-dioxane concentrations in 29 UCMR3 samples of surface water origin exceeded the maximum WWTP effluent value of 3.30 µg/L reported by Simonich et al. (2013) suggesting that some WWTP effluents contain 1,4-dioxane at substantially higher levels than previously reported.

Occurrence of 1,4-dioxane in surface water was assessed in several Japanese studies (Abe, 1999; Kawata et al., 2003, 2009; Simazaki et al., 2006; Tanabe et al., 2006). In a nationwide survey of Japanese drinking water sources, 1,4-dioxane was detected at levels  $\geq 0.05$  µg/L in 32 of 80 surface water samples, with an average concentration of 0.20 µg/L (Simazaki et al., 2006). In other studies, 1,4-dioxane concentrations in Japanese rivers ranged from  $<0.03$  to 16 µg/L (Abe, 1999; Kawata et al., 2003, 2009; Tanabe et al., 2006).

In Japanese wastewater effluents, 1,4-dioxane levels varied substantially (Abe, 1999). In a study performed in Korea, nine different WWTPs were studied for the occurrence of 1,4-dioxane. Four of the nine WWTPs were positive for 1,4-dioxane, and concentrations ranged between 1.14 and 23.6 µg/L and 0.76 and 18.1 µg/L for the influent and effluent, respectively.

### ***Landfill Leachate***

1,4-Dioxane is frequently detected in landfill leachate, groundwater beneath municipal and industrial landfills, and in landfill gas and landfill gas condensate. Landfills receiving vapor degreasing still bottoms, solvent wastes, paint filters, scintillation and other laboratory wastes, ink sludge, pesticide containers, household products with TCA as an ingredient, and industrial sludge from textile production, resin production, and cellulose acetate membrane production, have a higher prospect of 1,4-dioxane presence in leachate, gas, and affected groundwater (ATSDR, 2012). 1,4-Dioxane has been detected in landfill gas at a landfill in Westphalia, Germany (Mohr, 2010). DeWalle and Chain (1981) detected 1,4-dioxane in 37% of groundwater samples near the Army Creek Landfill in Wilmington, DE, at concentrations of 500 to 2400 µg/L (Zenker et al., 2003). In Japanese landfills, 1,4-dioxane was detected in 87.5% of leachate samples analyzed. Concentrations ranged from 1.1 to 109 µg/L with a reporting limit of 0.9 µg/L (Yasuhara et al., 2003)

### **Health Effects**

Information on health effects of 1,4-dioxane in humans are limited. The available data are derived from exposure studies primarily via inhalation of vapors, but may involve dermal exposure. Yet, the available data are sufficient to identify the liver and kidneys as the target organs for 1,4-dioxane toxicity. Toxicological studies revealed an increased incidence of nasal cavity and liver carcinomas in rats, liver carcinomas in mice, and gall bladder carcinomas in guinea pigs when exposed to 1,4-dioxane (ATSDR, 2012).

No data are available on bioaccumulation or bioconcentration. A low octanol water partition coefficient and high hydrophilicity suggest extremely low potential for bioaccumulation, and it is assumed that 1,4-dioxane, will not biomagnify significantly in aquatic organisms (Corporation and Group, 2007). Centers for Disease Control and Prevention (CDC) collected human blood specimens in 2007-2008 from a geographically-diverse populations of U.S. residents  $\geq 12$  years

old. In 2,053 human blood specimens analyzed no detectable concentrations of 1,4-dioxane were measured (ATSDR, 2012).

## **Treatment Options**

Because of its physico-chemical characteristics (Table 1), 1,4-dioxane is difficult to remove from water. The use of conventional treatment processes for water or wastewater treatment is either ineffective or infeasible. McGuire et al. (1978) investigated the removal of 1,4-dioxane via ferric chloride coagulation, powdered activated carbon adsorption, and permanganate oxidation. Results showed that no removal was achieved. Because of its low Henry's law constant, air stripping is also not effective for 1,4-dioxane removal (McGuire et al. 1978, Diguisseppi and Whitesides, 2007). To evaluate 1,4-dioxane's air stripping potential, a study conducted in California tested a cascading water column in a 40-foot-tall packed vertical stripping tower at a groundwater remediation site (Diguisseppi and Whitesides, 2007). Influent 1,4-dioxane concentrations ranged from 7.6 to 11.1 µg/L and effluent levels ranged from 7.0 to 10.0 µg/, using air: water ratios between 183 and 291. The maximum possible removal rate achieved was 10%, which was not sufficient to meet clean up goals, and repeatability was not guaranteed. (Diguisseppi and Whitesides, 2007). Advanced oxidation, adsorption, and biodegradation processes can be effective for 1,4-dioxane control and are discussed in more detail below.

### ***Advanced Oxidation Processes***

Advanced oxidation processes can be used independently or as a pre or post-treatment step in a remediation process or water treatment plant. AOPs rely on hydroxyl radicals to oxidize organic contaminants (Mohr, 2010). Two common AOPs include hydrogen peroxide in combination with ultraviolet (UV) light, and hydrogen peroxide in combination with ozone. In the presence of UV light, hydroxyl radicals are generated from hydrogen peroxide. Hydroxyl radicals are also generated when ozone reacts with hydrogen peroxide, even in the absence of UV light, as shown in equation 1 (Otto et al., 2007).



Adams et al. (1994) investigated the use of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> for the degradation of 1,4-dioxane. Experiments were conducted at near neutral pH values (7–9) with different combinations of O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub>. When used alone, neither O<sub>3</sub> nor H<sub>2</sub>O<sub>2</sub> readily oxidized 1,4-dioxane. However, when used together at molar ratios (H<sub>2</sub>O<sub>2</sub>/O<sub>3</sub>) between 0.5 to 1.0, 1,4-dioxane was effectively oxidized with an associated increase in biochemical oxygen demand, suggesting the formation of biodegradable oxidation products. Examples of projects that have implemented AOPs are summarized in Table 2.

**Table 2. Summary of full-scale, pilot-scale and bench scale advanced oxidation projects for 1,4-dioxane**

<b>Treatment Process Description</b>	<b>Scale Location</b>	<b>Concentration (ug/L)</b>	<b>Reference</b>
Hydrogen peroxide in combination with a ferrous iron salt (Fenton's reagent)	Bench scale US	<b>Influent:</b> 100 mg/L <b>Effluent:</b> 2.0 mg/L	(Kleka and Gonsior, 1986)
UV Hydrogen peroxide, granular activated carbon quenching	Full Scale Tucson, AZ	Not reported concentration (96% reduction)	(TrojanUV, 2015)
UV/Ozone, anaerobic pretreatment in some cases and aerobic post-treatment	Bench scale US		(Adams et al., 1994)
UV-Hydrogen peroxide	Full Sacramento, CA	Influent: 64.1 (collected in September of 2004) Effluent:<6.1 collected in September of 2004)	Reported by (Otto et al., 2007)
UV-Hydrogen peroxide	Full Ontario, Canada		Reported by (Otto et al., 2007)
UV-Hydrogen peroxide	Full, Ann Arbor, Michigan	Influent: 3,000-4,000 Effluent: ND to 10	Reported by (Otto et al., 2007)
Ozone + Hydrogen peroxide, pretreatment by air stripping	Pilot CA, US	Influent: 20.2 Effluent: <2	Reported by (Otto et al., 2007)
Ozone + Hydrogen peroxide	Full, CA, US	Influent: 15 Effluent: <0.94	Reported by (Otto et al., 2007)
Ozone + Hydrogen peroxide, pretreatment by air stripping	Full, Orange County, US	Influent:170 Effluent: <3	Reported by (Otto et al., 2007)

Although AOPs are capable of decreasing the concentration of 1,4-dioxane, potential limitations need to be considered before this treatment can be implemented. Some of these limitations are:

- Applications are restricted by the presence of scavengers such as carbonate, bicarbonate, and dissolved organic water .
- Presence of bromide in water containing 1,4-dioxane, may produce bromate after oxidation with ozone.
- Potential formation of aldehydes and organic acids (Adams et al., 1994)
- Hydrogen peroxide residual needs to be quenched.

### ***Adsorption Processes***

Adsorption involves concentrating contaminants on the surface of a sorbent such as GAC, thereby decreasing the concentrations of those contaminants in the water being treated (Otto et al., 2007). Adsorption processes have been demonstrated to be effective for removal of a large number of organic compounds (Corwin and Summers, 2012; Knappe et al., 1998; Li et al., 2002; Matsui et al., 2003, 2002a; Summers et al., 2013), but their effectiveness depends on the physico-chemical characteristics of the contaminant, initial concentration of contaminant, granular activated carbon characteristics (surface area, pore size distribution, hydrophobicity, surface chemistry), presence of competitors such as dissolved organic matter (DOM), and other pollutants, pH, temperature. For contaminated groundwater, Fotta (2012) evaluated the 1,4-dioxane removal effectiveness of four GACs prepared from bituminous coal, lignite, and coconut shells. Results showed that less than 1,000 bed volumes of water could be treated with all four GACs before complete breakthrough of 1,4-dioxane occurred, indicating that GAC adsorption is not a feasible treatment option for 1,4-dioxane removal in a full scale application. McGuire et al. (1978) tested GAC as a treatment option; percentage removal by adsorption was registered as 64%, but no bed life was reported by the authors.

Woodard and Mohr (2011) reported the removal of 1,4-dioxane by adsorption on Ambersorb 560, a synthetic carbonaceous resin, produced by thermal pyrolysis of sulfonated styrene-divinylbenzene copolymer. This resin was shown to be effective for the removal of 1,4-dioxane over a wide range of concentrations and operating conditions (Woodard and Mohr, 2011). Ambersorb 560 has a higher proportion of meso- and macropores compared to GAC, a more hydrophobic surface, and more uniform pore size distribution.

Two case studies were conducted to assess the effectiveness of Ambersorb 560 to remove 1,4-dioxane from groundwater. Removal to  $< 0.3 \mu\text{g/L}$  was achieved by ex-situ remediation using this resin. The first case located in Waltham, Massachusetts, treated 15 gallons per minute (gpm) of contaminated groundwater. The average influent 1,4-dioxane concentration was  $20 \mu\text{g/L}$ , effluent concentrations were consistently below detection. The second case study took place in St. Petersburg, Florida, where the system was designated to treat 80 gpm, and influent 1,4-dioxane concentrations ranged from 2,000 to 40,000  $\mu\text{g/L}$ . Effluent concentrations were reduced by four to five orders of magnitude. Ambersorb 560 can be regenerated *in-situ* by low pressure steam, microwave radiation, solvents, or hot gases (Woodard and Mohr, 2011). Regeneration was performed at the two sites by passing low-pressure steam through the bed, countercurrent to the direction of the process stream flow. After exiting the bed, the steam is condensed and decanted. This concentrate is passed through a small GAC vessel that is able to remove 1,4-dioxane at elevated 1,4-dioxane concentrations (Woodard and Mohr, 2011).

### ***Biological degradation***

Aerobic biotransformation of 1,4-dioxane can occur either metabolically, with 1,4-dioxane serving as the sole source of carbon and energy, or co-metabolically, with 1,4-dioxane degradation occurring after growth on an inducing substrate, such as propane or tetrahydrofuran (THF) (Mahendra and Alvarez-Cohen, 2006). Bacterial degradation of 1,4-dioxane appears to be catalyzed by monooxygenase enzymes (Mahendra and Alvarez-Cohen, 2006, Sales, 2012). Mahendra and Alvarez-Cohen (2006) tested 20 bacterial isolates, of which 13 were capable of biodegrading 1,4-dioxane. Only two strains were capable of growth on 1,4-dioxane as a sole carbon and energy source (*P. dioxanivorans* CB1190, *P. benzenivorans* B5). Co-metabolic transformation of 1,4-dioxane was observed by monooxygenase expressing strains that were induced with methane, propane, THF, and toluene (Mahendra and Alvarez-Cohen, 2006).

### **Regulations for 1,4-Dioxane**

1,4-Dioxane has received increased regulatory attention at both Federal and State levels in recent years. In February of 2008, 1,4-dioxane was included on the third drinking water contaminant candidate list (CCL3), and in May of 2012, it was included in the UCMR3.

Currently, no federal drinking water standard exists for 1,4-dioxane, but some states have implemented notification or guidance levels, as summarized in Table 3. For example, in the case of California, the notification is 1 µg/L, and wells have to be taken out of service when the 1,4-dioxane concentration exceeds 35 µg/L (CDPH, 2010).

**Table 3.State regulations for 1,4-Dioxane**

<b>State</b>	<b>Regulation</b>	<b>Concentration (µg/L)</b>	<b>Reference</b>
<b>California</b>	Drinking water notification level	1.0	(CDPH, 2010)
	Drinking water response level	35	(CDPH, 2010)
<b>Colorado</b>	Groundwater standard	3.0	(CDPHE, 2012)
<b>Connecticut</b>	Action level	3.0	(DPH, 2015)
	Drinking water guideline	20	(DPH, 2015)
<b>Massachusetts</b>	Drinking water guideline	0.3	(MassDEP,2015)
<b>Maine</b>	Drinking water maximum exposure guideline	4.0	(Maine CDC Maximum Exposure Guidelines ( MEGs ) for drinking water, 2008)
<b>New Hampshire</b>	Ambient groundwater quality standard	3.0	(New Hampshire, 2011)
<b>New York</b>	Drinking Water Standard	50	(NYCEP,2014)
<b>New Jersey</b>	Interim Specific Groundwater Criterion	3.0	(Post, 2008)
<b>Florida</b>	Groundwater criterion	3.2	(FDEP, 2016)
	Surface water cleanup target level	130	(FDEP, 2016)
<b>North Carolina</b>	Groundwater quality standard	3.0	(DEQ, 2016)
	Surface water supply standard	0.35	(DEQ, 2016)
<b>South Carolina</b>	Drinking Water Health Advisory	70	(SCDHEC, 2008)
<b>Rhode Island</b>	Drinking water guideline	6.1	(SCDHEC, 2008)

## **MATERIALS AND METHODS**

At the beginning of this study, samples were collected at 47 locations in the CFR watershed upstream and downstream of 14 WWTP discharges. Thereafter, monthly samples were collected for one year at 32 locations upstream and downstream of 9 WWTP discharges in the CFR watershed. Furthermore, composite samples were collected at three drinking water treatment plants (DWTPs) in the CFR basin (DWTP A, DWTP B, DWTP C) to quantify 1,4-dioxane concentrations in the source water and the finished drinking water. In this chapter the sampling procedures for surface water and drinking water are described.

### **Materials**

#### ***Bottles***

Samples were collected in 500-mL processed type III (soda-lime) amber glass bottles with solid top caps with fluoropolymer resin liner (catalog number: 89094-046, VWR International, Philadelphia, PA).

#### ***Sample Preservation Reagents***

Sodium sulfite (CASRN 7757-83-7), ACS grade, purchased from Thermo Fisher Scientific (Waltham, MA), was added to reduce free and combined chlorine in samples that had been disinfected with chlorine and/or chloramine (EPA, 2008). For consistency, sodium sulfite was added to all samples, regardless of whether or not a chlorine residual was present.

Sodium bisulfate (CASRN 7681-38-1), anhydrous, technical grade purchased from Sigma-Aldrich (St. Louis, MO), was added to acidify samples to  $\text{pH} < 4$  and act as a microbial inhibitor during sample shipping and storage (EPA, 2008).

Depending on the volume of the sampling bottle, preservation reagents were added as follows: first 50 mg of sodium sulfite in 1 L of sample and second 1 g of sodium bisulfate in 1 L of sample (EPA, 2008). To ensure confidence in preservative weight, the sample volume was always at least 500 mL. Preservation reagents were added in the field from small ziploc bags that were prepared prior to sampling.

#### ***Bridge Sampler***

Water samples were collected directly into the sample bottles using a bridge sampler shown in Figure 3. The sampler was developed during this study and tested for leaching and sorption of 1,4-dioxane. Results showed that the materials used to construct the sampler neither leached nor sorbed 1,4-dioxane.



**Figure 3. Bridge sampler for collecting river samples in this study. Glass sample bottles were placed into the perforated pipe and secured with a steel rod.**

### *Coolers and Cold Packs*

Coolers filled with ice and cold packs were used to transport samples. The water temperature was maintained below 10 °C during sample transport to the lab.

### *Chain of Custody Form*

Chain of custody forms were filled out in the field upon sample collection. Station ID, GPS coordinates, station location, sample ID, sample date and time, sample type, number of containers, indication of addition of preservatives, and comments were noted by the person in charge of sample collection.

## **Methods**

### *Bottle Preparation and Cleaning*

All sampling glassware was triple-rinsed in the laboratory with tap water and ultra-pure distilled and deionized water. Subsequently, bottles were baked at 400°C for 2 hours. Prior to sample collection, bottles were pre-rinsed once in the field with water from the sampling station.

## ***Labeling***

Labels were pre-printed before sample collection with sample ID, station ID, sample location and date. Upon sample collection GPS coordinates, collector's name and indication of preservative addition was noted by the person in charge of sample collection.

## ***Sample Collection Procedure***

### *Surface water*

1. Unscrew nut from the metal rod, and remove the metal rod from bridge sampler.
2. Place the sample bottle inside the bridge sampler and put back the metal rod and nut.
3. Take the bridge sampler and submerge it into the surface water body.
4. Take out the sampler from the water and discard bottle contents.
5. Repeat step 3 to collect sample.
6. Add to the sample 25 mg of sodium sulfite and mix until solid is dissolved.
7. Add 500 mg of sodium bisulfate and mix until solid is dissolved.
8. Cap the bottle
9. Label the bottle
10. Complete chain of custody Form
11. Place the sample bottle in the cooler

### *Drinking water*

1. Measure 100 mL raw water using a glass graduated cylinder, and pour it into a 2.5-L brown glass bottle. Repeat this procedure hourly within a 24-hour time frame. Upon completion, the total volume of the collected composite sample was 2.4 L.
2. From the 2.5L bottle, transfer approximately 500 mL of the composite sample to an amber sample bottle. To accomplish this, first flush the bottle by filling it up completely with composite sample, and discard it. Then fill it with another approximately 500 mL sample (fill to about the neck, but leave some headspace).
3. Add sodium sulfite salt (small Ziploc bag attached to the bottle, labeled S. Sulfite) to the water in the amber bottle. Cap the bottle and gently invert it until the content is well mixed. Wait for 5 minutes for the solid to dissolve.
4. Add sodium bisulfate salt (small Ziploc bag attached to the bottle, labeled as S. Bisulfate) to the water in the same amber bottle. Cap the bottle and gently invert it until the content is well mixed. Wait for 5 minutes for the solid to dissolve.
5. Using the preprinted label, label the amber bottle with corresponding sample ID, sampling date, start and end time, etc. Put the bottle in a refrigerator until weekly pick up.

### ***Sample Transportation***

Immediately after sampling, labeling, and chemical preservation, samples were placed in coolers on ice and cold packs. Sample submission forms were placed in a sealable waterproof bag and taped to the inside lid of the cooler.

### ***Receipt of Samples in the Laboratory***

Sample temperature were  $<10^{\circ}\text{C}$  at the time of arrival at the NCSU Environmental Engineering Research Laboratory. Sample temperature was verified upon sample arrival. Once samples were received, they were transferred to 40-mL VOA vials. Vials were tagged according to sample location and date.

### ***Quality Control/ Quality Assurance in Sample Collection***

#### ***Temperature Quality Control Check***

Each cooler contained a temperature quality control check. It was a container of ultrapure water stored in each cooler. The temperature was measured and recorded at the time of sample receipt in the laboratory. This temperature was used to represent the temperature of all samples in that cooler.

#### ***Sampling Blanks***

***Field Blanks*** – Field blanks were prepared by adding ultrapure water from the laboratory in sealed containers that were taken in coolers to the field. At a randomly selected sampling location (different for each sampling campaign), this water was poured into a 500mL sample container. Sodium sulfite and bisulfate were added to this container. The purpose of this blank was to assess contamination from field conditions during sampling. One field blank was collected per day per cooler and it was labeled as Field Blank with date and sampling location recorded.

***Trip Blanks*** – Trip blanks were prepared in the laboratory by adding ultrapure water to a 500mL sample container with all appropriate preservatives. This sample bottle was placed in the cooler, taken to the sampling site, and transported back to the laboratory without opening it. The purpose of this blank was to assess contamination during transportation. One trip blank was collected per day per cooler and was labeled as Trip Blank with date.

#### ***Field Duplicate Samples***

Field duplicate samples are two samples taken from the same sample location at the same time. Each bottle was given its own unique sample ID. The purpose of field duplicate samples was to provide a means of evaluating the relative precision of the sample collection and analysis procedure. One field duplicate was collected per day per cooler.

### *Matrix Spike and Matrix Spike Duplicate Samples*

Matrix spike and matrix spike duplicates are aliquots of samples that are augmented in the laboratory with a known concentration of analyte of interest. Extra bottles were collected to provide the laboratory with sufficient volume for matrix spikes. The purpose of matrix spikes and matrix spike duplicates was to evaluate the accuracy and reproducibility of the analytical technique that is used to quantify 1,4-dioxane concentrations in the background matrix of interest. Matrix spike/matrix spike duplicate were collected once per day per cooler and labeled as matrix spike or matrix spike duplicate with the original sample name.

### *Storage Blank*

This blank was prepared in the laboratory by adding ultrapure water to a 500mL sample container with all appropriate preservatives. This sample bottle was placed in the cold room that was used to store project samples. The purpose of this blank was to assess contamination during storage of samples. One storage blank was prepared for each sampling event. This sample never left the laboratory.

### *1,4-Dioxane QC Sample*

This sample was prepared in the laboratory by taking ultra-pure water and spiking it with a known concentration of 1,4-dioxane. This sample bottle was placed in the cooler, taken to the sampling site, and transported back to the laboratory without opening it. The purpose of this QC sample was to assess losses of 1,4-dioxane during sample transportation and storage. One 1,4-dioxane QC sample was prepared per cooler per day.

## **Analytical Methods**

*1,4-Dioxane* - Details of 1,4-dioxane determination are described in Chapter 4. Samples were analyzed within 28 days of collection.

*Conductivity* - Measurements were conducted based on Standard Method 2510 using a conductivity meter (Aquapro. Digital Water Tester. Model AP-2. HM Digital, Inc.).

*Total Dissolved Solids (TDS)* - The TDS concentration was calculated by multiplying the conductivity (microsiemens per centimeter -  $\mu\text{S}/\text{cm}$ ) by an empirical factor of 0.6 (Method 2510, Standard Methods for the Examination of Water & Wastewater).

*Total Organic Carbon (TOC)* - TOC was measured as non-purgeable organic carbon (NPOC) based on Standard Method 5310B (high-temperature combustion) using a Shimadzu VCH TOC analyzer. Samples collected were immediately acidified to  $\text{pH} < 2$ . For acidified samples, the holding time for this method is 28 days, all samples were analyzed within this time.

*pH* - pH was measured following Standard Method 4500-H+ (Standard Methods for the Examination of Water & Wastewater) using a pH -meter (Fisher ORION 2 STAR).

*Turbidity* - Turbidity was measured following Standard Method 2130 B (Standard Methods for the Examination of Water & Wastewater) using a HACH Turbidimeter 1720

### **External Data Sources**

Instantaneous and daily average streamflow were obtained from USGS stream gages. Releases from Jordan Lake dam were obtained by the US Army Corps of Engineers.

## **ANALYTICAL METHOD**

The analytical method for the determination of 1,4-dioxane was developed during this research and was published in Environmental Science and Technology (Sun et al., 2016).

### **Introduction**

The analysis of 1,4-dioxane presents a technical challenge because of the high affinity of 1,4-dioxane for water. USEPA has published several standard methods for the analysis of 1,4-dioxane in environmental samples including drinking water, soil, and municipal sludge (Sun et al., 2016). Different laboratories have modified these standard methods to achieve higher sensitivity. In Table A. 1, both standard methods and modifications are summarized. Liquid–liquid and solid phase extraction are the most commonly used sample preparation methods to achieve reporting limits below 1 µg/L, a level of sensitivity not easily achieved via other sample preparation techniques. However, extraction is time- and labor-intensive, requires large sample volumes, and generates solvent waste. Solid phase microextraction (SPME) is an alternative option but requires expensive fibers with limited lifetime. Another sample preparation method, purge-and-trap (P&T), is generally considered ineffective for 1,4-dioxane enrichment, and reporting limits are typically at least one order of magnitude higher than those achieved with solid phase or liquid–liquid extraction. Some P&T methods are capable of determining 1,4-dioxane concentrations as low as 1 µg/L by either purging for extended periods of time (20 min) at room temperature or shorter times (5-11 min) at elevated temperature; however, no information about method performance is available for applying these methods to different aqueous matrices. Similar to heated P&T, heated headspace sampling also promotes volatilization of 1,4-dioxane from aqueous solution for quantification at sub µg/L levels, but without active purging, the extraction time can be as long as 30 min (Sun et al., 2016).

