The impact of iodinated contrast media in hospital wastewater on drinking water quality in North Carolina

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ABSTRACT

Iodinated trihalomethanes (iodo-THMs) are an unregulated class of disinfection byproduct (DBP) of increasing public health concern due to their elevated toxicity in comparison to regulated THMs, even at their lower occurrence concentrations. Iodinated contrast media (ICM), specifically iohexol because of its prevalence in North Carolina, are a major source of iodine in surface waters that receive wastewater effluent due to their biological inactivity and persistence through wastewater treatment. Many of these waters feed downstream drinking water treatment plants (DWTPs). This study investigated whether the presence of iohexol in drinking water sources can lead to the formation of iodo-THMs in disinfected drinking water impacted by upstream medical waste discharges by determining the conditions under which iohexol releases iodine to form iodo-THMs and applying equivalent conditions to natural waters and DWTP samples. Using tryptophan as a surrogate for natural organic matter (NOM) in surface waters, reactions with chlorine in the presence and absence of up to 5 mg/L iohexol formed only chloroform, while similar reactions involving monochloramine yielded no detectable THMs. Samples collected from four points in a DWTP were characterized and confirmed the presence of tryptophan-like NOM, associated with wastewater effluent, in each sample. Subsequent reactions of source water, post-powdered activated carbon (PAC), and post-ozonation samples with chlorine and monochloramine (target disinfectant residual of 3 mg/L as Cl_2) in the presence and absence of 5 mg/L iohexol were evaluated to determine iodo-THM formation. Chlorination of samples showed formation of chloroform, bromodichloromethane, and dibromochloromethane, as well as two iodo-THMs, dichloroiodomethane and bromodiiodomethane, regardless of iohexol addition, while chlorodiiodomethane formed only after chlorination of source water in the presence of the iohexol. Chlorination of post-ozonation samples produced less iodo-THM formation compared to chlorination of source water and post-PAC samples. Though iodine was already present in sampled waters, chloramination yielded no quantifiable iodo-THMs even after iohexol addition, but yielded chloroform in reactions with source water, though at much lower concentrations than with equivalent disinfectant residuals after chlorination. These findings suggest that the combination of ozonation and monochloramine disinfection can decrease formation of iodo-THMs in drinking water; however, significant reduction of iodine-containing precursors in surface drinking water sources may only be possible with regulations on medical waste discharge into sewage systems, or with substitution of ICM alternatives that do not contain DBP precursors.

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INTRODUCTION

Conventional drinking water treatment

Since the implementation of drinking water treatment systems in the United States during the early twentieth century, rates of waterborne diseases such as typhoid fever and cholera, caused by microbial contaminants, have dropped dramatically. Most modern treatment includes a combination of coagulation and flocculation, sedimentation, filtration, and disinfection processes in order to treat surface or groundwater before distribution of drinking water to consumers. Figure 1 shows a schematic of these processes during conventional treatment. After the source water is pumped to a treatment facility, coagulation and flocculation processes are used to allow larger particles to clump together and settle. The water is then disinfected with chlorine and passed through a filter to remove smaller particles, after which ammonia is added and reacts with residual chlorine to form chloramines and continue disinfection. Finished water moves through a clearwell for contact with the disinfectant, after which fluoride is added to promote dental health, and corrosion inhibitors protect pipes in the distribution system. Water is then distributed in response to demand by consumers.

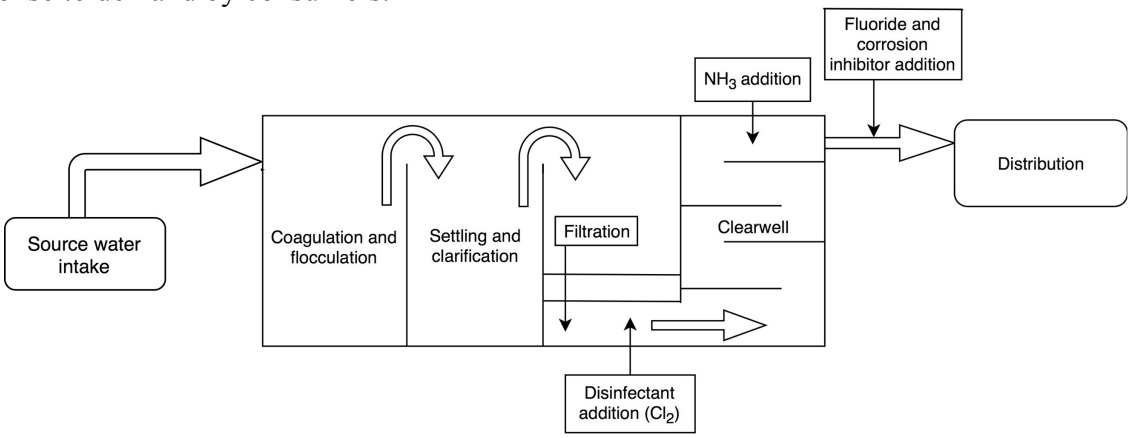

Figure 1. Schematic of a conventional drinking water treatment plant (DWTP), from the source water intake to the distribution system.

Disinfection is arguably the most important step in drinking water treatment in terms of protecting human health because of its ability to kill or deactivate pathogens that naturally occur in drinking water sources. The United States Environmental Protection Agency (U.S. EPA) established the Surface Water Treatment Rule (SWTR) in 1989, which requires public water systems to remove at least 99.9% of *Giardia lamblia* cysts, at least 99.99% of viruses, and at least 99% of *Cryptosporidium* during drinking water treatment from surface and groundwater sources (U.S. EPA, 2004). These criteria were established to protect against pathogens known to cause adverse human health effects.

Common disinfectants are chlorinated oxidants, such as chlorine or monochloramine, that kill or inactivate bacteria upon contact, and disinfectant residuals are maintained throughout the distribution system to continue pathogen control as water travels to consumers. Ammonia is often added in the clearwell to convert residual chlorine into chloramines, which provide a stable residual and produce lower levels of disinfection byproducts (DBPs) than free chlorine (Bichsel & von Gunten, 1999). Maximum residual disinfectant levels (MRDLs) were established by the U.S. EPA in 1996 in order to maintain appropriate microbial removal while also limiting disinfectant exposure and DBP formation. For both chlorine and monochloramine, MRDLs are

4.0 mg/L as Cl_2, and treatment plant compliance with this rule is based on running annual averages (USEPA, 2001).

Constituents of surface waters

Natural organic matter (NOM)

NOM exists in all surface drinking water sources and is a natural DBP precursor, though its properties can vary greatly depending on the water source. For example, changes in NOM concentrations in surface waters occur after heavy rainfall or runoff events. Humic substances, which include the organic compounds found in soil and sediment, constitute the majority of organic matter in natural waters – on average, up to 80% of the total dissolved organic carbon (DOC) (Boggs et al., 1985; Reuter & Perdue, 1977). DOC concentrations vary from less than 1 to greater than 50 mg/L as C in natural waters (Thurman, 1985). Amino acids are a subset of natural DOC and comprise a significant component – up to 13% – with concentrations generally varying from 100 to 500 μg/L in river water (Thurman, 1985). Due to amino acid prevalence, tryptophan has been used as a surrogate for nitrogen-containing NOM, which is associated with wastewater, in studies investigating DBP formation following disinfection of water (Owusu-Yaw, 1989; Li et al., 2019). The structure of tryptophan is shown in Figure 2 below.

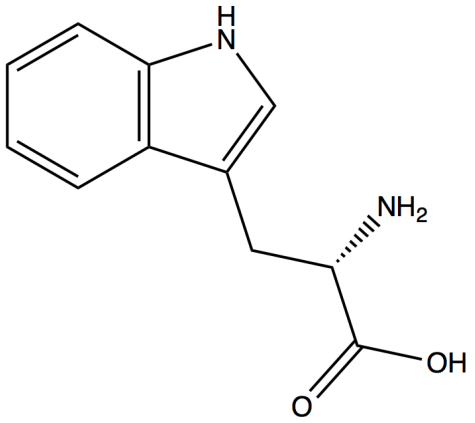

Figure 2. Chemical structure of tryptophan.

Though no currently regulated DBPs contain nitrogen, those that do, such as halonitromethanes, have been shown to be cytotoxic and genotoxic to mammalian cells and may threaten public health (Plewa et al., 2004a).

Pharmaceutical compounds in wastewater effluent

Pharmaceutical waste persistence through wastewater treatment

DBP precursors include not only NOM but also those from anthropogenic sources: for example, pharmaceutical compounds that persist through wastewater treatment. Wastewater treatment generally involves physical and biological processes to remove contaminants from sewage, but there is often incomplete removal, so contaminants may persist through treatment and be discharged into the environment. This contaminated wastewater may be reused by DWTPs that intake downstream from the same water source to which wastewater treatment plants discharge (Krasner et al., 2009). Figure 3 below shows a schematic of the linkage between medical waste, wastewater discharge and DWTP intake.

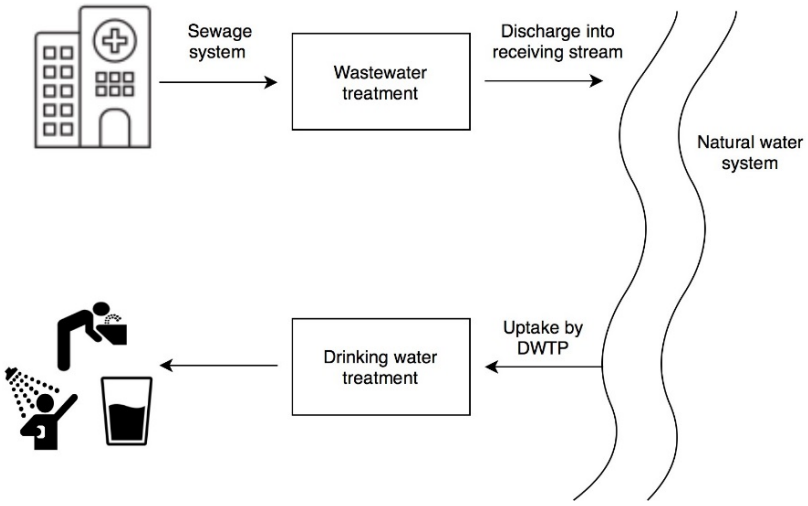

Figure 3. Schematic showing how anthropogenic chemicals can reach drinking water.

The presence of large molecular weight compounds in pharmaceutical waste adds a contaminant load that conventional wastewater treatment was not designed to remediate. Most pharmaceuticals are biologically active and might, therefore, be at least partially removed during biological treatment processes; however, iodinated X-ray contrast media are an example of a high molecular weight pharmaceutical agent used in medical imaging that are not biologically active and persist to a large extent through wastewater treatment (Hollender et al., 2009). These large, complex molecules take time to break down, so other carbon sources in wastewater are more efficiently broken down as a microbial food source during wastewater treatment.

Pharmaceutical waste regulations

The Clean Water Act (CWA), amended in 1972, was established by the U.S. EPA to protect water quality from point-source pollutants; however, the CWA allows those with National Pollutant Discharge Elimination System (NPDES) permits to discharge waste into waters of the United States (USEPA, 2002). Point sources are defined broadly as any discernible, confined conveyance or vessel from which pollutants are discharged, and waters of the United States refer to navigable waters, their tributaries, and oceans out to 200 miles (USEPA, 2002). NPDES permits specify acceptable pollution levels in discharge, and the permit holder must employ technologies to reduce pollution in their discharge in order to achieve these levels. Because hospitals and other medical facilities discharge waste into municipal sewer systems, they are not required to hold NPDES permits, so it is, therefore, left to the wastewater treatment facility to treat medical wastewater before discharge into a natural water system. This lack of regulation on medical wastewater paired with increasing pharmaceutical use leads to an increased pharmaceutical load in surface waters that cannot be remediated by conventional wastewater treatment. Moreover, the administration of diagnostic imaging chemicals to out-patients leads to a dispersion of these, mostly unmetabolized, materials into domestic sewage.

Iodine

Natural iodine sources

Formation of iodinated DBPs (iodo-DBPs) requires the presence of an iodine source in the water during disinfection. Iodine occurs naturally in many surface waters, though iodide and iodate are its only stable inorganic forms (Moran et al., 2002). Typical iodine concentrations in river water are about 5 μg/L (Moran et al., 2002), but concentrations above 50 μg/L can be found in some surface waters due to saltwater intrusion or the presence of particular rock formations (Weinberg et al., 2011). The main natural sources of iodine include oceanic iodine delivered atmospherically, iodine weathered from rocks, and iodine resulting from plant decomposition (Moran et al., 2002).

Anthropogenic iodine sources

Rivers located in areas with large amounts of water used for irrigation reported iodine concentrations greater than 30 μg/L, which could be due to agricultural techniques that disturb iodine present in rocks and soil (Moran et al., 2002). Iodine may also be introduced into the environment due to its presence in fertilizers, herbicides, and pesticides, as well as during nuclear fuel processing (Moran et al., 2002).

Another major anthropogenic source of iodine in surface waters is iodinated contrast media (ICM) from medical wastewater. ICM are common pharmaceuticals of large molecular weight used to improve soft tissue imaging, such as during computed tomography (CT) scans or magnetic resonance imaging (MRI). Table 1 below shows typical dosage concentrations of ICM in comparison to other pharmaceuticals. Iohexol, whose structure is shown in Figure 4, is one ICM commonly used in North Carolina that has previously been measured in surface waters (Duirk et al., 2011; Wendel et al., 2014). It has a total mass of 821.1 g/mol of which 46% is iodine.

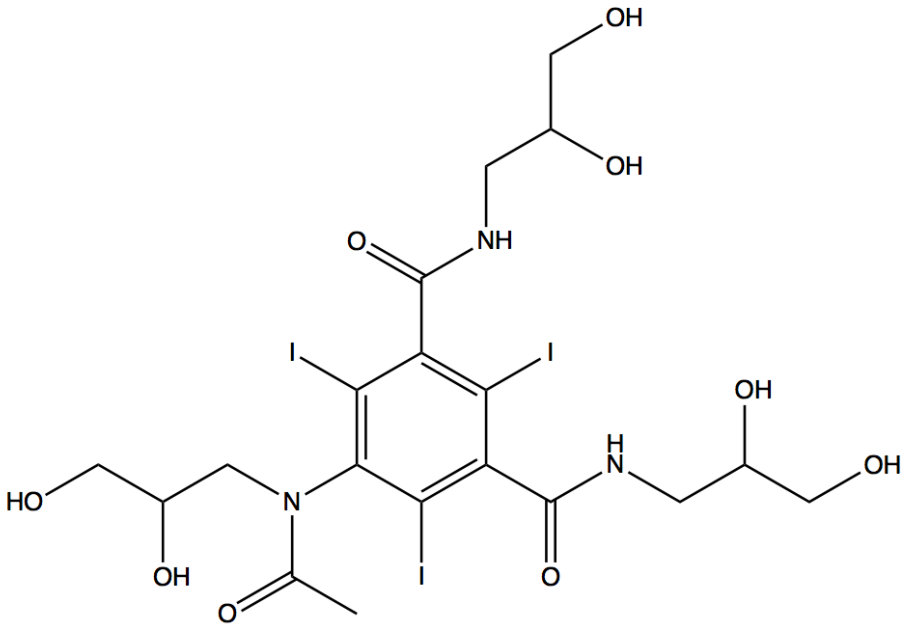

Figure 4. Chemical structure of iohexol.

Table 1. Common intravenous drugs and their maximum dosage.

Pharmaceutical compound	Maximum dose	Equivalent dose in average adult male	Reference
Iohexol (ICM)	250 mL (no absolute maximum dose)	75,000 mg	Medscape (2019)
Doxorubicin (chemotherapy)	50 mg/m^2	100 mg	Cheesman & Shields (2016)
Morphine	10 mg	10 mg	PAMI (2016)
Vancomycin	500 mg	500 mg	Medscape (2019)

ICM are dosed in extremely large concentrations and are designed to pass through the body without biotransformation; however, these properties also allow them to persist through wastewater treatment intact. Once discharged into surface waters, however, there is evidence that these agents break down as well as during oxidation once they enter DWTPs and release iodine, which reacts with disinfectants in the presence of NOM to produce toxic iodo-DBPs (Duirk et al., 2011; Kormos et al. 2011). There are no regulations currently in place to prevent these ICM from entering the wastewater system, so they constitute a significant anthropogenic iodine load in surface waters that receive treated effluent from municipal wastewater.

Bromine

Natural bromine sources

Bromine occurs naturally in both seawater and fresh water, with fresh water concentrations ranging from trace amounts to about 0.5 mg/L (Al-Mutaz, 2000). Common forms of bromine in surface waters include its presence in soluble salts as bromide, hydrobromic acid, hypobromous acid, bromous and bromic oxyacids (Cotton & Wilkinson, 1962). Elevated bromide concentrations in surface waters may be due to bromine leaching from NOM in soil (Yuita et al., 1982).

Anthropogenic bromine sources

Major anthropogenic factors contributing to the presence of bromine in surface waters are the presence of wastewater, sewage system leaks, and pesticide use (Winid, 2015). Agricultural activities and the use of pesticides containing bromine are associated with increased bromine concentrations in surface waters (Shomar, 2006). Landfill leachate and surface waters near landfills have also been shown to have elevated bromine concentrations of up to 160 mg/L, though this occurs mainly in urban areas where landfill leachate can penetrate drinking water sources (Milosevic et al., 2012).

Disinfection byproducts

Regulated disinfection byproducts

Hundreds of cytotoxic and genotoxic DBPs have been identified, though only eleven which were identified first are currently regulated in the United States (USEPA, 2001). Current regulations are set to limit concentrations of four trihalomethanes (THMs), five haloacetic acids (HAAs), chlorite, and bromate in drinking water distributed to community and non-transient non-community water systems. The four regulated THMs (THM4) are chloroform, bromodichloromethane, dibromochloromethane, and bromoform, with a total maximum contaminant level (MCL) of 0.080 mg/L in aggregate (USEPA, 2001). This regulation is enforced as a running annual average of total THMs and does not take into account the

individual toxicities of each compound. Previous studies have indicated an increased risk of bladder and colon cancers following THM exposure (Cantor et al., 1985; McGeehin et al., 1993; Black et al., 1996), as well as possible developmental and reproductive problems (Kramer et al., 1992; Bove et al., 1995). Exposure occurs not only when water is used for drinking purposes, but also during cooking, bathing, cleaning, and other daily activities that involve potable water use. THMs constitute a significant portion of total DBPs and are used as indicators for all potentially harmful compounds that form from the addition of chlorine to natural waters (CDC, 2016).

The 5 HAAs, monochloroacetic acid, dichoroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid, are also regulated as a running annual average with an MCL of 0.060 mg/L as total HAAs (USEPA, 2001). Bromate is regulated in DWTPs that use ozone as a disinfectant with an MCL of 0.010 mg/L, and chlorite is regulated in DWTPs that use chlorine dioxide as a disinfectant with an MCL of 1.0 mg/L (USEPA, 2001).

Iodinated disinfection byproducts

Iodo-DBPs are not currently regulated; however, they have been shown to have higher geno- and cytotoxicity compared to regulated DBPs, even at their lower occurrence concentrations (Plewa et al., 2004b; Richardson et al., 2008). Iodo-DBPs are most likely to form during chloramine disinfection, and to a lesser extent by chlorine and then ozone disinfection (Bichsel & von Gunten, 1999). Figure 5 shows a schematic representation of the formation of iodo-DBPs during chloramination.

