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January 25, 2016

To: Jay Zimmerman, Division of Water Resources Director

Through: Cyndi Karoly, Water Sciences Section Chief *CBK*

From: Carrie Ruhlman, Monitoring Coalition Coordinator *CR*  
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RE: DWR Results from a 1-year Study on 1,4-Dioxane in the Cape Fear River Basin

Attached please find the final report for the Division of Water Resources' initial 1-year study on 1,4-Dioxane in the Cape Fear River basin. Data contained in this report were collected from October 2014 through September 2015. Please contact Carrie Ruhlman (919-743-8411 or [carrie.ruhlman@ncdenr.gov](mailto:carrie.ruhlman@ncdenr.gov)) with any questions.

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# 1,4-Dioxane in the Cape Fear River Basin of North Carolina: An Initial Screening and Source Identification Study



## *Department of Environmental Quality*

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For more information on the Ambient Monitoring System and electronic copies of this publication:

<http://portal.ncdenr.org/web/wq/ess/eco/ams>

**North Carolina Department of Environmental Quality  
Water Sciences Section Mission Statement:**

The mission of the Water Sciences Section is to provide the Division with accurate information pertaining to waters of the state. Excellent service along with water quality monitoring and certification programs and analytical laboratory analyses that provide scientifically defensible data are the section's main avenues for accomplishing this mission. These activities support the management and protection of North Carolina's water resources for the health and welfare of the citizens of North Carolina and the economic well-being of the state.

## Abstract

1,4-dioxane is an emerging contaminant of concern that is being monitored in drinking water throughout the United States as part of the US Environmental Protection Agency's Third Unregulated Contaminant Monitoring Rule. In September 2015, the North Carolina Division of Water Resources completed the first year of a study designed to examine ambient concentrations and identify potential sources of 1,4-dioxane in major surface waters of the Cape Fear River basin.

Results of the 1-year study indicated four primary areas of elevated 1,4-dioxane in the upper portion of the Cape Fear River basin. Three of these "hot spots" are located immediately downstream of domestic wastewater treatment facilities, indicating that these facilities are conduits for 1,4-dioxane from domestic and industrial sources, into surface water. The fourth is located along a smaller stream, and potential local sources will be explored during the next phase of the Division's study. Because 1,4-dioxane is difficult to treat and remove, options for abatement and remediation of existing 1,4-dioxane inputs will also be explored in the next phase of the study.

## Keywords

1,4-Dioxane; Dioxane; Drinking water; Surface water; Wastewater; Cape Fear River basin; Unregulated Contaminant Monitoring Rule; UCMR3

## Introduction

1,4-Dioxane (C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>, CAS # 123-91-1) is a clear liquid with a faint, pleasant odor, that is highly miscible in water (ATSDR, 2012). It is a probable human carcinogen with drinking water advisory levels in place in several countries, including the United States (Mohr, 2010; Stepien, *et al.*, 2014). Though the U.S. Environmental Protection Agency (U.S. EPA) does not have an established maximum contaminant level for 1,4-dioxane in drinking water, they have established a drinking water health advisory with an associated, estimated lifetime cancer risk of one in one million at a concentration of 0.35 µg/L (U.S. EPA, 2012). North Carolina has a calculated human health criteria for 1,4-dioxane of 0.35 µg/L in water supplies and 80 µg/L in all other waterbodies (15A NCAC 02B.0208).

1,4-dioxane has historically been used as a solvent stabilizer, but is currently used for a wide variety of industrial and manufacturing purposes. 1,4-dioxane can be found in industrial solvents, paint strippers and varnishes and is often produced as a by-product of chemical processes to manufacture soaps, plastics and other consumer products (Stepien, *et al.*, 2014; U.S. EPA, 2015; Water Research Foundation, 2014).

Due to its physiochemical properties, 1,4-dioxane has a high mobility and is interminable in the environment. As a water quality contaminant, its persistence is due to an “indefinite solubility in water” (Stepien, *et al.*, 2014). Conventional drinking water treatment mechanisms have been found to be ineffective at removing 1,4-dioxane from source water. However, it can be removed via advanced oxidation processes applying a combination of hydrogen peroxide and other factors (Stepien, *et al.*, 2014; Water Research Foundation, 2014).