Objectives of this chapter are to present a rapid analytical method capable of quantifying aqueous 1,4-dioxane concentrations below the one-in-a-million cancer risk level of 0.35 µg/L; show method performance in a wide range of aqueous matrices using matrix spikes; and compare method performance to that of two EPA standard methods. Also, because of the growing concern about 1,4-dioxane occurrence and toxicity, it is possible that 1,3-dioxane may become a substitute. Therefore, a final objective was to determine whether the developed analytical method can separate these two isomers.

The method developed is based on the EPA method 522 of the EPA: “DETERMINATION OF 1,4-DIOXANE IN DRINKING WATER BY SOLID PHASE EXTRACTION (SPE) AND GAS CHROMATOGRAPHY/ MASS SPECTROMETRY (GC/MS) WITH SELECTED ION MONITORING (SIM)”, version 1 of September, 2008. The method was used with modifications as described below and in Sun et al. (2016).

### **Purge and Trap Settings**

For sample pre-concentration, the solid phase extraction step of EPA method 522 was replaced by a heated purge and trap step (Teledyne Tekmar, Stratum AQUATEK 100). For each analysis, 1 µL of 20 mg/L 1,4-dioxane-d8 in methanol was automatically added as IS into 5 mL sample.

The mixture was purged with helium at 60°C for 12 min, followed by dry purge at 20°C for 6 min. The purged chemicals were concentrated on a Teledyne Tekmar #9 trap for analysis and desorbed at 250°C for 1 min. The parameters were optimized to maximize sensitivity and minimize moisture carryover. Detailed P&T settings are listed in Table 4.

**Table 4. Setting for purge and trap system**

Variable	Value		Variable	Value
Valve Open Temp	150°C	<b>Desorb</b>	GC start	Start of desorb
Transfer Line Temp	150°C		Desorb Preheat Temp	245°C
Sample Mount Temp	90°C		Desorb Time	1.00 min
Purge Ready Temp	35°C		Desorb Temp	250°C
Condenser Ready Temp	40°C		Drain Flow	300 mL/min
Condenser Purge Temp	20°C		Bake Time	6.00 min
Standby Flow	20 mL/min	<b>Bake</b>	Bake Temp	280°C
Sparge Vessel Heater	ON		Condenser Bake Temp	200°C
<b>Purge</b> Pre-Purge time	0.5 min	<b>AQUATEk 100</b>	Bake Flow	200 mL/min
Pre-Purge Flow	40 mL/min		Pressurize Time	0.5 min
Preheat Time	2.00 min		Sample Transfer Time	0.35 min
Sample temp	60°C		Rinse Loop Time	1.00 min
Purge Time	12 min		Sweep Needle Time	1.00 min
Purge Temp	20°C		Bake Rinse	ON
Purge Flow	40 mL/min		Bake Rinse Cycles	3
Dry Purge Time	6.00 min		Bake Rinse Drain Time	0.35 min
Dry Purge Temp	20°C		Presweep Time	0.25 min
Dry Purge Flow	100 mL/min		Water Temp	90°C

### Gas Chromatography/Mass Spectrometry (GC/MS).

Upon desorption from the trap, analytes and IS were transferred to a gas chromatograph and ion trap mass spectrometer (CP-3800 GC coupled with Saturn 2200 MS, Agilent, Santa Clara, CA). A VF-624ms column (30 m × 0.25 mm × 1.4 μm, Agilent) was used for compound separation.

The MS was operated in electron ionization (EI) mode with selected-ion storage (SIS). Detailed settings of the GC/MS are summarized in Table 5.

**Table 5. GC/MS system settings**

<b>Parameter</b>	<b>Value</b>
Split ratio	40
Inlet temperature	200 °C
Carrier gas	1 mL/min helium
Oven temperature	started at 30 °C, held for 1.0 min, ramped at 20 °C/min to a final temperature of 200 °C and held for 10.0 min
MS detector on	4.5 to 6.5 minutes
Multiplier offset	200 V
Emission current	100 $\mu$ A
Scan time	0.6 sec
SIS mass range	55-66, 86-90 and 94-98
Ion storage level	48.0 m/z
Ion time factor	100%
Ion trap temperature	190°C
Manifold temperature	60°C
Transfer line temperature	220°C

## Chemicals

1,4-Dioxane (99.5%), 1,3-dioxane (98%), methanol (purge-and-trap grade), and anhydrous sodium sulfite (ACS grade) were purchased from Thermo Fisher Scientific (Waltham, MA). A commercial 1,4-dioxane standard (1 mg/mL in methanol) was purchased from Absolute Standard (Hamden, CT) to prepare quality control (QC) solutions. Deuterium-labeled 1,4-dioxane-d8 (99 atom % D) and anhydrous sodium bisulfate (technical grade) were purchased from Sigma-Aldrich (St. Louis, MO) (Sun et al., 2016).

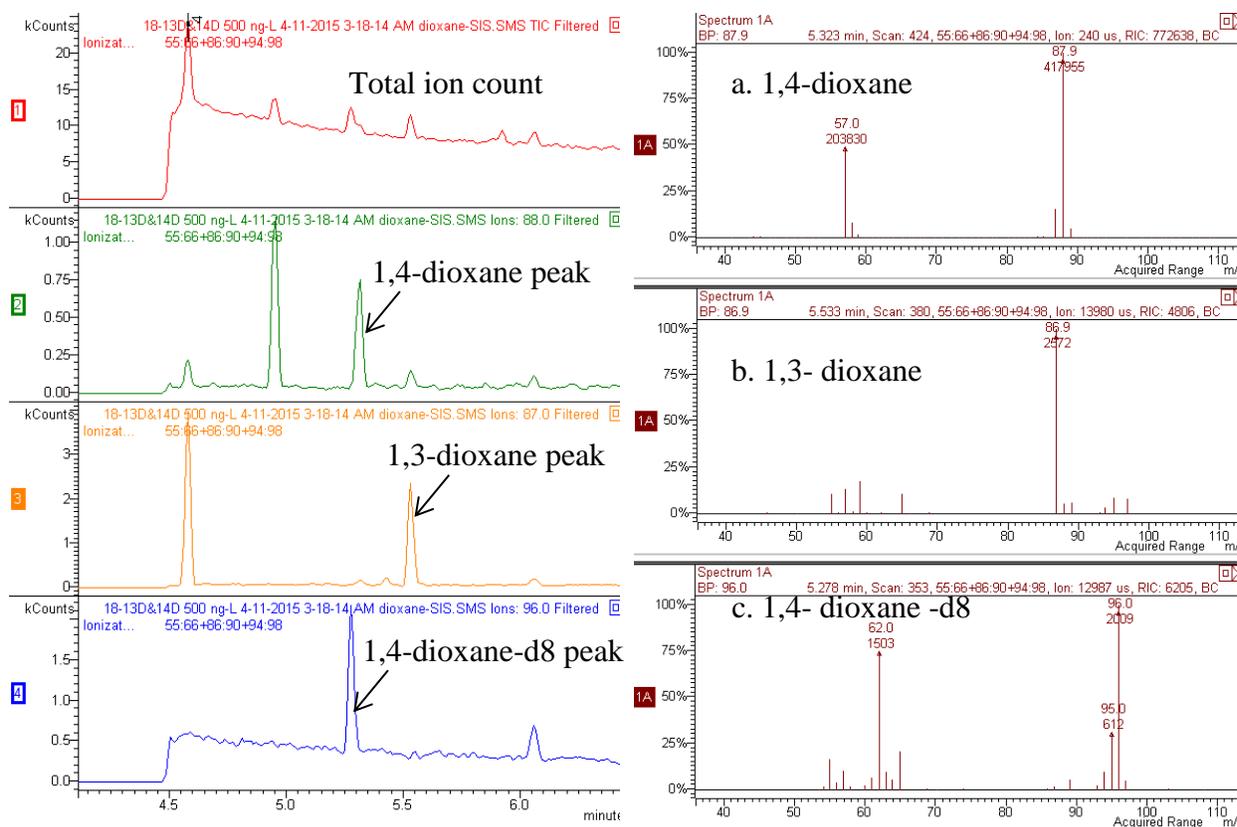
## Calibration Standards and Quality Control Samples

A stock standard solution (SSS) (1 mg/L) was prepared by dissolving neat 1,4-dioxane in ultrapure water and stored at 4°C. A primary dilution standard (PDS) was prepared from the SSS at 2000  $\mu$ g/L in ultrapure water on the same day of the calibration curve preparation. Duplicate calibration standards (0.15 - 300  $\mu$ g/L) were prepared from the PDS to build a nine-point calibration curve. Calibration standards were analyzed at the beginning and end of each sample batch. QC solutions (1 and 100  $\mu$ g/L in ultrapure water) were prepared from a standard solution obtained from a second source (1 mg/mL in methanol). To validate the calibration and method stability, a QC sample was analyzed after every 10-15 unknown samples (Sun et al., 2016).

## Method Performance

### Chromatogram and Mass Spectrum

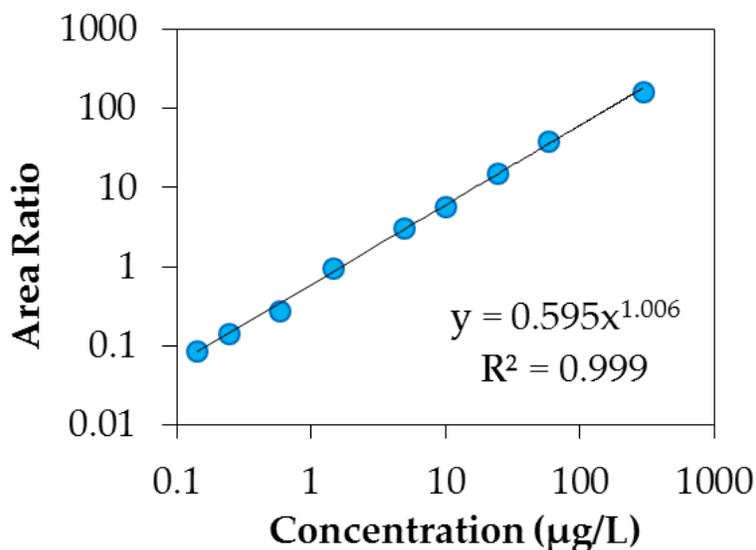
An example total ion chromatogram as well as the 1,4-dioxane, 1,4-dioxane-d8, and 1,3-dioxane mass chromatograms and corresponding mass spectra are shown in Figure 4. Peaks of all three compounds were obtained within 5.5 minutes, were symmetrical, and were clearly separated from one another as well as from background noise/other compounds in the samples. Ions with  $m/z$  of 88 and 96 served as quantitation ions (Q-ion) for 1,4-dioxane and 1,4-dioxane-d8, respectively. The ratio of secondary ion (57 for 1,4-dioxane, 62 for 1,4-dioxane-d8) to the Q-ion was constant across calibration solutions, QC solutions and environmental samples (RSD < 20% for 1,4-dioxane and <10% for 1,4-dioxane-d8). No 1,3-dioxane peak was detected in any of the environmental samples and thus no further quantitative analysis was performed. If 1,3-dioxane quantification is needed in other studies,  $m/z$  87 could serve as a quantitation ion. The total program run times for the P&T and GC were 31 and 19.5 min, respectively. Since the sample preparation (P&T) and quantification (GC/MS) operate in parallel, the average analytical time required per sample was 35 minutes.



**Figure 4.** Example total ion chromatogram, mass chromatograms, and associated SIS mass spectra for (a) 1,4-dioxane, (b) 1,3-dioxane, and (c) 1,4-dioxane-d8 in ultrapure water spiked at concentrations of 0.7, 0.6 and 4  $\mu\text{g/L}$ , respectively.

### Method Calibration

1,4-Dioxane calibration curves covered a concentration range of 0.15-300 µg/L, which was based on preliminary investigations of 1,4-dioxane concentrations in water matrices of interest. An example calibration curve is shown in Figure 5, and validation data for this curve are summarized in Table 6. Error, response factor and relative response factor for 1,4-dioxane calibration curve using 4 µg/L 1,4-dioxane-d8 as internal standard. The calibration curve was essentially linear for concentrations spanning more than 3 orders of magnitude. When the response factor and relative response factor (also referred to as calibration factor and response factor, respectively, in some references such as EPA Method 8000D) are constant (RSD <20% according to EPA Method 8000D), use of the linear model is generally considered appropriate over the calibration range. However, in this study, a power regression was found to produce a smaller error than linear regression when comparing concentrations back-calculated through the regression equation to the theoretical values. Thus, all quantification in this study was based on calibration equations developed from a power regression (Sun et al., 2016).



**Figure 5.** Calibration curve for 1,4-dioxane (0.15-300 µg/L) with 1,4-dioxane-d8 as the internal standard (4 µg/L).

**Table 6. Error, response factor and relative response factor for 1,4-dioxane calibration curve using 4 µg/L 1,4-dioxane-d8 as internal standard.**

<b>Concentration Spiked (µg/L)</b>	<b>Concentration back calculated through regression (µg/L) <sup>a</sup></b>	<b>Error % <sup>b</sup></b>	<b>RF <sup>c</sup></b>	<b>RRF <sup>d</sup></b>
<b>0.14</b>	0.15	5%	1430	2.47
<b>0.25</b>	0.24	-2%	1208	2.31
<b>0.58</b>	0.48	-18%	1464	1.94
<b>1.46</b>	1.63	12%	1731	2.67
<b>4.9</b>	5.19	6%	1414	2.54
<b>9.86</b>	9.67	-2%	1338	2.37
<b>24.5</b>	25.6	4%	1732	2.53
<b>58.6</b>	62.8	7%	1420	2.61
<b>291.9</b>	263.9	-10%	1271	2.22
<b>RSD<sup>e</sup></b>	/	/	13%	9%

**a: Calculated using the power regression equation shown in Figure 5**

**b. Error (%) =  $\frac{\text{Calculated concentration} - \text{Theoretical concentration}}{\text{Theoretical concentration}} \times 100\%$**

**c: Response factor, RF =  $\frac{\text{Peak area}}{\text{Theoretical concentration}}$**

**d: Relative response factor, RRF =  $\frac{\text{RF of analyte}}{\text{RF of IS}}$**

**e: Relative standard deviation of RF and RRF**

### *Minimum Reporting Level and Detection Limit*

The minimum reporting level (MRL) and detection limit (DL) for the developed method were determined as described in EPA Method 522. Briefly, the MRL was calculated using seven replicates of 1,4-dioxane-fortified ultrapure water at the proposed MRL (0.15 µg/L). The half range for the prediction interval of results (HR<sub>PIR</sub>) was determined using Equation 2, where S is the standard deviation, t<sub>(n-1, 1-α=0.99)</sub> is the Student's t value at the 99% confidence level with n-1 degrees of freedom (t=3.707), and n is the number of replicates (n=7).

$$HR_{PIR} = S \times t_{(n-1, 1-\alpha=0.99)} \times \sqrt{1 + \frac{1}{n}} \quad \text{Equation 2}$$

Then the upper and lower recovery limits of the Prediction Interval of Results (PIR = Mean + HR<sub>PIR</sub>) were calculated as shown in Equation 3 and 3. The Upper PIR must be ≤ 150% and the Lower PIR must be ≥ 50%.

$$\text{Upper PIR} = \frac{\text{Mean} + \text{HR}_{\text{PIR}}}{\text{Fortified concentration}} \quad \text{Equation 3}$$

$$\text{Lower PIR} = \frac{\text{Mean} - \text{HR}_{\text{PIR}}}{\text{Fortified concentration}} \quad \text{Equation 4}$$

With seven replicates of solution fortified at 0.15 µg/L, the calculated upper and lower PIR values were 98 and 78%, respectively, both meeting the criteria above. Thus the MRL for this method was determined to be 0.15 µg/L, which is lower than the excess one-in-a-million cancer risk level of 0.35 µg/L. The MRL is lower than that of all previously reported P&T methods and compares well with that of solid phase and solvent extraction methods shown in Table A. 1.

The DL was determined with seven replicates of ultrapure water fortified with 0.1 µg/L 1,4-dioxane and was calculated using Equation 5, where S,  $t_{(n-1, 1-\alpha=0.99)}$  and n are the same as defined for Equation 2. The DL calculated for this method is 0.056 µg/L.

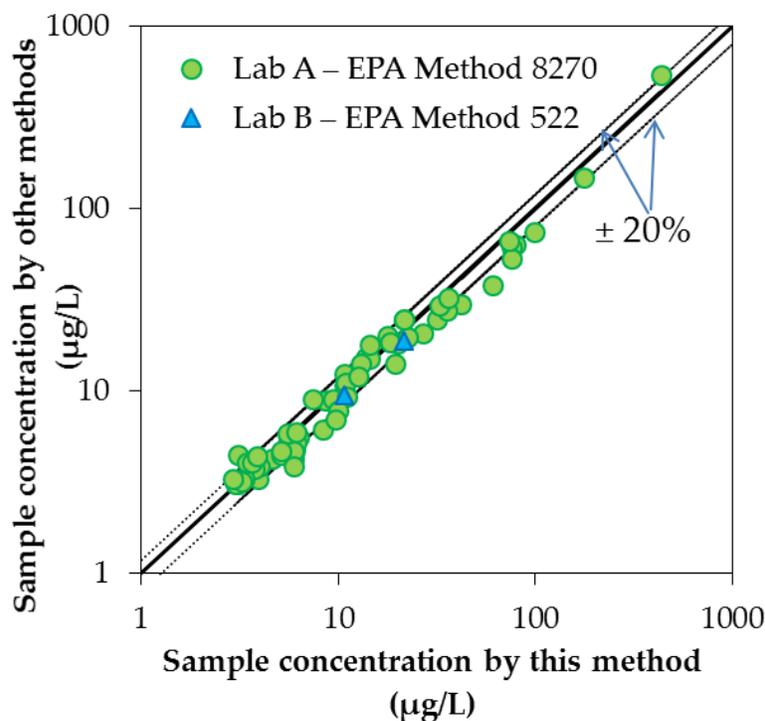
$$\text{DL} = S \times t_{(n-1, 1-\alpha=0.99)} \quad \text{Equation 5}$$

### ***Precision and Accuracy***

The reliability of this method was evaluated by analyzing samples of ultrapure water fortified with 1,4-dioxane at concentrations of 1 and 100 µg/L. Precision and accuracy were determined by the RSD and percent recovery, respectively. Seven fortified samples at each concentration were analyzed. RSDs were 6% at both concentrations, and recoveries were 112% and 101% of the spiked values at 1 and 100 µg/L, respectively, suggesting the method is both precise and accurate.

### **Comparison with Standard Methods**

An inter-laboratory comparison was performed to confirm the accuracy of the developed method. Surface water samples collected in NC were sent to two commercial labs for 1,4-dioxane quantification, and results were compared with those obtained by the method described herein (Figure 6). For sample preconcentration, Lab A used liquid-liquid extraction (Standard Method SW 846/EPA Method 8270, MRL = 3 µg/L) and Lab B used solid phase extraction (EPA Method 522, MRL = 0.07 µg/L). Among all 64 samples with results >MRL (Figure 6), the RSDs for inter-laboratory results ranged from 0 to 32%, and the average RSD was 10%. The agreement between data acquired using this method and other standard methods provides further validation of the analytical approach developed herein.



**Figure 6. Comparison of 1,4-dioxane concentration data obtained with the analytical method described herein and standard methods. Thick solid line represents perfect agreement.**

### Method Application to Environmental Samples

An important objective was to develop an analytical method that can accurately quantify 1,4-dioxane concentrations in a wide range of aqueous matrices. To demonstrate the capabilities of the method, matrix spike experiments were conducted with drinking water, groundwater, surface water, and WWTP effluent samples. Within each water matrix, background 1,4-dioxane concentrations were elevated in one sample and negligible/low in the other. Water quality characteristics of the matrices are summarized in Table 7.

**Table 7. Water quality characteristics of matrix spike samples**

Matrix	NPOC (mg/L)	pH	ALK (mg/L as CaCO <sub>3</sub> )	UV <sub>254</sub>	Conductivity (µS/cm)
Drinking water A	1.59	7.65	26.5	0.033	240
Drinking water B	1.88	7.55	36.5	0.031	145
Groundwater A	1.59	8.16	277.5	0.033	552
Groundwater B	0.08	7.92	152.5	0.004	662
Surface water A	6.43	7.39	46.7	0.226	133
Surface water B	3.80	7.44	26.7	0.168	160
Wastewater A	6.77	6.77	77.3	0.116	552
Wastewater B	19.66	7.54	113.7	0.597	1035

Each matrix was analyzed for its background 1,4-dioxane concentration, and then spiked at two 1,4-dioxane concentrations as shown in Table 8. For all matrices, RSDs were  $\leq 9\%$ , and recoveries of matrix spikes ranged from 86 to 115% with no discernible differences among the tested aqueous matrices. It should be noted that the recoveries for matrices with background 1,4-dioxane concentrations below the MRL of 0.15  $\mu\text{g/L}$  are reported by assuming the background concentration is either zero or MRL/2. The results shown in Table 8 suggest that the developed analytical method can be applied with confidence in a wide range of water quality contexts.

**Table 8. Precision and accuracy for 1,4-dioxane determinations in spiked water samples**

Matrix		Spiked concentration ( $\mu\text{g/L}$ )	Average measured concentration ( $\mu\text{g/L}$ ) (n=4)	RSD	Recovery <sup>a</sup>
<b>Drinking water</b>	A	0.00	<0.15		
		0.37	0.39	4%	106% / 86%
		0.75	0.71	5%	95% / 85%
	B	0.00	8.72	5%	
		5.02	13.38	4%	93%
		9.91	17.90	2%	93%
<b>Groundwater</b>	A	0.00	<0.15		
		0.36	0.35	5%	97% / 76%
		0.73	0.70	9%	95% / 85%
	B	0.00	1.36	6%	
		2.02	3.10	2%	86%
		4.89	6.02	2%	95%
<b>Surface water</b>	A	0.00	<0.15		
		0.37	0.43	7%	115% / 95%
		0.73	0.77	8%	104% / 94%
	B	0.00	58.08	3%	
		51.22	116.92	2%	115%
		99.71	165.82	3%	108%
<b>Wastewater</b>	A	0.00	2.15	9%	
		0.88	3.01	5%	99%
		1.87	3.99	5%	99%
	B <sup>b</sup>	0.00	118.45	5%	
		49.71	169.88	2%	103%
		99.53	230.66	4%	113%
<p>a: When background concentrations were &lt;MRL (i.e. &lt;0.15 <math>\mu\text{g/L}</math>), recovery is reported using two values: the first was calculated assuming a background concentration of zero, and the second was calculated assuming a background concentration of MRL/2 (= 0.075 <math>\mu\text{g/L}</math>).</p> <p>b: The background 1,4-dioxane concentration in wastewater B was beyond the calibration range, thus wastewater B was diluted 5 times and then used for the matrix spike tests</p>					

## **Conclusions**

Overall, the new analytical method described herein demonstrated high sensitivity, accuracy and precision. Compared to solid phase and solvent extraction methods, the fully automated heated P&T preconcentration step requires minimal sample volume, analysis time, and labor, and it produces no hazardous waste. The MRL for aqueous 1,4-dioxane was lowered to a level not previously achieved by published P&T methods, and the method was shown to accurately determine 1,4-dioxane concentrations in a wide range of environmental matrices. Thus, it has great potential to be applied in 1,4-dioxane occurrence and source identification studies, exposure assessment, fate and transport investigations, and treatment process evaluations.

# 1,4-DIOXANE OCCURRENCE IN THE CAPE FEAR RIVER WATERSHED OF NORTH CAROLINA

## *Abstract*

Recent data published by the USEPA show that seven of the twenty highest 1,4-dioxane concentrations in the US occur in drinking water derived from the Cape Fear River (CFR) basin in NC. 1,4-Dioxane is classified as a likely human carcinogen, and an excess  $10^{-6}$  cancer risk is associated with the lifetime consumption of drinking water with a 1,4-dioxane concentration of 0.35  $\mu\text{g/L}$ . The overarching goal of this research was to gain insights into the occurrence of 1,4-dioxane in surface water and drinking water in the CFR watershed. Specific objectives included to (1) identify possible sources of 1,4-dioxane, (2) establish temporal and spatial variability of 1,4-dioxane concentrations and mass flows, and (3) determine the fate of 1,4-dioxane in three surface water treatment plants. Forty-seven sampling points were strategically selected, across the CFR watershed to bracket possible sources, and monthly samples were collected over a period of one year. Results showed that discharges of three municipal wastewater treatment plants principally contributed to elevated 1,4-dioxane concentrations in the CFR basin. 1,4-Dioxane concentrations ranged from  $<0.15 \mu\text{g/L}$  in non-impacted surface water to  $1,760 \mu\text{g/L}$  downstream of a WWTP discharge. At three drinking water utilities, daily composite raw and finished water samples were also analyzed and collected over a period of 2 months to assess the fate of 1,4-dioxane in drinking water treatment plants. For two conventional water treatment plants, 1,4-dioxane concentrations were not attenuated, and average 1,4-dioxane concentrations in the finished water were 8.7 and 2.6  $\mu\text{g/L}$ . In the third utility, which employs raw and settled water ozonation, approximately 67% of the influent 1,4-dioxane was oxidized, but the average finished water 1,4-dioxane concentration of 1.2  $\mu\text{g/L}$  still remained above the one-in-a-million cancer risk level by a factor of 3.4.