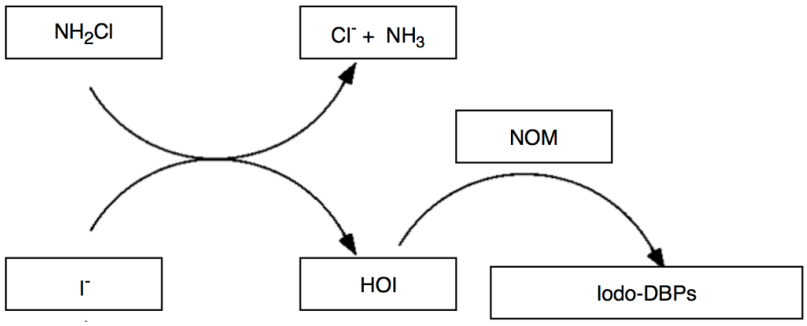

Figure 5. Formation of iodinated disinfection byproducts during chloramination processes (Adapted from Bichsel & von Gunten, 1999).

Iodo-DBP formation is dependent on the presence of both an iodine source and NOM during drinking water treatment. Monochloramine reacts with iodide to form hypoiodous acid, which then reacts with NOM to form iodo-DBPs (Bichsel & von Gunten, 1999).

The use of chloramine as a secondary disinfectant in drinking water has become more widespread in order to reduce the levels of regulated DBPs and decrease their public health impact; however, the risk of iodo-DBP formation in drinking water increases as chloramine use becomes more prevalent (Bichsel & von Gunten, 1999). Both Wendel et al. (2014) and Duirk et al. (2011) showed that reactions of ICM with chlorine in the absence of natural organic matter formed only trace amounts of iodo-DBPs. In reactions of ICM with chlorine in the presence of organic matter, iodate is the major iodine sink, while iodo-DBPs are an iodine sink for reactions with monochloramine (Bichsel & von Gunten, 1999). Because iodo-DBPs are not regulated, the increased use of chloramine could potentially increase drinking water toxicity and threaten human health.

Alternative treatment methods

Additional treatment processes are often used in the treatment of surface waters with compromised quality, such as during algal blooms that produce compounds impacting taste and odor. In addition to chlorine and chloramine, ozone is another commonly used disinfectant that treats taste and odor in drinking water, but all disinfectants can react with precursors in the water to form DBPs. Powdered activated carbon (PAC) and ozone are two alternative treatment methods employed to improve water quality beyond conventional treatment. Figure 6 shows a schematic of one train of alternative treatments incorporated into conventional treatment. After the source water is pumped to this treatment facility, PAC is added to begin removal of NOM and to treat taste and odor. Ozone is then used as a pre-disinfectant to remove color, oxidize organic compounds, and continue taste and odor treatment.

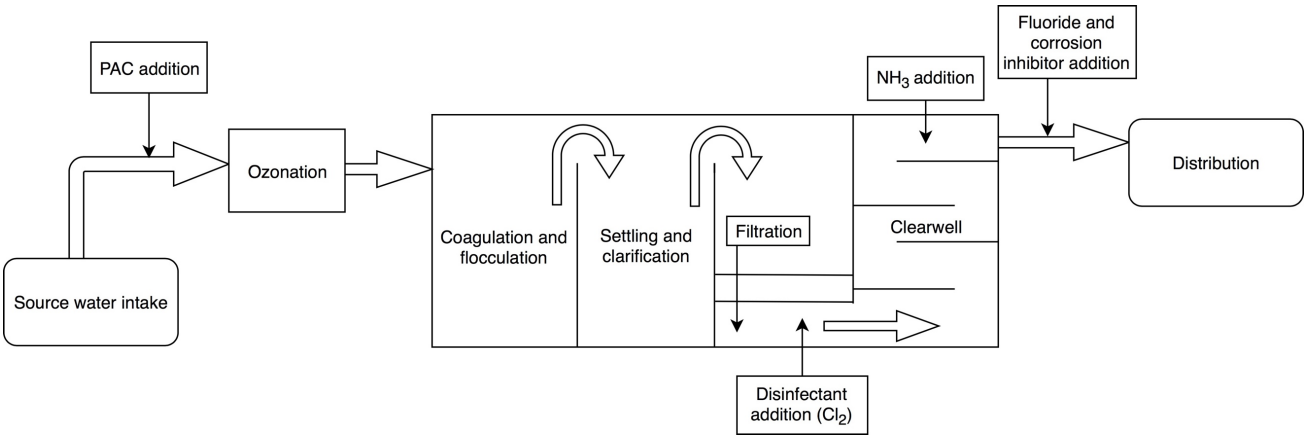

Figure 6. Schematic of a drinking water treatment plant with powdered activated carbon and ozone used prior to conventional treatment.

PAC and ozone have been shown to remove 86% and 90%, respectively, of the total load of analyzed pharmaceuticals from hospital wastewater (Kovalova et al., 2013). In addition to removing pharmaceutical compounds, ozone also acts as a disinfectant, while PAC only provides removal of some micropollutants (Kovalova et al., 2013). These alternative treatment methods can be employed in DWTPs that intake from the same water source to which wastewater treatment plants discharge upstream in order to further remove pharmaceutical contaminants.

Objectives

The lack of regulations on iodo-DBPs in drinking water and medical wastewater discharges, in addition to the increasing use of monochloramine as a disinfectant and increasing use of ICM for medical imaging, lead to an increased iodine load in surface waters that is not easily remediated by wastewater treatment. This study investigates whether the presence of iohexol in drinking water sources can lead to the formation of iodo-THMs, a subset of the total iodo-DBPs, in disinfected drinking water impacted by upstream medical waste discharges by addressing the following objectives:

1) Determine the conditions under which iohexol releases iodine to form iodo-THMs
2) Determine if these conditions are applicable to natural waters and drinking water treatment
3) Propose solutions to limiting iodo-THM formation in drinking water

MATERIALS AND METHODS

Chlorine and monochloramine solutions preparation

The sodium hypochlorite stock solution (Fisher Scientific, Pittsburgh, PA) was standardized prior to each use following Standard Method 4500-Cl B (Franson et al., 1999) in order to determine the free chlorine concentration. A solution of 0.01 N sodium thiosulfate (Fisher Scientific, Pittsburgh, PA) was titrated into a 50-mL Erlenmeyer flask containing 5 mL acetic acid (Fisher Scientific, Pittsburgh, PA), 1 g potassium iodide (Fisher Scientific, Pittsburgh, PA), and 100 µL NaOCl stock until the yellow color almost dissipated. 1 mL of starch indicator solution (Alfa Aesar, Ward Hill, MA) was then added to the flask, creating a blue color, and titration continued until the blue color disappeared. Free chlorine concentration was then calculated using the formula:

$$mg\ Cl\ as \frac{Cl_2}{mL} = \frac{A*N*35.45}{V}$$

where A = volume in mL of titrant used to titrate to endpoint, N = Normality of sodium thiosulfate titrant (0.01 N), and V = volume of NaOCl stock sample (0.1mL).

Monochloramine solutions were prepared by dissolving 0.084 g ammonium sulfate (Fisher Scientific, Pittsburgh, PA) in 50 mL laboratory grade water (LGW) (Dracor Water Systems, Durham, NC, USA), transferring to a 250-mL amber glass bottle with a stir bar and adjusting to pH 8 with 2 M NaOH (Fisher Scientific, Pittsburgh, PA). 1.25 mL of previously standardized NaOCl stock was then added dropwise to the solution slowly while stirring on a magnetic stir plate. Monochloramine (NH_2Cl) and dichloramine ($NHCl_2$) concentrations were determined using a Hewlett-Packard UV-Vis spectrophotometer (Palo Alto, CA) set to analyze at wavelengths of 245 and 295 nm, which correspond with the maximum absorption wavelengths for mono- and dichloramine, respectively. UV outputs were then translated into mono- and dichloramine concentrations using Beer's law:

$$A = \varepsilon Lc$$

where A = absorbance, ε = molar absorptivity (ε_{NH2Cl} = 445 L mol^{-1} cm^{-1} at 245 and 14 L mol^{-1} cm^{-1} at 295 nm, ε_{NHCl2} = 208 L mol^{-1} cm^{-1} at 245 nm and 267 L mol^{-1} cm^{-1} at 295 nm), L = length of path traveled by light (1-cm cuvettes), and c = solution concentration (M)

Chlorine and monochloramine demand tests with tryptophan as surrogate NOM

Preliminary demand tests were conducted using a HACH DR/890 datalogging colorimeter (HACH, Loveland, CO) to identify the correct dose of chlorine and monochloramine disinfectants to react with tryptophan (Acros Organics, New Jersey) and iohexol (Sigma-Aldrich, Darmstadt, Germany) in LGW in order to leave a 24-hour disinfectant residual of 3 mg/L as Cl_2. A 24-hour reaction was chosen as previous research has shown that up to 90% of the reaction demand, though dose dependent, occurs in this timeframe (Warton et al., 2006). A 3 mg/L as Cl_2 residual was targeted for both chlorine and monochloramine because the MRDLs are 4 mg/L as Cl_2, and a 3 mg/L residual reflects a treatment plant target concentration to remain below these values.

In these experiments, tryptophan was at an initial concentration of 15 mg/L to reflect a total organic carbon (TOC) concentration of about 10 mg/L as C, a level that is at the mid to high end in U.S. surface waters (Thurman, 1985). Iohexol was at an initial concentration of 5 mg/L in order to increase THM formation potential above detection limits. Disinfectants were dosed at several concentrations in order to attain the target residual in the selected time frame. Chlorine doses ranged from zero to 65 mg/L as Cl_2 because of the high demand for chlorine by amino acids (Hureiki et al., 1994), while monochloramine doses ranged from zero to only 15 mg/L as Cl_2 because there is less demand for monochloramine than chlorine by organic carbon in the same reaction timeframe (Bichsel & von Gunten, 1999).

Subsequent reactions were performed between monochloramine, tryptophan, and a gradient of iodide doses in order to determine iodo-THM formation from iodide rather than iohexol. These reactions were performed with monochloramine and not chlorine because monochloramine has been shown to form iodo-DBPs from reactions with iodide in the presence of organic matter, while the major iodine sink for similar reactions with chlorine is iodate (Bichsel & von Gunten, 1999). An iodide stock solution was prepared by dissolving 0.143 g potassium iodide (J.T. Baker Chemical Co., Phillipsburg, NJ) in 100 mL LGW for a stock concentration of 1.09 g/L as I. Iodide doses ranged from 0-25 μg/L as I to reflect concentrations typical in surface waters (Moran et al., 2002; Weinberg et al., 2011). Tryptophan was at a concentration of 15 mg/L, and monochloramine was dosed at 12 mg/L as Cl_2 as this was the dose required for a 24-hour residual of 3 mg/L as Cl_2, as determined by demand tests.

Reactions were performed headspace-free in 40-mL glass screw cap sample vials with open top caps and PTFE-lined silicone septa to prevent volatilization of any THM byproducts. After a 24-hour reaction, disinfectant residuals were measured as total chlorine using the HACH colorimeter, and samples for other analyte analysis were quenched with ascorbic acid to prevent change in their levels. Chlorine and monochloramine demands were calculated by subtracting the residual disinfectant concentration from the concentration dosed.

Collection and storage of water samples

Samples were collected March 1st, 2019 from a drinking water treatment plant (DWTP) at the following four points in the treatment process: source water intake, post-powdered activated carbon (post-PAC), post-ozonation (post-O_3), and finished water. Samples were collected for water characterization as well as for chlorine and monochloramine demand tests in the presence and absence of iohexol in 1-L amber glass bottles (Supelco, Bellefonte, PA) with screw caps and PTFE-lined silicone septa and were transported in a cooler with ice packs for preservation. Travel blanks containing only LGW without quenching agent were transported to the sample site as a control in order to mimic transportation and preservation conditions.

Another set of samples was collected on the same date from the same four points in 40-mL clear glass vials (I-Chem, Pasadena, TX) headspace-free for THM analysis. Approximately 25 mg ascorbic acid (Fisher Scientific, Pittsburgh, PA) was added to the 40-mL vials prior to sample collection as a disinfectant quenching agent to eliminate further THM formation. One sample of finished water had also been collected February 28th, 2019 in a 40-mL clear glass headspace-free vial containing approximately 25 mg ascorbic acid to compare THM formation in finished water from February to that from March, after the DWTP switched to chlorine disinfection. Another aliquot of finished water was collected for iodide and iodate analysis in a 250-mL amber glass bottle containing 25 mg sodium sulfite (Mallinckrodt, Dublin, Ireland) as a

disinfectant quenching agent. All samples were filtered through 0.45 μm polyamide membrane filters (Sartorius, Wood Dale, IL) and stored in the dark at 4° C until analysis.

Water sample characterization

Samples were analyzed for iodide and iodate using a Dionex (Sunnyvale, CA) ion chromatograph (IC) with Eluent Degas module, Gradient Pump module, conductivity detector, and Advanced Computer Interface. Mobile phase and acid regenerate solutions were prepared prior to IC sample analyses. The mobile phase was prepared as a solution of 4.8 mM Na_2CO_3 (Mallinckrodt, Dublin, Ireland) and 1.0 mM $NaHCO_3$ (Mallinckrodt, Dublin, Ireland) in LGW, and the regenerate was prepared by filtering 4 L of LGW and adding 5.5 mL of 36.8 N H_2SO_4 (Fisher Scientific, Pittsburgh, PA) for a concentration of 50 mN H_2SO_4. For these analyses, the chromatography was isocratic through a 4x250 mm AS-22 column (Dionex, Sunnyvale, CA) with a 4x50 mm AG22 guard column (Dionex, Sunnyvale, CA) at a flow rate of 1.0 mL/minute.

Samples were also analyzed for dissolved organic carbon (DOC) and total dissolved nitrogen (TDN) using a Shimadzu TOC-V_{CPH} and TOC-V_{CPN} Analyzer (Columbia, MD). DOC and TDN refer to concentrations of organic carbon and nitrogen after samples were passed through 0.45 μm polyamide membrane filters. The DOC stock standard was prepared as a solution of 1018 mg/L as C by dissolving 0.54095 g potassium hydrogen phthalate (Sigma-Aldrich, Darmstadt, Germany) in 250 mL LGW. The TDN stock standard was prepared as a solution of 1000 mg/L as N by dissolving 1.806 g potassium nitrate (EM Science, Gibbstown, NJ) in 250 mL LGW to prepare the calibration curve. Hydrochloric acid solution was prepared by adding 16.4 mL concentrated HCl (12.1 N) (Fisher Scientific, Pittsburgh, PA) to 100 mL LGW. A working solution was prepared as 100 mg/L as C, 100 mg/L as N, and 0.05 M HCl for pH adjustment to create calibration points.

Inductively coupled mass spectrometry (ICP-MS) with an SC2 DX Auto Sampler and Nexion computer software (Perkin-Elmer, Waltham, MA) was used to determine total iodine concentrations. ICP-MS data were collected from four 2017 sampling events of the same DWTP at the same sampling locations. Absorbance spectra were collected from each sample using a UV-Vis spectrophotometer (Hewlett-Packard, Palo Alto, CA) in order to calculate specific ultraviolet absorbance (SUVA), which is found by dividing the sample absorbance at 254 nm by its DOC concentration. Excitation emissions matrix (EEM) measurements on a Fluorolog-321 spectrofluorometer with charge-coupled device (Horiba, Kyoto, Japan) determined the presence of amino acids, specifically in the tryptophan-like region of EEMs ($\lambda ex/\lambda em \sim 220/303$ nm), in each sample. The peak-picking method for fluorescence was used to identify three fluorophores common in surface waters: Peak A (hydrophobic acid fraction) and Peak C (humic-like fraction), which are attributed to natural fluorescence once excited in surface waters (Coble, 1996), and Peak T (protein-like fraction), which is attributed to amino acid-like organic matter (Stedmon et al., 2003).

Chlorine and monochloramine demand tests with sampled waters

Demand tests were also conducted to identify the correct dose of chlorine and monochloramine disinfectants to react with the DWTP water samples in the presence and absence of iohexol in order to leave a 24-hour disinfectant residual of about 3 mg/L as Cl_2. Similar procedures were followed to those involving tryptophan as the surrogate NOM, but using DWTP sampled waters instead of a tryptophan solution. An iohexol working solution was prepared as 2000 mg/L from the 350 mg/mL as I Omnipaque solution (GE Healthcare, Chicago,

IL). From the working solution, iohexol was spiked into sampled waters at a concentration of 5 mg/L to increase the potential for release of iodine during reactions with disinfectants. Another set of reactions between sampled waters and spiked disinfectant in the absence of iohexol was used as a control. After 24 hours, disinfectant residuals were measured and samples prepared for THM analysis were quenched of residual disinfectant with ascorbic acid to prevent further THM formation after the desired reaction time.

THM analysis

THM analysis was performed on a Hewlett-Packard HP 6890 Series gas chromatograph (Hewlett-Packard, Palo Alto, CA) with micro electron capture detector (GC-μECD) after liquid-liquid extraction (LLE) of aqueous samples with methyl tert-butyl ether (MtBE) (EMD Chemicals, Burlington, MA). Table 2 shows the THMs analyzed in this study and their practical quantitation limits, which was their lowest detectable calibration point. THM 4 standards were in a calibration mix of 2000 μg/mL as each THM in methanol (Supelco, Bellefonte, PA), and iodo-THMs standards were prepared at 5000 mg/L as each iodo-THM (Orchid Cellmark, New Westminster, British Columbia, Canada) in MtBE.

Table 2. THM 4 and iodo-THMs calibration standards and quantitation limits.

	Acronym	Abbreviation	Compound	*CAS #	Practical quantitation limit
THM 4	TCM	Cl_3CH	chloroform	67-66-3	2.5 μg/L
	BDCM	$BrCl_2CH$	bromodichloromethane	75-27-4	2.5 μg/L
	DBCM	Br_2ClCH	dibromochloromethane	124-48-1	2.5 μg/L
	TBM	Br_3CH	bromoform	75-25-2	2.5 μg/L
iodo-THMs	DCIM	Cl_2ICH	dichloroiodomethane	594-04-7	0.5 μg/L
	BCIM	BrClICH	bromochloroiodomethane	3490-00-8	0.25 μg/L
	CDIM	ClI_2CH	chlorodiiodomethane	638-73-3	0.5 μg/L
	DBIM	Br_2ICH	dibromoiodomethane	593-94-2	0.5 μg/L
	BDIM	BrI_2CH	bromodiiodomethane	557-95-9	0.5 μg/L
	TIM	I_3CH	iodoform	75-47-8	5.0 μg/L

*CAS = Chemical Abstracts Service

Samples were extracted using LLE as described in the standard operating procedures (SOP) for halogenated volatiles presented in Appendix A. Briefly, all reaction and calibration point samples were measured to 30 mL in 40-mL glass vials and adjusted to pH 3.5 with 0.2 N H_2SO_4. 3 mL of extracting solvent (50 μg/L 1,2-dibromopropane in MtBE, 99+% pure, Sigma-Aldrich, Darmstadt, Germany) was added to each sample using a solvent dispenser bottle. Approximately 6 g sodium sulfate (Mallinckrodt, Dublin, Ireland) pre-baked at 400° C was then added to each sample and shaken vigorously for one minute. The samples were allowed to settle for 5 minutes before transferring the extract into 2-mL autosampler vials (Supelco, Bellefonte, PA, USA). Extract analysis was followed on the GC-μECD after a splitless injection volume of 2 μL at 200^o C using a ZB-1 column (Phenomenex, Torrance, CA,) with ultra-high purity helium

carrier gas (National Welders, Morrisville, NC) and ultra-high purity nitrogen makeup gas (National Welders, Morrisville, NC), using operating conditions described in the SOP.