As part of the Third Unregulated Contaminant Monitoring Regulation (UCMR3), the U.S. EPA requires public water systems to monitor a list of up to 30 unregulated contaminants in finished drinking water every five years. The data collected from this monitoring exercise are one of the primary sources of occurrence and exposure data that the U.S. EPA uses to determine regulations on these contaminants (UCMR3, 2012). 1,4-dioxane was included in the list of over 20 chemicals to be sampled, using specific analytical methods, at all water utility systems serving more than 10,000 or 100,000 people, during a 12-month period from January 2013 through December 2015. These chemicals, as well as two viruses, were also collected at a number of smaller public water systems (U.S. EPA, 2013).

The waters of the Cape Fear River basin supply drinking water to many counties in the state. According to UCMR3 data, this basin also exhibits some of the highest concentrations of 1,4-dioxane in finished drinking water. Therefore, it was chosen for the first 1,4-dioxane study by the North Carolina Division of Water Resources, with an initial objective of screening for ambient 1,4-dioxane concentrations in surface waters of the upper and middle Cape Fear River basin of North Carolina during all seasons. As the study progressed and areas with consistently elevated 1,4-dioxane were recognized (hereafter referred to as “hot spots”), the study developed a secondary objective of source identification.

## Methods

### Timeframe and Study Area

The original screening study included monthly sampling for one year (October 2014 – September 2015) at twelve stations throughout the Cape Fear River basin to capture seasonal and spatial variability in constituent concentrations and flow. In June of 2015, after which time sufficient data were available to

recognize distinct areas where 1,4-dioxane concentrations were elevated, source identification became a study objective. Seven monitoring stations were added to the monthly monitoring schedule at this point to evaluate these hot spots, and the study timeframe was extended for an additional year. Station information and location details can be found in Appendix A.

In September 2015, the first full year of sampling was completed. Monitoring locations were adjusted and frequency of monitoring was reduced to quarterly for the remainder of the study (October 2015 – May 2016), with objectives to further identify sources and spatial patterns of 1,4-dioxane, as well as to document surface water impacts of remediation and abatement efforts of those sources in the basin.

### Field Sampling and Procedure

Sampling was conducted according to methods described in North Carolina's Ambient Monitoring System (AMS) Quality Assurance Project Plan (QAPP) (NCDENR, 2014, Section B.2 and Appendices 7 and 8) and instructions provided by the contract laboratory for 1,4-dioxane sample collection and preservation. All samples were collected as near-surface (i.e. 0.1 meter depth) grab samples.

One sample was collected monthly for the analysis of 1,4-dioxane at each site. An additional sample was also collected at each site for NC State University. Quality assurance samples, including duplicates, matrix spikes and matrix spike duplicates, were collected quarterly at each of the stations on a rotating basis, and in accordance with the AMS QAPP (NCDENR, 2014).

During each sampling event, a multi-parameter meter (e.g. YSI Pro Plus with Quatro cable or similar) was used *in situ* to measure instantaneous water temperature, pH, specific conductance and dissolved oxygen values.

### Laboratory Procedure and Quality Control

Method SW-846 8270 SIM (selected ion monitoring) was used to evaluate the presence of 1,4-dioxane, with a practical quantitation limit (PQL) of 3 µg/L. Due to the absence of an approved method for surface water or wastewater-specific 1,4-dioxane sampling, the solid waste method was chosen to account for interferences that may exist in stream samples.

Quality control samples included duplicates, matrix spikes and matrix spike duplicates. Duplicates were analyzed to evaluate reproducibility of results. Matrix spikes were analyzed to evaluate surface waters receiving different types of inputs, including domestic wastewater effluent, dam release, urban stormwater and swamp waters, in which the potential for various types of interferences existed. Matrix spike duplicates were analyzed to evaluate reproducibility of spiked samples. Quality control samples were collected on a quarterly basis at rotating sites, including four stations in the original study and three stations in the source identification study per quarter.