## **Introduction**

In the past, 1,4-dioxane was widely used as a solvent stabilizer, and it is commonly thought of as a groundwater contaminant that co-occurs with chlorinated solvents. While 1,4-dioxane usage in the context of solvent stabilization has been decreasing, 1,4-dioxane continues to be used as an industrial solvent (e.g. textile industry, paper industry, production of specialty chemicals), and it is a by-product of manufacturing processes involving ethylene oxide (e.g. production of surfactants used in laundry detergents and shampoos, production of certain plastics). The US Environmental Protection Agency (USEPA) included 1,4-dioxane in the third contaminant candidate list (CCL3), and classified it as a “likely human carcinogen” by all routes of exposure. An excess one-in-a-million cancer risk is associated with lifetime consumption of drinking water containing 0.35  $\mu\text{g/L}$  1,4-dioxane. 1,4-Dioxane possess unique characteristics that explain its industrial utilization and environmental fate. Its cyclic structure with two opposed ether linkages results in a very stable structure, with high aqueous solubility, and high resistance to biodegradation. Moreover, its low Henry’s law constant and low octanol-water partition coefficient make it difficult to remove from water. Toxicological studies revealed an increased incidence of nasal cavity and liver carcinomas in rats, liver carcinomas in mice, and gall bladder carcinomas in guinea pigs when exposed to 1,4-dioxane (ATSDR, 2012).

1,4-Dioxane has emerged as a water contaminant of concern at numerous locations throughout the world (Table 9). In Japan, extensive research on the distribution and occurrence of 1,4-dioxane in drinking water, surface water, groundwater and landfill leachate has been conducted (Abe, 1999; Tanabe et al., 2006; Simazaki et al., 2006; Yasuhara et al., 2003). In a nationwide survey of 91 Japanese drinking water treatment plants, 1,4-dioxane was detected in 32 of 90 surface water derived samples, with an average concentration of 0.20 µg/L (Simazaki et al., 2006). In Europe, 1,4-dioxane has been found in surface waters of Germany, Poland, the Netherlands and the United Kingdom. Average concentrations in the finished water of two German drinking water treatment plants were 0.49 and 0.60 µg/L (Stepien et al., 2014). Extensive work has also focused on the occurrence of 1,4-dioxane in groundwater (Mohr, 2010; Mahendra and Alvarez-Cohen, 2006; Sales, 2012; Zenker et al., 2003). Furthermore, data published in 2016 from the third unregulated contaminant monitoring rule (UCMR3) illustrate that 3.0% of 36,479 drinking water samples collected from public water systems (PWSs) exhibited 1,4-dioxane concentrations >0.35 µg/L and 23% were from surface water origin (USEPA, 2016).

**Table 9. Global occurrence of 1,4-dioxane at different sources in the world**

Source	Location	Concentration (µg/L)	Reference
<b>Drinking water</b>	Durham, CT (Groundwater)	26	ATSDR, 2012
	Japan (Surface water)	Mean 0.20	Simazaki et al., 2006
	Kitakyusyu, Japan (surface water)	0.15	Abe, 1999
	Germany (Surface water)	0.49, 0.60	Stepien et al., 2014
	USA (Surface water)	<0.07 to 13.3	USEPA, 2016
	USA (Groundwater)	<0.07 to 33	USEPA, 2016
<b>Surface water</b>	Shinano River, Japan	Mean: 0.05	Tanabe et al., 2006
	Agano River, Japan	Mean: 0.11	Tanabe et al., 2006
	Kitakyushu, Japan	1.1 to 18	Kadokami et al., 1993
	Niigata, Japan	0.13 to 0.23	Kakegawa, 1995
	Nagano, Japan	0.42 to 1.5	Kakegawa, 1995
	Japan	Mean: 0.20	Simazaki et al., 2006
	Japan	0.10 to 16	Abe, 1999
<b>Groundwater</b>	Bedford, MA	2,100	Weimar, 1980
	Washtenaw, MI	212,000	ATSDR, 2012
	Circleville, Ohio	< 1.0 to 360	ATSDR, 2012
	California	1.1 to 109	Mohr, 2010
	Kanagawa, Japan	0 to 94.8	Abe, 1999
	Japan	<0.05 to 5.6	Simazaki et al., 2006
	Japan	<0.1 to 94.8	Abe, 1999
<b>Wastewater</b>	Ann Arbor, MI (domestic)	2.0 to 3.0	Zenker et al., 2003

Source	Location	Concentration ( $\mu\text{g/L}$ )	Reference
	US (domestic)	0.30 to 3.30	Simonich et al., 2013
	Japan (domestic)	0.21 to 0.39	Tanabe et al., 2006
	Hiratsuka, Japan (industrial)	4020	Abe, 1999
	Hiratsuka, Japan (domestic)	0.40 to 1.1	Abe, 1999
	Hiratsuka, Japan (industrial)	0.80 to 46	Abe, 1999
	Hiratsuka, Japan (domestic)	0.80 to 1.1	Abe, 1999
	Hiratsuka, Japan (domestic)	3.6 to 97	Abe, 1999
	Hiratsuka, Japan (domestic)	1.7 to 3.0	Abe, 1999
	Hiratsuka, Japan (domestic)	1.0 to 88	Abe, 1999
<b>Landfill Leachate</b>	Japan	1.1 to 109	Yasuhara et al., 2003
	Japan	0.80 to 198	Yasuhara et al., 2003
	Japan	19.6 to 775	Yasuhara et al., 2003
	Japan	0.13 to 13.8	Yasuhara et al., 2003
	Wilmington, DE	0.5 to 2.4	DeWalle and Chian, 1981
	Gloucester, Canada	~300-2000	Lesage et al., 1990

1,4-Dioxane mass loading studies have been conducted in Japan and Germany. Tanabe et al. (2006) quantified mass flows in two rivers in Japan; average mass flows over a period of eleven months were 3.5 and 1.5 kg/d in the Agano River and Shinano River, respectively. Average stream flow in the Agano River was reported as 372 m<sup>3</sup>/s, whereas in the Shinano river it was 350 m<sup>3</sup>/s. Stepien et al. (2014) collected daily 24-hour composite samples in three German rivers (Oder, Rhine and Main river) for a period of two weeks. The highest average mass loads were 134.5 kg/d (Rhine river), 34.1 kg/d (Oder river) and 6.5 kg/d (Main river). Results show that loads of 1,4-dioxane in two locations of the Oder river were not constant over time during March and August of 2012. Except for these two locations, loads of 1,4-dioxane at the Oder, Rhine and Main river were similar. In April of 2013, when the discharge was almost three times higher than in August of 2012, the mass flows of 1,4-dioxane in the Oder river remained comparable at all sampling locations (Stepien et al., 2014).

Research has been conducted to investigate removal of 1,4-dioxane by physical, chemical and biological processes (Table 10). Stepien et al (2014) investigated the presence of 1,4-dioxane in two drinking water treatment (DWT) facilities (Table 10). Results demonstrated that neither bank filtration nor purification of the raw water (for description of the treatment process, refer to Table 10) was capable of measurable 1,4-dioxane removal. McGuire et al. (1978) investigated

treatment of 1,4-dioxane with ferric chloride coagulation, powdered activated carbon adsorption, permanganate oxidation, and chlorination. None of the studied processes was capable of achieving significant 1,4-dioxane removal (Table 10), but 67% removal was achieved when GAC was incorporated into the treatment. Data collected at the Orange County Water District in Southern California indicated that 1,4-dioxane partially passes through reverse osmosis membranes (USEPA, 2013). Advanced oxidation processes (AOP) are capable of 1,4-dioxane control at bench scale and full scale (Adams et al., 1994; Kleka and Gonsior, 1986; TrojanUV, 2015).

Biodegradation of 1,4-dioxane at sub- $\mu\text{g/L}$  levels is currently in the research stage. Monooxygenase expressing bacteria degraded 1,4-dioxane by cometabolism in the presence of tetrahydrofuran, butane or ethane (Mahendra and Alvarez-Cohen, 2006). Other processes shown to be effective for removing 1,4-dioxane include photocatalysis using titanium dioxide, sonication with or without UV irradiation and electrolysis. However, these techniques have very limited drinking water application and can be prohibitively expensive (WRF, 2014).

**Table 10. Removal of 1,4-dioxane by different water treatment processes**

<b>Treatment Process Description</b>	<b>Location</b>	<b>Concentration (ug/L)</b>	<b>Reference</b>
Bank filtration ozonation, aeration, and a two layer activated carbon filtration.	Full scale Germany	<b>Raw water:</b> 0.67 µg/L (75% bank filtration and 25% groundwater recharge) <b>Finished water:</b> 0.49 µg/L	(Stepien et al., 2014)
Natural filtration ozonation, sand/gravel filtration, activated carbon filtration, physical decalcification, and disinfection with chlorine dioxide	Full scale Germany	<b>Raw water:</b> 0.65 µg/L, surface water <b>Finished water:</b> 0.6 µg/L	(Stepien et al., 2014)
Ferric chloride coagulation, powdered activated carbon, permanganate oxidation	Bench scale US	<b>Influent:</b> 5.0 mg/L <b>Effluent:</b> 5.0 mg/L	(Mcguire et al., 1978)
Granular carbon	Bench scale US	<b>Influent:</b> 5.0 mg/L <b>Effluent:</b> 1.8 mg/L	(Mcguire et al., 1978)
Hydrogen peroxide in combination with a ferrous iron salt (Fenton's reagent)	Bench scale US	<b>Influent:</b> 100 mg/L <b>Effluent:</b> 2.0 mg/L	(Kleka and Gonsior, 1986)
UV Hydrogen peroxide, granular activated carbon quenching	Full Scale Tucson, AZ	Not reported concentration (96% reduction)	(TrojanUV, 2015)
Ozone + Hydrogen peroxide, pretreatment by air stripping	Pilot CA, US	<b>Influent:</b> 20.2 <b>Effluent:</b> <2	Reported by (Otto et al., 2007)
Ozone + Hydrogen peroxide	Full, CA, US	<b>Influent:</b> 15 <b>Effluent:</b> <0.94	Reported by (Otto et al., 2007)
Ozone + Hydrogen peroxide, pretreatment by air stripping	Full, Orange County, US	<b>Influent:</b> 170 <b>Effluent:</b> <3	Reported by (Otto et al., 2007)

The overarching goal of this research was to gain insights into the occurrence of 1,4-dioxane in surface water and drinking water in the CFR watershed. Specific objectives included to (1) identify possible sources of 1,4-dioxane, (2) establish temporal and spatial variability of 1,4-dioxane concentrations and mass flows, and (3) determine the fate of 1,4-dioxane in three surface water treatment plants two employing conventional treatment processes and one employing advanced treatment processes, including raw and settled water ozonation, biological activated carbon filtration and disinfection by medium pressure ultraviolet (MP-UV) light.

## **Materials and Methods**

### ***Chemicals and Reagents***

1,4-Dioxane (99.5%, CAS No. 123-91-1), methanol (purge-and-trap grade), and sodium sulfite anhydrous (ACS grade) were purchased from Thermo Fisher Scientific (Waltham, MA). 1,4-Dioxane-d8 (99%, CAS No. 17647-74-4), and sodium bisulfate anhydrous (technical grade) were purchased from Sigma-Aldrich (St. Louis, MO). A commercial 1,4-dioxane standard (1 mg/mL in methanol) was purchased from a second source (Absolute Standard, Hamden, CT) to prepare quality control (QC) samples.

### ***Analytical Method***

The method used for determination of 1,4-dioxane in water samples was recently described by Sun et al. (2016). Briefly, heated purge-and-trap (P&T) preconcentration (AQUATek 100 autosampler, Stratum PTC, Teledyne Tekmar, Mason, OH) followed by gas chromatography (GC)/ion-trap mass spectrometry (MS) with selected-ion storage (CP-3800 GC and Saturn 2200 MS, Agilent, Santa Clara, CA) was used to measure 1,4-dioxane concentrations in aqueous samples. A 5-mL sample volume was heated and the purged chemicals were collected by a sorbent trap (Teledyne Tekmar #9). Mass-labeled 1,4-dioxane-d8 was used as internal standard (IS) for quantification. A capillary column (30 meter  $\times$  0.25 mm  $\times$  1.4  $\mu$ m, Agilent VF-624ms) was used for compound separation.

Calibration standards were prepared according to EPA method 522. A stock standard solution (SSS) (1 mg/L) was prepared by dissolving neat 1,4-dioxane in ultrapure water, and the SSS was stored at 3°C. A primary dilution standard (PDS) was prepared from the SSS at 2000  $\mu$ g/L in ultrapure water on the day of the calibration curve preparation. A nine-point calibration series was built from the PDS, and duplicate calibrations (0.15 - 300  $\mu$ g/L) were run at the beginning and end of each quantification batch. In each analysis, 1  $\mu$ L of 20 mg/L 1,4-dioxane-d8 in methanol was automatically added as the IS. Peak area ratios of 1,4-dioxane to the IS were used for quantification, and calibration curves were described with a log linear regression (Sun et al. 2016). QCs were prepared at concentrations of 1 and 100  $\mu$ g/L, and a QC sample was analyzed after every 10-15 unknown samples.

## *Watershed Description and Sampling Plan*

### *Surface Water*

Samples were collected in the CFR basin of North Carolina (NC) the largest river basin in NC, draining 23,700 square kilometers. The Haw and Deep Rivers originate in the north central part of the state and their confluence forms the Cape Fear River, which flows in a southeasterly direction until it reaches the Atlantic Ocean. Local water authorities estimate that as many as 1.5 million residents obtain drinking water from surface water resources within this basin (Nakayama et al., 2007). Initially, 47 sampling points were strategically selected upstream and downstream of 14 wastewater treatment plants (WWTPs). The majority of sampling points were distributed along the Haw, Deep, and Cape Fear Rivers, covering more than 400 km of river. The preliminary survey of 47 locations and 14 WWTP discharges was completed to gain insight into which locations had the potential to be 1,4-dioxane sources in the CFR watershed. Based on results of the preliminary survey, 32 river sampling locations were selected based on either high concentration and/or concentrations increasing across point source discharges. A total of 600 samples were collected between October of 2014 and October of 2015.

### *Drinking Water Treatment Plants*

Samples were also collected at three municipal drinking water treatment plants (DWTPs). Relevant information about the population served, capacity, process configuration and source water for each DWTP is listed in Table 11. All three DWTPs studied use conventional drinking water treatment. In addition, DWTP C uses ozonation (raw water and settled water), biological filtration and medium pressure UV disinfection. Daily composite raw and finished water samples were collected at DWTP A and DWTP B for a period of eight weeks. Sampling was conducted between March 17, 2015 and May 12, 2015. Per plant, 144 samples were analyzed: 56 raw water samples, 56 treated water samples and 32 QA/QC samples (duplicates, matrix spikes). Samples for DWTP C were collected for 6 weeks between April 14, 2015 and May 25, 2015; 126 samples were analyzed: 49 raw water samples, 49 finished water samples and 28 QA/QC samples.

**Table 11. Relevant information of the DWTPs studied**

<b>Parameter</b>	<b>Plant A</b>	<b>Plant B</b>	<b>Plant C</b>
<b>Population served</b>	3,743	204,410	112,067
<b>Capacity (MGD)</b>	2.50	39.5	35.0
<b>Process configuration</b>	Coagulation-flocculation, sedimentation, filtration, free chlorine, chloramine	Powdered activated carbon (<5 mg/L), coagulation-flocculation, sedimentation, filtration, free chlorine, chloramine	Pre-ozone, coagulation-flocculation, sedimentation, intermediate ozone, biological filtration, UV, free chlorine
<b>Source Water</b>	Haw River	Cape Fear River	Cape Fear River

### *Sampling Procedure*

Surface water and composite water samples were collected following directions described in EPA method 522. Pre-cleaned and baked amber glass bottles (500 mL, VWR International, Philadelphia, PA) were used to collect samples. Surface water samples were collected directly into the sample bottles using a bridge sampler designed and constructed by the authors. Composite samples were collected by adding 100 mL of sample every hour during 24 hours to complete a total volume of 2.4 L. Sodium sulfite (50 mg/L, to remove free and combined chlorine) and sodium bisulfate (1 g/L, to lower the pH and inhibit microbial activity) were added to all samples as preservation reagents at the time of sample collection (EPA, 2008). Samples were stored at 4°C and analyzed within 28 days of sample collection. Blanks and quality control standard samples (temperature blank, trip blank, 1,4-dioxane QC, field duplicate, matrix spike and matrix spike duplicates) were included with each batch of samples collected, to ensure the quality of the collection and analysis processes. Prior to analysis of the water samples, blanks and calibration standards were analyzed. All blank samples registered as ND for 1,4-dioxane, duplicate samples were within ±20% of difference, and matrix spike recovery was within the ±30% difference required by EPA Method 522 (EPA 2008).

## **Results and Discussion**

### *Source Identification*

Surface water samples were collected upstream and downstream of nine WWTP discharge locations (labeled 1-9 in Figure 8) in the CFR watershed of NC. Although 1,4-dioxane concentration data at each sampling location varied from month to month, the distribution pattern between upstream and downstream locations bracketing individual discharge points remained the same. As shown in Figure 7 and Figure 8, WWTP discharges 2, 5, and 9 were important contributors to elevated instream 1,4-dioxane concentrations. Upstream concentrations were

relatively low for all three discharge points (<MRL to 1.0 µg/L at H-11, 0.7-4.5 µg/L at site D-7, and 0.8-4.0 µg/L at site SB-2). However, downstream of the discharge points, 1,4-dioxane concentrations were one to two orders of magnitude higher (1.0-1,760 µg/L for site H-10, 2.8-78 µg/L for site D-6, and 4.85-436 µg/L for site SB-1). The results for sampling points H-10, D-6 and SB-1 illustrate that WWTP discharges can be important point sources that contribute to elevated instream 1,4-dioxane concentrations.

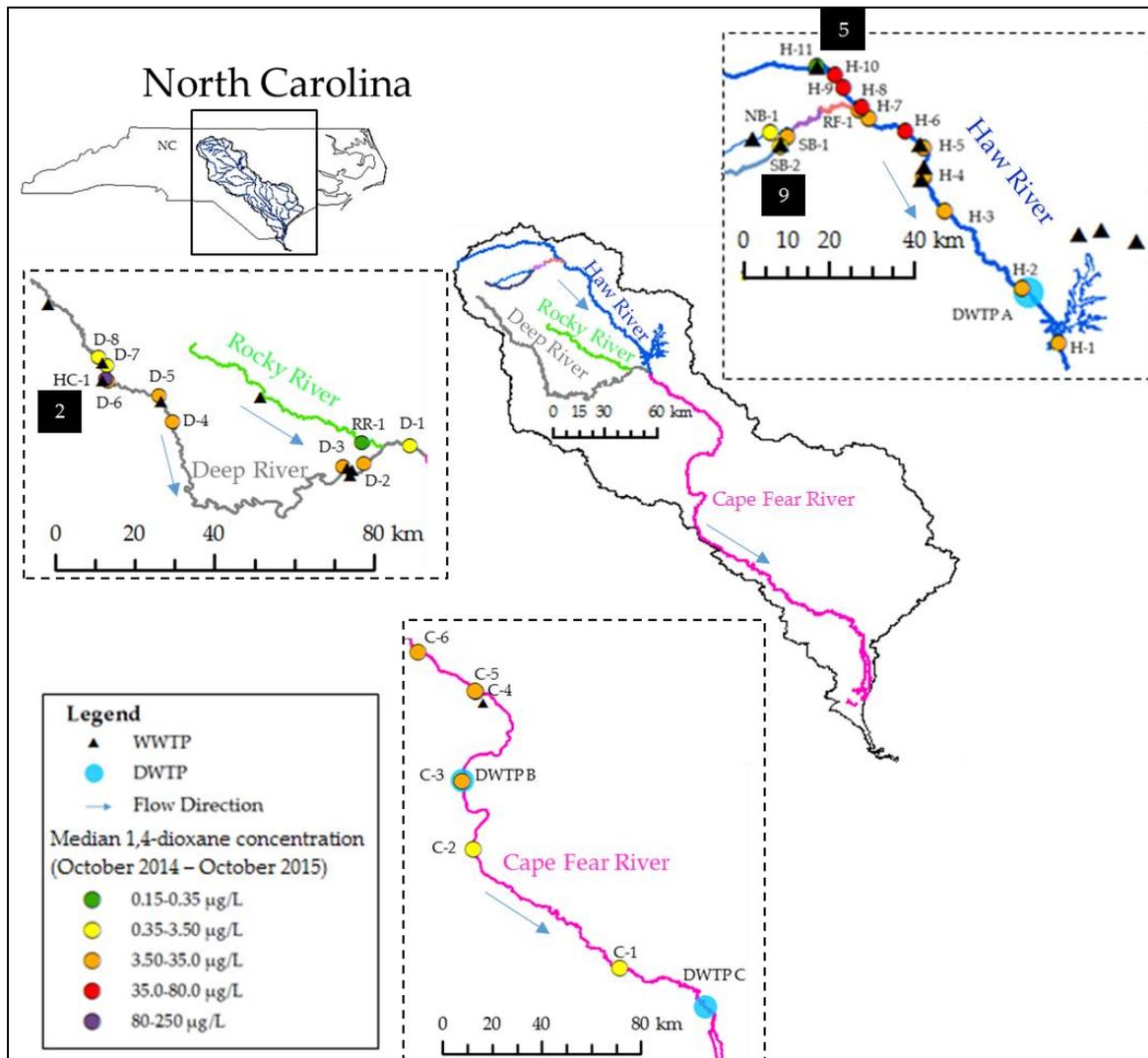
However, not all WWTP discharges led to increases in instream 1,4-dioxane concentrations. As illustrated in Figure 8, upstream and downstream of WWTP discharge 1, 3, 4, 6, 7 and 8, 1,4-dioxane concentrations were similar. For the case of WWTP discharges 3, 4, 6, 7, and 8, both upstream and downstream concentrations were high (>3.0 µg/L, Table 12); while for WWTP discharge 1, both upstream and downstream concentrations were lower (median concentrations of 2.0 µg/L at points D-7 and D-8, Table 12).

### *Temporal and Spatial Variability of Instream 1,4-Dioxane Concentrations*

Monthly stream samples were collected upstream and downstream of 9 WWTP discharges to investigate the occurrence and fate of 1,4-dioxane in surface waters of the CFR watershed. The area of study, surface water sampling points, and WWTP discharge locations are shown in Figure 7. Sampling points were coded according to the name of the stream (C: Cape Fear River, D: Deep River, RR: Rocky River, HC: Hasketts Creek, H: Haw River, RF: Reedy Fork Creek, SB: South Buffalo Creek, NB: North Buffalo Creek) followed by the sampling point number on that stream. Numbering of sampling points in each stream began at the most downstream sampling point; i.e., C-1 represents the most downstream sampling point on the Cape Fear River. In Figure 7, sampling points are color coded according to the median concentration measured during the one-year sampling campaign (three locations were sampled over 9 months, see Table 12). Median instream concentrations of 1,4-dioxane varied from < 0.15 to 1,760 µg/L. Minimum, average, median and maximum 1,4-dioxane concentrations for each sampling location are shown in Table 12. River distance was measured from the intake location of DWTP C (Figure 7). The highest 1,4-dioxane concentration, 1,760 µg/L, was measured on September 9, 2015 at H-10 located 10 km downstream of WWTP discharge 5.

1,4-Dioxane concentrations in the Deep River exhibited a variable profile along the river. Median concentrations of 2.0 µg/L were measured in the upper reaches at locations D-8 and D-7. Five kilometers downstream of these locations, median 1,4-dioxane concentration increased by a factor of ~10 (to 20.1 µg/L at location D-6), demonstrating the impact of WWTP discharge 2 (Figure 7). At location D-1 (134 km downstream of location D-6) the median 1,4-dioxane concentration was 3.5 µg/L, suggesting dilution from tributaries and lack of point source contributions in this stretch. As an example of dilution, the Rocky River joins the Deep River at kilometer 300 (between locations D-1 and D-2). Median concentration of 1,4-dioxane at D-2 was 4.9 µg/L, while it was 3.5 µg/L at D-1. The median concentration at point RR-1 was < 0.15 µg/L (during 2014-2015 stream flow of the Rocky River was on average 10% of the flow in the Deep River).

For the Haw River, the median 1,4-dioxane concentration was 0.20  $\mu\text{g/L}$  at location H-11; 10 kilometers downstream the median concentration was 76  $\mu\text{g/L}$  (location H-10) showing the impact of WWTP discharge 5. Moreover, the median concentration in South Buffalo Creek (Figure 7 and Table 12) at SB-2 was 1.81  $\mu\text{g/L}$ ; 5 km downstream, the median concentration was 25.8  $\mu\text{g/L}$  (SB-1). As shown in Figure 7, South Buffalo Creek flows into Reedy Fork Creek, a tributary to the Haw River. As the river flows towards Jordan Lake, the median concentration of 1,4-dioxane decreased, in fact 89 kilometers from location H-10 the median concentration 1,4-dioxane concentration was 6.5  $\mu\text{g/L}$  (H-1).