RESULTS AND DISCUSSION

Demand test results for tryptophan reactions

The goal of these experiments was to identify the correct dose of chlorine and monochloramine to react with tryptophan and iohexol in LGW in order to leave a 24-hour residual of about 3 mg/L as Cl_2. Table 3 shows the gradient of chlorine doses reacted with 15 mg/L tryptophan in the presence and absence of 5 mg/L iohexol and their associated 24-hour total chlorine residuals.

Table 3. 24-hour disinfectant demand test results for reactions of chlorine with 15 mg/L tryptophan in the presence and absence of 5 mg/L iohexol.

Chlorine dose (mg/L as Cl_2)	**Chlorine residual after reaction with tryptophan (mg/L as Cl_2)**	**Chlorine residual after reaction with tryptophan and iohexol (mg/L as Cl_2)**	**Chlorine demand by tryptophan (mg/L as Cl_2)**
0	0.0	0.0	0.0
30	1.3	-	-
60	1.9	-	-
65	4.4	2.3	60.6

The 65 mg/L as Cl_2 dose left a free chlorine residual of 4.4 mg/L as Cl_2 after a 24-hour reaction with tryptophan, which was close to the target residual of 3 mg/L as Cl_2 and the regulated MRDL of 4.0 mg/L as Cl_2 for chlorine (USEPA, 2001). Because the HACH colorimeter can only measure total chlorine concentrations up to 2.0 mg/L as Cl_2, samples had to be diluted prior to measuring residuals. This dose left close enough to the target residual and was, therefore, used in subsequent reactions with both tryptophan and iohexol in order to determine the formation potential of THMs. Because the 65 mg/L as Cl_2 dose left a residual close to the target value, other doses were excluded from subsequent reactions with tryptophan and iohexol, which is why data are not included Table 3. After the reaction of chlorine with tryptophan and iohexol, the free chlorine residual was 2.3 mg/L as Cl_2, which is close to the target residual of 3 mg/L as Cl_2.

Table 4 shows the gradient of monochloramine doses reacted with 15 mg/L tryptophan in the presence and absence of either 5 mg/L iohexol or 25 μg/L iodide and their 24-hour total chlorine residuals. The monochloramine solution was dosed as total chlorine and residuals were measured as total chlorine. Iodide was used in reactions with monochloramine and tryptophan as its reaction is slow enough to be able to form iodo-DBPs, while iodate is the major iodine sink for similar reactions with chlorine (Bichsel & von Gunten, 1999).

Table 4. 24-hour disinfectant demand test results for reactions of different doses of monochloramine as total chlorine with 15 mg/L tryptophan in the presence and absence of 5 mg/L iohexol or 25 μg/L iodide.

Total Cl_2 dose (mg/L as Cl_2)	**Total Cl_2 residual after reaction with tryptophan (mg/L as Cl_2)**	**Total Cl_2 residual after reaction with tryptophan and iohexol (mg/L as Cl_2)**	**Total Cl_2 residual after reaction with tryptophan and iodide (mg/L as Cl_2)**	**Total Cl_2 demand by tryptophan**
0	0.0	0.0	0.0	0.0
5	0.1	-	-	-
12	4.2	3.3	4.8	7.8
15	5.0	-	-	-

The 12 mg/L as Cl_2 dose left a total chlorine residual of 4.2 mg/L as Cl_2 after reacting for 24 hours with tryptophan, which is close to the target residual of 3 mg/L as Cl_2. This dose was chosen for subsequent reactions with tryptophan and either iohexol or iodide in order to determine THM formation potential, which is why data from other doses are not included in Table 4. After reactions of monochloramine, tryptophan, and iohexol, the total chlorine residual was 3.3 mg/L as Cl_2, and 4.8 mg/L as Cl_2 in the reaction with iodide instead of iohexol. These residuals are also close to both the target residual of 3 mg/L as Cl_2 and the MRDL of 4.0 mg/L as Cl_2 for monochloramine (USEPA, 2001). The demand was 1.5 mg/L as Cl_2 greater in reactions with iohexol than in iodide reactions, which could be due to the presence of additional organic matter within iohexol that could react with monochloramine to increase demand. The iodide concentration was also about 92 times lower than the concentration of iohexol as I. These test results show that there was more demand for chlorine than monochloramine by tryptophan, which is consistent with previous kinetics studies indicating a faster reaction with chlorine than monochloramine by NOM (Bichsel & von Gunten, 1999).

THM analysis results for tryptophan reactions

When the reaction conditions for the target residual in the demand tests were repeated, monochloramine at 12 mg/L as Cl_2 with tryptophan at 15 mg/L in the presence and absence of iohexol at 5 mg/L did not yield any detectable THM4 or iodo-THMs; however, reactions of chlorine at 65 mg/L as Cl_2 with these concentrations of tryptophan and iohexol yielded chloroform (Cl_3CH) as shown in Table 5.

Table 5. THM yield from reactions of chlorine, iohexol, and tryptophan.

Chlorine dose	**Iohexol dose**	**Tryptophan dose**	**Cl_3CH yield***
0 mg/L	5 mg/L	15 mg/L	< 2.5 μg/L
65 mg/L	5 mg/L	15 mg/L	309 ± 30 μg/L

*Concentration values averaged from analysis of duplicate samples.

Chloroform was the only THM formed and at a concentration of 309 μg/L, which is consistent with literature which suggests that chlorine as a disinfectant is more likely to form THM4 than iodo-THMs (Bichsel & von Gunten, 1999). This concentration was determined as an extrapolation of the calibration curve, as the highest calibration point for THM4 was 100 μg/L. Reactions of chlorine with tryptophan in the absence of iohexol were not analyzed for THMS.

Iodide is rapidly oxidized by chlorine to form HOI which can then further react with excess HOI to form iodate, but both HOI and HOCl can react with tryptophan to form iodinated and chlorinated THMs (Bichsel & von Gunten, 1999). However, the presence of HOCl in large excess compared to any HOI that could have formed from the iodine released by iohexol caused chloroform to form at much higher concentrations than iodinated THMs. Under these reaction conditions, iodine was not released from iohexol to form iodo-THMs. In order to form iodo-THMs, chloroform would have to either be substituted by HOI, or HOI could partially react with tryptophan to form iodo-THMs rather than be furthered to iodate.

Reactions of chlorine or monochloramine with iohexol in the absence of tryptophan did not produce any detectable THM4 or iodo-THMs. This is consistent with previous studies suggesting that a source of organic matter must be present in order to form THMs (Duirk det al., 2011; Wendel et al., 2014).

Table 6 shows THMs formed after a 24-hour reaction of monochloramine, tryptophan, and varying concentrations of iodide.

Table 6. Iodoform yield from reactions of monochloramine with tryptophan and varying concentrations of iodide.

Monochloramine dose	Iodide dose	Tryptophan dose	I_3CH yield*
12 mg/L	0 μg/L	15 mg/L	< 1.0 μg/L
12 mg/L	2.0 μg/L	15 mg/L	< 1.0 μg/L
12 mg/L	25 μg/L	15 mg/L	12.3 ± 1.6 μg/L

*Concentration values averaged from analysis of duplicate samples.

Iodoform was the only THM formed and at a concentration of 12.3 μg/L after a 24-hour reaction between monochloramine, tryptophan, and 25 μg/L iodide. An iodoform concentration of 12.3 μg/L as iodoform is equivalent to 11.9 μg/L as I, which translates to 47.6% yield of the original iodide dose. The equivalent yield from a 2.0 μg/L iodide dose in Table 6 above would be 0.98 μg/L as iodoform, which is below its practical quantitation limit of 5.0 μg/L.

Because reactions between the same dose of monochloramine with iohexol rather than iodide did not form THMs, these results suggest that, based on percent yield from the iodide reactions, iohexol would have to release at least 10.2 μg/L iodide in a reaction with monochloramine at 12 mg/L and tryptophan at 15 mg/L in order to form a detectable concentration of iodoform. An iohexol concentration of 5 mg/L as iohexol is equivalent to 2.3 mg/L as I. In reactions with monochloramine and tryptophan, iohexol released less than 0.4% of its iodine (10.2 μg/L iodide needed divided by the iohexol concentration of 2.3 mg/L as I) and did not form THMs.

Iodide is also oxidized to HOI by monochloramine, though this reaction is much slower than oxidation by chlorine (Bichsel & von Gunten, 1999). This gives more potential for the formation of iodo-THMs because HOI reacts with available tryptophan rather than other HOI to form iodate. This is seen in the formation of iodoform from the reaction of monochloramine, iodide, and tryptophan. The pathway of iodo-DBP formation from monochloramine can be seen in Figure 3.

Water characterization

Samples were collected from a single DWTP in March 2019 at the source water intake, post-PAC, post-ozonation, and finished water points in the treatment process. These sample

location points can be seen in Figure 4. Water characterization was carried out in order to describe the water quality changes after treatment steps within the plant.

Ion chromatography results

Ion chromatography was used to determine concentrations of iodide and iodate in the DWTP samples. Sample chromatograms and calibration curves can be found in Appendix B. Samples were matrix-spiked with 100 μg/L as iodate and the chromatograms compared with those for a 100 μg/L as iodate standard and the unspiked samples. Though there were chromatographic peaks present in the DWTP samples at a similar retention time to that of the iodate standard, it is clear from the matrix spikes where there was no increase in area in comparison to the unspiked samples that iodide and iodate were not detectable in the samples. These chromatograms and raw data are shown in Appendix B.

Total iodine

Total iodine concentrations were determined using ICP-MS to analyze samples collected from the same DWTP and sample locations in another project in order to show trends of total iodine removal following each treatment step. Though this is historical data, overall trends in total iodine should remain the same. Table 7 shows total iodine concentrations from ICP-MS analysis in each DWTP sample.

Table 7. Total iodine concentrations in each DWTP sample.

Sample	Total iodine concentration* (μg/L as I)	% Total iodine removed from previous sample location
Travel blank	< 0.5 μg/L	-
Source water intake	9.8 ± 0.9	-
Post-PAC	1.3 ± 0.8	87%
Post-O_3	1.0 ± 0.6	23%
Finished water	1.0 ± 0.6	0%

*Concentration values averaged from 3 replicates in a 2017 sampling event

Although iodide and iodate were not detectable in samples, because their detection limit was 25 μg/L, they could constitute a portion of the total iodine that was not able to be seen during ion chromatography analysis. PAC is the first treatment step following intake and accounted for removal of 87% of the total iodine present in the source water. PAC removes organic compounds, which would significantly decrease total iodine concentrations if the majority of iodine is contained within organic compounds. PAC is not removed prior to ozonation, so the increased contact time between PAC and organics during ozonation may result in lower total iodine concentrations. Ozonation does not physically remove organics, but it may transform DBP precursors as well as transform PAC into a form that makes adsorption easier.

Dissolved organic carbon and total dissolved nitrogen

Samples were analyzed for DOC and TDN, which are important water quality parameters as they are surrogate measures for precursors of DBP formation. Table 8 shows DOC and TDN concentrations in each DWTP sample. Sample calibration curves can be found in Appendix C.

Table 8. Dissolved organic carbon and total nitrogen concentrations in each DWTP sample.

Sample	DOC concentration* (mg/L as C)	TDN concentration* (mg/L as N)	% DOC removed from previous sample location	% TDN removed from previous sample location
Travel blank	< 0.1	< 0.1	-	-
Source water intake	4.4 ± 0.01	0.64 ± 0.02	-	-
Post-PAC	3.9 ± 0.01	0.54 ± 0.03	11.4%	15.6%
Post-O_3	4.1 ± 0.01	0.61 ± 0.01	0.0%	0.0%
Finished water (March 2019)	1.0 ± 0.01	0.34 ± 0.02	75.6%	44.3%

*Concentration values averaged from duplicate samples

The source water had the highest levels of DOC and TDN at 4.4 mg/L as C and 0.64 mg/L as N, which was expected because this sample had not yet undergone any treatment process. Typical DOC concentrations in lakes range from less than 1 mg/L to about 25 mg/L as C (Thurman, 1985), and TDN concentrations in surface waters ranged from about 0.5 mg/L to 7.0 mg/L as N in a study of the Mississippi river basin (Rus et al., 2012). Though samples were collected during a period of heavy and prolonged rainfall, DOC and TDN were at the low end of the range for surface waters.

Each treatment step has an associated change in water quality that is reflected in the DOC and TDN concentration changes from source water to finished water. DOC and TDN generally decrease as treatment progresses. PAC is used to remove NOM and treat taste and odor problems early in the treatment process and is subsequently removed during sedimentation; however, some particulate PAC may persist through the treatment. Because PAC is not removed from the water before continuing other treatments and ozonation does not physically remove particulates, it is not abnormal for DOC to increase or remain the same following PAC addition.

The most significant change in DOC and TDN concentrations was seen in finished water. Treatment steps between ozonation and finished water are coagulation and flocculation, settling and clarification, filtration, and disinfection. Previous studies have indicated 60-80% removal of DOC by coagulation and flocculation (Gone et al., 2009; Heiderscheidt et al., 2016), with the hydrophobic fractions more efficiently removed (Bolto et al., 1999). This would account for the significant removal of DOC seen between ozonation and finished water. Total organic carbon (TOC) concentrations in finished water were reported by the DWTP in 2017 as having a removal ratio of up to 1.9 (Personal Communication, 2019), which would indicate a finished water DOC concentration of 2.3 mg/L as C if the source water had a DOC concentration of 4.4 mg/L. A DOC concentration of 1.0 mg/L as C was measured for the finished water sample collected in March 2019, and this decreased concentration in comparison to average DOC concentrations from the DWTP may be due to heavy rainfall which likely diluted the DOC in the plant waters. Also, this measurement was based on only one sampling event, while the DWTP computes removal efficiencies as averages of multiple samples collected in each reporting period.

UV-254 and SUVA

Samples were analyzed for UV absorbance at 254 nm (UV-254), which was used to calculate specific ultraviolet absorbance (SUVA), a water quality parameter normalized to DOC content that has been shown to be correlated with aromatic carbon content as well as with NOM

removal (Weishaar et al., 2003). Table 9 shows UV-254 absorbance values obtained for each DWTP sample. SUVA was calculated by dividing the UV-254 value by the DOC concentration shown in Table 8, and then multiplying by 100 to convert cm to m.

Table 9. UV-254 and calculated SUVA values for each DWTP sample.

Sample	UV-254 (cm^{-1})	SUVA (L/mg-m)
Travel blank	0.0	-
Source water intake	0.200	4.54
Post-PAC	0.169	4.33
Post-O_3	0.132	3.19
Finished water (March 2019)	0.0136	1.36

SUVA is a water quality parameter that is normalized for DOC in each sample. A lower SUVA value indicates the presence of lower molecular weight DOC, and SUVA is also correlated with the hydrophobic organic acid fraction of DOC (Spencer et al., 2012). SUVA decreased following each treatment step, indicating aromatic DOC removal. The low SUVA value for the finished water sample compared to other sampling points indicates higher finished water quality than at other points in the treatment plant due to DOC removal.

Excitation-emission matrices

EEMs are three-dimensional plots that show fluorescence intensity at a given excitation and emission wavelength and are useful for characterizing DOC in an aqueous sample. Figures 7-10 below are EEMs of each filtered DWTP sample. On each EEM, the x-axis represents emission wavelength in nm, the y-axis represents excitation wavelength in nm, and the z-axis (color) represents peak intensity in Raman units (RU). The peaks labeled A, C, and T are each correlated with a different component of DOC common in surface waters. Peak A corresponds with the hydrophobic acid fraction, Peak C corresponds with the humic-like fraction, and Peak T corresponds with the hydrophobic base or protein-like fraction. Peak T is correlated with wastewater effluent due to the presence of proteins and amino acids in human waste.

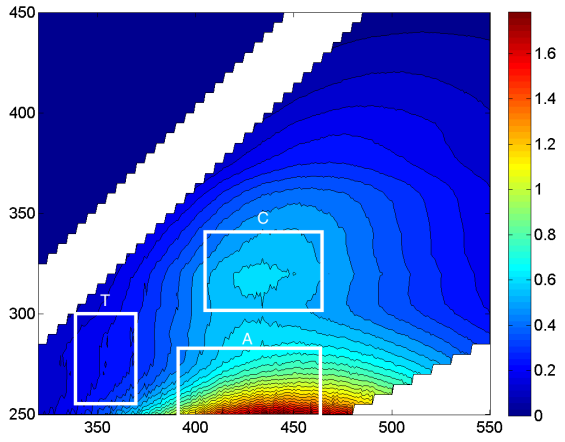

Figure 7. EEM for source water intake sample.

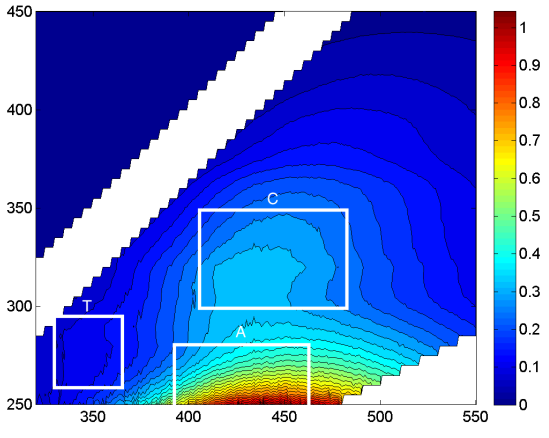

Figure 8. EEM for post-PAC sample.

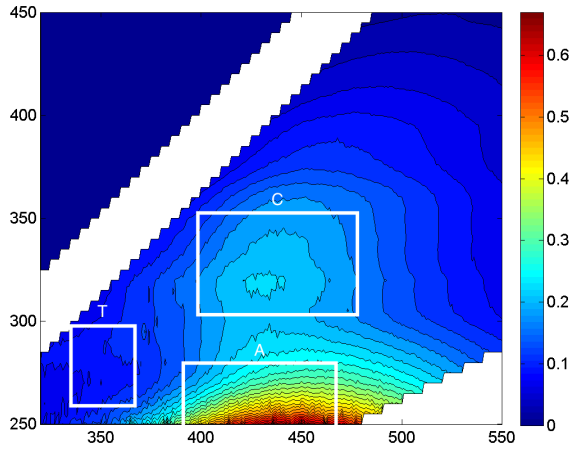

Figure 9. EEM for post-O_3 sample.