### Data Analysis

Data analysis was performed only on DWR sample results to determine ambient concentrations of 1,4-dioxane in surface waters throughout the Cape Fear River basin, to compare results with calculated evaluation levels and to identify hot spots that may be contributing to the exceedance of evaluation levels throughout the basin.

Additionally, where available, stream flow data from United States Geological Society (USGS) gages at or near sampling stations were downloaded as an explanatory variable. Surface discharge appears to be inversely related to 1,4-dioxane concentration in some cases.

Monthly results were analyzed to determine the mean, median, max and min. These results were then plotted on an interactive online map (<http://arcg.is/1dJa1Nq>), to identify potential areas of concern. The map was used to identify hot spots and possible sources of 1,4-dioxane, including:

- Domestic and industrial point-source discharges;
- Active and inactive hazardous waste facilities;
- Active and inactive landfills;
- Pre-regulatory landfills;
- Known 1,4-dioxane contaminated groundwater plumes;
- Wastewater outfalls from groundwater remediation sites;
- Permitted non-discharge facilities;
- Airports;
- Brownfields; and
- Manufactured gas plants.

## Results

Overall, four hot spots were identified from data collected between October 2014 and September 2015. These areas had maximum ambient 1,4-dioxane concentrations ranging from 171 µg/L to 1030 µg/L, mean concentrations of 42.6 µg/L to 350.5 µg/L, and may be contributing to downstream exceedances of the calculated criteria.

Three of the four hot spots are located downstream of domestic wastewater treatment facilities (WWTF), and one is downstream of an inactive textile manufacturing site. Summarized results for all stations can be found in Appendix B.

## Geographic Distribution of 1,4-Dioxane

While results in excess of the calculated criteria were observed throughout the Haw, Deep and Cape Fear Rivers, there is reason to believe that the major sources of 1,4-dioxane are originating in the upper watersheds of the Haw and Deep Rivers, as this is where the highest concentrations were observed (Appendix C).

## Discussion

Seven of the 19 monitored locations routinely returned results at or below method detection limits (MDLs), indicating that the background concentration of 1,4-dioxane is below 3 µg/L. The highest measured concentrations were observed below WWTFs, suggesting that the most significant contributions to ambient surface water concentrations were coming from wastewater effluent originating from sources upstream, since 1,4 dioxane is not used in or created by wastewater treatment process. Thus, it is likely that 1,4 dioxane is being discharged into industrial waste streams and passing through WWTF treatment processes with varying levels of removal efficiency prior to entering surface waters.

It has been found that certain industrial processes are more likely to utilize or create 1,4-dioxane as a by-product, such as esterification and subsequent polycondensation used to create polyethylene terephthalate (PET) plastics (Popoola, 1991) or the synthesis of those plastics in the manufacturing of polyesters (Zenker, *et al.*, 2003). Therefore, WWTFs with such industries discharging to their collection system may expect to see greater loading of this contaminant in both their influent and effluent streams.

As 1,4-dioxane is an emerging contaminant of concern, municipal water and wastewater treatment facilities are generally not equipped to remove it through their treatment processes. Due to the high aqueous solubility and resistance of 1,4-dioxane to biodegradation, conventional treatment processes are generally ineffective at removal (Zenker, *et al.*, 2003). Installation and operation of advanced treatment processes, such as those using hydrogen peroxide, ozone and/or ultra-violet photo-oxidation, all known to be effective for 1,4-dioxane removal at either WWTFs or drinking water systems, are anticipated to be prohibitively expensive for local governments and the citizens served by public utilities (*Ibid*). Therefore, the most prudent approaches to reducing 1,4-dioxane concentrations in surface water and drinking water are likely to be reduction, elimination and/or capture and treatment at industrial sources using or generating 1,4-dioxane if possible.