**Figure 7. Surface water sampling sites in the CFR basin and associated median 1,4-dioxane concentrations. Labels adjacent to sampling sites correspond to location identities listed in Table 3.**

Concentrations of 1,4-dioxane in the CFR also decreased over the length of the river, location C-6 located 5 km downstream of the confluence of the Deep and Haw river showed a median concentration of 4.3  $\mu\text{g/L}$ , the stream flow at this point was on average 90  $\text{m}^3/\text{s}$ ; 207 km

downstream of the confluence, the median concentration was 2.7 µg/L at location C-1, streamflow at this location was on average 140 m<sup>3</sup>/s. The results presented above suggest that 1,4-dioxane concentrations in the CFR were primarily affected by 1,4-dioxane inputs from the Haw and Deep river and dilution from the tributaries.

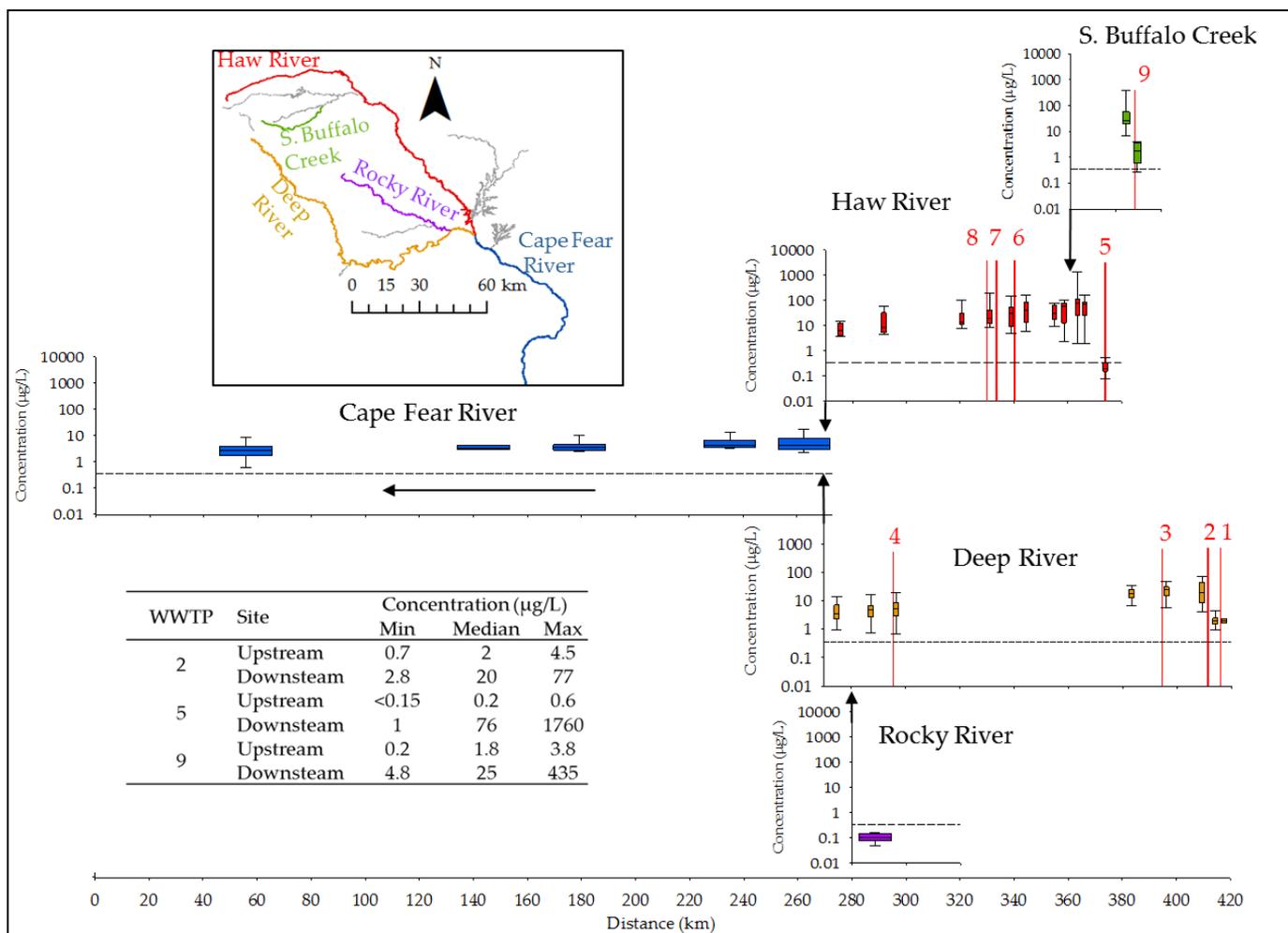
Temporal and spatial variability of 1,4-dioxane over the one-year sampling campaign is shown in Figure 8. At a given location, concentrations varied temporally over a wide range, in some cases by two or three orders of magnitude (see locations H-10, D-6, SB-1). These results suggest that the mass input of 1,4-dioxane through the discharges of WWTPs 2, 5 and 9 was highly variable; variability in streamflow can also contribute to the variability in 1,4-dioxane concentrations, but variability in streamflow was not sufficiently large to explain the range in 1,4-dioxane concentrations alone.

Concentrations of 1,4-dioxane at location H-2 varied from 3.8 (May 12, 2015) to 70 µg/L (August 11, 2015). For location H-1, downstream of Jordan Lake dam, the minimum 1,4-dioxane concentration was 3.9 (April 14, 2015) and the maximum was 13 µg/L (December 13, 2015), suggesting that temporal variability is smaller downstream of Jordan Lake, a large drinking water reservoir. At location D-1, the lowest 1,4-dioxane concentration was 0.9 µg/L (October 12, 2015) and the maximum was 16.0 µg/L (April 14, 2015); for C-6, located 5 km from the confluence of the Haw River and the Deep River, the minimum 1,4-dioxane concentration was 2.2 µg/L (July 7, 2015) and the maximum was 19 µg/L (October 30, 2014), suggesting that the temporal variability of 1,4-dioxane concentrations at locations D-1, H-1 and C-6 was similar. Finally, location C-1, 219 kilometers downstream of location C-6, registered a minimum 1,4-dioxane concentration of 0.6 (July 7, 2015) and maximum of 8.0 µg/L (May 5, 2015).

**Table 12. Minimum, average, median and maximum 1,4-dioxane concentrations at individual sampling locations. Results based on monthly samples collected over a one-year sampling campaign unless otherwise indicated.**

<b>River</b>	<b>Sample Location ID</b>	<b>River km<sup>p</sup></b>	<b>Min</b>	<b>Mean</b>	<b>Median</b>	<b>Max</b>
<b>Cape Fear CFR<sup>a</sup></b>	C-1 <sup>a</sup>	56	0.60	3.20	2.70	8.00
<b>Cape Fear CFR<sup>a</sup></b>	C-2 <sup>a</sup>	144	1.20	4.00	3.20	11.0
<b>Cape Fear CFR</b>	C-3	179	2.40	4.20	3.50	11.0
<b>Cape Fear CFR</b>	C-4	235	3.10	5.60	4.20	14.0
<b>Cape Fear CFR</b>	C-5	236	3.20	5.60	4.50	14.0
<b>Cape Fear CFR</b>	C-6	263	2.20	6.20	4.30	19.0
<b>Deep</b>	D-1	275	0.90	5.20	3.50	16.0
<b>Deep</b>	D-2	287	0.60	5.90	4.90	18.0
<b>Deep</b>	D-3	296	0.30	7.00	5.40	25.0
<b>Deep</b>	D-4	383	4.00	19.7	17.8	36.0
<b>Deep</b>	D-5	396	4.30	25.1	26.1	49.0
<b>Hasketts Creek</b>	HC-1	412	66.9	388	240	1405
<b>Deep</b>	D-6	409	2.80	29.2	20.1	78.0
<b>Deep</b>	D-7	414	0.70	2.20	2.00	4.50
<b>Deep*</b>	D-8*	416	1.40	2.00	2.00	2.60
<b>Haw<sup>a</sup></b>	H-1 <sup>a</sup>	275	3.90	8.00	6.50	13.0
<b>Haw</b>	H-2	292	3.80	19.0	8.20	70.0
<b>Haw</b>	H-3	320	6.80	29.1	13.6	108
<b>Haw</b>	H-4	331	7.60	46.2	19.7	201
<b>Haw</b>	H-5	339	5.10	45.1	29.9	163
<b>Haw</b>	H-6	344	5.90	57.0	38.9	164
<b>Haw</b>	H-7	355	9.12	37.9	30.3	77.0
<b>Haw</b>	H-8	359	1.45	50.9	59.8	105
<b>Haw</b>	H-9	366	1.21	61.0	68.1	177
<b>Haw</b>	H-10	364	1.05	215	76.6	1760
<b>Haw</b>	H-11	374	<0.15	0.26	0.20	1.00
<b>North Buffalo Creek</b>	NB-1	391	0.20	4.46	1.13	18.0
<b>South Buffalo Creek</b>	SB-1	385	4.85	78.0	25.8	436
<b>South Buffalo Creek</b>	SB-2	390	0.18	1.91	1.81	4.00
<b>South Buffalo Creek</b>	SB-3	410	3.59	23.3	30.2	44.0
<b>South Buffalo Creek</b>	SB-4	408	1.00	9.21	5.12	26.0
<b>South Buffalo Creek</b>	SB-5	407	0.60	11.0	8.55	29.0
<b>South Buffalo Creek</b>	SB-6	409	1.32	14.9	16.3	38.0
<b>Big Alamance Creek</b>	BAC-1	330	0.30	5.80	1.80	34.0
<b>Reedy Fork</b>	RF	359	9.67	38.1	27.0	84.0
<b>Rocky River</b>	RR-1	288	<0.15	<0.15	<0.15	<0.15

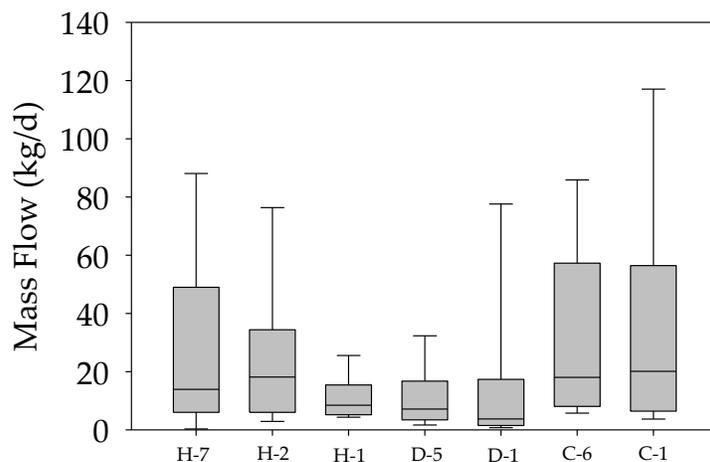
\*5 month sampling data, <sup>a</sup> 9 month sampling data <sup>p</sup> Distance measured from DWTP C location shown in Figure 7



**Figure 8. Spatial and temporal variability in 1,4-dioxane concentrations. The Haw and Deep River join at kilometer 277 to form the Cape Fear River. River Kilometer 0 is the intake of DWTP C near Wilmington, NC. Red solid lines represent WWTP discharges. Dashed line shows the  $10^{-6}$  excess cancer risk level/NC surface water quality standard ( $0.35 \mu\text{g/L}$ ).**

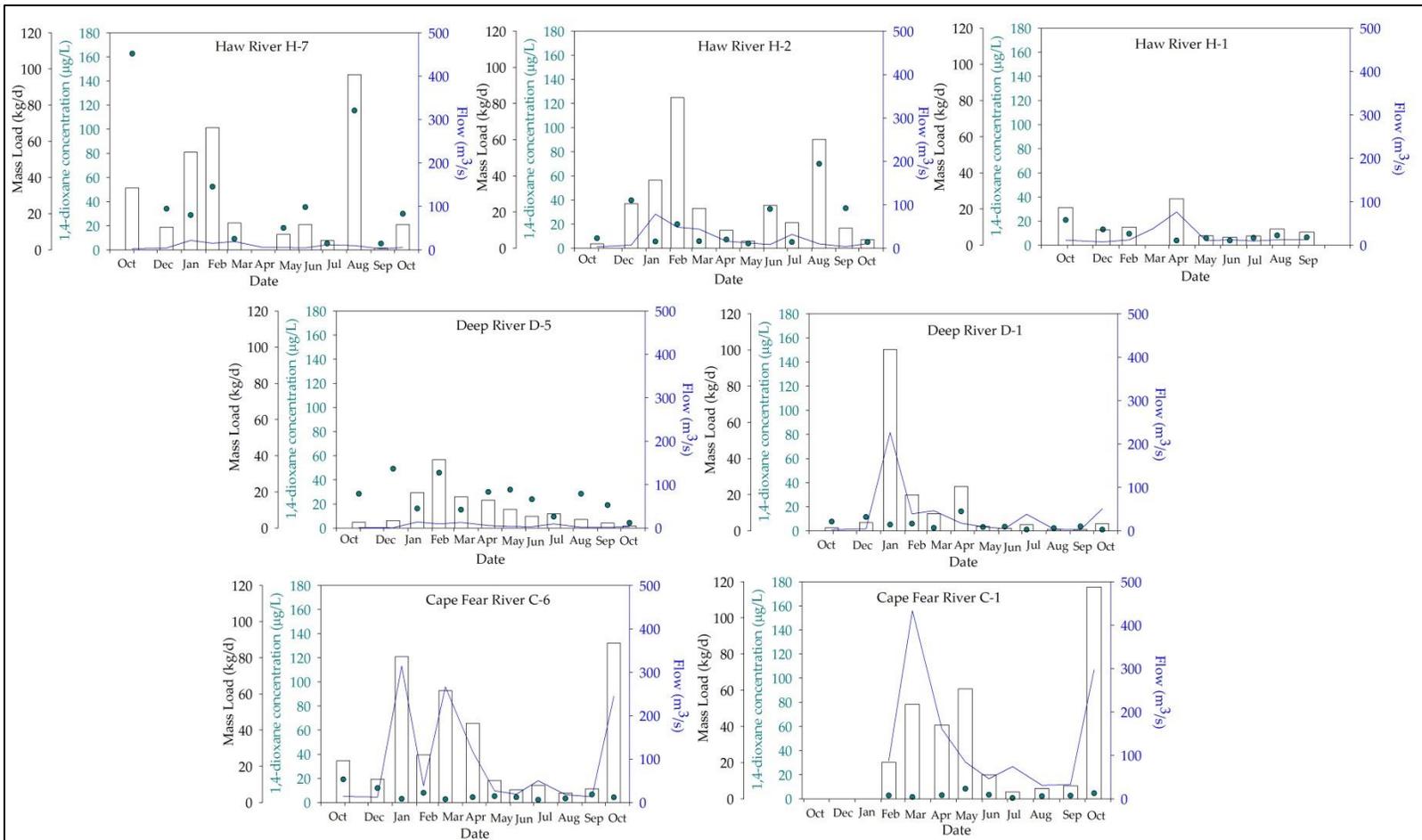
Based on the concentrations measured and the stream flow of the river (for sampling points where data of instantaneous and average stream flow were available), the daily mass flows of 1,4-dioxane in the Haw River, Deep River and CFR were calculated (Figure 9 and Figure 10). Mass flow of 1,4-dioxane in the rivers exhibited high variability. For the Haw River, mass flow of 1,4-dioxane at location H-7 (located 19 km downstream of WWTP discharge 5) varied from 1.0 (September 14, 2015) to 97 kg/d (August 11, 2015), and the median mass flow was 14.4 kg/d. Moving downstream at location H-2 (upstream of Jordan Lake) the mass flow of 1,4-dioxane ranged from 2.4 (October 30, 2015) to 83 kg/d (February 2, 2015), with a median mass flow of 18 kg/d. At location H-1 located downstream Jordan Lake and 17 kilometers from location H-2, mass flow of 1,4-dioxane ranged from 4.3 (June 9, 2015) to 25.6 kg/d (April 4, 2015), with a median mass flow of 8.5 kg/d. The results obtained at H-1 suggest that Jordan Lake reduced the variability in mass flows, and a lower median mass flow at H-1 compared to H-2 suggests 1,4-dioxane accumulated in Jordan Lake.

For the Deep River, mass flow of 1,4-dioxane at location D-5 (20 kilometers from WWTP discharge 2) varied from 0.9 (December 12, 2014) to 14.1 kg/d (January 13, 2015), and the median mass flow of 1,4-dioxane was 3.5 kg/d. At location D-1, 121 kilometers downstream of location D-5, mass flow of 1,4-dioxane ranged from 0.7 (August 11, 2015) to 100 kg/d (January 13, 2015), with a median mass flow of 3.7 kg/d. Finally for the Cape Fear River at location C-6 (located 5 kilometers from the confluence of the Haw and the Deep River), mass flows were between 5.1 (August 11, 2015) and 88 kg/d (October 12, 2015), with a median mass flow of 18 kg/d. At location C-1, 207 kilometers downstream location C-6, mass flows of 1,4-dioxane were between 20 (February 10, 2015) and 117 kg/d (October 12, 2015), with a median mass flow of 20 kg/d. The high temporal variability of mass flows of 1,4-dioxane in the three rivers suggest the presence of point sources with highly variable 1,4-dioxane releases.



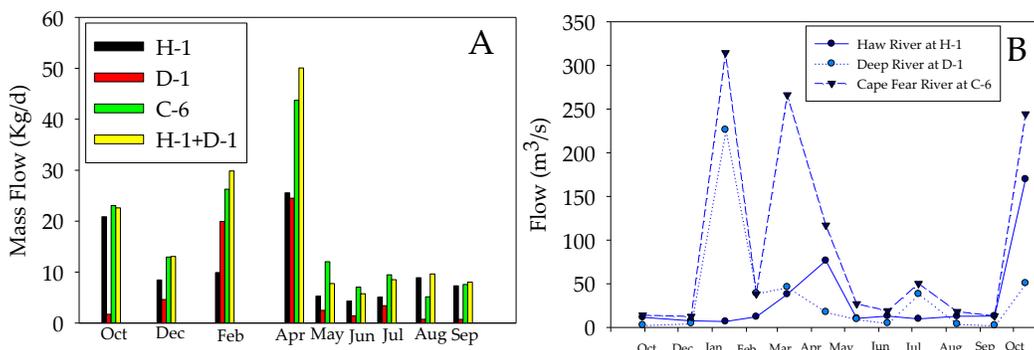
**Figure 9. Mass flows of 1,4-dioxane at seven locations in the CFR watershed.**  
**Note: At C-1 and H-1 mass flow calculations were performed for nine months.**

No correlations between 1,4-dioxane concentrations and stream flows were found (Figure 10). It was not possible to assume that the higher the stream flow, the lower the 1,4-dioxane concentration in the surface water as would be anticipated based on a constant 1,4-dioxane loading being attenuated by varying dilution amounts.



**Figure 10. Mass flows of 1,4-dioxane as well as contributing 1,4-dioxane concentrations and stream flows at seven locations in the CFR watershed. Hollow bars represented mass flows, green circles represent 1,4-dioxane concentrations and lines represent stream flow. Going from left to right, graphs represent upstream to downstream direction. Note: At C-1 and H-1 mass flow calculations were performed for nine months.**

A mass balance was performed using location H-1 downstream of Jordan Lake, which is located 6.6 km upstream of the confluence with the Deep river, location D-1 which is located 4.4 km upstream of the confluence, and location C-1 which is situated on the CFR 6.2 km downstream of the confluence of the Haw and Deep Rivers. Reasonable agreement was found between the mass flow of 1,4-dioxane measured at point C-6 and the addition of the mass loads for the two tributaries (H-1+D-1), demonstrating that 1,4-dioxane behaves conservatively. For all months except February, mass flows in the Haw River were higher than in the Deep River.



**Figure 11. A) Mass loads of 1,4-dioxane (kg/d) near the confluence where the Haw river (H-1) and Deep river (D-1) form the Cape Fear River (C-6). Data labeled as H-1+D-1 is the sum of the mass loads of the two tributaries. B) Stream flow of the three rivers. Based on available 1,4-dioxane data, mass balance comparisons could only be made for nine months.**

1,4-Dioxane mass loads calculated in this research were compared with studies performed by Stepien et al. (2014) and Tanabe et al. (2006) in three German and two Japanese rivers, respectively. All average mass loads in NC rivers were higher compared to these studies, except for the Rhine River in Germany. As shown in Table 13, concentrations of 1,4-dioxane in NC rivers were higher (by a factor of 8.7 at least) and stream flows were lower (by a factor of 1.6 at least) compared to Stepien et al. (2014) and Tanabe et al. (2006). In aggregate, the results in Table 13 illustrate that the mass loads of 1,4-dioxane in the CFR watershed are similar to those calculated for two German rivers (Oder, Rhine). However, 1,4-dioxane concentrations in the CFR watershed were substantially higher because of lower stream flows in the CFR watershed.

**Table 13. Maximum 1,4-dioxane concentration, stream flow and average mass load in USA, Germany and Japan.**

Location	River Name	Max. 1,4-dioxane concentration (µg/L)	Stream flow (m <sup>3</sup> /s)	Average Mass Load (kg/d)	Reference
NC, USA	Deep	35.8	18.0	29.5	This study
	Haw	69.9	37.1	83.2	
	CFR	19.2	94.5	88.1	
Germany	Rhine	2.20	3050	134.5	Stepien et al., 2014
	Oder	0.86	316	34.1	
	Main	0.70	156	6.5	
Japan	Shinano	0.26	372	3.5	Tanabe et al., 2006
	Agano	0.10	350	1.5	

Note: Maximum concentration is neither related with average streamflow or average mass load.

### *Occurrence of 1,4-Dioxane in Drinking Water*

To explore temporal variations in 1,4-dioxane concentrations at a finer resolution, 24-hour composite samples were collected daily at three DWTPs. Both raw and finished water was sampled at each utility to assess not only temporal variability in 1,4-dioxane concentrations but also the fate of 1,4-dioxane during full-scale drinking water treatment.

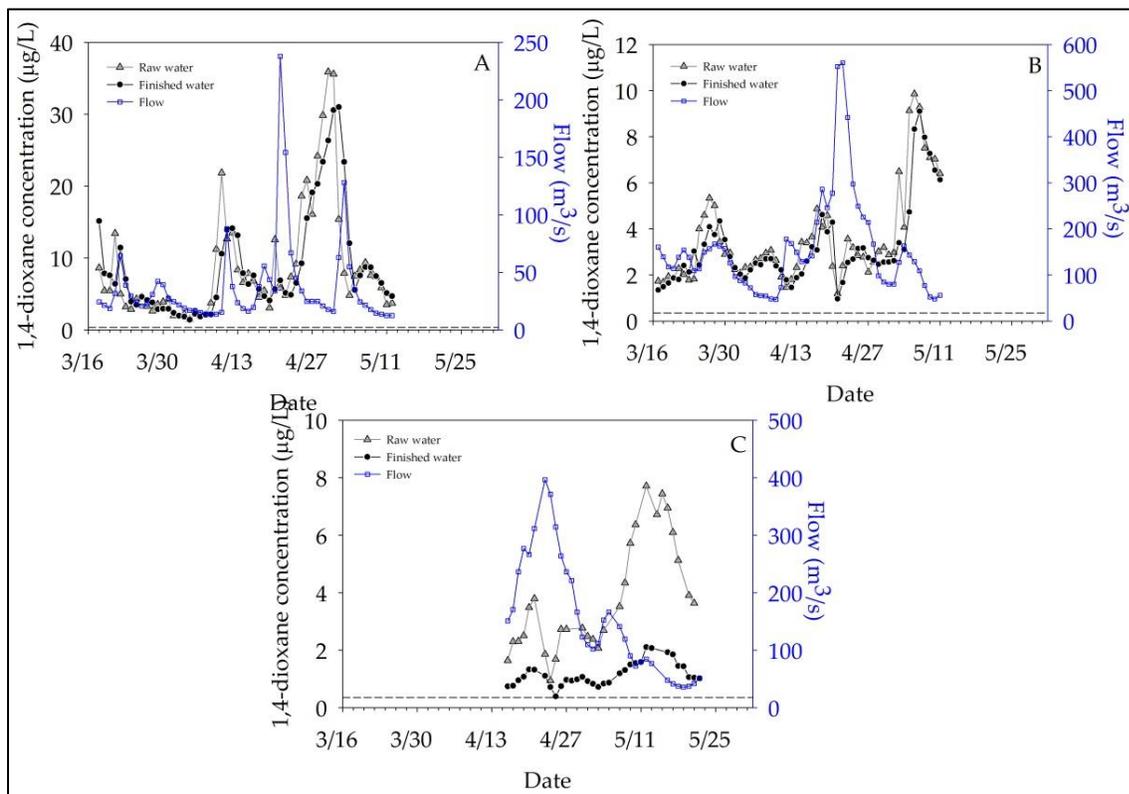
Raw and treated water 1,4-dioxane concentrations exceeded the NC stream water quality standard and the one in a million cancer risk level at all the three studied DWTPs (Figure 12). The average concentration for raw water in DWTP A (Figure 12a), treating Haw River water, was 8.8 µg/L (25 times the NC stream water quality standard and the 10<sup>-6</sup> excess cancer risk level), whereas the maximum concentration was 36 µg/L. For the same DWTP the average finished water concentration was 8.7 µg/L (25 times the NC stream water quality standard and the 10<sup>-6</sup> excess cancer risk level) and the maximum concentration was 31 µg/L.