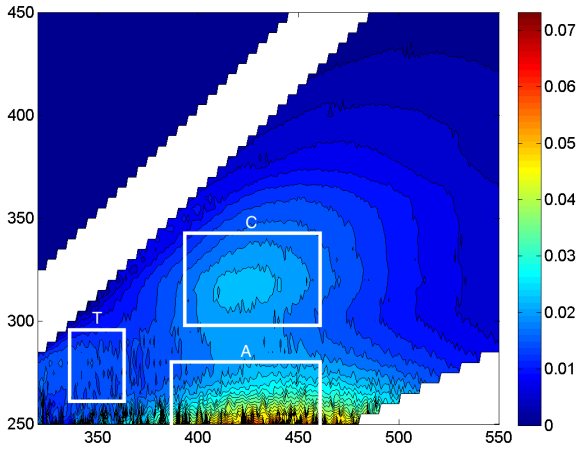

Figure 10. EEM for finished water sample

Table 10 shows the EEM peak intensities in Raman units (RU) of each DWTP sample using the peak-picking method in which peak intensities are recorded within a region of interest. Though peak intensities are not concentrations themselves, they describe DOC, where a larger peak value indicates a larger concentration of that DOC fraction in the water sample.

Table 10. EEM peak intensities of sampled waters using the peak-picking method.

Sample	Peak A intensity (RU)	Peak C intensity (RU)	Peak T intensity (RU)	Percent of DOC in Peak T region*
Source water intake	1.77	0.50	0.20	8.1%
Post-PAC	1.01	0.27	0.11	7.9%
Post-O_3	0.68	0.20	0.09	9.3%
Finished water (March 2019)	0.07	0.02	0.02	18.2%

*Calculated by dividing Peak T fraction by the sum of Peak A, C and T fractions.
RU = Raman Units

Peak T was present in all samples, suggesting the persistence of tryptophan-like dissolved organic matter through the DWTP. Each peak or DOC component decreased proportionally through each treatment step; however, Peak T constituted a larger portion of DOC in the finished water than in other samples. This may be due to the efficiency of hydrophobic acid DOC removal by coagulation and flocculation in comparison to other types of DOC (Bolto et al., 1999), as Peak A's intensity decreased by 91% between post-ozonation and finished water. Peak C, the humic-like fraction, also saw a 90% decrease in peak intensity between post-ozonation and finished water, while Peak T's intensity decreased 78%. Dotson & Westerhoff (2009) found that 70% of total amino acids were removed during coagulation and settling, which is consistent with these results because of the association between Peak T and amino acids.

Results from water characterization indicate changes in water quality associated with each treatment step. Historical data from the 2017 samples related to earlier showed a total

iodine concentration of 9.8 μg/L as I in the source water, which decreased dramatically after PAC addition. The mean concentration of total iodine in river water is about 5 μg/L (Moran et al., 2002), and the presence of iodine in the source water at an elevated concentration indicates that it is impacted by wastewater and likely contains iohexol-like organic compounds as a result of upstream discharge from documented medical facility waste. The source water also had a DOC concentration of 4.4 mg/L as C, which decreased by 11.4% after PAC addition. PAC removes organic compounds and total iodine, both of which are iodo-DBP precursors. Ozonation does not remove DBP precursors but transforms them. DOC in finished water decreased by 75.6% from post-ozonation, though all other treatment processes occur in between ozonation and finished water. Water characterization indicated higher finished water quality in comparison to other treatment steps.

THM presence in DWTP samples

THMs were quantified in each sample in order to determine their presence throughout the DWTP, but especially in finished water after disinfection. Table 11 shows the THMs quantified from each DWTP sample. Beginning in March, the DWTP switches from chloramines to chlorine disinfection during a month-long chlorine burn period. Finished water from February, therefore, represents the use of chloramines for disinfection, while finished water from March represents the use of chlorine disinfection. The DWTP reported chloramine residuals in finished water ranging from 1.6-4.24 mg/L as Cl_2 (MRDL = 4 mg/L) and chlorine residuals ranging from 0.76-2.87 mg/L as Cl_2 (MRDL = 4 mg/L) in 2017. The two regulated and 3 iodo-THMs shown in the table were the only detectable THMs in the samples. Sample chromatograms and calibration curves can be found in Appendix A.

Table 11. THM* characterization of DWTP samples.

Sample	**THM4**		**Iodo-THMs**		
	$BrCl_2CH$	Br_2ClCH	Cl_2ICH	BrClICH	Br_2ICH
Travel blank	< 2.5 μg/L	< 2.5 μg/L	< 0.5 μg/L	< 0.25 μg/L	< 0.5 μg/L
Source water intake	< 2.5 μg/L	< 2.5 μg/L	< 0.5 μg/L	< 0.25 μg/L	< 0.5 μg/L
Post-PAC	< 2.5 μg/L	< 2.5 μg/L	< 0.5 μg/L	< 0.25 μg/L	< 0.5 μg/L
Post-O_3	< 2.5 μg/L	< 2.5 μg/L	< 0.5 μg/L	< 0.25 μg/L	< 0.5 μg/L
Finished water (February 2019)	6.8 ± 1.0 μg/L	< 2.5 μg/L	2.7 ± 0.2 μg/L	6.6 ± 0.8 μg/L	1.1 ± 0.3 μg/L
Finished water (March 2019)	2.5 ± 1.0 μg/L	4.2 ± 0.2 μg/L	4.1 ± 0.1 μg/L	10.1 ± 0.4 μg/L	1.1 ± 0.1 μg/L

*Concentration values averaged from duplicate samples

THMs were not detected in the source water, post-PAC, or post-O_3 samples because these treatment steps occur prior to disinfection. The presence of both bromine- and iodine-containing THMs in the finished water indicates a source of bromine and iodine either in the source water or introduced during treatment. The total concentration of iodine found in iodo-THMs in March finished water was about 8.0 μg/L as I, which is greater than the total iodine concentration measured in finished water in 2017 of 1.0 μg/L.

Chloroform was not detected in any sample, which may be due to its volatility and could have been lost during sampling or instrumental analysis. The finished water sample collected in February had a THM4 concentration of 6.8 μg/L while for the March sampling it was 6.7 μg/L, both of which are in compliance with the MCL of 80 μg/L regulation (USEPA, 2001). The sum of the measured iodo-THM concentrations exceeded THM4 concentrations by 3.8 μg/L in February and by 8.6 μg/L in March. The presence of iodo-THMs at higher concentrations than THM4 indicates inadequate removal of iodine sources prior to disinfection.

Beginning on March 1st for one month, the DWTP switched from monochloramine to chlorine disinfection which is reflected in the changes in THM concentrations. After beginning the chlorine burn, the concentration of bromodichloromethane decreased, but the concentrations of dibromochloromethane, dichloroiodomethane, and bromochloroiodomethane increased. This could be due to normal fluctuations in source water quality or changes in flow of water through the DWTP in response to demand, and an increased disinfectant contact time in the clearwell would result in formation of THMs at higher concentrations.

Disinfectant demand test results for DWTP samples spiked with iohexol

Demand tests were conducted to identify the appropriate dose of chlorine to react with DWTP sampled waters in the presence and absence of an iohexol spike and leave a 24-hour residual of about 3 mg/L as Cl_2. A gradient of chlorine doses ranging from 15 to 65 mg/L as Cl_2 was used in order to determine this dose. This range was selected based on previous experiments involving tryptophan at 15 mg/L in which the chlorine dose required to leave a 24-hour 3 mg/L as Cl_2 residual was 65 mg/L as Cl_2. A tryptophan dose of 15 mg/L as tryptophan is equivalent to 9.7 mg/L as C. Because each sample had a DOC concentration of about 4 mg/L as C, or about 40% of the DOC in the previous tryptophan dose, it was assumed that 40% of the previous chlorine dose of 65 mg/L as Cl_2 would be necessary to leave the same residual of 3 mg/L as Cl_2. The selected doses, however, left residuals much greater than 3 mg/L as Cl_2, so only the lowest chlorine dose of 15 mg/L as Cl_2 was selected for further THM analysis.

Table 12 shows the residuals and demand for 3 of the DWTP samples after a 24-hour reaction with 15 mg/L chlorine in the presence and absence of 5 mg/L iohexol.

Table 12. 24-hour chlorine demand test results for DWTP samples in the presence and absence of iohexol.

Sample	Cl_2 dose (mg/L as Cl_2)	Cl_2 residual after reaction with sample (mg/L as Cl_2)	Cl_2 residual after reaction with sample and 5 mg/L iohexol (mg/L as Cl_2)	Cl_2 demand by sample (mg/L as Cl_2)
Source water	15	10.1	9.5	4.9
Post-PAC	15	10.3	11.2	4.7
Post-O_3	15	10.7	11.7	4.3

The target residual of 3 mg/L as Cl_2 was not met even with the lowest chlorine dose of 15 mg/L as Cl_2; however, since THM formation was to be maximized, a residual of about 10 mg/L as Cl_2 is adequate. The demand for chlorine by each water sample was less than 5 mg/L as Cl_2, while the demand for chlorine by tryptophan in previous reactions was greater than 60 mg/L as Cl_2. This is due to a larger DOC concentration in the tryptophan reactions than the DWTP sample reactions, as well as differences in EEMs of tryptophan and DWTP samples. The Peak T

region constitutes all of tryptophan's DOC as tryptophan is the Peak T standard, while Peak T in the source water, post-PAC, and post-O_3 samples only constituted 8-9% of the DOC. The addition of iohexol to the samples did not impact chlorine demand indicating that it likely had little reaction with chlorine.

Table 13 shows the monochloramine demand in each sample (measured as total chlorine) at a 5 mg/L as Cl_2 dose in the absence and presence of iohexol and their associated 24-hour total chlorine residuals. A gradient of monochloramine doses ranging from 5 to 10 mg/L as Cl_2 was used in order to determine the appropriate dose required to leave a 24-hour residual of about 3 mg/L as Cl_2. Previous experiments involving tryptophan indicated that a monochloramine dose of 12 mg/L as Cl_2 was necessary to react with tryptophan at 15 mg/L and leave the target residual. It was again assumed that 40% of the previously used monochloramine dose of 65 mg/L as Cl_2 would be necessary to leave the same residual of 3 mg/L as Cl_2. The lowest monochloramine dose of 5 mg/L as Cl_2 left a residual greater than the target, so this dose was selected for further THM analysis.

Table 13. 24-hour monochloramine demand test results (measured as total chlorine) for DWTP samples in the presence and absence of iohexol.

Sample	Total Cl_2 dose (mg/L as Cl_2)	Total Cl_2 residual after reaction with sample (mg/L as Cl_2)	Total Cl_2 residual after reaction with sample and 5 mg/L iohexol (mg/L as Cl_2)	Total Cl_2 demand by sample (mg/L as Cl_2)
Source water	5	4.1	4.2	0.9
Post-PAC	5	4.2	4.3	0.8
Post-O_3	5	4.5	4.4	0.5

A monochloramine dose of 5 mg/L as Cl_2 left a residual of 4.1-4.5 mg/L as Cl_2 after a 24-hour reaction with each DWTP sample. These results are consistent with previous results suggesting the demand for monochloramine is much less than the demand for chlorine. The residuals were similar to the MRDL of 4 mg/L as Cl_2 for monochloramine. The addition of iohexol to the samples did not impact total chlorine demand again suggesting that it may have little to no reaction with the disinfectant under the treatment conditions employed.

THM analysis results for disinfectant reactions of DWTP samples with added iohexol

THM analysis was performed to quantify THM concentrations after 24-hour reactions of DWTP samples with the selected chlorine or monochloramine dose described in the previous section in the presence and absence of iohexol. Table 14 shows the THMs formed from the reactions of chlorine with DWTP samples in the presence and absence of iohexol at 5 mg/L.

Table 14. 24-hour THM formation results for chlorination of DWTP samples in the presence and absence of iohexol.

Sample	Cl_2 dose	Iohexol dose	THM4* (μg/L)			Iodo-THMs* (μg/L)		
			Cl_3CH	$BrCl_2CH$	Br_2ClCH	Cl_2ICH	ClI_2CH	BrI_2CH
Travel blank	15 mg/L	0 mg/L	< 2.5	< 2.5	< 2.5	< 0.5	< 0.5	< 0.5
Travel blank	15 mg/L	5 mg/L	< 2.5	< 2.5	< 2.5	< 0.5	< 0.5	< 0.5
Source water	15 mg/L	0 mg/L	239 ± 41	67 ± 17	3.7 ± 0.1	6.5 ± 0.2	< 0.5	7.1 ± 2.8
Source water	15 mg/L	5 mg/L	361 ± 13	37 ± 13	3.5 ± 0.1	5.8 ± 0.2	0.74 ± 0.05	11.1 ± 1.0
Post-PAC	15 mg/L	0 mg/L	237 ± 36	41 ± 17	3.2 ± 0.1	4.9 ± 0.5	< 0.5	7.4 ± 0.1
Post-PAC	15 mg/L	5 mg/L	369 ± 56	55 ± 15	3.6 ± 0.2	5.3 ± 0.5	< 0.5	10.2 ± 1.1
Post-O_3	15 mg/L	0 mg/L	212 ± 55	47 ± 11	9.1 ± 0.4	1.0 ± 0.1	< 0.5	4.9 ± 0.1
Post-O_3	15 mg/L	5 mg/L	297 ± 21	75 ± 12	11 ± 1.0	1.2 ± 0.1	< 0.5	6.9 ± 0.2

*Concentration values averaged from duplicate samples

Chloroform formed at greater concentrations than other THMs after every reaction. Chloroform concentrations were extrapolated from the calibration curve, as the highest THM4 calibration point was 100 μg/L. THM4 concentrations exceeded the MCL of 80 μg/L, which is why other treatment steps are necessary to remove THM precursors prior to disinfection. The addition of iohexol did not seem to impact the concentration or characterization of THMs formed, except in the reaction with the source water sample. In the absence of iohexol, the reaction of source water with chlorine did not form a detectable concentration of chlorodiiodomethane, but in the presence of iohexol, chlorodiiodomethane formed at a concentration of 0.74 μg/L. These results are consistent with the results from previous reactions of tryptophan as surrogate NOM with chlorine and iohexol, except formation of bromine-containing THMs in the plant waters was likely due to the presence of bromide which was not present in the earlier laboratory-prepared solutions. Previous reactions of chlorine with iohexol in the absence of organic matter did not produce detectable THMs. A carbon source is, therefore, necessary for THM formation, which is seen in the results of Table 14 where DOC was present in each sample.

The addition of iohexol generally increased formation of chloroform and bromodiiodomethane within each sample. An increase in chloroform concentration could be due to the addition of organic matter contained within iohexol to each sample. However, chlorination of iohexol in the absence of NOM did not produce detectable THMs. Bromodiiodomethane concentrations could have increased due to the release of iodine from iohexol, though the same trends are not seen among other iodo-THMs. Iohexol increased formation of chlorodiiodomethane in only the source water sample, which could be due to the release of iodine from iohexol in the presence of organic matter prior to treatment by PAC.

Previous sample analysis, whose results are presented in Table 11, showed the presence of bromochloroiodomethane and dibromoiodomethane in finished water but these DBPs did not form in reactions where the same water was spiked with iohexol. The results of chloramine reactions of plant waters with and without added iohexol shown in Table 15, however, formed chlorodiiodomethane, bromodiiodomethane, and chloroform that were not present in finished water samples. The presence of iodo-THMs in the finished water samples and after sample reactions with chlorine indicates inadequate removal of iodine-containing precursors prior to disinfection. The total iodine present in iodo-THMs in finished water (Table 11) was about 8.0 μg/L as I, and the total iodine concentrations present in iodo-THMs shown in Table 14 were 6.5, 5.7, and 2.4 μg/L as I for source water, post-PAC, and post-O_3 samples following chlorination in the absence of an iohexol spike, respectively. This follows the decreasing total iodine trend after each treatment step seen in Table 7.

Similar formation of bromodichloromethane, dibromochloromethane, dichloroiodomethane, and bromodiiodomethane was seen among source water intake and post-PAC samples after chlorination, regardless of iohexol presence. Post-O_3, however, decreased both dichoroiodomethane and bromodiiodomethane formation. This indicates that ozonation may have transformed the organic matter into a form that does not as easily produce iodo-THMs.

Table 15 shows those THMs formed from the reactions of monochloramine with DWTP samples in the presence and absence of iohexol at 5 mg/L.

Table 15. 24-hour THM formation results for chloramination of DWTP samples in the presence and absence of iohexol.

Sample	NH_2Cl dose	Iohexol dose	Cl_3CH yield*	ClI_2CH yield*
Travel blank	5 mg/L	0 mg/L	< 2.5 μg/L	< 0.5 μg/L
Travel blank	5 mg/L	5 mg/L	< 2.5 μg/L	< 0.5 μg/L
Source water intake	5 mg/L	0 mg/L	2.6 ± 0.5 μg/L	< 0.5 μg/L**
Source water intake	5 mg/L	5 mg/L	3.5 ± 0.7 μg/L	< 0.5 μg/L**
Post-PAC	5 mg/L	0 mg/L	< 2.5 μg/L	< 0.5 μg/L**
Post-PAC	5 mg/L	5 mg/L	3.4 ± 1.0 μg/L	< 0.5 μg/L**
Post-O_3	5 mg/L	0 mg/L	< 2.5 μg/L	< 0.5 μg/L**
Post-O_3	5 mg/L	5 mg/L	< 2.5 μg/L	< 0.5 μg/L**

*Concentration values averaged from duplicate samples
**Peaks detectable but not quantifiable

The only quantifiable THM from the reactions of monochloramine with the DWTP samples was chloroform. Chlorodiiodomethane peaks were detectable but not quantifiable as they were below the practical quantitation limit of 0.5 μg/L. The presence of chlorodiiodomethane could be confirmed by increasing contact time of monochloramine with DWTP samples or by increasing the concentrations of precursors. The chloroform concentrations from these reactions were nearly two orders of magnitude lower than from the chlorine reactions (Table 14), which is due to differences in reaction kinetics and demand of chlorine and monochloramine. The addition of iohexol increased chloroform formation in the post-PAC sample, which may be due to the presence of additional organic matter from iohexol in the

sample. In the post-O_3 samples, there was no chloroform formation, indicating possible transformation of organic matter by ozonation into a form that makes THM formation less likely.

In the previous lab-controlled chlorination experiments of DWTP samples, chlorodiiodomethane only formed when iohexol was spiked into the source water sample and reacted with chlorine, shown in Table 14. In these experiments, chlorodiiodomethane was detectable regardless of the presence of an iohexol spike. This indicates that an iodine source was already present in the sampled waters and contributed to formation of iodo-THMs, which was also shown in the total iodine characterization data. The total iodine concentrations present in iodo-THMs from these reactions were below detection limits. Based on these results, it seems that iohexol is not a major source of iodine in the formation of iodo-THMs following chloramination; however, the use of chlorine as a pretreatment could be detrimental as iodo-THMs formed following chlorination, regardless of additional iohexol.

CONCLUSIONS

This project evaluated the formation potential of iodo-THMs in surface waters that receive pharmaceutical wastewater effluent by addressing the following objectives:

1) Determine the conditions under which iohexol (one of the most widely used ICM in the state of North Carolina) releases iodine in controlled laboratory media.

In this study, iodo-THMs formed only in reactions of monochloramine with tryptophan (a source of natural organic matter and nitrogen) in the presence of iodide, and the only iodo-THM that formed was iodoform. Based on percent yield from these reactions, iohexol (5 mg/L) would have to release about 10 μg/L iodide (about 0.2% of its mass) in a reaction with monochloramine at 12 mg/L and tryptophan at 15 mg/L in order to form a detectable concentration of iodoform. No other THMs were formed in these reactions. However, chlorine reacted with tryptophan in the presence of iohexol to produce chloroform, but no detectable iodo-THMs were measured. Since iohexol was added at 5 mg/L into a subset of all of these samples and no iodo-THMs were detected, it appears that iohexol is not a major source of iodide under the laboratory conditions evaluated.