## Management Implications and Future Actions

Successful abatement of 1,4-dioxane in Cape Fear River basin drinking water sources will require partnerships between the Division, municipal utility departments and industries within the basin. Further research into options for replacement of 1,4-dioxane-containing compounds in industrial processes, as well as capture and treatment technologies that could be implemented in industrial and domestic wastewater treatment systems, is warranted. Such research has already begun locally through studies funded by the National Science Foundation, Water Resources Research Institute and Urban Water Consortium.

The DWR will continue to monitor 1,4-dioxane concentrations at selected locations within the Cape Fear River basin through May of 2016, with the objectives of further understanding fluctuations in concentrations, identifying sources and documenting in-stream responses to source abatement efforts. As funding becomes available, the study should also be expanded into the Neuse and Yadkin River basins, in areas that have returned UCMR results for 1,4-dioxane above the calculated human health criteria for water supply waterbodies.

## Acknowledgements

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*All hyperlinks accessible as of January 7, 2016.*

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**APPENDIX A**  
**DWR Monitoring Station Locations**

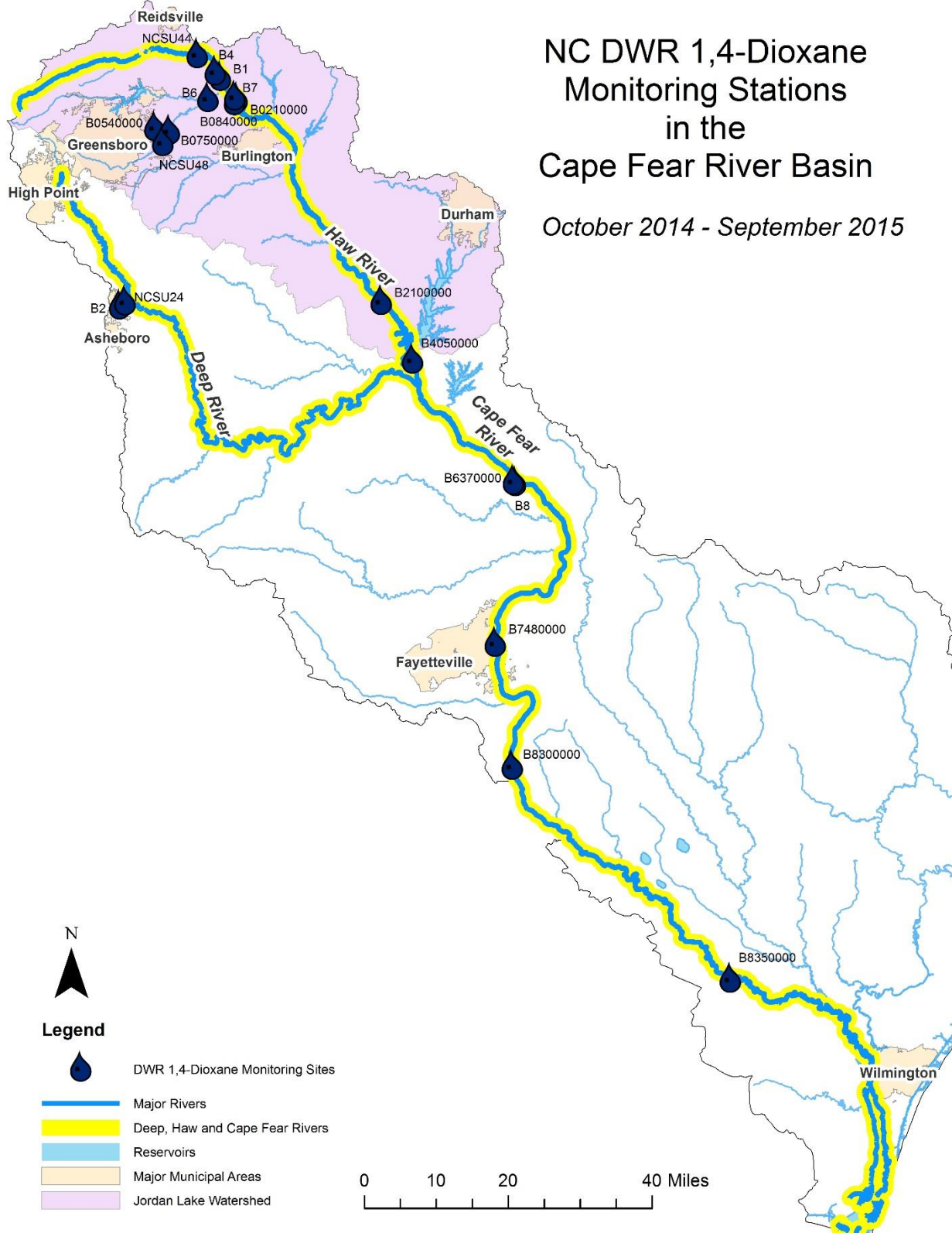
STATION ID	STATION LOCATION	COUNTY	LATITUDE	LONGITUDE	NC STREAM CLASS <sup>1</sup>	Monitoring Dates
NCSU44	Haw River at NC 150 near Reidsville	Rockingham	36.2673	-79.6037	WS-IV NSW	Jun 2015 - Sept 2015
B4	Haw River at Troxler Mill Road near Reidsville	Rockingham	36.2329	-79.5588	WS-IV NSW	Jun 2015 - May 2016
B1	Haw River at SR 1712 (Brooks Bridge Road)	Guilford	36.2219	-79.5456	WS-V NSW	Oct 2014 - May 2016