Results for the DWTP B (Figure 12b), located on the CFR further downstream, show an average 1,4-dioxane concentration for raw water of 2.8 µg/L (7 times the NC stream water quality standard and the 10<sup>-6</sup> excess cancer risk level) and a maximum raw water concentration of 10.2 µg/L. In the finished water the average 1,4-dioxane concentration was 2.6 µg/L (7 times the NC stream water quality standard and the 10<sup>-6</sup> excess cancer risk level) and the maximum concentration was 9.8 µg/L.

1,4-Dioxane concentrations in raw and finished water from DWTPs A and B showed that conventional drinking water treatment was not effective for removing 1,4-dioxane. Similar results were found by McGuire et al. (1978) and Stepien et al. (2014). McGuire et al. (1978) did not find removal of 1,4-dioxane using ferric chloride coagulation, powdered activated carbon and permanganate oxidation. Stepien et al. (2014) tested raw water and finished water from two

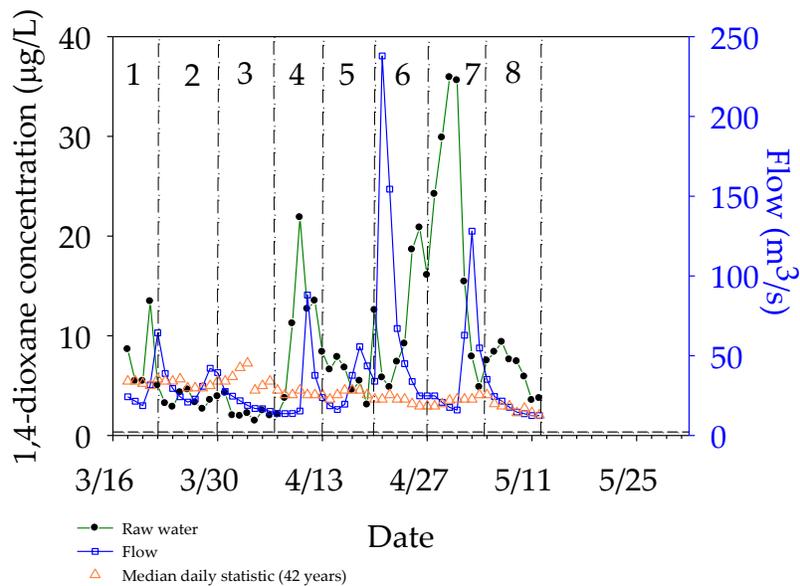
German DWTPs (DWTP1 and DWTP2). Raw water concentrations of 1,4-dioxane were 0.67 and 0.65  $\mu\text{g/L}$  at DWTP 1 and DWTP 2, respectively; whereas treated water concentrations of 1,4-dioxane were 0.49 and 0.60  $\mu\text{g/L}$  at DWTP 1 and DWTP 2, respectively. These results illustrate that neither bank filtration nor the available unit processes at the two DWTPs were capable of achieving substantial removal (Stepien et al., 2014).

Composite sampling results for DWTP C, located near the mouth of the CFR, are summarized in Figure 12c. This DWTP employs raw and settled water ozonation. The average raw water 1,4-dioxane concentration was 3.8  $\mu\text{g/L}$ , and the maximum was 7.7  $\mu\text{g/L}$ . The average 1,4-dioxane concentration in finished water was 1.2  $\mu\text{g/L}$  and the maximum 2.1  $\mu\text{g/L}$ . On average, the two ozonation steps oxidized 67% of the influent 1,4-dioxane in this DWTPs, suggesting that ozonation is somewhat effective for 1,4-dioxane oxidation in surface water. Barndök et al. (2014) demonstrated that  $\text{O}_3$  is able to oxidize 1,4-dioxane in synthetic water, with 88% oxidation achieved at pH 9. These results suggest that production of hydroxyl radicals ( $\text{OH}\cdot$ ), favored at high pH, leads to the oxidation of 1,4-dioxane. Numerous studies have shown that advanced oxidation processes (AOPs) such as ozone ( $\text{O}_3$ )/hydrogen peroxide ( $\text{H}_2\text{O}_2$ ); UV/ $\text{H}_2\text{O}_2$ ; and Fenton's reagent can effectively oxidize 1,4-dioxane (Adams et al., 1994; Safarzadeh-Amiri et al., 1997; Son et al., 2009; Stefan and Bolton, 1998; Suh and Mohseni, 2004; Vescovi et al., 2010).



**Figure 12. Raw water and finished water composite sampling results and river discharge for a) DWTP A, b) DWTP B, and c) DWTP C. Dotted line represents the NC stream water quality standard and the  $10^{-6}$  excess cancer risk level of 0.35  $\mu\text{g/L}$  1,4-dioxane**

Precipitation events caused high stream flows in the Haw River (intake of DWTP A) on several occasions during the study period. To illustrate variations in stream flow and possible effects on 1,4-dioxane concentrations, raw water 1,4-dioxane concentrations at the intake of DWTP A are shown together with median daily stream flow and the 42-year median stream flow in Figure 13. While high stream flow events at the end of week 1, and during weeks 6 and 7 led to a dilution of elevated 1,4-dioxane concentrations, this pattern was not observed during the high stream flow event during week 4, when 1,4-dioxane concentrations remained high during the period of high stream flow. Also, low 1,4-dioxane concentrations coincided with low stream flows in week 3. Overall, the results in Figure 13 illustrate that 1,4-dioxane concentrations did not correlate well with stream flow. Instead, variability in 1,4-dioxane source contributions was the principal driver behind variability in 1,4-dioxane concentrations.



**Figure 13. Raw water concentrations of 1,4-dioxane at DWTP A (dots), streamflow of Haw river (lines) and median daily statistic (42 years) (triangles).**

In the case of DWTP B, stream flow in the CFR was strongly influenced by water releases from Jordan Lake Dam, and high releases resulted in high flow events during weeks 5 and 6 (Figure 12B). Overall, raw water concentrations of 1,4-dioxane at DWTP B were lower compared to raw water concentrations at DWTP A (concentrations ranged from 1.2 to 9.9 µg/L in the raw water of DWTP B and from 1.5 to 36 µg/L in the raw water of DWTP A). At DWTP B, high flow events coincided with low concentrations of 1,4-dioxane (week 6), but some high flow events coincided with high concentrations of 1,4-dioxane (week 5), again suggesting that streamflow is not a good indication of 1,4-dioxane concentrations.

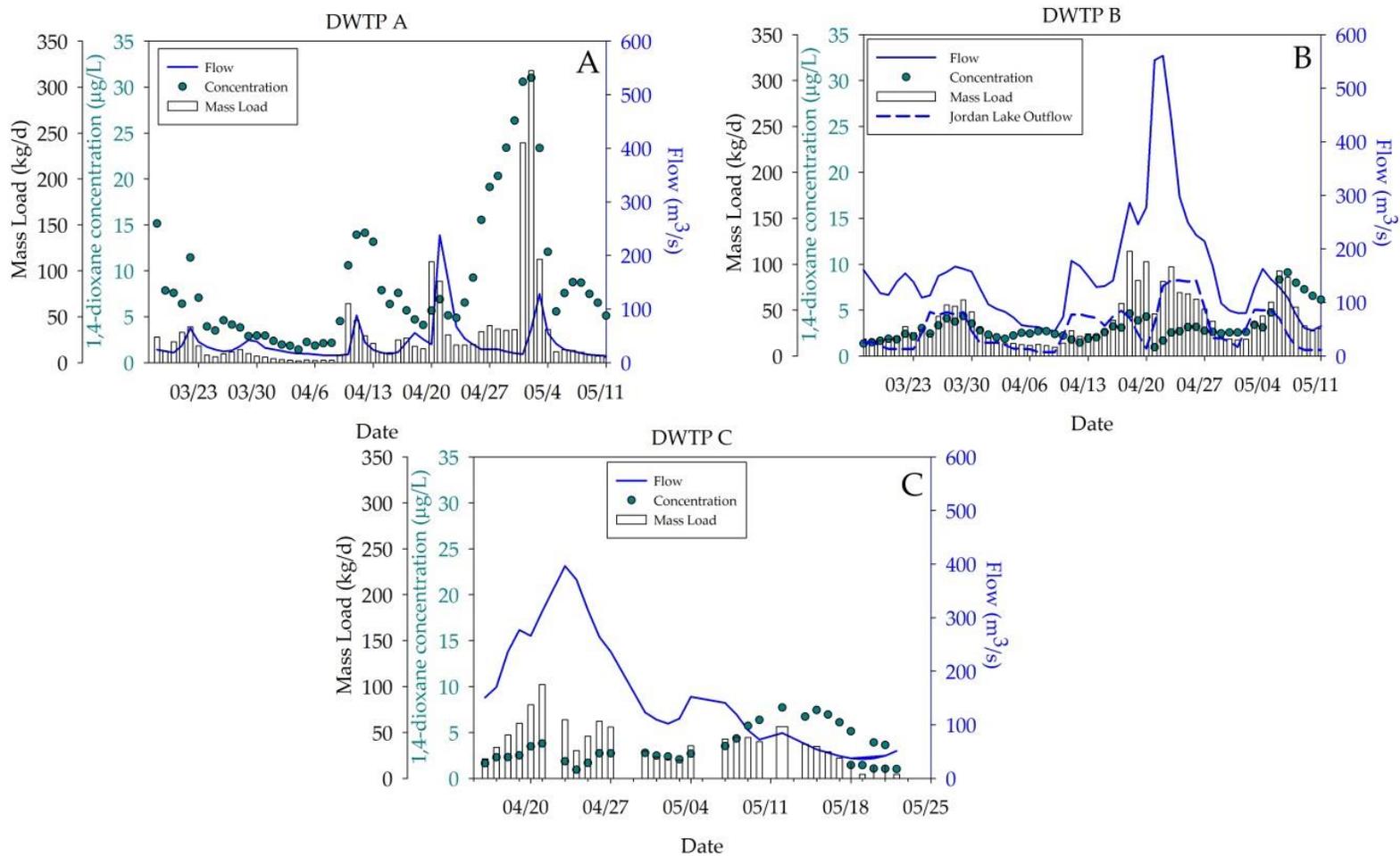
To obtain 1,4-dioxane mass flows, daily raw water concentrations of 1,4-dioxane at DWTPs A, B and C were used and multiplied by mean daily stream flow at the sampling location (DWTP A and DWTP C) or the closest USGS stream gage with flow data (DWTP B). The range, median and average of 1,4-dioxane mass flows at the three DWTPs are presented in Table 14. At DWTP

A, mass flows ranged from 2.1 to 279 kg/d with a median value of 14.4 kg/d, at DWTP B the mass flows were between 10.7 and 136 kg/day with a median value of 32.2 kg/d, and at DWTP C mass flows were between 12.6 to 102 kg/day with a median value of 36.4 kg/d. The median values suggest that 1,4-dioxane mass flows increased in a downstream direction. The large increase in median mass flow of 1,4-dioxane between DWTP A and DWTP B was primarily a result of the mass load being contributed by the Deep River. The smaller increase between DWTP B and DWTP C was likely due to wastewater discharges between the two communities. As illustrated by Simonich et al. (2013), all municipal wastewater treatment plant effluents contain some 1,4-dioxane from the use of consumer products.

As illustrated in Figure 14, mass flows fluctuated most dramatically from day to day at DWTP A (upstream of Jordan Lake), while smaller fluctuations were observed at DWTP B and DWTP C (downstream of Jordan Lake). High mass flows at DWTP A indicate the presence of one or more important 1,4-dioxane source(s) upstream of the intake of DWTP A, and the variability in 1,4-dioxane mass flows suggests non-constant 1,4-dioxane inputs into the Haw River.

**Table 14. Range of 1,4-dioxane mass flows at DWTP A, DWTP B, and DWTP C.**

<b>1,4-dioxane mass flow (kg/d)</b>	<b>DWTP A</b>	<b>DWTP B</b>	<b>DWTP C</b>
<b>Minimum</b>	2.1	10.7	12.6
<b>Median</b>	14.4	32.2	36.4
<b>Average</b>	32.0	44.6	40.2
<b>Maximum</b>	279	136	102



**Figure 14. Daily mass flows from two drinking water treatment plants. a) DWTP A and b) DWTP B c) DWTP C. In DWTP A and b samples collected from March 2015 through May 2015; in DWTP C samples collected from April 2015 to May 2015.**

## Conclusions

- Results of the stream sampling campaign conducted between October 2014 and October 2015 showed that concentrations of 1,4-dioxane exceeded the North Carolina stream water quality standard throughout almost the entire length of the Haw, Deep, and Cape Fear Rivers. Downstream of three municipal wastewater treatment plant discharges, median concentrations of 1,4-dioxane were 77 µg/L in the Haw River, 26 µg/L in both South Buffalo Creek and the Deep River. The maximum 1,4-dioxane concentration was 1,760 µg/L and was measured downstream of a wastewater treatment plant discharge on the Haw River. Results of this study confirm the need for 1,4-dioxane monitoring and discharge controls.
- High temporal and spatial variability was observed in 1,4-dioxane concentration and mass flows. The variability in mass flows points to variability in 1,4-dioxane releases by point sources. Variability in 1,4-dioxane releases was also a key determinant of 1,4-dioxane concentrations with variability in streamflow playing a lesser role.
- Median 1,4-dioxane concentrations decreased in a downstream direction with increasing distance from the identified sources. The decreasing 1,4-dioxane concentrations can be explained by dilution from tributaries that did not contain measurable levels of 1,4-dioxane.
- Conventional drinking water treatment processes were ineffective for 1,4-dioxane attenuation. Average concentrations in the finished water of DWTPs A, B, and C exceeded by a factor of ~25, ~7 and ~3.5, respectively, the  $10^{-6}$  cancer risk level of 1,4-dioxane (0.35 µg/L). Ozone was able to oxidize 67% of the influent 1,4-dioxane in DWTP C, indicating that ozonation of surface water is somewhat effective for 1,4-dioxane oxidation.
- Future work needs to focus on source identification and source control to decrease the release of 1,4-dioxane into the environment and drinking water supplies.

## OZONATION AND ADVANCED OXIDATION PROCESSES FOR 1,4-DIOXANE CONTROL

Few water treatment options are available for the control of 1,4-dioxane. As illustrated in Chapter 5, ozonation of raw and coagulated/settled CFR water oxidized about two-thirds of the influent 1,4-dioxane. This result was unexpected because ozone was ineffective in previous studies investigating 1,4-dioxane control in groundwater (e.g. Adams et al. 1994). Prior research has suggested, however, that advanced oxidation processes (AOPs) are an effective treatment option for 1,4-dioxane control. Two common AOPs are the peroxone ( $O_3/H_2O_2$ ) and the UV/ $H_2O_2$ , in which hydrogen peroxide ( $H_2O_2$ ) is irradiated with ultraviolet (UV) light. Both AOPs generate highly reactive hydroxyl ( $\bullet OH$ ) radicals.

The goal of this study therefore was to assess the ability of  $O_3$ ,  $O_3/H_2O_2$ , and UV/ $H_2O_2$  processes to oxidize 1,4-dioxane in surface water. For  $O_3$ , we hypothesized that the oxidation of 1,4-dioxane will occur via  $\bullet OH$  radical production from the reaction between ozone and dissolved organic matter. Experiments were designed to identify the effects of 1,4-dioxane concentration, organic matter characteristics, pH, and ozone to total organic carbon ( $O_3:TOC$ ) ratio on 1,4-dioxane transformation. Furthermore, the potential benefits of employing advanced oxidation processes ( $O_3/H_2O_2$ , UV/ $H_2O_2$ ) for 1,4-dioxane oxidation in conventionally treated surface water were investigated.

### Introduction

Prior research on treatment options for 1,4-dioxane control were primarily conducted in a groundwater remediation context. Adams et al. (1994) conducted oxidation experiments in synthetic waters simulating contaminated groundwater. The work illustrated that  $O_3$  alone was not feasible for treatment of 1,4-dioxane; however, when combined with  $H_2O_2$ ,  $\bullet OH$  radicals were formed that effectively transformed 1,4-dioxane. Results of Adams et al. (1994) highlighted that molecular  $O_3$  reacts only very slowly with 1,4-dioxane ( $k_{O_3}=0.32 M^{-1}s^{-1}$ , Hoigne & Bader 1983) while  $\bullet OH$  radicals readily oxidize 1,4-dioxane ( $k_{OH}=2.5-3.1 \times 10^9 M^{-1}s^{-1}$ ). Suh et al. (2004) studied the application of  $O_3/H_2O_2$  under varying initial 1,4-dioxane concentrations, pH values, and  $H_2O_2:O_3$  ratios. Results demonstrated again that  $O_3$  alone was not viable for groundwater treatment of 1,4-dioxane. However, upon addition of  $H_2O_2$ , the enhanced production of  $\bullet OH$  radicals led to effective 1,4-dioxane oxidation. Additionally, UV/ $H_2O_2$  has been studied for 1,4-dioxane control. For example, Stefan and Bolton (1998) demonstrated in a deionized water matrix that effective transformation of 1,4-dioxane could be achieved by UV/ $H_2O_2$ , and oxidation pathways were identified. The application of UV/ $H_2O_2$  was further tested by TrojanUV (2015) for 1,4-dioxane control in an Arizona groundwater. The results of their study demonstrated for a  $H_2O_2$  dose of 15 mg/L that >97% 1,4-dioxane oxidation was achieved.

These studies have provided insight into groundwater treatment options for 1,4-dioxane. However, recent UCMR3 data (USEPA 2016) and the results in Chapter 5 illustrate that 1,4-dioxane is also an important surface water contaminant (USEPA 2016). Thus, surface water treatment options for the control of 1,4-dioxane need to be identified. Results from groundwater studies are not directly transferable to a surface water treatment context, primarily because (1)

the concentration of dissolved organic matter (DOM) is typically higher in surface water than in groundwater and (2) the character of DOM in surface water differs from that in groundwater.

Surface water in the Cape Fear River (CFR) basin is characterized by moderate TOC concentrations and low alkalinity. Hence, we hypothesized that oxidation of 1,4-dioxane is feasible during ozonation of CFR water because (1) DOM functional groups promote •OH radical formation and (2) scavenging of •OH radicals by bicarbonate/carbonate is low. Numerous studies have investigated the decomposition of ozone in aqueous solution (*e.g.*, Sonntag and Schuchmann, 1994; Staehelin and Hoigne, 1982; Tomiyasu et al., 1985). In aqueous solution ozone reacts with hydroxide ions (OH<sup>-</sup>), resulting in the formation of hydroxyl (•OH) radicals. However, in the presence of dissolved organic matter (DOM), this OH<sup>-</sup> pathway no longer dominates. Instead the direct reaction of ozone with specific moieties within the DOM dominate ozone decomposition (Buffle et al., 2006). Of the direct reaction between ozone and DOM, only a fraction result in •OH radical formation. Nöthe et al. (2009) demonstrated that ozone reacts with electron-rich aromatic components of DOM, yielding •OH radicals. For example, aromatic lignin compounds, commonly present in the composition of DOM, have been demonstrated to react with ozone to form •OH radicals (Mvula et al., 2009). Furthermore, •OH radical formation is not a steady-state process and decreases as the ozone concentration in solution decreases (Gonzales et al., 2012). Also, Elovitz and von Gunten (2000) demonstrated that the type and concentration of DOM greatly affect ozone and •OH radical exposure. The yield of •OH radicals varies substantially from one water source to another such that •OH formation must be assessed for each water matrix studied (Nöthe et al., 2009; von Sonntag and von Gunten, 2012). Prior research has also demonstrated that bicarbonate and carbonate, the principal contributors to the alkalinity of most natural waters, effectively scavenge •OH radicals. As a result, AOPs are less effective in high alkalinity waters.

Otto et al. (2007) highlights limitations associated with employing AOPs to surface water treatment. One important limitations involves the presence of bromide, which is also present at elevated concentrations in the CFR basin (Greune 2014). When adding ozone to surface water, the resulting combination of molecular O<sub>3</sub> and •OH radicals can oxidize bromide to bromate, which is classified as a probable human carcinogen (Otto et al. 2007) with a maximum contaminant level (MCL) of 10 µg/L in drinking water. Thus ozonation of surface water with elevated bromide concentrations can be problematic. Ozonation and AOPs can also produce biodegradable organic by-products such as aldehydes and organic acids. Biodegradable organic matter can be readily controlled in biofilters following ozonation or AOPs. Thus, by-product formation needs to be kept in mind when considering the implementation of ozonation and AOPs.

## Materials and Methods

### *Chemicals*

1,4-Dioxane (99.5%) was obtained from Thermo Fisher Scientific (Waltham, MA). A stock solution of 1,4-dioxane was prepared at a concentration of 11,769 µM (104 mg/L) in deionized water and stored in 2-mL glass vials at 4°C in the dark. For GC/MS analysis, an internal standard, deuterium-labeled 1,4-dioxane-d8 (99 atom % D) was obtained from Sigma-Aldrich

(St. Louis, MO). For the preparation of quality control samples, a 1,4-dioxane standard (1 mg/mL in methanol) was purchased from Absolute Standard (Hamden, CT). Benzaldehyde (99%), which was used to quantify ozone concentration in solution, was obtained from Sigma-Aldrich (St. Louis, MO). The ozone quenching agent trans-cinnamic acid (99%) was obtained from Sigma-Aldrich (St. Louis, MO). Sodium phosphate monobasic monohydrate (98%) and sodium phosphate dibasic heptahydrate used for buffering solutions was purchased from Sigma-Aldrich (St. Louis, MO). Potassium indigo trisulfonate (Sigma-Aldrich, St. Louis, MO) was used in the indigo colorimetric method for determining the concentration of ozone stock solutions concentration was obtained from. Hydrogen peroxide (30%) was obtained from Fisher Chemical (Fair Lawn, NJ). Ascorbic acid (99%), a quenching agent for hydrogen peroxide, was obtained from Alfa Aesar (Ward Hill, MA). Sodium bicarbonate (99%) was purchased from Sigma-Aldrich (St. Louis, MO).

### ***Water collection***

One drinking water and one surface water impacted by wastewater effluent were used. The drinking water source was Cape Fear Public Utility Authority (Wilmington, NC) from which raw Cape Fear River (raw CFR) water and settled Cape Fear River (settled CFR) water were collected. The surface water source impacted by wastewater effluent was South Buffalo Creek water (Greensboro, NC). Upon collection, raw CFR and settled CFR waters were stored in individual 55-gal stainless steel drums at 4°C. The South Buffalo Creek water was stored in a 5-gal jug at 4°C. The dissolved organic carbon (DOC) concentrations of raw CFR water and settled CFR water, and South Buffalo Creek water were measured to be 6.814, 3.383, and 12.878 mg/L, respectively. Alkalinities for the raw CFR water, settled CFR water, and South Buffalo Creek water were 21, 12, 101 mg/L as CaCO<sub>3</sub>.

### ***Analytical Methods***

#### ***Purge-and-trap GC-MS – 1,4-Dioxane***

Concentrations of 1,4-dioxane were determined by heated purge-and-trap gas chromatography-mass spectrometry. 1,4-dioxane and internal standard were extracted from aqueous samples by a Stratum AQUATEK 100 P&T system (Teledyne Tekmar, Mason, OH). For analysis, 1 µL of a 20 mg/L internal standard, 1,4-dioxane-d<sub>8</sub> in methanol, was automatically dosed into 5 mL of sample. Following desorption from the trap, 1,4-dioxane and internal standard were transferred to a gas chromatography with ion trap mass spectrometer (CP\_3800 GC coupled with Saturn 2200 MS, Agilent, Santa Clara, CA). A VF-624ms column (30 m × 0.25 mm × 1.4 µm, Agilent) was employed for compound separation. The MS was operated in electron ionization mode with selected-ion storage. A full list of purge-and-trap GC-MS operating parameters has been provided in Sun et al. (2016).

#### ***HPLC-DAD – Benzaldehyde***

Benzaldehyde concentrations were quantified using a Waters high performance liquid chromatography with dual wavelength absorbance detector (Milford, MA). The eluent used was a 65:35 (v/v%) 0.05 mM phosphate buffer pH 2.2 to acetonitrile. Employing a flow rate of 0.43

mL/min solutions were loaded onto a Discovery RP-Amide C16 HPLC Column (25 cm × 3 mm, 5µm) for separation of benzaldehyde. Following elution from the column sample was passed through a Waters DAD 2487, which was set for detection of benzaldehyde at two wavelengths, 233 and 254 nm.