2) Determine if the laboratory conditions evaluated in objective (1) are applicable to natural waters and drinking water treatment.

Samples collected from four treatment points (source water, post-PAC, post-O_3, and finished water) in an NC surface DWTP were characterized and confirmed the presence of tryptophan-like organic matter and iodine in each sample. Finished water samples collected in February 2019, when chloramine was used for final disinfection, contained bromodichloromethane (6.8 ± 1.0 μg/L), dichloroiodomethane (2.7 ± 0.2 μg/L), bromochloroiodomethane (6.6 ± 0.8 μg/L), and dibromoiodomethane (1.1 ± 0.3 μg/L), which indicates the presence of bromine in addition to iodine in the source water. Iodine had been detected in samples collected from the same DWTP and locations in 2017, the source of which could have been iohexol or other unknown compounds. This also indicates precursor differences between the type of NOM present in the surface water and tryptophan, as previous reactions addressed under objective (1) using tryptophan as surrogate NOM did not yield THMs following chloramination. The tryptophan-like Peak T region in DWTP samples following EEM analysis constituted less than 10% of the DOC in source water, post-PAC, and post-O_3 samples.

Reactions of monochloramine (5 mg/L as Cl_2) with source water samples resulted in formation of chloroform (2.6 ± 0.5 μg/L in the absence of iohexol, 3.5 ± 0.7 μg/L in the presence of iohexol) regardless of iohexol addition, though chloroform was not detected in finished water. This may have been due to the 77% decrease in DOC from source water to finished water which would decrease chloroform formation, though ionorganic iodine must have persisted through treatment in order to produce iodo-THMs, as PAC removes the majority of organic compounds. Chloramination, dosed at 5 mg/L as Cl_2, of post-PAC samples also yielded chloroform (3.4 ± 1.0 μg/L) but only when 5 mg/L iohexol was added, possibly due to the presence of additional organic matter from iohexol in the sample. Post-O_3 samples had no chloroform formation following chloramination, indicating possible transformation of organic matter by ozonation into a form that makes THM formation less likely. Post-O_3 samples decreased SUVA by 26% and EEM peak intensities decreased by 20-33% in comparison to post-PAC samples, indicating DOC removal and transformation.

Chloramination of source water, post-PAC and post-O_3 samples showed chromatographic peaks for chlorodiiodomethane though the concentrations were not quantifiable as they were below the practical quantitation limit of 0.5 μg/L. Chlorodiiodomethane at this level was detectable regardless of whether iohexol was added into the sample, indicating that an iodine source was already present in the sampled waters and contributed to formation of iodo-THMs.

Finished water samples collected in March during the chlorine burn period in which chlorine is used for final disinfection contained bromodichloromethane (2.5 ± 1.0 μg/L), dibromochloromethane (4.2 ± 0.2 μg/L), dichloroiodomethane (4.1 ± 0.1 μg/L), bromochloroiodomethane (10.1 ± 0.4 μg/L), and dibromoiodomethane (1.1 ± 0.1 μg/L). These are the same THM species as those detected when chloramine was used for final disinfection except for the additional dibromochloromethane (4.2 ± 0.2 μg/L). In comparison to the finished water samples collected in February during chloramination, in March finished water samples, the concentration of bromodichloromethane decreased by 4.3 ± 2.0 μg/L, but the concentrations of dibromochloromethane, dichloroiodomethane, and bromochloroiodomethane increased by 4.2 ± 0.2 μg/L, 1.4 ± 0.3 μg/L, and 3.5 ± 1.2 μg/L, respectively. This could be due to fluctuations in source water quality, PAC or ozone dosing, or changes in flow of water through the DWTP in response to demand, and an increased disinfectant contact time in the clearwell would result in formation of THMs at higher concentrations. Reactions of tryptophan with chlorine in the experiments of objective (1) yielded only chloroform, indicating differences between the carbon precursor in the NOM present in surface water and plant samples and that in tryptophan.

Chlorination of source water, post-PAC, and post-O_3 samples showed formation of chloroform (361 ± 13 μg/L in the presence of iohexol and 239 ± 41 μg/L in absence of iohexol), bromodichloromethane (37 ± 13 μg/L in the presence of iohexol and 67 ± 17 μg/L in absence of iohexol), and dibromochloromethane (3.5 ± 0.1 μg/L in the presence of iohexol and 3.7 ± 0.1 μg/L in absence of iohexol), as well as two iodo-THMs, dichloroiodomethane (5.8 ± 0.2 μg/L in the presence of iohexol and 6.5 ± 0.2 μg/L in absence of iohexol) and bromodiiodomethane (11.1 ± 1.0 μg/L in the presence of iohexol and 7.1 ± 2.8 μg/L in the absence of iohexol), regardless of whether iohexol was added, while chlorodiiodomethane (0.74 ± 0.05 μg/L) formed only after chlorination of source water in the presence of 5 mg/L iohexol. This could be due to release of iodine by iohexol when added to the source water matrix that reacted with chlorine and NOM to produce iodo-THMs, which may not have occurred in other samples due to decreases in DOC. Similar trends of dichloroiodomethane and bromodiiodomethane formation were seen among chlorinated source water and post-PAC samples regardless of iohexol presence. The post-O_3 step, however, decreased these iodo-THM concentrations, indicating that ozonation may have transformed NOM into a form that does not provide the carbon precursor to produce iodo-THMs.

3) Propose solutions to limiting iodo-THM formation in drinking water.

Ozonation seemed to decrease iodo-THM formation in comparison to PAC treatment and source water samples, indicating that this treatment step plays an important role in the transformation of NOM to a form that makes iodo-THM formation less likely. However, reduction of iodine-containing precursors in surface drinking water sources is necessary to significantly decrease iodo-THM formation. Because conventional wastewater treatment cannot adequately remove large molecular weight ICM from water before discharging into surface waters that can be upstream DWTP sources, it should be the responsibility of either drug manufacturers or medical facilities to reduce ICM waste. This could include the implementation

of regulations on medical waste before it enters the wastewater system or the production of ICM alternatives that do not contain DBP precursors. Policy should consider who should reasonably be expected to bear the financial burden in order to limit the presence of ICM in surface waters.

THM formation also decreased when monochloramine was used as a disinfectant compared to chlorine. The implementation of PAC and ozonation and the use of monochloramine as a disinfectant could, therefore, be useful for DWTPs to decrease their formation of iodo-THMs and to protect public health, especially if doses are optimized for the specific treatment plant. Other advanced treatment options, such as reverse osmosis or membrane filtration, could also be used to reduce DBP precursors prior to disinfection. The use of chlorine as a primary disinfectant is potentially detrimental, as contact time between finished water and chlorine prior to ammonia addition to form chloramines could lead to increased formation of iodo-THMs. The use of ozonation and the implementation of advanced treatment processes, however, are costly and raise the question of whether the burden of protecting water sources should fall on the drinking water consumer (i.e. through increased rates from the utility) or on the manufacturers and users of ICM.

Future work:

To fully address objective (1), future studies in which disinfectant contact times or concentrations of iohexol or tryptophan are increased are necessary in order to determine if iodine can be released by iohexol. Other iodo-DBP measurements, such as iodo-acids, should also be included in order to account for formation of any iodo-DBP, not just iodo-THMs.

For objective (2), chlorodiiodomethane formed at 0.74 ± 0.05 μg/L after chlorination of source water in the presence of 5 mg/L iohexol. Chloramination (5 mg/L as Cl_2) of source water, post-PAC and post-O_3 samples showed chromatographic peaks for chlorodiiodomethane though the concentrations were not quantifiable as they were below the practical quantitation limit of 0.5 μg/L. Future studies are necessary to confirm chlorodiiodomethane formation by increasing disinfectant contact time, concentrating samples, or increasing the dose of iohexol.

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APPENDIX A

Standard operating procedure for THM analysis, sample chromatogram, and calibration curve

Prepared by: Bonnie Lyon
10/20/08

Standard Operating Procedure for Halogenated Volatile and Haloacetamide Analysis

Halogenated Volatiles

Abbrev.	Compound	CAS #	mol. wt. (g/mol)
$CHCl_3$	chloroform	67-66-3	119.38
TCAN	trichloroacetonitrile	545-06-2	144.39
DCAN	dichloroacetonitrile	3018-12-0	109.94
$BrCl_2CH$	bromodichloromethane	75-27-4	163.83
TCA	chloral hydrate	302-17-0	165.40
11 DCP	1,1-dichloropropanone	513-88-2	126.97
TCNM	Trichloronitromethane (chloropicrin)	76-06-2	164.38
Br_2ClCH	dibromochloromethane	124-48-1	208.28
BCAN	bromochloroacetonitrile	83463-62-1	154.39
111TCP	1,1,1-trichloropropanone	918-00-3	161.42
$CHBr_3$	bromoform	75-25-2	252.73
DBAN	dibromoacetonitrile	3252-43-5	198.85

Haloacetamides

Abbrev.	Compound	CAS #	mol. wt. (g/mol)
DIAM	diiodoacetamide	5875–23–0	310.85
BIAM	bromoiodoacetamide	62872–36–0	263.86
CIAM	chloroiodoacetamide	62872–35–9	219.41
DBAM	dibromoacetamide	598–70–9	216.86
TBAM	tribromoacetamide	594–47–8	295.75
BCAM	bromochloroacetamide	62872–34–8	172.41
DBCAM	dibromochloroacetamide	855878–13–6	251.31
BDCAM	bromodichloroacetamide	98137–00–9	206.85
BAM	bromoacetamide	683–57–8	137.96
DCAM	dichloroacetamide	683–72–7	127.96
TCAM	trichloroacetamide	594–65–0	162.40

Equipment

- Clear 60-mL, clean, prewashed glass screw cap sample vials with polytetrafluoroethylene (PTFE)-lined silicone septa. Clean vials by washing with Alconox powder detergent solution, rinsing with tap water, and soaking in a 10% ACS-grade HNO_3 bath overnight. The vials should then be rinsed at least three times with tap water and then rinsed three times with laboratory grade water (LGW) and dried in a 180°C oven for at least 24 hours. Repeat the same steps for cleaning the caps and septa except oven temperature should be set at 80°C.
- Gas tight syringes: 25 µL, 50 µL, 100 µL, 250 µL
- 50-250 µL Dade Model J micropipetter fitted with clean glass capillary tips

- Eight 100-mL glass volumetric flasks with glass stoppers
- 1-L amber bottle mounted with 10-mL pump pipetting dispenser containing PFTE transfer line
- 23-cm disposable glass Pasteur pipettes
- Rubber Pasteur pipette bulb
- pH indicator strips pH 0-6 – colorpHast, EMD Chemicals, (Fisher Scientific – catalog #M95863)
- GC vials - 12x32 mm 1.8-mL Amber glass vials, Laboratory Supply Distributors, (catalog #20211ASRS-1232)
- GC Caps - 11 mm seal w/ Red Teflon® faced silicone septa, 40 Mils thick, Supelco (catalog #27360-U)
- GC vial inserts – 5x30 mm Flat Bottom LVI, Laboratory Supply Distributors, (catalog #20870-530)
- Hand crimper for sealing gas chromatography autosampler vials
- Vortexer
- Teflon tape
- Stainless steel scupula

Instrumentation

Gas Chromatograph

- Hewlett-Packard GC5890 Series II with autosampler/autoinjector tower, located in Baity Laboratory L03
- Capillary Column: HP-1 (Agilent) 30 m length x 0.25 mm inner diameter, 1.0-µm film thickness
- Electron Capture Detector (ECD): Hewlett-Packard Model ECD
- Data System: Hewlett-Packard ChemStation

GC Gases

- Carrier Gas-Ultra High Purity (UHP) helium (He) available through UNC Scientific Storerooms (catalog # SG62350)
- Makeup Gas-Ultra High Purity (UHP) nitrogen (N_2) available through UNC Scientific Storerooms (catalog # SG62750)

GC Supplies

Septa- (Restek, Bellafonte, PA) 11-mm diameter Thermolite Septa (catalog #20365)

- Injector Liner Sleeves- (Supelco, Bellafonte, PA) Split/Splitless Injector Sleeve with deactivated glass wool, 4 mm inner diameter (catalog #20486,05)
- Column Ferrules- (J&W) graphite/vespel 0.5 mm ferrules (catalog #5002025)
- Autosampler Syringes- 10 µL Agilent tapered needle syringe

Reagents

- Laboratory Grade Water (LGW)
- Extraction solvent: OmniSolv Methyl-t-Butyl Ether, EMD Chemicals, (Fisher Scientific – catalog # MMX08266)

- Sodium sulfate (Na_2SO_4), Mallinckrodt, granular, ACS grade (catalog #8024) from Scientific Storeroom. Bake at 400°C in muffle furnace for 24 hours in a shallow, porcelain dish covered with aluminum foil. Store in glass-stoppered bottle in dessicator.
- Solvent for dilution of standards: OmniSolv Methyl-t-Butyl Ether (EMD Chemicals, Fisher Scientific – catalog # MMX08266)
- Methanol (for rinsing glassware) HPLC grade
- L-Ascorbic Acid (for quenching residual Cl_2) Certified ACS grade (Fisher Scientific – catalog #A61-25)
- Sulfuric Acid (for pH adjustment) Certified ACS Plus (Fisher Scientific – catalog #A300-212)

Standards

- THM Calibration Mix, 2000 µg/mL each in methanol. (Supelco, Bellafonte - catalog # 48140-U)
- EPA 551B Halogenated Volatiles Mix, 2000 µg/mL each in methanol (Supelco, Bellafonte - catalog # 4-8046)
- Chloral Hydrate, 1000 µg/mL in acetonitrile (Supelco, Bellafonte - catalog # 47335-U)
- Internal Standard (IS): Aldrich (Milwaukee, WI) 1,2-dibromopropane neat standard, 99+% (catalog #14,096-1)
- Bromoacetamide (98%), Acros Organics (catalog # 291100050)
- Dichloroacetamide (98%), Acros Organics (catalog # 113050100)
- Trichloroacetamide (99%), Acros Organics (catalog # 202920250)
- Bromochloroacetamide, CanSyn Chemical Corporation
- Bromodichloroacetamide, CanSyn Chemical Corporation
- Tribromoacetamide, CanSyn Chemical Corporation
- Chloroiodoacetamide, CanSyn Chemical Corporation
- Dibromochloroacetamide, CanSyn Chemical Corporation
- Dibromoacetamide, CanSyn Chemical Corporation
- Diiodoacetamide, CanSyn Chemical Corporation
- Bromoiodoacetamide, CanSyn Chemical Corporation

Samples

Samples should be collected headspace-free in pre-cleaned 60 mL glass vials with screw caps and PTFE-lined silicone septa containing 1.4 mg ascorbic acid. Samples should be filled head-space free and holding vial at an angle so halogenated volatiles do not escape through volatilization. Store samples in fridge at 4°C. Samples should be extracted within 24 hours of quenching.

Procedure

Internal Standard

Stock solution of Internal Standard (IS) at ~2000 µg/mL in MtBE - prepared by injecting 10µL of the neat standard and injecting into a 5 mL volumetric flask containing MtBE, fill to line with MtBE.

Primary dilution at 100µg/mL: prepared by injecting 250µL of IS stock solution using a micropipette into a 5 mL volumetric flask containing MtBE, fill to line with MtBE.

Extracting solution at 50 µg/L or 100 µg/L (depending on what expected concentration of analytes in samples): calculate how much extracting solvent will be needed for all of your samples and calibrations (3 mL for each sample and calibration). Make from primary dilution, and prepare more than needed because there may be bubbles in the dispenser that you need to clear, and will need to pump a few times to start out.

Halogenated Volatiles Calibration Standards

These are prepared as a mix of THM4, 551B Halogenated Volatiles and chloral hydrate.

Calibration Standard #1: 100 µg/mL, 100 µL of each THM4 and EPA551B stock calibration mix and 200 µL of chloral hydrate to 2 mL volumetric flask containing MtBE, fill to line with MtBE.

Calibration Standard #2: 1 µg/mL, 20 µL of Calibration Standard #1 into 2 mL volumetric flask containing MtBE, fill to line with MtBE.

Haloacetamide Stock & Calibration Standards

Primary dilution stock: 2000 µg/mL. Prepared from solid standards of each haloacetamide. Weigh out 20 mg of each compound, dissolve in 10 mL high purity MtBE.

Calibration Standard #1: 20 µg/mL, 20 µL of primary dilution stock into 2 mL volumetric flask containing MtBE, fill to line with MtBE.

Calibration Standard #2: 1 µg/mL, 100 µL of Calibration standard #1 into 2 mL volumetric flask containing MtBE, fill to line with MtBE.

1. Transfer standards to a 2-mL amber glass vial and store in laboratory standards freezer at -15°C.

2. Check calibration standards a few days before extraction. Make up two dilutions (50µg/L and 1µg/L) in MtBE containing internal standard. Standards should be monitored for degradation and contamination by comparing standard chromatographic peak area values obtained on the performance evaluated designated GC to those obtained during initial calibration of standard. The responses obtained on the same instrument are normalized relative to the freshly prepared internal standard to account for instrument detector drift and the values for each compound stored on a spreadsheet on the GC computer and backed-up to the external hard drive. New standards should be made from the stock solution if check exceeds 20% drift. If the drift persists, purchase new stock solutions from two suppliers and compare the responses making a note of the stock batch number.

3. Prepare a laboratory reagent blank (the level 1 calibration standard - see step 6) and the laboratory fortified blank (level 3 calibration standard – see step 6) at the beginning of each day and analyze on the GC before extracting samples. If QC criteria fail, troubleshoot and correct the problem, reanalyzing these check standards before proceeding to the next step.

4. Prepare calibration standards in 100 mL LGW according to the range of concentrations expected in the samples. Examples for halogenated volatiles and haloacetamides are shown below.

Example of Halogenated Volatile Calibrations

Level	Calibration standard	Volume Cal. std. added (µL) to 100 mL LGW	Analyte conc. (µg/L)
1	--	0	0
2	1 µg/mL	10	0.1
3	1 µg/mL	100	1
4	100 µg/mL	10	10
5	100 µg/mL	20	20
6	100 µg/mL	50	50
7	100 µg/mL	100	100
8	100 µg/mL	200	200

Example of Haloacetamide Calibrations

Level	Calibration standard	Volume Cal. std. added (µL) to 100 mL LGW	Analyte conc. (µg/L)
1	--	0	0
2	1 µg/mL	10	0.1
3	1 µg/mL	50	0.5
4	20 µg/mL	25	5
5	20 µg/mL	50	10
6	20 µg/mL	125	25
7	20 µg/mL	250	50

5. Prepare matrix spike (MS) and matrix spike duplicate (MSD) in 25mL samples → should be ~2-3 times halogenated volatile levels in samples.

6. Measure 30 mL from all calibration standards using a 50mL measuring cylinder starting from lowest to highest concentration and then follow with the samples all in duplicate and transfer into 60 mL vials. Rinse cylinder 3 times with LGW and once with sample to be measured next between each. Pour at an angle so halogenated volatiles are not lost through volatilization.

7. Adjust all samples and calibrations to approximately pH 3.5 with 0.2 N H_2SO_4. (Amount required for pH adjustment will likely be different for calibrations compared to samples. Use remaining 30 mL aliquot from 60 mL vial to determine how much H_2SO_4 will be needed.)