B7	Haw River at NC 87	Alamance	36.1826	-79.5101	WS-V NSW	Jun 2015 - May 2015
B0210000	Haw River at SR 1561 Hub Mill Road	Alamance	36.1786	-79.5042	WS-V NSW	Oct 2014 - May 2016
B0540000	North Buffalo Creek at SR 2832 near Greensboro	Guilford	36.1199	-79.7082	WS-V NSW	Oct 2014 - Sept 2015
NCSU48	South Buffalo Creek at Richardson Village Way at McLeansville	Guilford	36.0896	-79.6880	WS-V NSW	Jun 2015 - Sept 2015
B0750000	South Buffalo Creek at SR 2821 at McLeansville	Guilford	36.1128	-79.6718	WS-V NSW	Oct 2014 - May 2016
B6	Reedy Fork at NC-61 near Ossipee	Guilford	36.1792	-79.5763	WS-V NSW	Jun 2015 - May 2016
B0840000	Reedy Fork at NC-87 at Ossipee	Alamance	36.1730	-79.5103	WS-V NSW	Oct 2014 - May 2016
NCSU24	Haskett Creek at WOW Road near Asheboro	Randolph	35.7681	-79.7790	C	Jun 2015 - May 2016
B2	Haskett Creek at Hub Morris Road near Asheboro	Randolph	35.7599	-79.7919	C	Jun 2015 - Sept 2015
B2100000	Haw River at SR 1713 near Bynum (near Pittsboro intake)	Chatham	35.7717	-79.1450	WS-IV NSW	Oct 2014 - May 2016
B4050000	Haw River below Jordan Lake Dam near Moncure	Chatham	35.6534	-79.0673	WS-IV	Oct 2014 - Sept 2015
B6370000	Cape Fear River at US-401 at Lillington	Harnett	35.4065	-78.8135	WS-IV	Oct 2014 - May 2016
B7480000	Cape Fear River at Hoffer WTP intake at Fayetteville	Cumberland	35.0825	-78.8638	WS-IV CA	Oct 2014 - May 2016
B8	Cape Fear River at Harnett County Public Utilities intake	Harnett	35.4092	-78.8189	WS-IV CA	Oct 2014 - May 2016
B8300000	Cape Fear River at William O. Huske Lock near Tar Heel	Bladen	34.8349	-78.8226	WS-IV	Oct 2014 - Sept 2015
B8350000	Cape Fear River at Lock 1 near Kelly	Bladen	34.4038	-78.2932	WS-IV Sw	Oct 2014 - May 2016

<sup>1</sup>NC Stream classifications at study locations included Water Supplies (WS-IV and WS-V) and Critical Areas (CA) near drinking water intakes, Nutrient Sensitive Waters (NSW), waters protected for aquatic life and secondary recreation (C) and Swamp waters (Sw).

