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Occurrence, monitoring and removal of drinking water contaminants by advanced technologies

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OCCURRENCE, MONITORING AND REMOVAL OF DRINKING WATER CONTAMINANTS BY ADVANCED TECHNOLOGIES

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ABSTRACT

In order to maintain drinking water primary standards compliance under the USEPA Stage 2 Disinfectant Disinfection Byproducts Rule, drinking water treatment plants (DWTPs) are switching from free chlorine (FC) to chloramines (MCA). Concerns are raised as MCA disinfection has been linked N-nitrosamine formation. N-nitrosamines are a group of nitrogenous DBPs (N-DBPs) which are highly carcinogenic in comparison to regulated DBPs (THMs and HAAs, generated by FC disinfection). Also in the forefront of drinking water concerns are other emerging drinking water contaminants such as perchlorate. Perchlorate is a contaminant which can enter drinking water from natural deposits or through introduction by anthropogenic actives and applications which the USEPA has decided to regulate.

To contend with current drinking water issues, two major areas were targeted: (1) perchlorate removal and (2) drinking water DBP and emerging contaminant formation by an alternative disinfectant (peracetic acid, PAA). Perchlorate monitoring was performed at higher risk DWTP locations within the state of Missouri with levels below the estimated regulatory limit (4 μg/L or higher). Perchlorate removal from drinking water was also studied by adsorptive materials: powdered activated carbons (PACS) and clays. Out of all the materials studied, one clay (TC-99) had efficient removal with quick kinetics. PAA disinfection was studied to determine the formation of THMs, HAAs, HNMs, perchlorate, bromate, and N-nitrosamines. In comparison to FC and/or MCA, PAA disinfection yielded significantly less of the monitored contaminants, with the majority remaining below their respective detection limits.

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1. INTRODUCTION

1.1. WATER RESOURCES

Water resources are impacted by urban, agricultural and industrial activities alike. Some examples include pesticide/herbicide application, industrial waste discharge, and various sources of runoff. Contamination by these activities is not only a concern on-site, but contaminate transportation and percolation can lead to widespread issues. However, water contamination is not limited to synthetic contamination entering our natural resources. Drinking water treatment facilities (DWTFs) draw in source water containing many of these contaminants, along with natural organic matter (NOM), which have the potential to serve as precursors to disinfection by-products (DBPs) upon chemical treatment.

1.2. CONVENTIONAL DRINKING WATER TREATMENT PROCESS

Conventional drinking water treatment includes coagulation, flocculation, sedimentation, and filtration (**Figure 1.1**).[1] To remove colloidal and suspended particulate matter, a coagulant (aluminum sulfate, ferric chloride, or cationic polymers) is added to assist in flocculation and sedimentation which reduce turbidity and natural organic matter (NOM). These processes can also be optimized with the addition of coagulant aids including calcium hydroxide, calcium carbonate, or anionic/nonionic polymers.

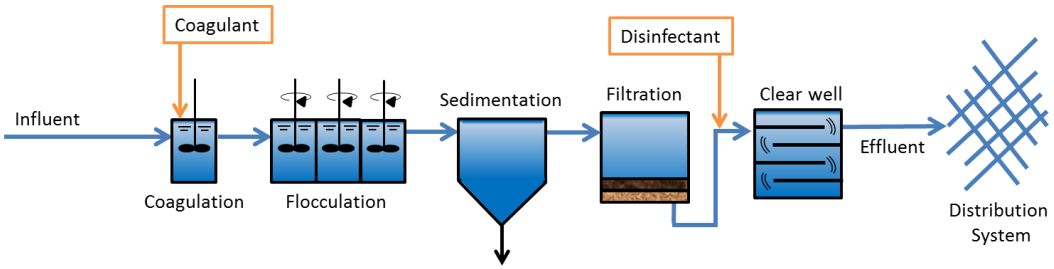

Figure 1.1. Schematic of conventional drinking water treatment

The water then undergoes filtration (rapid sand filtration) before the secondary disinfectant is added. Ultimately, NOM and other DBP precursors can be removed by the DWTFs treatment process. Removal can be achieved by entrapment by flocs formed during flocculation and settled out during sedimentation, or by sand filtration. Sand filtration has several mechanisms of removing particulates: (1) straining, (2) interception, (3) sedimentation, and (4) diffusion. Some DWTFs also opt to utilize dual media filters, where activated carbon can be added to further assist in removal of NOM and DBP precursors. Ultimately, a disinfectant is added to the filter effluent to not only to purify the water, but also to maintain a disinfectant residual throughout the distribution system.