8. Add 3 mL extracting solvent from a solvent dispenser bottle to each 30 mL aliquot. Make sure there are no bubbles in the dispenser addition line.

9. Add ~6 g pre-baked sodium sulfate to each 30 mL sample/calibration standard. (6 g can be measured out in pre-measured marked 10 mL glass beaker) Vortex samples for 1 minute immediately after adding sodium sulfate to avoid clumping. Let samples settle for 5 minutes.

10. Using a disposable 23-cm glass Pasteur transfer ~1.5 mL from the middle of the MtBE layer (top layer) to a GC autosampler vial. Do not transfer any sodium sulfate crystals as they will clog the GC. Cap and crimp vial. Fill three GC vials for each sample (one for halogenated volatile analysis, one for haloacetamide analysis, and one backup), and two GC vials with each calibration (since you will have separate halogenated volatile and haloacetamides calibrations – need one for analysis and one backup). Use GC vial inserts. Store in the laboratory freezer at -15°C in a tray covered in aluminum foil if not analyzed immediately. Also fill two autosampler vials with MtBE and 2 vials of extracting solvent containing MtBE + IS. Analyze within 4 weeks.

11. Analyze according to specified GC method (see GC temperature programs below) on the designated GC. Instructions for GC use for this method are provided by the instrument that is available at the time.

Quality Control

Precision is measured as the average and relative percent difference (RPD) of the duplicate analyses of each sample. RPD should be less than 10% otherwise sample has to be flagged as suspect. The coefficient of variation of all the internal standard responses for the complete set of samples must be less than 15%. Individual samples responsible for elevating this value above the threshold should be flagged and considered suspect.

A calibration check standard is prepared in the mid-range of the standard calibration curve and is injected every 10 samples. If the detector response for this sample varies more than 10% from the previous injection, all samples analyzed between the two injections are flagged for investigation.

Each sample bottle set is accompanied by replicate field and travel blanks.

In cases with unknown or mislabeled samples, we will first attempt to determine what sample identification actually is, based on received samples and shipping list information. If a reasonable idea of the sample is determined, it will be analyzed and those data will be qualified in reports and future data analyses.

GC-ECD analysis on Hewlett-Packard GC5890 Series II:
Injector:
Syringe size = 10µL; Injection volume = 2µL
Wash solvent = MtBE; Pre-injection washes = 3; Post-injection washes = 3; Pumps = 3
Injector Temperature = 200°C; Injection splitless (split after 0.5 min)

Oven/Column:
Oven equilibration time = 3 min; Oven max °C = 300°C
Gas = He; Column flow = 1mL/min
Column type = DB1 (Agilent), 30.0m length, 0.25mm inner diameter, 1µm film thickness
Split flow = 1mL/min; Split ratio = 1:1

Halogenated Volatiles Oven Temperature program (Total time = 55.75 min)

	Velocity (°C/min)	**Temp. (°C)**	**Time (min)**
Initial	-	35	22
Level 1	10	145	2
Level 2	20	225	10
Level 3	20	260	5

Electron Capture Detector (ECD), Detector temperature = 290°C, Injector temp: 117°C

Haloacetamides Oven Temperature program (Total time = 59.60 min)

	Velocity (°C/min)	**Temperature (°C)**	**Time (min)**
Initial	-	37	1
Level 1	5	110	10
Level 2	5	280	0

Electron Capture Detector (ECD), Detector temperature = 300°C

Chromatogram for 20 µg/L as iodo-THMs and 100 µg/L as THM4 standards

Data File C:\HPCHEM\1\DATA\LS030419\018F1801.D Sample Name: 20ugL_ITHM_2

```
======================================================================
Injection Date  : 3/5/2019 7:15:09 AM          Seq. Line :  18
Sample Name     : 20ugL_ITHM_2                  Location : Vial 18
Acq. Operator   : LES                             Inj :   1
Acq. Instrument : Instrument 1                Inj Volume : 2 µl
Acq. Method     : C:\HPCHEM\1\METHODS\LS_HVOL.M
Last changed    : 7/10/2017 8:59:12 PM by KES
Analysis Method : C:\HPCHEM\1\METHODS\STANDBY.M
Last changed    : 5/7/2017 3:16:04 PM by KES
                  (Results are from a previously saved Batch)
BL created 09/29/11 from 5890 GC method, for newly reimaged 6890 computer
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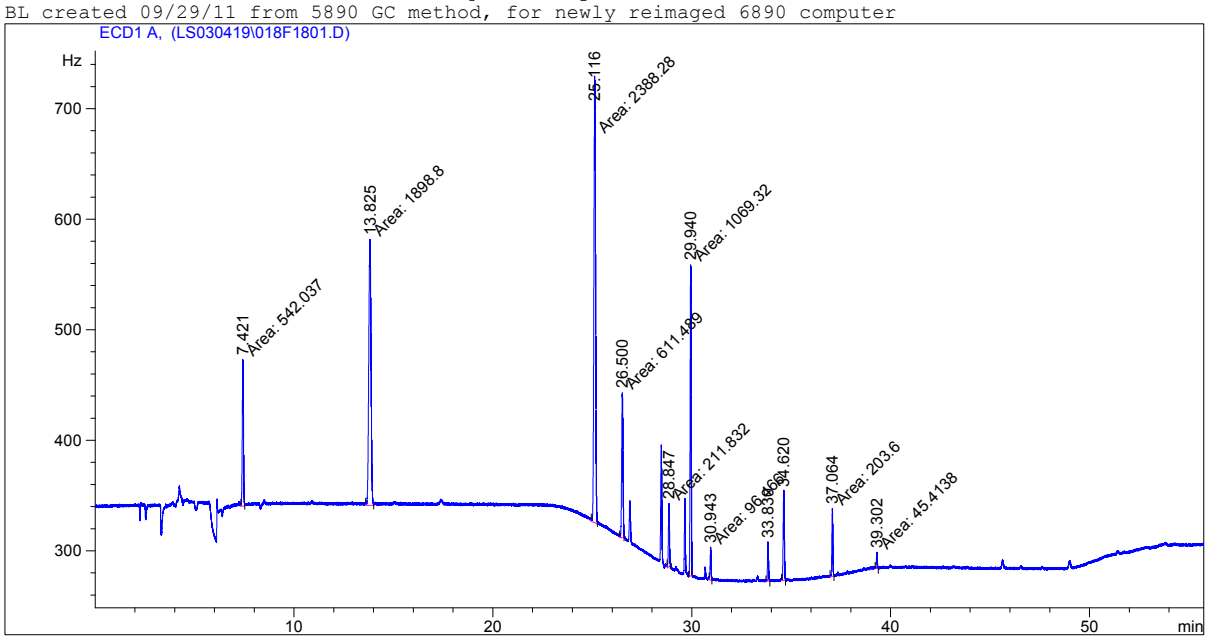



```
======================================================================
                        Area Percent Report
======================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

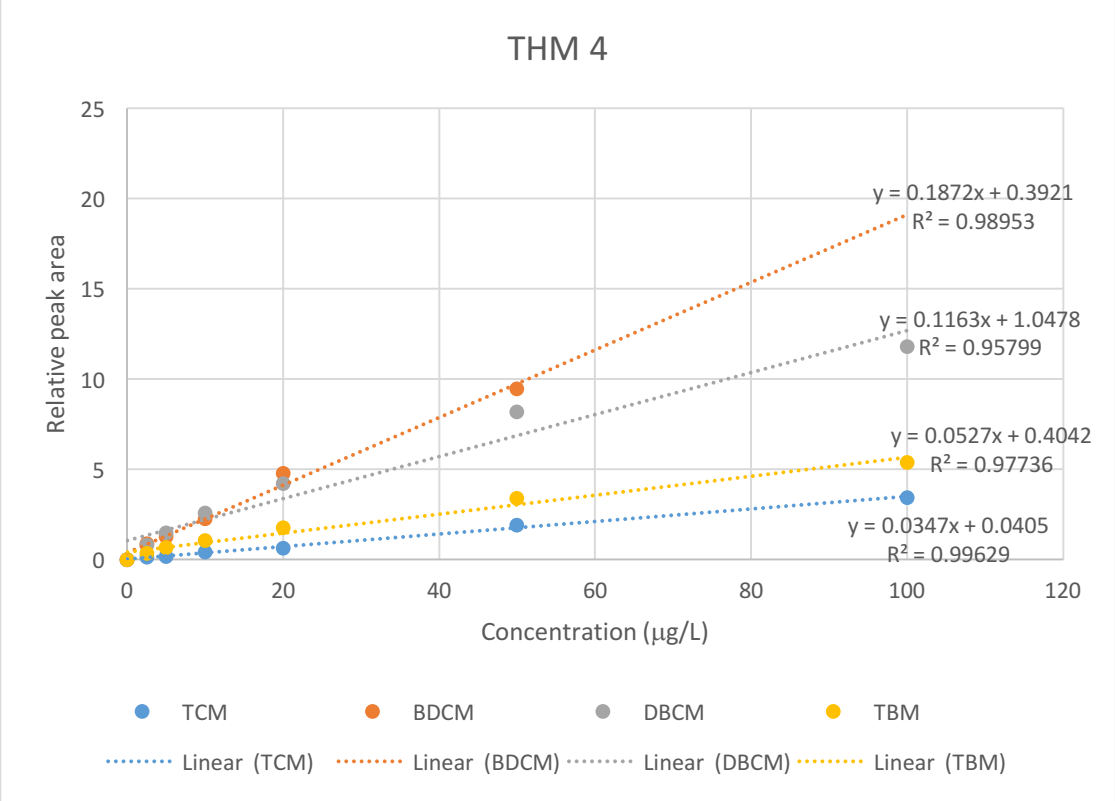

Signal 1: ECD1 A,

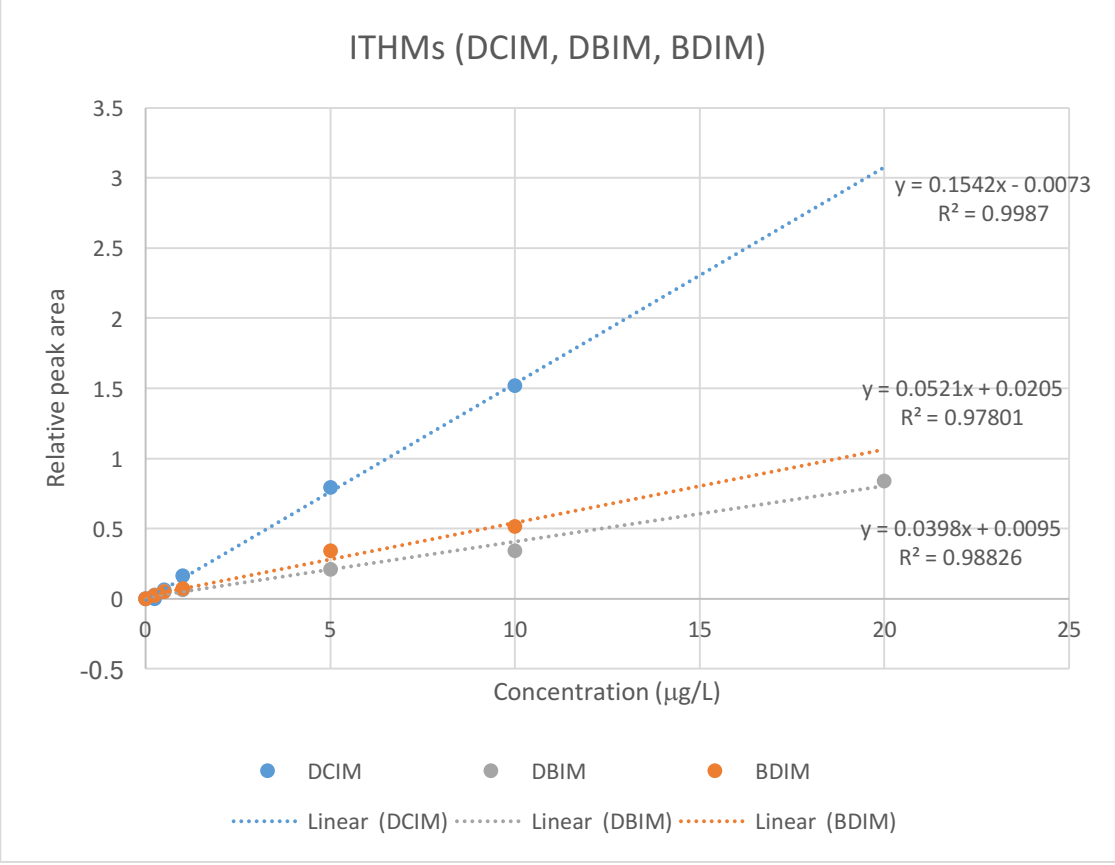
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [Hz*s]      [Hz]        %
----|-------|----|-------|----------|----------|--------|
   1   7.421 MM    0.0681  542.03748  132.59473  7.20112
   2  13.825 MM    0.1314 1898.80029  240.75114 25.22609
   3  25.116 MM    0.0985 2388.28369  403.97769 31.72902
   4  26.500 MM    0.0777  611.48895  131.18739  8.12380
   5  28.847 MM    0.0618  211.83208   57.11553  2.81425
   6  29.940 MM    0.0633 1069.32104  281.52087 14.20623
   7  30.943 MM    0.0546   96.46598   29.45123  1.28158
   8  33.830 VP    0.0423  125.44280   35.25813  1.66654
   9  34.620 VBA   0.0506  334.44150   80.95306  4.44315
  10  37.064 MM    0.0555  203.59985   61.10021  2.70488
  11  39.302 MM    0.0520   45.41381   14.55255  0.60334

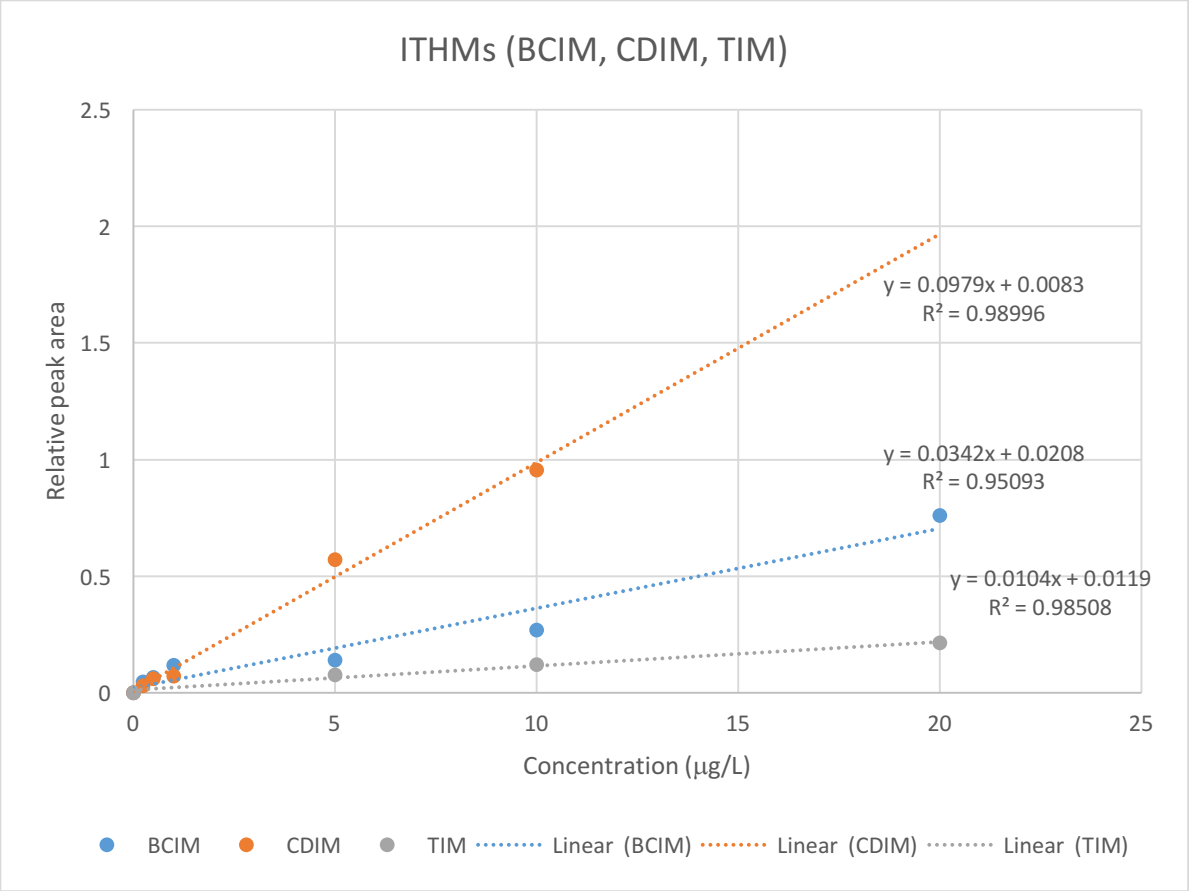
Totals :                  7527.12748 1468.46254