### ***Ozone Stock Solution***

Ozone stock solutions were generated prior to each experiment. Research grade oxygen, purchased from Airgas (Radnor, PA), was passed through an ozone generator (G-11, Pacific Ozone, Benicia, CA). The outlet gas stream from the ozone generator was then bubbled through DI water, at a pH of 2, in a glass flask that was placed in an ice bath. Typical stock solution concentrations ranged from 20-29 mg/L. Prior to dosing reactors the ozone stock solution concentration was quantified by employing an indigo colorimetric test, and measured on a spectrophotometer at a wavelength of 600 nm. Based on the concentration of ozone stock solution a volume of stock solution was determined in order to achieve a desired ozone to TOC ratio in the reactor.

### ***Batch Ozonation Experiments***

Batch ozonation experiments were conducted in 20 mL vials. Vials were filled with a water which had been prepared with an initial 1,4-dioxane concentration (5 µm), buffered with 20 mM phosphate buffer to desired pH, if required sodium bicarbonate was added to achieve a desired alkalinity, and for ozone peroxide experiments hydrogen peroxide was dosed to achieve hydrogen peroxide to ozone ratios of 2:1, 1:1, and 1:2. A PTFE-coated magnetic stir bar was added to reactors to provide continuous mixing. Based on the calculated ozone stock solution concentration reactors were dosed with a given volume of ozone stock solution to achieve a desired ozone to TOC ratio. Individual reactors were allowed to mix for predetermined times after addition of ozone (10 sec, 20 sec, 30 sec, 1min, 2 min, 5 min, and 10 min). The ozone residual in the reactors were quenched with 2 mL of 2 mM cinnamic acid. For the t=0 sample, cinnamic acid was added to the vial prior to ozone dosing. Following the experiment 2 mL aliquots of each reactor were taken for analysis of ozone residuals on the HPLC-DAD. The method determined benzaldehyde concentrations which can be directly related to ozone residual (Dodd et al. 2006). An additional aliquot of sample was taken for analysis of residual 1,4-dioxane concentration on GC-MS.

### ***Batch UV/H<sub>2</sub>O<sub>2</sub> Experiments***

Batch UV/H<sub>2</sub>O<sub>2</sub> experiments were conducted in pyrex dishes. A working solution was created in filtered settled Cape Fear River water to which 1,4-dioxane was dosed at a concentration of 5 µM and the pH was buffered with 20 mM phosphate buffer. To each pyrex dish 50 mL of sample were added and a PTFE-coated magnetic stir bar was added to provide continuous mixing. The collimated beam apparatus was set up to follow the method created by Bolton and Linden (2003). The reactor was placed in the collimated beam apparatus and then hydrogen peroxide was dosed to achieve a desired initial hydrogen peroxide concentration ranging from 010 mg/L. The reactor door was then closed and the solution was irradiated with UV light for a predetermined fluence dose which can be related to an exposure time. Following the irradiation

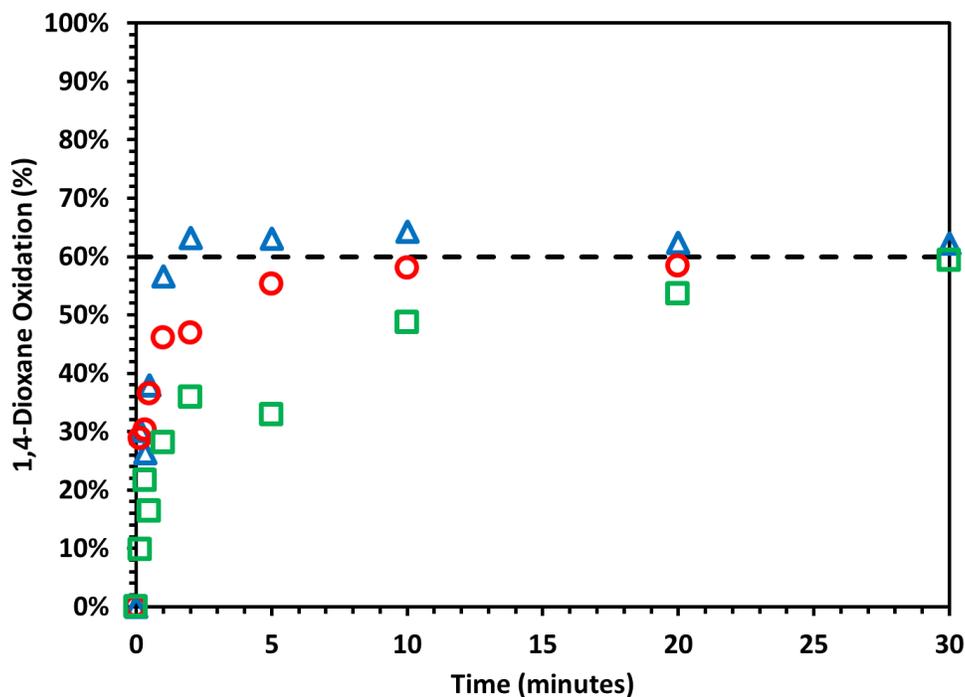
period, residual hydrogen peroxide was quenched with 1 mL of 13.125 mg/L ascorbic acid. An aliquot of solution was then taken for analysis of 1,4-dioxane residual concentration on GC-MS.

## Results and Discussion

Batch ozonation experiments were conducted on raw Cape Fear River (rCFR) water, settled Cape Fear River (sCFR) water, and South Buffalo Creek (SBC) water. Experiments were performed to assess the effect of pH across the 3 to 7 range, alkalinity from 21 to 300 mg/L as CaCO<sub>3</sub>, ozone to TOC ratio, hydrogen peroxide dose, 1,4-dioxane concentration, and DOM composition.

### *Effect of Solution pH on 1,4-Dioxane Oxidation by Ozone*

Batch ozonation experiments in rCFR water were conducted at solution pH values of 3, 5.7, and 7 and an O<sub>3</sub>:TOC ratio of ~0.65. Percent oxidation of 1,4-dioxane is shown in Figure 15 as a function of time for each pH value.

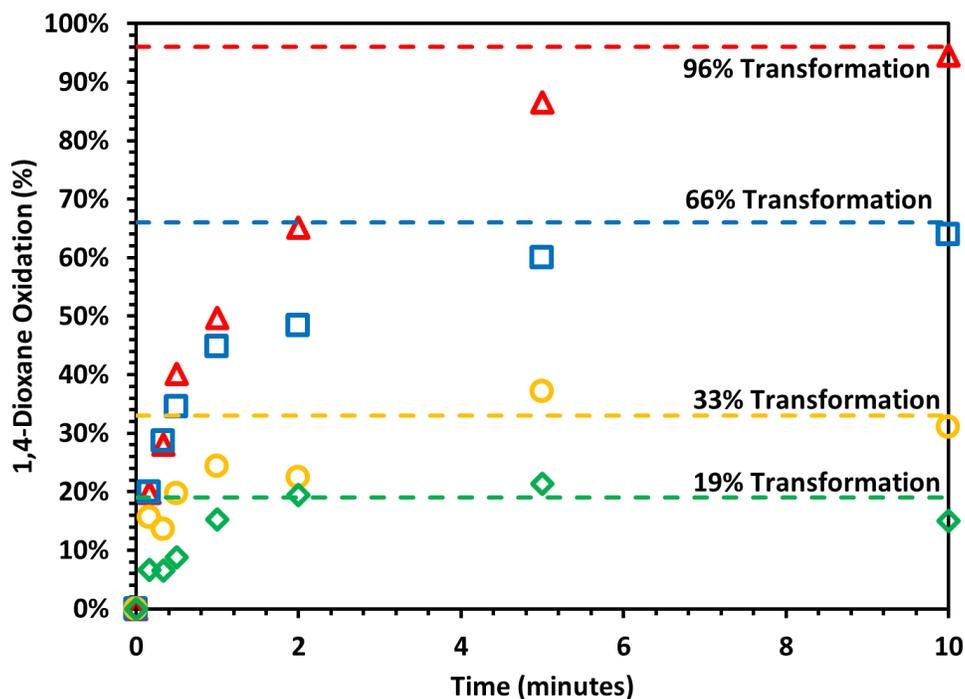


**Figure 15. Effect of solution pH on 1,4-dioxane oxidation by ozone in raw Cape Fear River water.** ( $\Delta$ ) pH=7.02,  $[O_3]=7.08 \times 10^{-5}$  M, O<sub>3</sub>:TOC=0.60, Alkalinity= 21 mg/L as CaCO<sub>3</sub>; ( $\square$ ) pH= 5.67,  $[O_3]=7.93 \times 10^{-5}$  M, O<sub>3</sub>:TOC=0.67, Alkalinity= 21 mg/L as CaCO<sub>3</sub>; ( $\circ$ ) pH= 3.03,  $[O_3]=8.02 \times 10^{-5}$  M, O<sub>3</sub>:TOC=0.67, Alkalinity= 21 mg/L as CaCO<sub>3</sub>. Dashed line represents 58% transformation.

Results in Figure 15 illustrate that regardless of solution pH, the extent of 1,4-dioxane oxidation was similar (~58% at pH 7 and 5.7, slightly lower at pH 3). However, the rate of 1,4-dioxane oxidation increased with increasing solution pH. These results agree with the observations of Elovitz et al. (2000), who demonstrated that an increase in solution pH leads to reduced  $O_3$  exposure while  $\bullet OH$  radical exposure was maintained. For the three different pH values, similar  $\bullet OH$  radical exposures were calculated from the 1,4-dioxane oxidation data ( $2.8 \times 10^{-10}$  to  $3.2 \times 10^{-10} M \cdot s$ ). The faster rate of 1,4-dioxane oxidation at higher solution pH values can be explained by the faster initiation of hydroxide-initiated ozone decay and an associated increase in the formation rate of  $\bullet OH$  radicals. Because experiments were conducted in the presence of DOM and alkalinity, changes in solution pH also changed the degree of (de)protonation of DOM moieties and the bicarbonate/carbonic acid equilibrium. As shown below, the shift from bicarbonate to carbonic acid with decreasing pH likely had only a small effect on 1,4-dioxane oxidation. It is possible, however, that deprotonated DOM moieties contributed to faster  $\bullet OH$  radical formation rates and a faster rate of 1,4-dioxane oxidation.

### *Effect of Ozone:TOC Ratio on 1,4-Dioxane Oxidation*

Additional batch ozonation experiments were conducted in sCFR water to assess the effect of  $O_3$  dose and  $O_3$ :TOC ratio on 1,4-dioxane oxidation. Experiments were performed at  $O_3$ :TOC ratios ranging from 0.19 to 1.25 mg  $O_3$ /mg TOC (Figure 16).



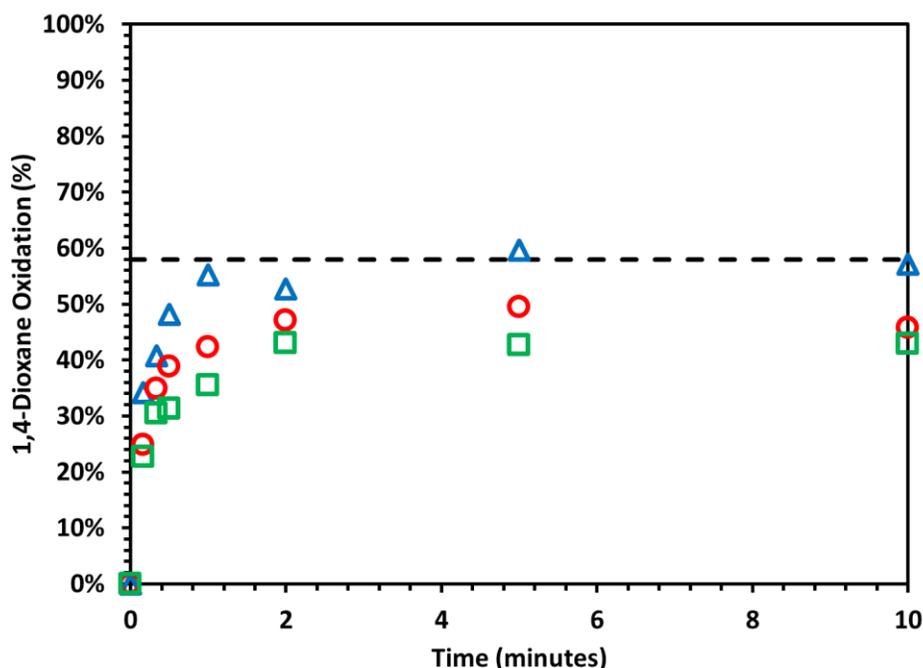
**Figure 16. Effect of  $O_3$ :TOC ratio on 1,4-dioxane oxidation in settled Cape Fear River water.** ( $\Delta$ ) pH=6.80,  $[O_3]=7.38 \times 10^{-5} M$ ,  $O_3$ :TOC=1.25; ( $\square$ ) pH= 6.99,  $[O_3]=4.12 \times 10^{-5} M$ ,  $O_3$ :TOC= 0.64; ( $\circ$ ) pH=7.12,  $[O_3]=2.34 \times 10^{-5} M$ ,  $O_3$ :TOC=0.34; ( $\diamond$ ) pH= 7.16,  $[O_3]=1.37 \times 10^{-5} M$ ,  $O_3$ :TOC=0.19. Alkalinity=12 mg/L as  $CaCO_3$ .

After 10 minutes of reaction time, when the O<sub>3</sub> residual was either small or non-detectable, the extent of 1,4-dioxane ranged from ~20% at an O<sub>3</sub>:TOC ratio of 0.19 to ~95% at an O<sub>3</sub>:TOC ratio of 1.25 (Figure 16). The corresponding O<sub>3</sub> doses were 0.7 and 3.5 mg/L, respectively. Changing the O<sub>3</sub>:TOC ratio from 0.19 to 1.25 increased the •OH radical exposure from 1.3×10<sup>-11</sup> to 1.1×10<sup>-9</sup> M\*s, respectively. Results obtained at an O<sub>3</sub>:TOC ratio of 1.25 illustrate that ozonation of sCFR could be a viable treatment alternative for 1,4-dioxane control.

Furthermore, a comparison of 1,4-dioxane oxidation results in rCFR (Figure 15) and sCFR (Figure 16) at an O<sub>3</sub>:TOC ratio of ~0.65 and pH~7 illustrate improved 1,4-dioxane in sCFR water compared to rCFR water. The improved 1,4-dioxane oxidation in sCFR may be attributable to the lower alkalinity of sCFR and/or differences in DOM character after coagulation.

### *Effect of Alkalinity on 1,4-Dioxane Oxidation*

The alkalinity of surface water can vary temporally at a given location (e.g. lower alkalinity during storm events) and geographically, depending on local geology. To assess how alkalinity affects the oxidation of 1,4-dioxane, rCFR water with a native alkalinity of 21 mg/L as CaCO<sub>3</sub> was amended with NaHCO<sub>3</sub> to reach alkalinities of 157 and 314 mg/L as CaCO<sub>3</sub>. Batch ozonation experiments were conducted at an O<sub>3</sub>:TOC ratio of ~0.60 and pH ~7, and results are presented in Figure 17.

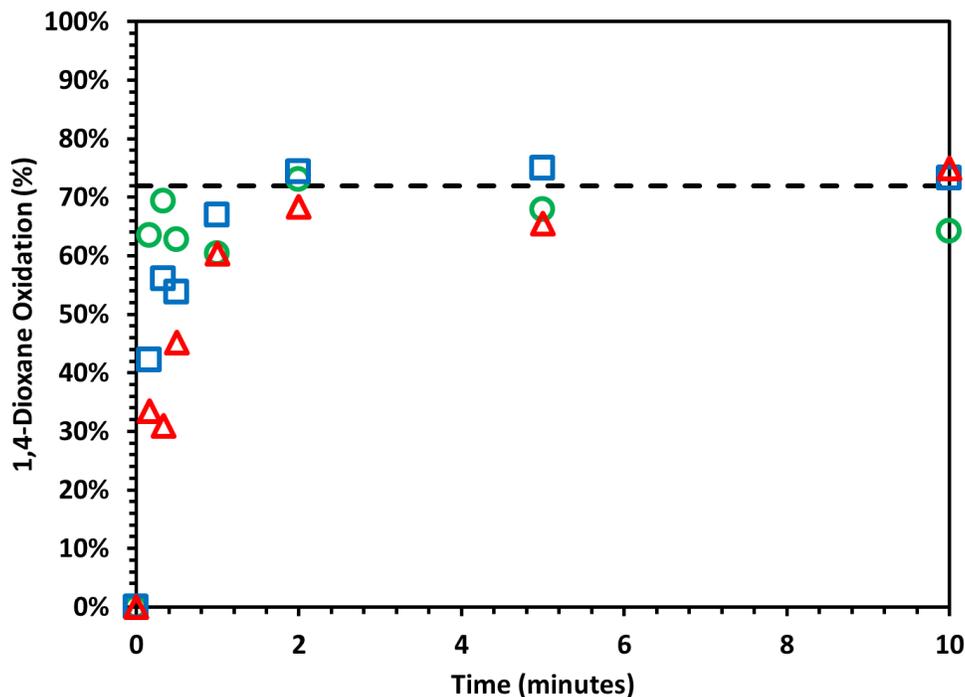


**Figure 17. Oxidation of 1,4-dioxane in Raw Cape Fear River water for different levels of alkalinity.** (Δ) pH=7.02, [O<sub>3</sub>]=7.08×10<sup>-5</sup> M, O<sub>3</sub>:TOC=0.59, Alkalinity=21 mg/L as CaCO<sub>3</sub>; (○) pH= 6.96, [O<sub>3</sub>]=7.33×10<sup>-5</sup> M, O<sub>3</sub>:TOC=0.60, Alkalinity=157 mg/L as CaCO<sub>3</sub>; (□) pH= 7.00, [O<sub>3</sub>]=7.09×10<sup>-5</sup> M, O<sub>3</sub>:TOC=0.58, Alkalinity=313 mg/L as CaCO<sub>3</sub>. Dashed line represents 58% transformation.

Results presented in Figure 17 demonstrate that the extent of 1,4-dioxane oxidation decreased from 58 to 43% as the alkalinity was increased from 21 to 314 mg/L as CaCO<sub>3</sub>. The 1,4-dioxane data further suggest that the •OH radical exposure decreased from 3.16×10<sup>-10</sup> to 1.96×10<sup>-10</sup> M-s as the alkalinity increased from 21 to 314 mg/L as CaCO<sub>3</sub>. The lower extent of 1,4-dioxane transformation in the water with the higher alkalinity can be attributed to higher concentrations of bicarbonate and carbonate, which will scavenge •OH radicals (Elovitz and von Gunten 2000).

### *Effect of Hydrogen Peroxide Addition*

Previous work demonstrated AOPs effectively oxidized 1,4-dioxane in groundwater (Adams et al., 1994; Suh et al., 2004). However, no data are available to assess the effect of H<sub>2</sub>O<sub>2</sub> addition on 1,4-dioxane oxidation during ozonation of surface water. Batch ozonation experiments were therefore conducted in sCFR at pH 7 and an O<sub>3</sub>:TOC ratio of ~0.5 to determine the effect of H<sub>2</sub>O<sub>2</sub> addition on 1,4-dioxane oxidation. H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> ratios of 1:2, 1:1, and 2:1 were evaluated (Figure 18).



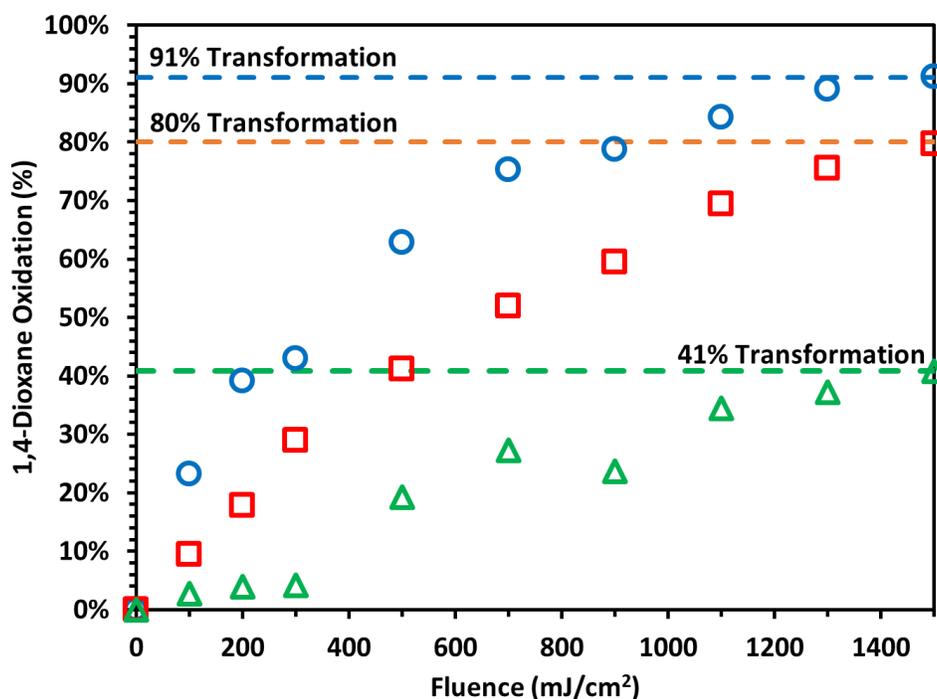
**Figure 18. Effect of H<sub>2</sub>O<sub>2</sub> addition on 1,4-dioxane oxidation during ozonation of settled Cape Fear River water.** (Δ) pH=7.09, [O<sub>3</sub>]=3.60×10<sup>-5</sup> M, H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub>=1:2, O<sub>3</sub>:TOC=0.52; (□) pH= 7.09 [O<sub>3</sub>]=3.13×10<sup>-5</sup> M, H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub>=1:1, O<sub>3</sub>:TOC=0.45; (○) pH= 7.09 [O<sub>3</sub>]=3.13×10<sup>-5</sup> M, H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub>=2:1, O<sub>3</sub>:TOC=0.47. Alkalinity=12 mg/L as CaCO<sub>3</sub>. Dashed line represents 72% transformation.

The results in Figure 18 demonstrate that the addition of hydrogen peroxide achieved similar extent of oxidation regardless of the applied H<sub>2</sub>O<sub>2</sub>:O<sub>3</sub> ratio. Compared to results in Figure 16, the addition of H<sub>2</sub>O<sub>2</sub> improved the extent of 1,4-dioxane oxidation. For example, in settled water ozonation at an O<sub>3</sub>:TOC ratio of 0.64 yielded 66% oxidation of 1,4-dioxane; however, upon

addition of H<sub>2</sub>O<sub>2</sub> at an O<sub>3</sub>:TOC ratio of 0.45-0.52 the AOP process was able to achieve approximately 72% transformation of 1,4-dioxane. Furthermore, the 1,4-dioxane data suggest that the •OH radical exposure increased from 3.48×10<sup>-10</sup> M\*s for ozonation only to an average of 4.35×10<sup>-10</sup> M\*s for ozone/H<sub>2</sub>O<sub>2</sub>.

### UV/H<sub>2</sub>O<sub>2</sub> Treatment

A viable treatment option for 1,4-dioxane control in groundwater is the UV/H<sub>2</sub>O<sub>2</sub> process. However, its applicability for 1,4-dioxane control in a surface water treatment context has not been demonstrated. In Figure 19, 1,4-dioxane oxidation data obtained with the UV/H<sub>2</sub>O<sub>2</sub> process in coagulated, settled, and filtered CFR water are summarized. Three H<sub>2</sub>O<sub>2</sub> concentrations (2 mg/L, 6 mg/L, and 10 mg/L) and fluence values up to 1500 mJ/cm<sup>2</sup> were studied.



**Figure 19. UV/H<sub>2</sub>O<sub>2</sub> oxidation of 1,4-dioxane in settled/filtered Cape Fear River water.** (○) Filtered settled water, pH=7.09, [H<sub>2</sub>O<sub>2</sub>]=10 mg/L; (□) Filtered settled water, pH=7.09, [H<sub>2</sub>O<sub>2</sub>]=6 mg/L; (△) Filtered settled water, pH=7.10, [H<sub>2</sub>O<sub>2</sub>]=2 mg/L. Alkalinity=12 mg/L as CaCO<sub>3</sub>.

Results presented in Figure 19 demonstrate that 1,4-dioxane oxidation was strongly dependent on H<sub>2</sub>O<sub>2</sub> dose and that both a high H<sub>2</sub>O<sub>2</sub> dose and a high UV dose (fluence) was required to reach substantial levels of 1,4-dioxane oxidation. To surpass 90% 1,4-dioxane oxidation in coagulated, settled, and filtered CFR necessitated an H<sub>2</sub>O<sub>2</sub> dose of 10 mg/L in combination with a UV fluence of 1500 mJ/cm<sup>2</sup>. In the UV/H<sub>2</sub>O<sub>2</sub> process, rate of 1,4-dioxane concentration is affected by the steady state •OH radical concentration. Here, steady state •OH radical concentrations were 2.1×10<sup>-7</sup> M, 6.0×10<sup>-7</sup> M, and 9.6×10<sup>-7</sup> M for H<sub>2</sub>O<sub>2</sub> doses of 2 mg/L, 6 mg/L, and 10 mg/L, respectively. Overall, the UV/H<sub>2</sub>O<sub>2</sub> results show that its application for 1,4-dioxane control in settled/filtered CFR would be very costly as a result of the high H<sub>2</sub>O<sub>2</sub> and UV dose requirements.