# APPENDIX A DWR Monitoring Station Locations

## NC DWR 1,4-Dioxane Monitoring Stations in the Cape Fear River Basin

*October 2014 - September 2015*



## APPENDIX B

### 1,4-Dioxane Results Summary

Station	Location	Stream Class	Eval Level (µg/L)	# of Results	1,4-Dioxane (µg/L)				Load (lbs/day)
					Min	Median	Max	Mean	Median
<b>Haw River above Reedy Fork</b>									
NCSU44	Haw River at NC 150 near Reidsville	WS-IV NSW	0.35	5	<3	<3	<3	<3	
B4	Haw River at Troxler Mill Rd near Reidsville	WS-IV NSW	0.35	4	35	169	1030	351	
B1	Haw River at SR 1712 (Brooks Bridge Rd)	WS-V NSW	80	13	3	33	149	46	
B7	Haw River at NC 87	WS-V NSW	80	4	12	23	51	27	
B0210000	Haw River at SR 1561 Hub Mill Rd.	WS-V NSW	80	13	3	38	100	42	
<b>Buffalo Creek and Reedy Fork</b>									
B0540000	North Buffalo Creek at SR 2832 near Greensboro	WS-V NSW	80	12	<3	<3	<3	<3	0.4
NCSU48	S. Buffalo Creek at Richardson Village Way	WS-V NSW	80	4	<3	<3	<3	<3	
B0750000	South Buffalo Creek at SR 2821 Harvest Rd at McLeansville	WS-V NSW	80	15	9	25	543	80	
B6	Reedy Fork at NC 61 near Ossipee	WS-V NSW	80	4	11	20	45	24	
B0840000	Reedy Fork at NC-87 at Ossipee	WS-V NSW	80	13	7	45	100	43	
<b>Hasketts Creek</b>									
B2	Hasketts Creek at Hub Morris Rd near Asheboro	C	80	4	<3	<3	<3	<3	
NCSU24	Hasketts Creek at W.O.W. Rd.	C	80	4	147	269	478	291	
<b>Haw River below Reedy Fork</b>									
B2100000	Haw River at SR 1713 near Bynum (near Pittsboro intake)	WS-IV NSW	0.35	13	<3	13	66	18	32
B4050000	Haw River below Jordan Dam near Moncure	WS-IV	0.35	13	3	7	25	9	
<b>Cape Fear River</b>									
B8	Cape Fear River at Harnett County Public Utilities intake	WS-IV CA	0.35	13	<3	5	15	6	24
B6370000	Cape Fear River at US-401 at Lillington	WS-IV	0.35	15	<3	4	15	6	24
B7480000	Cape Fear River at Hoffer WTP intake at Fayetteville	WS-IV CA	0.35	12	<3	3	11	4	
B8300000	Cape Fear River at William O. Huske Lock near Tar Heel	WS-IV	0.35	12	<3	3	11	4	36
B8350000	Cape Fear River at Lock 1 near Kelly	WS-IV Sw	0.35	14	<3	3	6	4	32

<sup>1</sup> The evaluation level for 1,4-dioxane is based on stream classification. The water supply EL is 0.35 µg/L, except WS-V in the Jordan Lake watershed. The EL for Jordan Lake WS-V and all other waters is 80 µg/L.

<sup>2</sup> The number of results corresponds to period of sampling. Most stations were sampled monthly from October 2014-September 2015 (n=12-15); additional stations were sampled by DWR monthly from June 2015-September 2015 (n=4-5).

<sup>3</sup> Concentration values may be inflated for stations with results below the contract lab PQL of 3 µg/L. Non-detect results were set equal to the PQL for this summary.

<sup>4</sup> Loads were calculated only at stations collocated with a USGS stream flow gage, and may also be inflated at stations with non-detect results.

# APPENDIX C

## Mean 1,4-Dioxane Concentrations