 Results obtained with enhanced integrator!
```

Calibration curves for THM4 and iodo-THMs






ITHMs (BCIM, CDIM, TIM)
Relative peak area
Concentration (µg/L)
y = 0.0979x + 0.0083
R² = 0.98996
y = 0.0342x + 0.0208
R² = 0.95093
y = 0.0104x + 0.0119
R² = 0.98508
BCIM
CDIM
TIM
Linear (BCIM)
Linear (CDIM)
Linear (TIM)

APPENDIX B

Standard operating procedure for ion chromatograph analysis, sample chromatograms, and calibration curve.

DIONEX ION CHROMATOGRAPH
STANDARD OPERATING PROCEDURE
Prepared July 2009 by Ryan Kingsbury

Initial Startup:

1. Fill all eluent bottles and the regenerant bottle with the appropriate solutions.
2. Turn on pressure at the Helium tank
3. Turn the eluent degas module ON. Set all bottles to SPARGE and turn each individual bottle to ON. Loosen the cap on each bottle.
4. Verify that gas is flowing out of each sparge line that is turned on. Connect the sparge lines to the bottles. Allow the eluents to sparge for 20 minutes
5. While the eluents are sparging, take out the suppressor and remove the caps on all four ports
6. Hydrate the suppressor membranes by using a syringe and the luer-lok adapter to push ~5 mL LGW through the REGEN IN port and ~3 mL through the ELUENT OUT port. Be careful not to push through the ELUENT OUT port too fast or you may damage the membrane
7. Uncap the ends of the regenerant and eluent lines in the sink
8. Install the suppressor in the cabinet and connect the REGEN OUT port of the suppressor to the appropriate line
9. Connect the column and guard column to the injection assembly
10. When sparging is complete, remove the sparge lines. Tighten the caps on the bottles and switch them to PRESSURIZE. Adjust the regulator on the degas module to 7 +/- 2 psi
11. Turn the pump ON
12. Prime the pump. For each eluent bottle, set the flow to 100% and 1.0 mL/min. Turn the silver bar on the pump perpendicular to the pump face and attach a 3 mL syringe. Press START and draw about 3 mL from the port into the syringe. Discard. Repeat two more times or until no air bubbles are seen. On the third time, loosen the black knob and push the syringe contents back into the pump while tapping on the clear tube to remove any air bubbles. Re-tighten the knob.
13. Begin pumping eluent through the system at 1.0 mL/min. As soon as you see eluent dripping out of the column line, connect it to the ELUENT IN port of the suppressor.
14. When you see eluent emerge from the ELUENT OUT port of the suppressor, connect it to the detector.
15. Tighten the cap and the gas line connection on the regenerant bottle. Carefully turn on pressure to the regenerant bottle at the regulator, watching to see when regenerant begins to flow in the line. When regenerant begins to flow, connect the line to the REGEN IN port of the suppressor.
16. Adjust the pressure until the desired regenerant flow rate is achieved (measure flow out of the REGEN OUT line in the sink with a graduated

cylinder and a watch). Consult the suppressor manual for optimal regenerant flow rates for each eluent strength.

17. Turn the ACI and Detector ON. Turn the cell OFF.
18. Allow the system to equilibrate for 30 minutes
19. Turn the cell ON. Record the baseline conductivity and the pump back-pressure in the log book.
20. Run samples.

Short Term (Daily operation) Shutdown:

1. Flush the system with LGW at 1.0 mL/min for 10 minutes.
2. Turn the cell OFF. Turn the detector OFF.
3. STOP and turn off the pump
4. Turn off pressure to the regenerant bottle at the regulator. Loosen the regenerant bottle cap to relieve the pressure. Re-tighten the cap.
5. Cap the ends of the eluent and regenerant lines in the sink to keep them from drying out.
6. Leave the Eluent Degas Module ON with pressure to the eluent and LGW bottles.

Short Term (Daily operation) Startup:

1. Uncap the ends of the regenerant and eluent lines in the sink
2. Turn on pressure to the regenerant bottle at the regulator. Adjust until the desired regenerant flow rate is achieved (measure flow with a graduated cylinder in the sink)
3. Turn the pump ON
4. Prime the pump. For each eluent bottle, set the flow to 100% and 1.0 mL/min. Turn the silver bar on the pump perpendicular to the pump face and attach a 3 mL syringe. Press START and draw about 3 mL from the port into the syringe. Discard. Repeat two more times or until no air bubbles are seen. On the third time, loosen the black knob and push the syringe contents back into the pump while tapping on the clear tube to remove any air bubbles. Re-tighten the knob.
5. Begin pumping eluent through the system at 1.0 mL/min
6. Turn the ACI and Detector ON. Turn the cell OFF.
7. Allow the system to equilibrate for 30 minutes
8. Turn the cell ON. Record the baseline conductivity and the pump back-pressure in the log book.
9. Run samples.

Long Term (> 1 week) Shutdown:

1. Flush the system with LGW at 1.0 mL/min for 10 minutes
2. Turn the cell OFF. Turn the detector OFF.
3. STOP the pump.
4. Turn off pressure to the regenerant bottle at the regulator. Loosen the regenerant bottle cap to relieve the pressure.

5. Remove the suppressor. Cap both ends of the regenerant out line. Cap the ELUENT IN and ELUENT OUT ports with the original plugs.
6. Using a disposable syringe and the luer-lok adapter in the drawer, push 5-6 mL of LGW through the REGEN IN port on the suppressor.
7. Cap the REGEN IN and REGEN OUT ports with the original plugs.
8. Connect the column directly to the detector. Flush the system with operating eluent for 10 minutes.
9. Remove the column and guard column. Cap the ends with the original caps and place in their respective boxes. Be careful not to tap, drop, or otherwise shock the columns as this will disturb the packing.
10. Connect the detector directly to the injection assembly. Flush the system with LGW at 9.9 mL/min for 10 minutes.
11. STOP and turn OFF the pump.
12. On the eluent degas module, switch all bottles to SPARGE. Loosen the caps to relieve the pressure. Switch the entire module OFF. Switch each bottle OFF. Switch all bottles to PRESSURIZE. Turn off the gas supply.

USEFUL INFORMATION FROM DIONEX MANUALS

General:
-You should not inject more than 50 nM of any single analyte onto the column (for AS-19), as this can affect the linearity of the response
-Be sensitive to the source of LGW used to prepare eluents and especially standards. Dionex recommends that the water have a resistance at least of 18.2 megaohm-cm. At the time of this writing, LGW from the Weinberg lab had noticeably lower ionic content (and produced a much better baseline) than LGW from the Singer lab.

Eluent Preparation:
-Use high quality (Fisher Certified) liquid NaOH, not pellets. The pellets have too much potential for contamination
-store the solution under a nitrogen atmosphere and limit exposure to air as much as possible in order to avoid carbonate intrusion
-use the following table to determine the weight of NaOH to add to 1 L of water:

Table 6

Dilution of 50% (w/w) NaOH to Make Standard AS19 Eluents

50% (w/w) NaOH g (mL)	Concentration of NaOH Eluent (mM)
0.40 (0.26)	5
1.6 (1.04)	20
8.00 (5.25)	100
160.00 (104.6)	2 M

Regenerant Notes:

Dionex recommends for typical
anion applications a sulfuric acid regenerant concentration between 25 mN and 75 mN and for typical cation applications a
TBAOH regenerant concentration of between 50 mN and 100 mN. It should be noted that there will be a small leakage of
regenerant ions into the eluent channel and is dependent primarily on the concentration of the regenerant used. A lower
regenerant concentration is preferred at a relatively higher flow rate since it produces a lower level of leakage hence a lower
background, than a higher regenerant concentration at a lower flow rate.

Table 3
Matching Regenerant Concentration and Flow Rate to Eluent Concentration and Flow Rate for the 4-mm AMMS 300 in the Chemical Suppression Mode

Eluent	Eluent Flow Rate (mL/min)	Regenerant Flow Rate (mL/min)	Regenerant Conc (mN H_2SO_4)
1.8 mM Na_2CO_3/1.7 mM $NaHCO_3$	0.5–2.0	3–5	25
2.7 mM Na_2CO_3/0.3 mM $NaHCO_3$	0.5–2.0	3–5	25
3.5 mM Na_2CO_3/1.0 mM $NaHCO_3$	0.5–2.0	3–5	25
9.0 mM Na_2CO_3	0.5–2.0	3–5	50
1.0 - 100 mM NaOH	0.5–1.5	3–10	50–100
1.0 - 100 mM KOH	0.5–1.5	3–10	50–100
1.0 - 20 mM $Na_2B_4O_7$	0.5–2.0	5–10	50
20 - 50 mM $Na_2B_4O_7$	0.5 - 1.5	10-May	50-100

Chromatogram of 100 µg/L as iodide and iodate standard

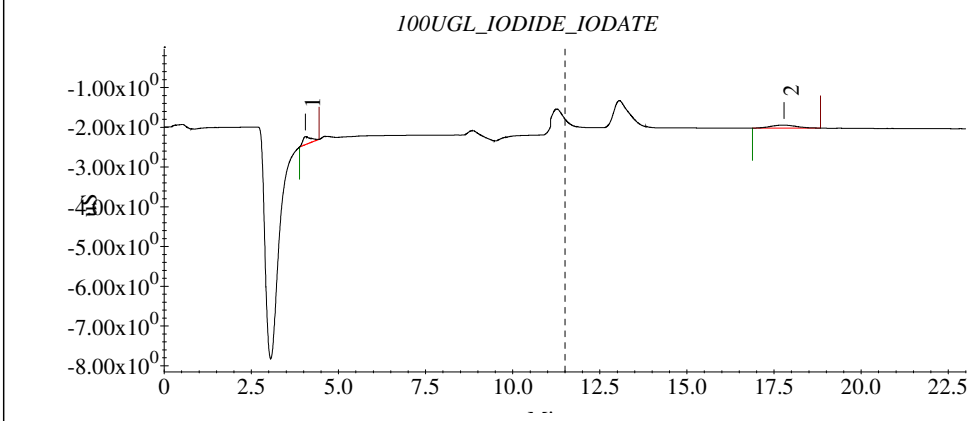
Sample Analysis Report

Sample Name : 100UGL_IODIDE_IODATE
Data File Name : C:\PEAKNET\DATA\LAUREN\190318\100UGL_IODIDE_IODATE_013.DXD

Method File Name : C:\PeakNet\method.aci\Lauren\ANIONS_AS-22_IODIDE.MET
Date Time Collected : 3/18/2019 6:36:58 PM

Peak Information : All Peaks

Peak #	Component Name	Retention Time	Amount (ug/L)	Peak Area	Peak Height
1	Iodate	4.05	177.61	3154000	201714
2	Iodide	17.79	116.72	3960400	76930



Chromatogram of finished water sample

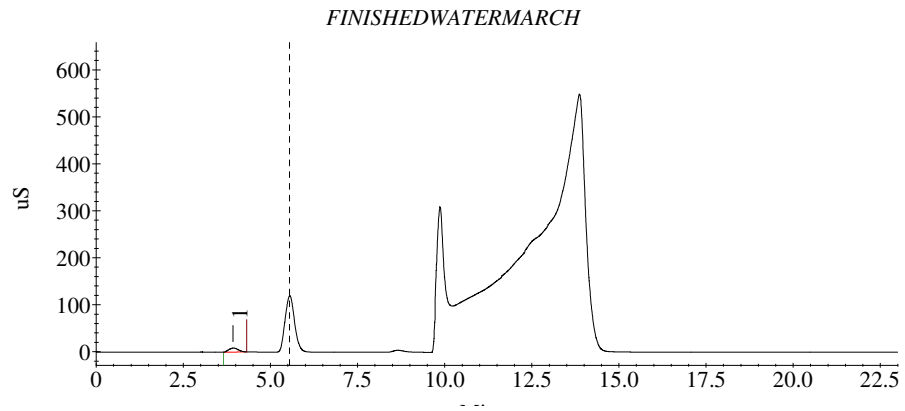
Sample Analysis Report

Sample Name : FINISHEDWATERMARCH
Data File Name : C:\PEAKNET\DATA\LAUREN\190318\FINISHEDWATERMARCH_004.DXD

Method File Name : C:\PeakNet\method.aci\Lauren\ANIONS_AS-22_IODIDE.MET
Date Time Collected : 3/18/2019 2:14:49 PM

Peak Information : All Peaks

Peak #	Component Name	Retention Time	Amount (ug/L)	Peak Area	Peak Height
1	Iodate	3.92	7157.96	160680112	8419458



Chromatogram of finished water sample containing 100 µg/L as iodide and iodate matrix spike

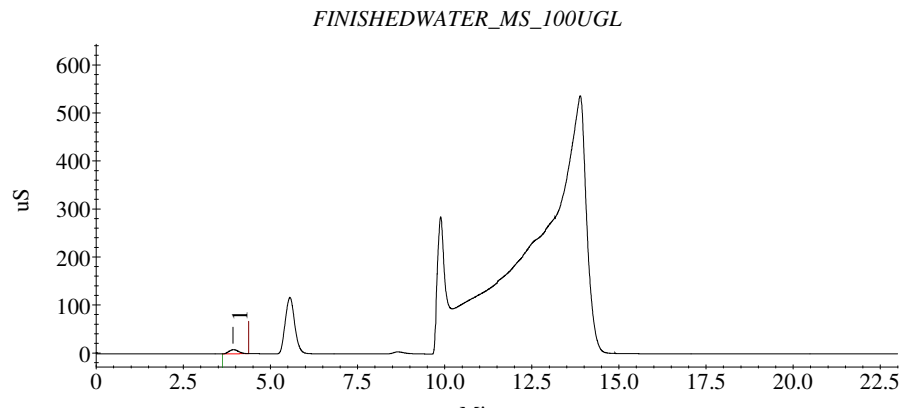
Sample Analysis Report

Sample Name : FINISHEDWATER_MS_100UGL
Data File Name : C:\PEAKNET\DATA\LAUREN\190318\FINISHEDWATER_MS_100UGL_010.DXD

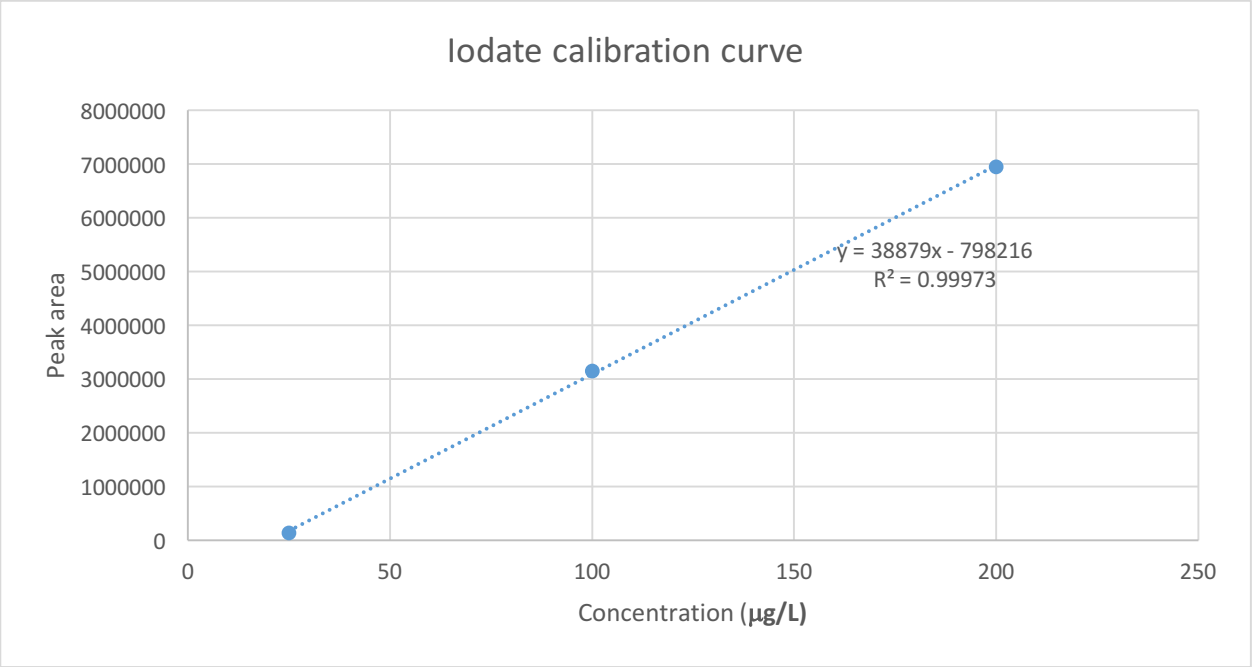
Method File Name : C:\PeakNet\method.aci\Lauren\ANIONS_AS-22_IODIDE.MET
Date Time Collected : 3/18/2019 5:17:03 PM

Peak Information : All Peaks

Peak #	Component Name	Retention Time	Amount (ug/L)	Peak Area	Peak Height
1	Iodate	3.92	7171.65	160989080	8371219



Iodate calibration curve



APPENDIX C

Standard Operating Procedure for Total/Dissolved Organic Carbon (TOC/DOC) and Total Nitrogen (TN) analysis in aqueous samples, raw data, and calibration curve

This instrument is housed in MHRC room 1111 together with other instruments. Access to this room is only provided to those who have been trained, observed, and demonstrated competence and who have been approved by Dr Weinberg. You are expected to prepare samples and standards in your own laboratory and only use the space in this laboratory assigned to the instrument. Do not use anything else in the laboratory. After use, the space around the instrument must be cleaned

Standards Preparation

Dissolved Organic Carbon (DOC) Stock Standard (1,000 mg/L as C)

- Dissolve 2.125 g Potassium Hydrogen Phthalate in 1-L lab grade water (LGW); mix with a magnetic stir bar
- Store in fridge in amber bottle with PTFE-lined septa/cap. Good for 2 months

Total Nitrogen (TN) Stock Standard (1000 mg/L as N)

- Dissolve 7.219 g Potassium nitrate in 1-L LGW; mix with a magnetic stir bar
- Store in fridge in amber bottle with PTFE-lined septa/cap. Good for 2 months

HCl solution (2 N)

- Carefully add 41 mL concentrated HCl (12.1 N) to LGW in a 250 mL volumetric flask.
- Fill to line with LGW and carefully invert 3 times. Store in amber bottle with PTFE-lined septa/cap.

DOC Working Solution (100 mg/L as C)

- Pipette 10-mL of DOC Stock Standard into a 100 mL volumetric flask; fill to line with LGW; invert stoppered flask three times
- Store in fridge in amber bottle with PTFE-lined septa/cap. Good for 1 week

DOC/TN Working Solution (100 mg/L as C, 100 mg/L as N, 0.05 M HCl)

- Pipette 10-mL of DOC Stock Standard, 10 mL of TN Stock Standard, and 2.5 mL of 2 M HCl into a 100 mL volumetric flask; fill to line with LGW; invert stoppered flask three times
- Store in fridge in amber bottle with PTFE-lined septa/cap. Good for 1 week

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Calibration Points should be made fresh for every run

- To make 0.5 mg-C/L Calibration Point, pipette 0.5 mL of DOC Working Solution into a 100-mL volumetric flask; fill to line with LGW; invert stoppered flask three times
- Additional Calibration Points are made in an analogous fashion

Procedure

Notes:
*The concentrations of the samples need to be **less than 10 mg/L** as C or N – you should first test a highly diluted sample to make sure you will be in the correct range.
*If you do not plan to analyze your water samples soon after you collect them, adjust to pH 4.5 and store them in the fridge.
*Before you contemplate running samples, you need to talk to Dr Weinberg about the type of samples you will be running – to make sure they will not compromise the instrument.

1. Prepare calibrations (for example: 0, 0.5, 5, 10 mg C and N/L) and samples (dilute if necessary – concentration needs to be less than 10 mg/L as C or N).

2. Pour your samples and calibrations into acid-washed TOC vials. If you use the shared vials you should indicate in the logbook how many you use and the date they are returned to the inventory.

3. Acidify all samples and calibrations to pH 2-2.5 using 2 N HCl. A typical surface water requires about 2-4 drops of 2 N HCl if using 24 mL sample vials, but you need to test your actual sample matrix using a pH meter to be sure you adjust the pH to this value. Cover each vial with aluminum foil. Calibration points prepared using LGW from Weinberg lab typically require ~6 drops of 2 N HCl (but you should check the pH using an extra aliquot with the pH meter).