Furthermore, an additional treatment step would be needed to quench the H<sub>2</sub>O<sub>2</sub> residual leaving the UV reactor.

# REMOVAL OF 1,4-DIOXANE FROM TAP WATER BY POINT-OF-USE TREATMENT DEVICES

## *Abstract*

The purpose of this research was to assess 1,4-dioxane removal by point-of-use (POU) treatment devices. Conventional drinking water treatment is ineffective for 1,4-dioxane control. As a result, many residents in the Cape Fear River basin receive drinking water with elevated 1,4-dioxane concentrations. Granular activated carbon (GAC) can adsorb 1,4-dioxane from water, but a short GAC service life makes GAC adsorption a costly and impractical treatment option in a centralized water treatment facility. Activated carbon-based POU treatment devices, which treat only the small fraction of household water use associated with drinking and cooking, may be an effective option for 1,4-dioxane removal. In this research, two commercial pitcher filters, a custom pitcher filter containing a tailored adsorbent, and two commercial refrigerator filters were evaluated. Filters were operated until they reached 125% of the manufacturer expected lifetime or until the flow dropped to <60% of the initial flow, whichever occurred first. Experiments were conducted with spiked tap water at either constant or variable influent 1,4-dioxane concentrations. Average removals for the two commercial and the custom pitcher filter were 24%, 42% and 72%, respectively after treating 128 L (34 gal). For the two refrigerator filters that are capable of treating a larger water volume, average removals were 15% and 80% after treating 302 L (80 gal). Results for pitcher filters showed that percent 1,4-dioxane removal was independent of the initial 1,4-dioxane concentration. Desorption of 1,4-dioxane occurred in all POU devices when a period of high influent 1,4-dioxane concentration was followed by a period of low influent 1,4-dioxane concentration and diminished the overall benefit of POU treatment. In the custom pitcher filter, desorption of 1,4-dioxane was less pronounced. Overall, commercially available POU treatment devices exhibited limited effectiveness for 1,4-dioxane removal from tap water, especially under variable 1,4-dioxane concentrations. A POU device containing the tailored resin was more effective, but in the tested configuration, it would not be able to lower 1,4-dioxane concentrations to 0.35 µg/L when receiving water with the 1,4-dioxane concentrations observed in finished drinking water of three communities in the CFR watershed.

## **Introduction**

Increasingly stringent maximum contaminant levels (MCLs), costs for advanced treatment of large volumes of water, occurrence of emerging contaminants, and water quality deterioration in distribution systems are some of the drivers for the adoption of in-house water filtration systems to treat water for direct human consumption (Cotruvo, 2003). Studies show that a considerable number of consumers in North America have concerns about tap water safety. Taste and odor problems are a frequent cause of customer complaints. A survey conducted by the Public Health and Safety Organization revealed that 82% of 1,000 consumers reported concerns about trace levels of emerging contaminants in drinking water. Pesticides and herbicides are of greatest concern, followed by prescription drugs, detergents and flame retardants (Rick, 2014).

Because most concerns are associated with the consumption of drinking water, point of use (POU) treatment of water used for drinking/cooking purposes only may represent one possible solution. Most potable water is used as “service water” for nonpotable purposes. Less than 1% of

potable water generated in the United States is used for drinking and cooking (Cotruvo, 2003). Future safe drinking water paradigms may shift towards providing the right quality of water for the intended application; in other words, the highest quality water is used for consumption and high-exposure use (i.e., bathing), and the remaining water for nonpotable applications is treated to a lesser standard to save energy, chemical, and infrastructure costs (Anumol et al., 2015).

Consumers have reason to be concerned about chemical exposure in their drinking water. Data from the third Unregulated Contaminant Monitoring Rule (UCMR-3) indicate that 1,4-dioxane has been detected in 3.1% of drinking water samples nationwide at concentrations above the  $10^{-6}$  cancer risk level of 0.35  $\mu\text{g/L}$  (USEPA, 2015). Results presented in Chapter 5 showed that 1,4-dioxane concentrations in NC drinking water can exceed 30  $\mu\text{g/L}$ . Conventional treatment (coagulation, sedimentation, filtration, chlor(am)ination) is not effective for 1,4-dioxane control (McGuire et al., 1978 ; Simazaki et al., 2006). Because of its low volatility, 1,4-dioxane is not well removed by air stripping technologies (Moyer, 2008; EPA, 2014; McGuire et al., 1978). Pilot-scale data obtained with granular activated carbon (GAC) adsorbers illustrate that only between 500 and 1,000 bed volumes of groundwater can be treated prior to 1,4-dioxane breakthrough (Fotta, 2012). As a result, GAC would require replacement or regeneration on a weekly basis when the empty bed contact time (EBCT) of the adsorber is 15 minutes. With such short bed life, GAC treatment for 1,4-dioxane control is infeasible in centralized water treatment facilities. Powdered activated carbon (PAC) adsorption processes will likely require PAC doses that are too high (>100 mg/L) to be practical and economically feasible at the utility scale (McGuire et al., 1978). Data collected at the Orange County Water District in Southern California indicate that 1,4-dioxane also passes through reverse osmosis membranes (USEPA, 2013). As a result, advanced oxidation processes (AOP) such as ozonation with  $\text{H}_2\text{O}_2$  addition or UV/ $\text{H}_2\text{O}_2$  oxidation may be the only established treatment options that are effective for 1,4-dioxane control. AOPs are energy-intensive and expensive, requiring significant capital investment and upgrade of existing infrastructure (Anumol et al., 2015). POU treatment devices employing carbonaceous adsorbents can provide an effective barrier at the household scale for emerging contaminants because POU devices treat only a small fraction of the total domestic demand (Anumol et al., 2015). Therefore, POU devices may offer an avenue to remove 1,4-dioxane from drinking water in communities affected by elevated 1,4-dioxane concentrations.

A POU treatment device is any unit installed on a single water tap or refrigerator to provide a barrier against both microbial and chemical contaminants (Anumol et al., 2015; Mohamed et al., 2010). The ability of POU devices to attenuate microbial and conventional chemical contaminants (lead, copper, and zinc) has been demonstrated (e.g., Ahmedna et al. 2004a; Ahmedna et al. 2004b; Deshommes et al., 2010; Cleland, 2010; Carrière et al., 2011), but studies on their feasibility to treat emerging organic contaminants are in the research stage (e.g. Anumol et al., 2015). Several states in the US allow for communities to meet water standards through the use of proven POU devices instead of centralized treatment. In Washington DC, thousands of POU devices were distributed to treat high levels of lead in drinking water (Anumol et al., 2015). Likewise, POU treatment devices were distributed in Flint, MI after citizens were exposed to lead via tap water. These cases demonstrate the flexibility of POU treatment devices and their applicability in situations where centralized treatment systems are not able to protect public health.

The aim of this study was to determine the effectiveness of four commercial POU devices and one custom pitcher filter containing a tailored adsorbent for removing 1,4-dioxane from tap water. Specific objectives included to 1) compare the effectiveness of different POU devices and 2) assess the performance of select filters under constant and variable 1,4-dioxane concentrations with a focus on determining possible 1,4-dioxane desorption when a period of low 1,4-dioxane concentration follows a period of high 1,4-dioxane concentrations. As shown in Chapter 5, the temporal variability in 1,4-dioxane concentrations in tap water of several communities in the CFR watershed is high (affected by both source variability and stream flow), making the potential for desorption an important POU performance consideration.

## **Materials and Methods**

### *Selection of POU Devices*

Four commercial POU devices and one custom POU device were tested. Commercial POU devices included two pitcher filters (P-POU) (Brita® Monterrey 11-cup filter and PUR™ Classic 11-Cup Water Filter) and two refrigerator filters (R-POU) (EveryDrop™ Ice & Water refrigerator filter and Frigidaire® PureSource Ultra®). P-POU and R-POU devices were selected because of their widespread use. In the US, 34% of POU users own an R-POU device and 27% a P-POU device (Intel, 2012). P-POUs brands were selected based on consumer usage; 38% use Brita and 19% PUR (Intel, 2014). R-POU devices were selected based on commercial availability and in the case of one (EveryDrop) for its wide compatibility with different refrigerator brands.

The two commercial P-POU devices contained both granular activated carbon (GAC) and ion exchange resins (IX) (Brita, 2016; PUR, 2016). While the exact amount of GAC and IX resin in each filter is proprietary business information, separation of the adsorbents was performed finding that Brita and PUR contained on a dry mass basis 55% and 67% (w/w) of GAC, respectively. The R-POU devices employed solid block activated carbon (SBAC) technology. The volume of carbon was calculated as 102 cm<sup>3</sup> and 270 cm<sup>3</sup> for the EveryDrop and Frigidaire R-POUs, respectively. Each POU had an exhaustion time specified by the manufacturer that corresponds to a volume of water that can be treated by the filter, i.e., the manufacturer's expected lifetime (MEL). The MEL values for the selected POU devices are presented in Table 15.

A tailored POU device was built by opening a Brita cartridge, removing the adsorbent materials and replacing them by a carbonaceous resin designed for 1,4-dioxane removal (Ambersorb 560, Dow Chemical Company) produced by thermal pyrolysis of sulfonated styrene-divinylbenzene copolymer. This resin is effective for the removal of 1,4-dioxane over a wide range of concentrations and operating conditions (Woodard and Mohr, 2011). The volume of resin added was equal to the volume of adsorbent contained in the original cartridge. Measured bed densities for the adsorbents are shown in Table 15.

**Table 15. Characteristics of the POU devices studied**

Type	MEL	Filter	Total Mass of Adsorbent (g)	Mass of carbonaceous adsorbent (g)	Mass of IX Resin (g)	Bed Density g/cm <sup>3</sup>
P-POU	151 L (40 gal)	Brita	52.8	28.9	23.9	0.56
		PUR	55.8	37.6	18.2	0.54
		Tailored Resin	54.3	54.3	0.0	0.53
R-POU	757 L (200 gal)	Frigidaire	192.7	192.7	0.0	0.72
		EveryDrop	68.2	68.2	0.0	0.67

**Experimental Setup**

Each filter was tested in accordance with NSF/ANSI Standard 53 guidelines (NSF/ANSI, 2011). Fifty-five gallons (208 L) of feed solution were prepared by adding NaCl to Raleigh, NC, tap water to reach a total dissolved solids (TDS) concentration of ~300 mg/L. 1,4-Dioxane was added from a primary dilution standard (PDS) (1000 mg/L) to achieve a concentration of about 50 µg/L (high concentration) or 5 µg/L (low concentration). Each 208 L (55-gal) solution was mixed for one hour using an overhead mixer prior to use. Conductivity was measured and monitored to establish completely mixed conditions after the addition of NaCl and 1,4-dioxane. Turbidity, pH, total organic carbon (TOC) and temperature were measured for each 208 L (55-gal) solution. All feed water quality parameters requirements for POU experiments complied with requirements of NSF ANSI standard 53 (Table 16).

**Table 16. Water parameters measured and required by the by the NSF ANSI standard 53**

Parameter	Measured feed water quality	NSF ANSI standard 53 specification
TDS (mg/L)	280 - 300	200-500
Turbidity (NTU)	0.2 - 0.42	< 1
pH	7.5 - 8.0	7.0-8.0
TOC (mg/L)	1.2 - 1.8	> 1.0
Temperature (°C)	18-18.6	17.5-22.5
1,4-dioxane (µg/L)	~50 (high) and ~5 (low)	N/A

Prior to the experiment, each POU device was preconditioned with the exposure water as recommended by the manufacturer and NSF/ANSI 53. For P-POU devices, 2 gallons (7.57 L) of

water were treated per day in eight one-quart (0.95-L) batches. The minimum rest period between batches was 30 seconds. The R-POU devices were connected to a gear pump that pushed water through the devices at a fixed pressure of 40 psi. A 50/50 on/off cycle (20 minutes on, 20 minutes off) was used, and up to 55 gallons of water were processed per day.

Flow rate was measured for each POU device at regular intervals. NSF/ANSI 53 guidelines (NSF/ANSI 53, 2011) state that filters with a performance indication device must be operated to 120% MEL. In this study, tests were discontinued after 125% of the MEL or if the flow rate of a device fell to below 60% of its maximum flow. Samples for 1,4-dioxane analysis were collected in VOA vials for each POU device in percentage increments of 5% of the MEL until 125% of the MEL was reached. Influent samples from the 55-gallon solutions were collected periodically to verify that no measurable 1,4-dioxane losses occurred during the experiment. Samples were stored at 4°C immediately after collection. An MEL of 0% was considered to be the starting point after the preconditioning of the POU device with test water (NSF/ANSI 53, 2011).

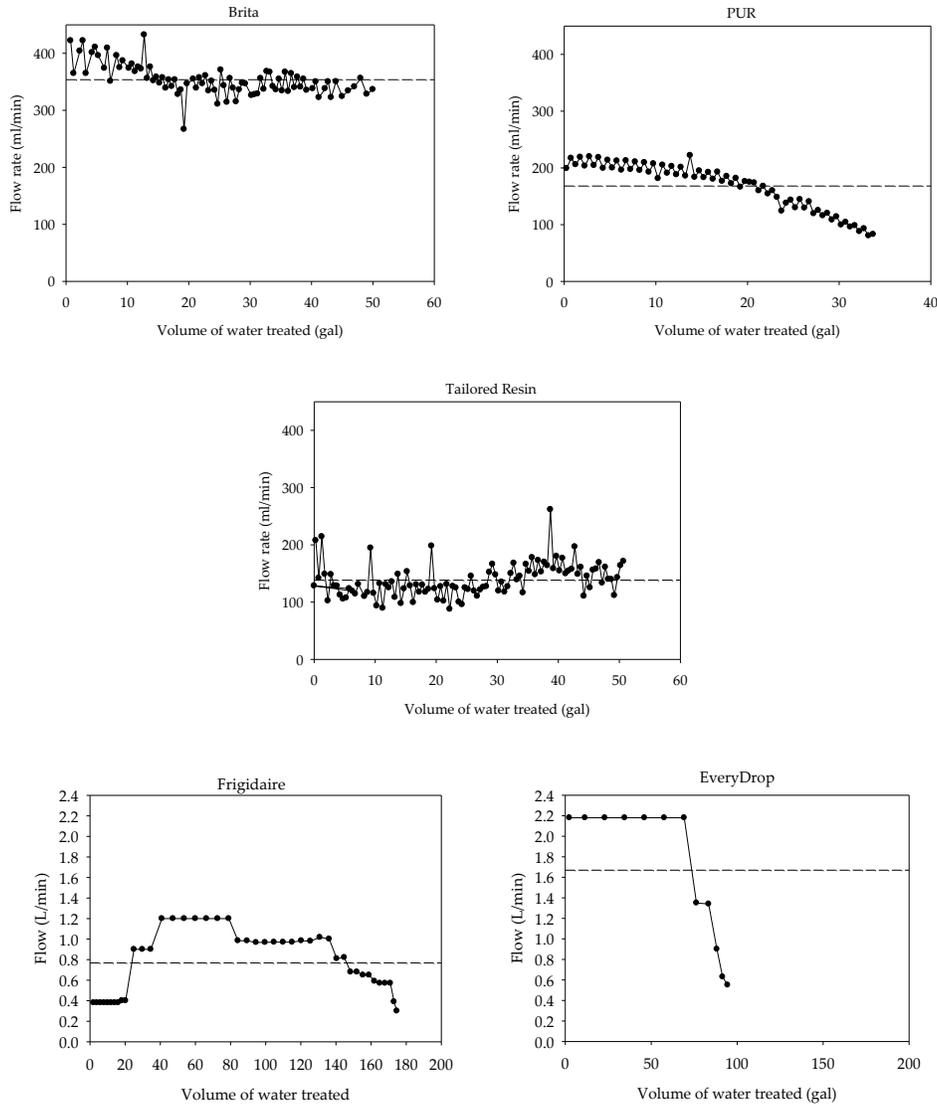
### ***Water Quality Analyses***

The method used for determination of 1,4-dioxane in water samples was recently published by Sun et al. (2016) and is described in Chapter 4. Briefly, heated purge-and-trap (P&T) preconcentration (AQUATEk 100 autosampler, Stratum PTC, Teledyne Tekmar, Mason, OH) followed by gas chromatography (GC)/ion-trap mass spectrometry (MS) with selected-ion storage (CP-3800 GC and Saturn 2200 MS, Agilent, Santa Clara, CA) was used to measure 1,4-dioxane concentrations in aqueous samples. A 5-mL sample volume was heated, and the purged chemicals were collected by a sorbent trap (Teledyne Tekmar #9). Mass-labeled 1,4-dioxane-d8 was used as internal standard (IS) for quantification. A capillary column (30 meter × 0.25 mm × 1.4 μm, Agilent VF-624ms) was used for compound separation. Methods for determination of conductivity, TDS and TOC are described in Chapter 3.

## **Results and Discussion**

### ***Flow rates***

Among the P-POUs, the average flow rate for the Brita filter was highest (0.36 L/min). Average flow rates of the PUR (0.17 L/min) and the Tailored Resin (0.13 L/min) P-POUs were 49 and 36% of that obtained with the Brita Filter. Flow in the PUR P-POU decreased to <40% of its initial flow rate prior to reaching 125% of the MEL. In line with the manufacturer's specifications, the two R-POUs operated at much higher flow rates and treated larger water volumes than the P-POU filters. At a constant pressure of 2.7 atm (40 psi) (NSF/ANSI 53, 2011), average flow rates for Frigidaire and EveryDrop were 0.8 and 1.6 L/min, respectively. The flow rate of the EveryDrop device drop rapidly from 2.2 to below 0.4 L/min at approximately 40% of the MEL, resulting in early termination of the experiment. The Frigidaire filter produced variable flow rates through the test: starting with a flow of 0.4 L/min, progressively increasing to a flow of 1.2 L/min (Figure 20). After treating 302 L (80 gal) the flow dropped until reaching the starting value of 0.4 L/min.

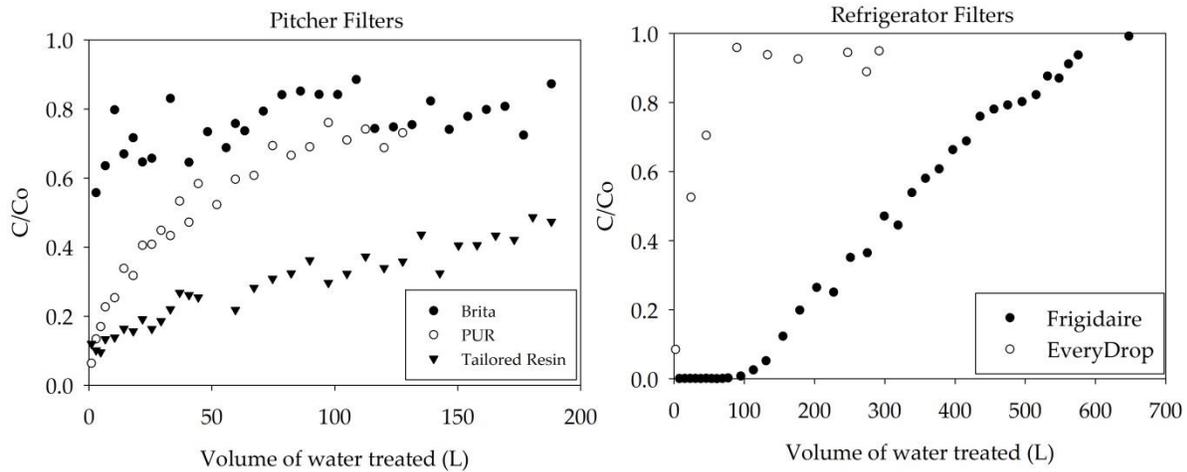


**Figure 20. Flow rates for three P-POUs and two R-POUs**

***Adsorption of 1,4-Dioxane by POU Treatment Devices at Constant Concentration***

To evaluate the performance of POU devices for 1,4-dioxane removal, experiments were initially conducted at a constant influent concentration of  $\sim 50 \mu\text{g/L}$ . The performance of each POU device is illustrated in Figure 21 by plotting the 1,4-dioxane concentration ( $C$ ) in the treated water relative to that in the influent water ( $C_0$ ). As shown in Figure 21, the Brita P-POU produced immediate 1,4-dioxane breakthrough of almost 60%. For the PUR and Tailored Resin P-POUs, immediate breakthrough was also observed, but only at  $\sim 10\%$ . As the volume of water treated increased, 1,4-dioxane breakthrough increased and reached a final relative concentration of 87% after treating 189 L (50 gal) with the Brita, 73% after treating 128 L (34 gal) with the PUR, and 49% after treating 189 L (50 gal) with the tailored resin P-POUs (Figure 21). For the R-POUs, immediate 1,4-dioxane breakthrough was at almost 10% for the EveryDrop filter and at

0.2% for the Frigidaire filter (Figure 21). The Frigidaire filter was able to maintain >99% 1,4-dioxane removal for 100 L of water treated. Complete 1,4-dioxane breakthrough was reached at 131 L (34 gal) for the the EveryDrop and at 646 L (171 gal) for the Frigidaire R-POUs.



**Figure 21. Relative concentration vs. volume of water treated per POU device studied. Dotted line represents cessation of the test for P-POU PUR and R-POU EveryDrop.**

Average removal was calculated by dividing the mass of 1,4-dioxane adsorbed by the mass of 1,4-dioxane fed. Average percentage removal for each POU device at different MELs is presented Table 17. After treating 129 L (34 gal), the P-POU containing the tailored resin showed the highest removal of 1,4-dioxane from tap water (74%), followed by Pur (44%), and Brita (25%). For the R-POUs, the Frigidaire filter removed on average 85% after treating 303 L (80 gal) while the EveryDrop removed 17% (Table 17).

**Table 17. Average percent 1,4-dioxane removal at different MEL percentages for P-POUs and R-POUs**

P-POU	Percentage 1,4-dioxane removal at different percentages of manufacturer expected lifetime (MEL) and corresponding water volume		
	85% MEL	100 % MEL	125% MEL
	129 L (34 gal)	151 L (40 gal)	189 L (50 gal)
<b>Brita</b>	25%	24.5%	24%
<b>PUR</b>	44%	-	-
<b>Tailored Resin</b>	74%	72%	68%
R-POU	Percentage 1,4-dioxane removal at different percentages of manufacturer expected lifetime (MEL) and corresponding water volume		
	10% MEL	40% MEL	85% MEL
	76 L (20gal)	303 L (80 gal)	644 L (170 gal)
<b>Frigidaire</b>	>99%	85%	61%
<b>EveryDrop</b>	37%	17%	-

Because the POU devices varied in terms of adsorbent type, adsorbent mass, and hydraulic configuration 1,4-dioxane adsorption capacities for the carbonaceous adsorbents were compared by calculating solid-phase concentration at 50% breakthrough. A value of  $C/C_0=0.5$  was selected because none of the P-POUs reached complete breakthrough at the stopping criterion (125% MEL, flow <40% of maximum flow). Results for the P-POUs show that the 1,4-dioxane adsorption capacity of the carbonaceous adsorbents increased in the order of Brita < PUR < tailored resin (Table 18). In other words, the 1,4-dioxane adsorption capacity of the tailored resin exceeded that of the GACs in the Brita and PUR filters by factors of ~ 27 and 3.6, respectively. The low adsorption capacity of the GAC in the Brita filter was likely attributable to the high flow rate through the filter (Figure 20), which immediately led to high levels of 1,4-dioxane breakthrough (Figure 21). For the R-POUs, the SBAC in the Frigidaire filter exhibited a 1,4-dioxane adsorption capacity that was ~6 times that of the SBAC in the EveryDrop filter. Overall, the tailored resin exhibited the highest 1,4-dioxane adsorption capacity, exceeding that of the SBAC in the Frigidaire filter by a factor of almost 2.

**Table 18. Volume of water treated to ~50% 1,4-dioxane breakthrough and comparison of 1,4-dioxane adsorption capacities of the studied carbonaceous adsorbents at 50% breakthrough of 1,4-dioxane**

Type	Filter	Volume Treated (L)	Corresponding C/Co	Mass Fed (mg)	Mass Adsorbed (mg)	Adsorbent mass (g)	Capacity q (µg/g)
P-POU	Brita	3	0.57	0.18	0.13	28.89*	4.56
	PUR	38	0.53	1.89	1.27	37.58*	34.0
	Tailored Resin	189	0.49	9.73	6.63	54.34	122
R-POU	Frigidaire	336	0.54	15.7	12.7	192.7	66.1
	EveryDrop	24	0.53	1.0	0.7	68.15	10.7

\*Values for GAC. Total mass of adsorbent shown in Table 15

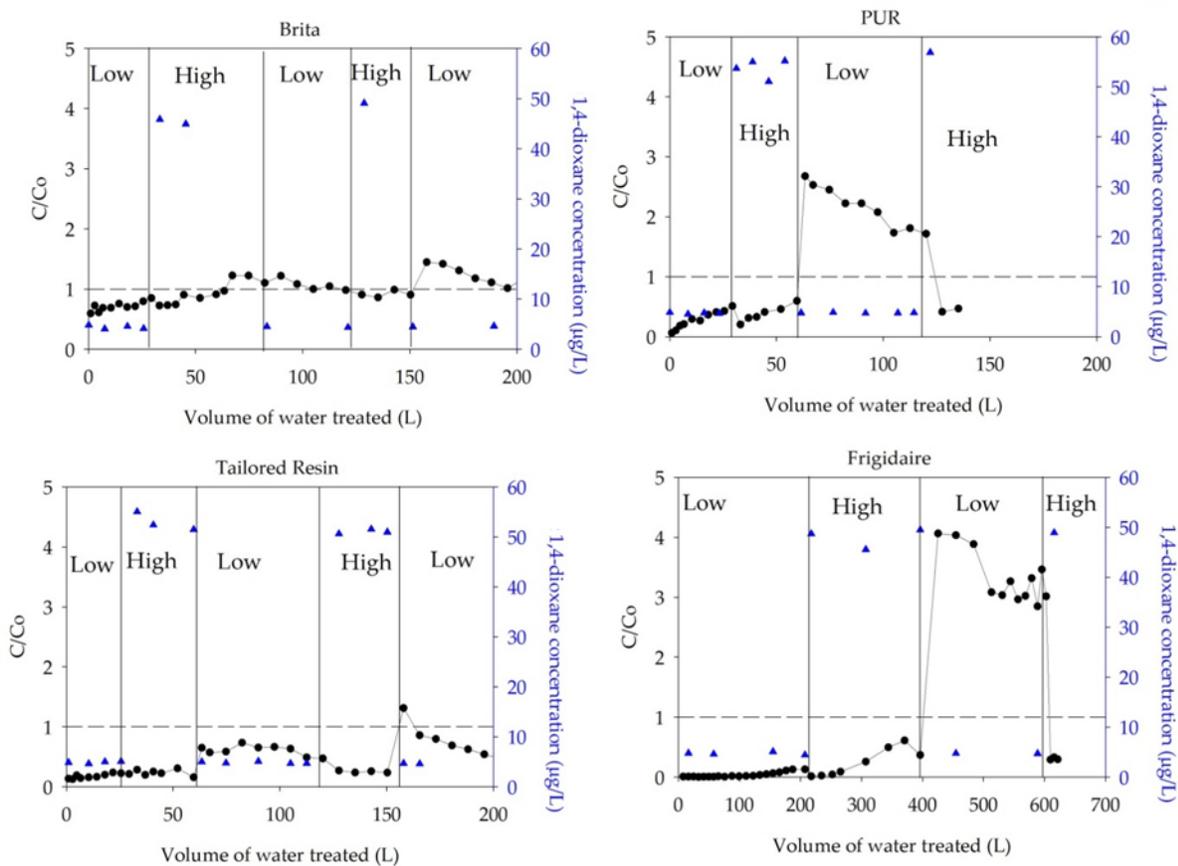
### *Adsorption of 1,4-Dioxane by POU Treatment Devices at Variable Concentration*

As illustrated in Chapter 5, 1,4-dioxane concentrations in drinking water derived from the CFR watershed exhibit high temporal variability. As a result, it is important to assess the performance of POU treatment devices under variable 1,4-dioxane concentrations. Of particular interest is the possible desorption of 1,4-dioxane when a period of low 1,4-dioxane concentrations is followed by a period of high 1,4-dioxane concentrations. This assessment is less critical for drinking water derived from groundwater as groundwater concentrations of 1,4-dioxane are not expected to exhibit high temporal variability.

Experiments were performed with the three P-POU filters and the Frigidaire R-POU. Experiments were initiated with a relatively low influent 1,4-dioxane concentration (~5 µg/L). Results of the initial POU performance were compared to those obtained at an initial 1,4-dioxane concentration of ~50 µg/L (discussed in the previous section) to determine whether percent 1,4-dioxane removal is affected by the initial 1,4-dioxane concentration. After a period of feeding water containing 5 µg/L 1,4-dioxane, the POU feeds were alternated between high (~50 µg/L) and low (~5 µg/L) 1,4-dioxane concentrations.

Results for the POU experiments at variable concentrations are shown in Figure 22. The Brita P-POU exhibited immediate breakthrough of almost ~60%, and desorption was observed starting with the second period of low influent concentration of 1,4-dioxane. The extent of desorption was relatively low because little 1,4-dioxane was removed in the preceding phases. The PUR P-POU exhibit an immediate breakthrough of 6% and desorption was observed when switching from an influent concentration of 50 µg/L to an influent concentration of 5 µg/L at the point where 54 L of water had been filtered. Breakthrough at this point was 267% and the P-POU kept releasing 1,4-dioxane throughout the entire low influent concentration period. The tailored resin P-POU exhibited immediate breakthrough of 13% and maintained a high level of removal, both during low and high influent concentration periods, until 60 L of water was treated. When the

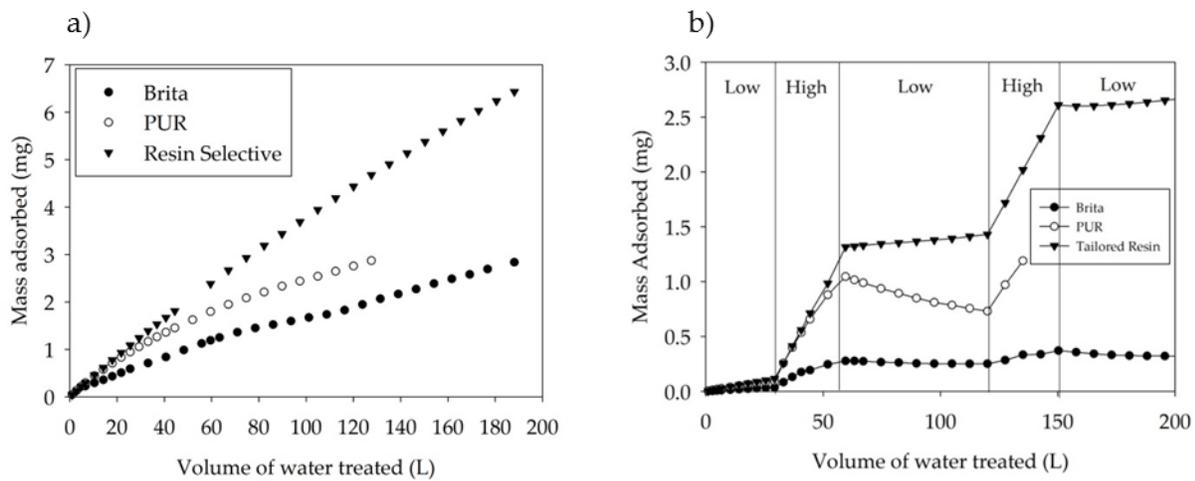
influent concentration was switched from 50 to 5 µg/L, the tailored resin exhibited a performance decrease, but only on one occasion did the 1,4-dioxane concentration in the filtered water exceed the influent concentration (104% at 158 L). But the filter recovered rapidly and 1,4-dioxane removal was 48% after 200 L of water had been treated. Finally, for the Frigidaire (R-POU) filter, 5% breakthrough was observed after treating 150 L. At 400 L, the influent was switched from a high to a low influent concentration of 1,4-dioxane. At that moment, a breakthrough value of 403% was measured. In other words, an influent 1,4-dioxane concentration of 4.8 µg/L resulted in a filtrate concentration of 19 µg/L. Throughout the entire low influent concentration period, breakthrough levels of 1,4-dioxane in the filtrate remained above ~300% of the influent value. Overall, the results presented in Figure 22 highlight that the tailored resin exhibited the lowest extent of 1,4-dioxane desorption when exposed to variable influent concentrations of 1,4-dioxane.



**Figure 22. Performance of POU devices at variable influent concentration of 1,4-dioxane. Points represent relative concentrations, triangles represent influent concentration, solid vertical lines represent change in the influent concentration, and dashed horizontal lines represent a relative concentration equal to 1.**

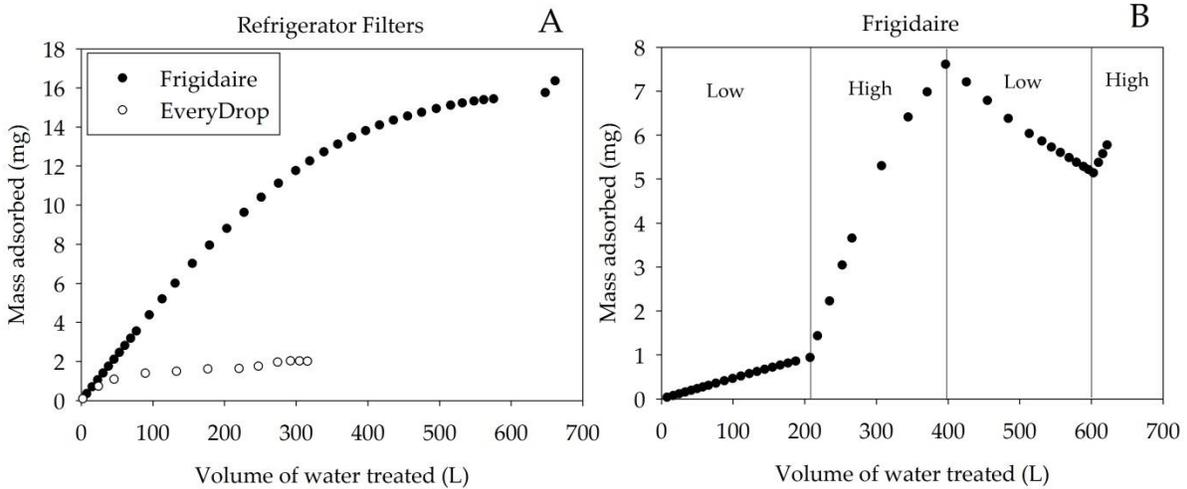
**Mass Adsorbed of the POU Treatment Devices at Influent Constant and Variable Concentrations of 1,4-Dioxane.**

Mass adsorbed at constant and variable concentration for the P-POUs is shown in Figure 23. At a constant influent concentration of 1,4-dioxane, the mass adsorbed after treating 128 L with the tailored resin exceeded that of the GACs in the Brita and PUR filters by factors of ~ 2.4 and 1.7, respectively. In contrast, at variable influent concentrations of 1,4-dioxane, the mass adsorbed after treating 128 L with the tailored resin exceeded that of the GACs in the Brita and PUR filters by factors of ~ 6.2 and 1.7, respectively. When a period of low influent concentration followed one of high influent concentration (between 60 and 120 L), the effectiveness of the tailored resin was reduced, but 1,4-dioxane continued to adsorb. In contrast, 41% of the mass of previously adsorbed 1,4-dioxane was desorbed from the PUR filter between 60 and 120 L.



**Figure 23. Mass of 1,4-dioxane adsorbed from tap water by three P-POUs for a) constant influent concentrations of 63, 48, and 51  $\mu\text{g/L}$  for Brita, PUR, and tailored resin P-POUs, respectively, and b) variable influent 1,4-dioxane concentrations (Low  $C_0 = 4.7 \mu\text{g/L}$ , High  $C_0 = 48 \mu\text{g/L}$  for Brita P-POU; Low  $C_0 = 4.9 \mu\text{g/L}$ , High  $C_0 = 51 \mu\text{g/L}$  for PUR P-POU; and Low  $C_0 = 4.7 \mu\text{g/L}$ , High  $C_0 = 48 \mu\text{g/L}$  for tailored resin P-POU).**

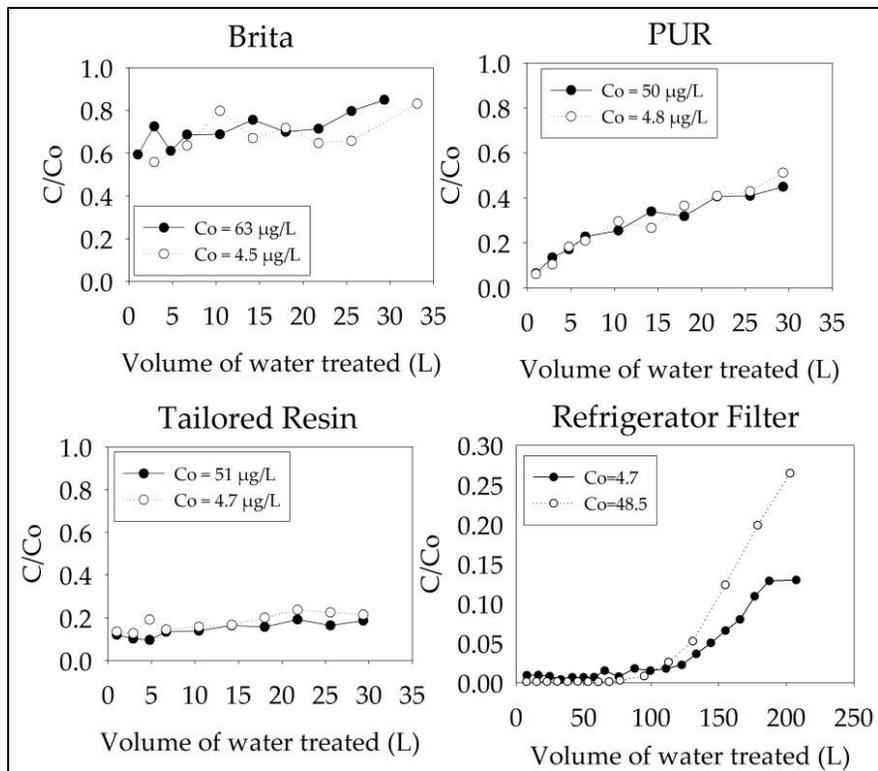
The mass adsorbed by the R-POUs at constant and variable concentrations is shown in Figure 24. At a constant influent concentration, the Frigidaire R-POU was able to adsorb 12 of 16 mg 1,4-dioxane fed (after treating 357 L), whereas the EveryDrop R-POU adsorbed only 2.0 mg out of 15 mg fed. Under variable influent concentrations the Frigidaire R-POU filter desorbed 2 of 11 mg 1,4-dioxane (after treating 602 L), reducing its overall benefit.



**Figure 24. Mass of 1,4-dioxane adsorbed from tap water for two R-POU for A) constant influent 1,4-dioxane concentrations of 46 and 42  $\mu\text{g/L}$  for Frigidaire and EveryDrop, respectively, and B) variable influent 1,4-dioxane concentration (Low  $C_0 = 4.7 \mu\text{g/L}$ , High  $C_0 = 48 \mu\text{g/L}$ ).**

### *Effect of Initial 1,4-Dioxane Concentration*

Percent 1,4-dioxane removal was independent of the initial 1,4-dioxane concentration during the initial phase of P-POU operation (Figure 25). This result concurs with findings of others studies that evaluated the removal of organic contaminants with higher molecular weights from surface water (Knappe et al., 1998; Rossner Campos, 2008). The theoretical basis for this behavior has been explained using Ideal Adsorption Solution Theory (IAST) and the Pore and Surface Diffusion Model equations (Knappe et al., 1998; Matsui et al., 2002a, 2002b). For the R-POU,  $C/C_0$  was independent of  $C_0$  for the first 110 L, but then more rapid breakthrough for the experiment with the higher influent 1,4-dioxane concentration was observed. The latter result suggests that the R-POU performance was not only affected by the adsorption of background organic matter but also by the accumulated mass of adsorbed 1,4-dioxane.



**Figure 25. Relative concentration of 1,4-dioxane in the filtrate when feeding high and low 1,4-dioxane concentrations in the POU influent.**

## Conclusions

- Removal of 1,4-dioxane varied greatly among POU devices with different adsorbent types, adsorbent mass, and hydraulic configuration.
- At a constant influent concentration, average removals for the two commercial and the custom pitcher filter were 25%, 44% and 74%, respectively, after treating 128 L (34 gal). For the two refrigerator filters that are capable of treating a larger water volume, average removals were 17% and 85% after treating 303 L (80 gal).
- Adsorption capacities were compared at 50% breakthrough. Results showed that the tailored resin exhibited the highest 1,4-dioxane adsorption capacity (122  $\mu\text{g}$  of 1,4-dioxane/g of adsorbent), whereas the adsorbent in the Brita P-POU showed the lowest (4.5  $\mu\text{g}$  of 1,4-dioxane/g of adsorbent). The latter result was likely attributable to the high flow rate through the filter, which immediately led to high levels of 1,4-dioxane breakthrough.
- Results for pitcher filters showed that percent 1,4-dioxane removal was independent of the initial 1,4-dioxane concentration.
- Desorption of 1,4-dioxane occurred in all POU devices, when a period of high influent 1,4-dioxane concentration was followed by a period of low influent 1,4-dioxane concentration and diminished the overall benefit of POU treatment for the commercial filters tested. In the custom pitcher filter, desorption of 1,4-dioxane was less pronounced.

- Overall, commercially available POU treatment devices exhibited limited effectiveness for 1,4-dioxane removal from tap water, especially under variable 1,4-dioxane concentrations. A POU device containing the tailored resin was more effective, but in the tested configuration, it would not be able to lower 1,4-dioxane concentrations to 0.35 µg/L when receiving water with the 1,4-dioxane concentrations observed in finished drinking water of three communities in the CFR watershed..

### **Future work**

Research should be conducted to characterize the adsorbent materials used in this research in order to identify adsorbent properties that govern 1,4-dioxane removal.

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## APPENDICES

### APPENDIX A: Analytical Methods for 1,4-Dioxane

**Table A. 1 Summary of analytical methods for determining aqueous 1,4-dioxane concentrations from (Sun et al., 2016)**

Reference	Sample preparation	Sample volume	Quantification method	Environmental sample tested	Calibration range	Detection limit	Minimum reporting limit / limit of quantitation
<b>USEPA Method 8260</b>	Direct injection, azeotropic distillation or vacuum distillation	5 or 25 mL	GC-MS	Designed for liquid and solid waste, but no method validation data shown	1-100 µg/L (azeotropic distillation)	12 µg/L (azeotropic distillation)	Not available
<b>USEPA Method 8270*</b>	Liquid-liquid extraction	1 L	GC-MS	Designed for solid waste matrices, soils, air sampling media and water samples, but no data shown	Not available	Not available	Not available
<b>USEPA Method 1624</b>	Purge-and- trap	5 mL	GC-MS, with isotopic dilution	Designed for waters, soils, and municipal sludges, but no data shown	Not available	50 µg/L	Not available
<b>USEPA Method 522</b>	Solid phase extraction	500 or 100 mL	GC-MS with SIM	Drinking water	0.04-20 µg/L	0.020-0.026 µg/L	0.036-0.047 µg/L
<b>Kadokami et al (1990) <sup>1</sup></b>	Solid phase extraction on activated carbon with acetone and	1 L	GC-MS in SIM mode	River water and seawater	Not available	0.024 µg/L	Not available

Reference	Sample preparation	Sample volume	Quantification method	Environmental sample tested	Calibration range	Detection limit	Minimum reporting limit / limit of quantitation
	dichloromethane as the elution solvents						
<b>Grimmett &amp; Munch (2009)</b> <sup>2</sup>	Solid phase extraction on activated carbon columns with dichloromethane as the elution solvent	0.5 L	GC-MS in SIM mode	Drinking water, surface water, groundwater	2-1000 µg/L	36 or 47 ng/L, depending on extraction methods	20 or 26 ng/L, depending on extraction methods
<b>Kawata et al. (2001)</b> <sup>3</sup>	Solid phase extraction on activated carbon fiber felt cartridges with acetone as the elution solvent	0.5 L	GC-MS	Groundwater, surface water	Not available	0.02 µg/L	Not available
<b>Isaacson (2006)</b> <sup>4</sup>	Solid phase extraction on activated carbon disks with acetone as the elution solvent	50-150 mL	GC-MS/MS	Groundwater	0.31-3100 µg/L	0.13 µg/L	0.31 µg/L
<b>Stepien &amp; Püttmann (2013)</b> <sup>5</sup>	Solid phase extraction on activated	0.5 L	GC-MS in SIM mode	Surface water	0.040-20 µg/L	0.010 µg/L in ultrapure water and	0.034 µg/L in ultrapure water and

Reference	Sample preparation	Sample volume	Quantification method	Environmental sample tested	Calibration range	Detection limit	Minimum reporting limit / limit of quantitation
	coconut charcoal cartridges with dichloromethane as the elution solvent					0.016 µg/L in environmental samples	0.052 µg/L in environmental samples
<b>Shirey and Linton (2006)</b> <sup>6</sup>	Solid phase microextraction on carboxen-polydimethylsiloxane fibers in heated headspace or direct immersion in solution	5-8 mL	GC-MS	None	0.5-100 µg/L	2.5 µg/L without background subtraction, 0.5 µg/L with background subtraction	0.5 µg/L
<b>Nakamura and Daishima (2005)</b> <sup>7</sup>	Headspace solid phase microextraction at 60 °C on three types of fibers	10 mL	GC-MS in SIM mode	Tap water, river water	5-100 µg/L	1.2 µg/L	Not available
<b>Jochmann et al. (2006)</b> <sup>8</sup>	Headspace solid-phase dynamic extraction on four types of fibers	10 mL	GC-MS	Alcoholic beverages	Not available	0.8 - 1.2 µg/L depending on extraction materials	Not available

Reference	Sample preparation	Sample volume	Quantification method	Environmental sample tested	Calibration range	Detection limit	Minimum reporting limit / limit of quantitation
<b>Shin &amp; Lim (2011)</b> <sup>9</sup>	Heated headspace sampling for 30 min at 90 °C	5 mL	GC-MS in SIM mode	Drinking water (raw and finished)	0.1-20 µg/L	0.02 µg/L	Not available
<b>Li et al. (2011)</b> <sup>10</sup>	Frozen liquid-liquid micro-extraction with methylene chloride	0.2 mL	GC-MS in SIM mode	Groundwater	25-1600 µg/L	1.6 µg/L	Not available
<b>Yoo et al (2002)</b> <sup>11</sup>	Purge-and-trap for 20 min	25 mL	GC-MS/MS	Drinking water, surface water, groundwater, wastewater	1-30 µg/L	0.2 µg/L	Not available
<b>Michigan SOP (2009)</b> <sup>12</sup>	Heated purge-and-trap for 11 min at 40 °C	25 mL	GC-MS in SIM mode	Designed for drinking water, surface water, groundwater, wastewater, but no data shown	0.5-200 µg/L	Not available	Not available
<b>Teledyne Tekmar application note (2009)</b> <sup>13</sup>	Heated purge-and-trap for 5 min at 60 °C	25 mL	GC-MS in SIM mode	None	1-100 µg/L	Not available	0.275 µg/L
<b>Epstein et al. (1987)</b> <sup>14</sup>	Heated purge-and-trap for 11 min at 50 °C	5 mL	GC-MS in SIM mode	None	2-200 µg/L	Not available	Not available

Reference	Sample preparation	Sample volume	Quantification method	Environmental sample tested	Calibration range	Detection limit	Minimum reporting limit / limit of quantitation
	with sodium sulfate						
<b>Epstein et al. (1987)</b> <sup>14</sup>	Solid phase extraction on charcoal tube with carbon disulfide and methanol as the elution solvent	4 L	GC-FID	None	0.26-518 mg/L in organic solvents, aqueous concentration not available	<1 µg/L	Not available
<b>Park et al (2005)</b> <sup>15</sup>	Liquid-liquid extraction by methylene chloride and sodium chloride.	10 mL	GC-MS in SIM mode	Drinking water (raw and finished)	1-100 µg/L	0.2 µg/L	Not available
<b>Park et al (2005)</b> <sup>15</sup>	Heated purge – trap for 11 min at 40 °C	5 mL	GC-MS in SIM mode	Drinking water (raw and finished)	25–500 µg/L	25 µg/L	Not available
<b>Park et al (2005)</b> <sup>15</sup>	Solid phase extraction on activated carbon cartridge with acetone as the elution solvent	200 mL	GC-MS in SIM mode	Drinking water (raw and finished)	0.1–50 µg/L	6 µg/L	Not available

Reference	Sample preparation	Sample volume	Quantification method	Environmental sample tested	Calibration range	Detection limit	Minimum reporting limit / limit of quantitation
<b>Draper et al (2000)</b> <sup>16</sup>	Heated purge – trap for 11 min at 30 °C	25 mL	GC–MS in SIM mode	None	10–5000 µg/L	8.6 µg/L	Not available
<b>Draper et al (2000)</b> <sup>16</sup>	Direct aqueous injection	~1 µL	GC–FID	None	2-500 mg/L	2 mg/L	Not available
<b>Draper et al (2000)</b> <sup>16</sup>	Continuous liquid–liquid extraction with dichloromethane	1 L	GC–MS with ion trap	Surface water, groundwater, tap water	Multiple calibration ranges	0.2-3.1 µg/L, depending on analytical methods	Not available
<b>*: Method 8270 does not list 1,4-dioxane as a analyte, but is often used to quantify 1,4-dioxane.</b>							