4. Start the system: Before using the instrument, check a day or two in advance that the head pressure on the air tank is above 500psi by opening the regulator attached to the air tank and reading the pressure. If it is not, consult with whoever is responsible for the instrument so that a new gas tank can be ordered. Use only UHP air ("air grade zero"). On the day of use turn on computer (login Weinberg Lab, password chocolate), turn on TOC analyzer, and open the air tank at the regulator.

5. Check the system:
Open Software (TOC ControlV)
Sample table (User = TOC; password = UNC)
File → New → sample run → (TC/IC-TN 24mL system (default) or use TC/IC-TN 40mL if using 40 mL sample vials)
Instrument → connect → use PC settings
Check the following on the instrument:

(a) Carrier gas flow = 150 (TOC analyzer)
(b) Pressure = 200 (TOC analyzer)
(c) Continuous bubbles in the plastic bottle (TOC analyzer)
(d) N flow ~ 0.5 (Nitrogen unit)
(e) Fill the humidifier tank with laboratory grade water (LGW) of TOC < 0.5ppm water if it is empty or almost empty.

Instrument → Background monitor → run and wait for all points to be checked and green (about 20 mins)

6. Create your calibration curve

For TOC/DOC:
File → New → Calibration curve → 24mL system (default) → NPOC (for Non Purgeable Organic Carbon)
Standard
TOC
Linear Regression (uncheck the 'zero shift')
Check 'multiple injections'
Put the number of standards and the range of the concentrations
Injection volume of 100 µL
Adjust the concentrations of each standard and save

For TN:
File → New → Calibration curve → 24mL system (default) → TN
Standard
TN
Linear Regression (uncheck the 'zero shift')
Check 'multiple injections'
Put the number of standard and the range of the concentrations
Injection volume of 100 µL
Adjust the concentrations of each standard and save

7. Create your sequence
(a) First excel cell → insert autogenerate→ choose your method → put 3-4 blank LGW vials to rinse the system
(b) Run a 5 mg/L as C and N standard after LGWs. You will record the area counts for these in the logbook and do the same for a 5 mg/L as C and N standard at the end of your run.
(c) Click on next excel cell → insert calib curve NPOC → enter the vial #s in the ASI vial view
(d) Next excel cell → insert calib curve TN → enter the vial #s
(e) Next excel cell → insert auto generate → choose your method → enter the number of samples and start vial # (only after the standards) → Enter your sample name in the excel cells→ Save as your sequence
*be sure to run another 5 mg/L as C and N standard after all of your samples and a LGW blank. Run 3 LGW blanks after this standard too.

8. Check the system: Recheck the previous signals, if all lights are green,
Maintenance → replace flow line content (cleans the syringe)

9. Run the sequence
Instrument → Start → Shut down → make sure external acid addition is checked → run

10. Instrument will shut down once sample run is finished, but you need to come in and manually turn off the gas tank at the regulator when run is done.

11. In the logbook by the instrument, record the method and calibration you used next to your name and the date. When your samples have finished running, record the calibration curve

information: slope, y-intercept, R^2, and the area counts for the first non-zero calibration point area. Also record the area counts for the 5 mg/L standards at the start and end of your run. If the response is different, alert the student who oversees the instrument use and be prepared to help troubleshoot. You should similarly alert this person if your calibration line and sensitivity diverges from the values recorded in the previous 3 months.

12. After running your samples, remove vials from instrument immediately and clean them. Any vial containing environmental samples (tap water or dirtier) needs to be rinsed and put in the 10% nitric acid bath overnight. Then rinse at least 3x with LGW and dry in 180^{o}C oven overnight. Any vial containing LGW or standards made up in LGW can be rinsed 3x with LGW and dried in 180^{o}C oven overnight.

13. Maintenance – All users are expected to contribute their time in maintaining the instrument, troubleshooting problems, and providing resources to replace consumables. By using this instrument you agree to order and charge your account for replacement of instrument consumables.

DOC/TDN raw data

Instr.Information

System	TC/IC-TN 24 mL vials
Detector	Combustion
Catalyst	TC/TN
Cell Length	long

Sample

Sample Name:	rinse
Sample ID:	rinse
Origin:	KES_NPOC+TN.met
Chk. Result	

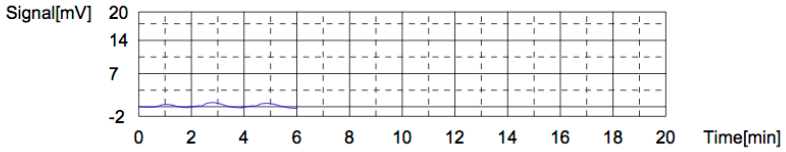
Type	Anal.	Dil.	Result
Unknown	NPOC/TN	1.000	NPOC:0.4493mg/L TN:0.1111mg/L

1. Det

Anal.: NPOC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	2.198	0.1674mg/L	100uL	1	E	bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 6:08:25 PM
2	4.925	0.4615mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 6:10:56 PM
3	4.699	0.4371mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 6:13:31 PM

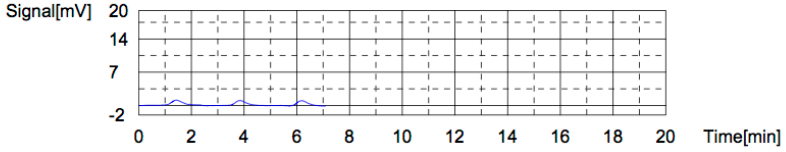
Mean Area 4.812
Mean Conc. 0.4493mg/L



Anal.: TN

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	3.211	0.1112mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 6:08:25 PM
2	2.956	0.1012mg/L	100uL	1	E	bl_tn.2012_03_08_14_11_32.cal	3/4/2019 6:10:56 PM
3	3.209	0.1111mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 6:13:31 PM

Mean Area 3.210
Mean Conc. 0.1111mg/L



Sample

Sample Name:	rinse
Sample ID:	rinse
Origin:	KES_NPOC+TN.met
Chk. Result	

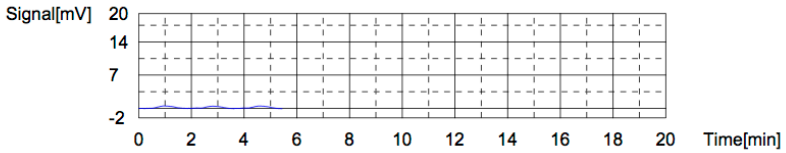
Type	Anal.	Dil.	Result
Unknown	NPOC/TN	1.000	NPOC:0.1451mg/L TN:0.08190mg/L

1. Det

Anal.: NPOC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	1.964	0.1422mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 7:03:59 PM
2	1.693	0.1129mg/L	100uL	1	E	bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 7:06:16 PM
3	1.834	0.1282mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 7:08:58 PM

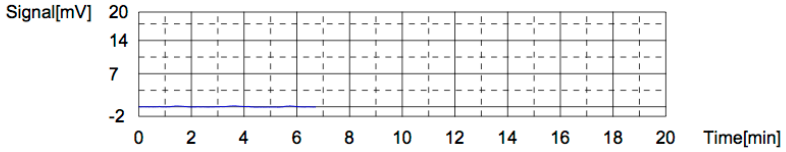
Mean Area 1.899
Mean Conc. 0.1352mg/L



Anal.: TN

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	0.6029	0.00934mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 7:03:59 PM
2	0.4232	0.00233mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 7:06:16 PM
3	0.8829	0.02028mg/L	100uL	1	E	bl_tn.2012_03_08_14_11_32.cal	3/4/2019 7:08:58 PM

Mean Area 0.5131
Mean Conc. 0.00584mg/L



Cal. Curve

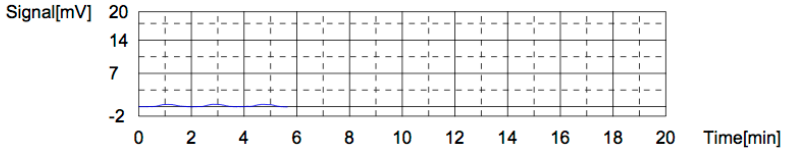
Sample Name: NPOC
Sample ID: NPOC
Cal. Curve: les_npoc_2019_03_04.2019_03_04_19_08_59.cal

Type	Anal.
Standard	NPOC

Conc: 0.000mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	1.827	100uL	1	*******	E	3/4/2019 7:17:32 PM
2	2.051	100uL	1	*******		3/4/2019 7:19:37 PM
3	2.065	100uL	1	*******		3/4/2019 7:21:42 PM

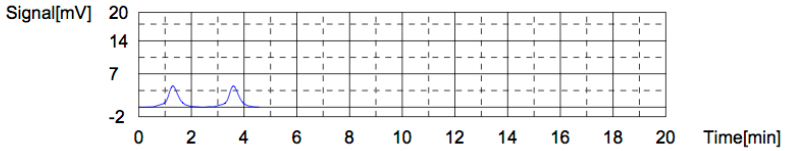
Acid Add. 1.500%
Sp. Time 90.00sec
Mean Area 2.058



Conc: 0.1000mg/L

No.	Area	Inj. Vol.	Aut. Dil.	Rem.	Ex.	Date / Time
1	3.589	100uL	1	*******	E	3/4/2019 7:30:28 PM
2	3.392	100uL	1	*******		3/4/2019 7:32:41 PM
3	3.349	100uL	1	*******		3/4/2019 7:35:00 PM

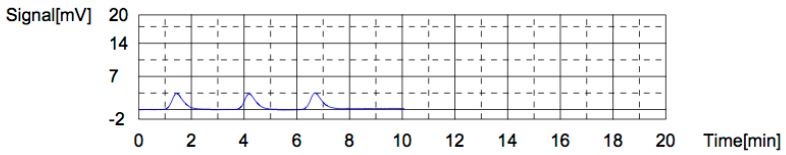
Mean Area 12.85
Mean Conc. 1.316mg/L



Anal.: TN

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	10.61	0.4001mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 10:15:56 PM
2	9.989	0.3759mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 10:18:37 PM
3	12.52	0.4747mg/L	100uL	1	E	bl_tn.2012_03_08_14_11_32.cal	3/4/2019 10:23:38 PM

Mean Area 10.30
Mean Conc. 0.3880mg/L



Sample

Sample Name: Post ozone 1
Sample ID: rinse
Origin: KES_NPOC+TN.met
Chk. Result

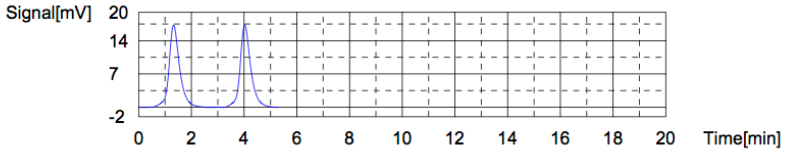
Type	Anal.	Dil.	Result
Unknown	NPOC/TN	1.000	NPOC:5.249mg/L TN:0.6373mg/L

1. Det

Anal.: NPOC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	49.36	5.254mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 10:33:14 PM
2	49.27	5.244mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 10:36:18 PM

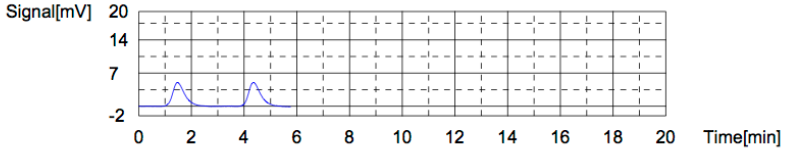
Mean Area 49.31
Mean Conc. 5.249mg/L



Anal.: TN

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	16.62	0.6348mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 10:33:14 PM
2	16.75	0.6399mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 10:36:18 PM

Mean Area 16.69
Mean Conc. 0.6373mg/L



Sample

Sample Name: Finished water March 1
Sample ID: rinse
Origin: KES_NPOC+TN.met
Chk. Result

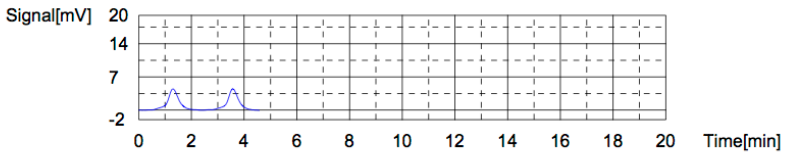
Type	Anal.	Dil.	Result
Unknown	NPOC/TN	1.000	NPOC:1.336mg/L TN:0.3384mg/L

1. Det

Anal.: NPOC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	13.13	1.346mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 10:01:08 PM
2	12.93	1.325mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 10:03:46 PM

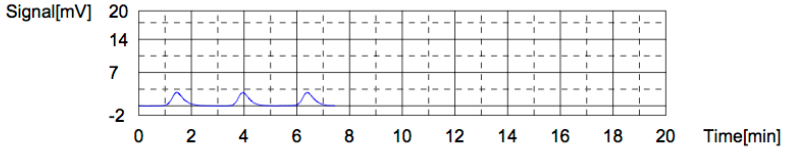
Mean Area 13.03
Mean Conc. 1.336mg/L



Anal.: TN

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	9.005	0.3374mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 10:01:08 PM
2	8.600	0.3216mg/L	100uL	1	E	bl_tn.2012_03_08_14_11_32.cal	3/4/2019 10:03:46 PM
3	9.052	0.3393mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 10:06:28 PM

Mean Area 9.029
Mean Conc. 0.3384mg/L



Sample

Sample Name: Finished water March 2
Sample ID: rinse
Origin: KES_NPOC+TN.met
Chk. Result

Type	Anal.	Dil.	Result
Unknown	NPOC/TN	1.000	NPOC:1.316mg/L TN:0.3880mg/L

1. Det

Anal.: NPOC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	12.93	1.325mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 10:15:56 PM
2	12.76	1.307mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 10:18:37 PM

Sample

Sample Name: Post ozone 2
Sample ID: rinse
Origin: KES_NPOC+TN.met
Chk. Result

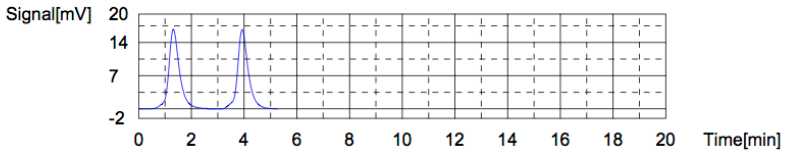
Type	Anal.	Dil.	Result
Unknown	NPOC/TN	1.000	NPOC:5.079mg/L TN:0.6157mg/L

1. Det

Anal.: NPOC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	47.59	5.063mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 10:46:02 PM
2	47.89	5.095mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 10:48:55 PM

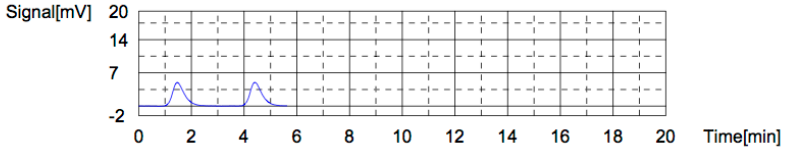
Mean Area 47.74
Mean Conc. 5.079mg/L



Anal.: TN

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	16.21	0.6188mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 10:46:02 PM
2	16.05	0.6125mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 10:48:55 PM

Mean Area 16.13
Mean Conc. 0.6157mg/L



Sample

Sample Name: Post PAC 1
Sample ID: rinse
Origin: KES_NPOC+TN.met
Chk. Result

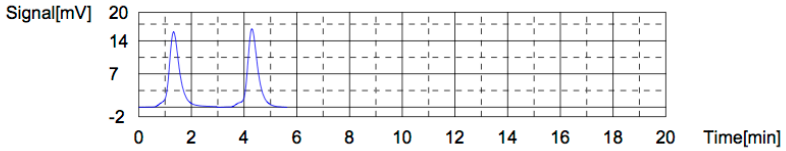
Type	Anal.	Dil.	Result
Unknown	NPOC/TN	1.000	NPOC:4.848mg/L TN:0.5913mg/L

1. Det

Anal.: NPOC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	45.03	4.787mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 10:58:41 PM
2	46.16	4.909mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 11:01:48 PM

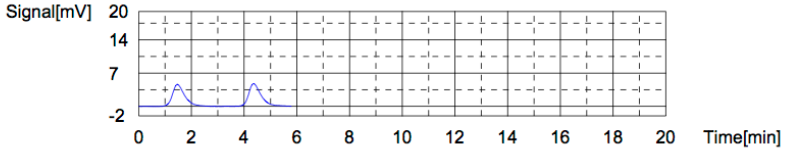
Mean Area 45.59
Mean Conc. 4.848mg/L



Anal.: TN

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	15.30	0.5832mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 10:58:41 PM
2	15.71	0.5993mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 11:01:48 PM

Mean Area 15.51
Mean Conc. 0.5913mg/L



Sample

Sample Name: Post PAC 2
Sample ID: rinse
Origin: KES_NPOC+TN.met
Chk. Result

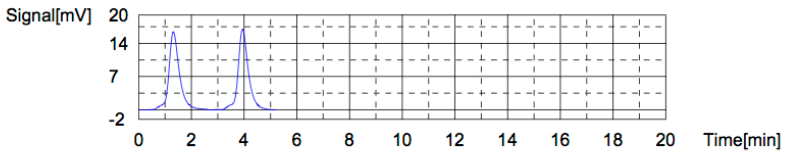
Type	Anal.	Dil.	Result
Unknown	NPOC/TN	1.000	NPOC:4.913mg/L TN:0.5208mg/L

1. Det

Anal.: NPOC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	45.84	4.874mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 11:11:13 PM
2	46.55	4.951mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 11:14:13 PM

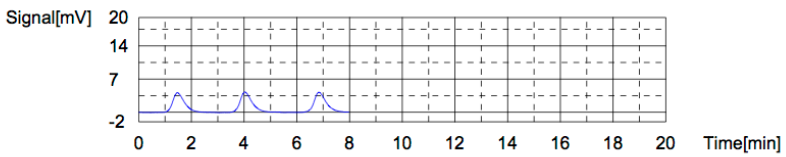
Mean Area 46.20
Mean Conc. 4.913mg/L



Anal.: TN

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	12.97	0.4923mg/L	100uL	1	E	bl_tn.2012_03_08_14_11_32.cal	3/4/2019 11:11:13 PM
2	13.79	0.5243mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 11:14:13 PM
3	13.61	0.5173mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 11:17:01 PM

Mean Area 13.70
Mean Conc. 0.5208mg/L



Sample

Sample Name: Jordan lake intake 1
Sample ID: rinse
Origin: KES_NPOC+TN.met
Chk. Result

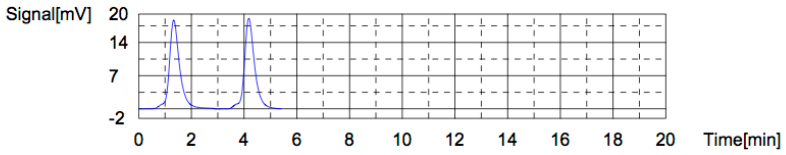
Type	Anal.	Dil.	Result
Unknown	NPOC/TN	1.000	NPOC:5.487mg/L TN:0.6373mg/L

1. Det

Anal.: NPOC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	51.16	5.448mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 11:26:36 PM
2	51.89	5.527mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 11:29:30 PM

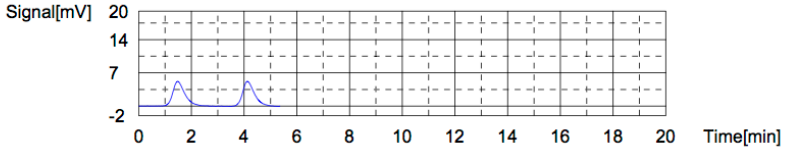
Mean Area 51.53
Mean Conc. 5.487mg/L



Anal.: TN

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	16.48	0.6293mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 11:26:36 PM
2	16.89	0.6453mg/L	100uL	1		bl_tn.2012_03_08_14_11_32.cal	3/4/2019 11:29:30 PM

Mean Area 16.69
Mean Conc. 0.6373mg/L



Sample

Sample Name: Jordan lake intake 2
Sample ID: rinse
Origin: KES_NPOC+TN.met
Chk. Result

Type	Anal.	Dil.	Result
Unknown	NPOC/TN	1.000	NPOC:5.503mg/L TN:0.6736mg/L

1. Det

Anal.: NPOC

No.	Area	Conc.	Inj. Vol.	Aut. Dil.	Ex.	Cal. Curve	Date / Time
1	51.03	5.434mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 11:38:55 PM
2	52.31	5.572mg/L	100uL	1		bl_npoc.2012_03_08_12_51_51.cal	3/4/2019 11:41:58 PM

DOC and TDN calibration curves