1.3. DRINKING WATER DISINFECTION BY-PRODUCT REGULATIONS

DWTFs most often use primary disinfection to achieve the required log removal; however, it is also utilized for the removal of ammonia contained within the source water. Consequently, primary disinfection of source water which contains DBP precursors, such as NOM, increases the formation potential of DBPs. This is a growing concern as the

United States Environmental Protection Agency (USEPA) drinking water DBP regulations become increasingly stringent and DWTFs are forced to meet DBP compliance concentrations.

In response to research supporting the carcinogenic effects of trihalomethanes (THMs), the United States Environmental Protection Agency (USEPA) issued the THM Rule in 1979.[2] The THM Rule regulated four THMs at a maximum contaminant level (MCL) of 100 μg/L: trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM). In 1998, the USEPA issued Stage 1 of the Disinfectants/DBPs (D/DBPs) Rule which reduced the total THM MCL to 80 μg/L, along with the additional regulation of five haloacetic acids (HAA-5, 60 μg/L), bromate (10 μg/L), and chlorite (1 mg/L).[3] Under Stage 1, determination of DBP running annual averages (RAAs) for a DWTF required samples to be obtained across the distribution system and the average concentration of the entire distribution system would be used in the determination of whether compliance was achieved. In 2012, the USEPA implemented the Stage 2 D/DBPs Rule which strengthened Stage 1 as it tightened the compliance monitoring.[4] In Stage 2 the DWTP monitoring was adjusted by requiring an initial distribution system evaluation (IDSE) to identify the highest DBP concentration sampling points within the distribution system. At these points, the DWTF were required to meet compliance based on the locational running annual average (LRAA). In response to increasingly more stringent DBP regulations, DWTFs are looking for other treatment options to maintain or obtain compliance.

1.4. DRINKING WATER DISINFECTANTS

There are several known groups of regulated, unregulated, and emerging DBPs formed by drinking water disinfection (**Table 1.1**).[1] The formation of each is dependent upon a combination of water parameters such as pH, temperature, NOM, disinfectant, disinfectant dosage, and contact time.[5] FC disinfection became fundamental for water disinfection in the early 1900's to reduce water borne illnesses.[1,6] However, since then implementation and regulation of other disinfectants by the USEPA have expanded to include: ozone, chlorine dioxide, and MCA.

Ozone disinfection is able to effectively destroy chemicals that cause color, taste and odor within drinking water.[1] However, the formation of bromate within water containing bromide is very rapid. Ozone also produces non-halogenated by-products from the NOM within the water which can promote bacterial growth within the distribution system due to the highly biodegradable availability.[1] Chlorine dioxide is also a strong oxidant, which yields the least amount of known DBPs and considerably less THMs and HAAs than FC. Yet, chlorate and chlorite concentrations within water disinfected with chlorine dioxide are a concern, whether they were formed upon disinfection or present within the source water.

In the United States, FC is the most widely utilized disinfectant for drinking water disinfection. FC has the most numerous and widest variety of DBPs known to be generated from drinking water disinfection, however, it has been the most widely studied. Studies have shown FC to have the potential to form THMs, haloacetic acids (HAAs), halonitromethanes (HNMs), haloacetonitriles (HANs), haloketones (HKs), and aldehydes.[1] However, among the DBPs produced, THMs and HAAs are the most prevalent and of greatest concern.

Table 1.1. Drinking water disinfectants and their by-products

Disinfectant	Known By-products Formed
Free Chlorine	Trihalomethanes (THMs)
	Haloacetic acids (HAAs)
	Halonitromethanes (HNMs)
	Haloacetonitriles (HANs)
	Haloketones (HKs)
	Aldehydes
Monochloramine	N-Nitrosamines
	Cyanogen halides
Ozone	Bromate
	Bromoform
	Aldehydes
Chlorine dioxide	Chlorite
	Chlorate

Drinking water disinfection by MCA has occurred over the past 90 years.[7] The advantages of MCA, in comparison to FC, are the higher residual concentrations attainable and lower DBP formation – both of which result from the slower kinetics and less reactive nature with NOM. However, not all DWTFs are able to switch to MCA due to limitation of contact time (required log removal) or metal pipe corrosion resulting in leaching of toxic substances, such as lead.[7] For DWTFs which do not have the previous concerns, MCA usage is an advantageous. The drawback to MCA disinfection is the known reaction between MCA and N-nitrosamine precursors (secondary, tertiary, and quaternary amines) yielding N-nitrosamines.[8,9] N-nitrosamines, although unregulated, are of great concern due to their high carcinogenicity (0.7 ng/L NDMA).[10]

1.5. EMERGING DRINKING WATER CONTAMINANTS

As analytical instrumentation continues to advance, improved sensitivity is achieved, and identification of previously undetected chemicals increase, the detection emerging drinking water contaminants will persist. Within the last century, as contaminant detection limits have progressed from parts per hundred to parts per trillion, the USEPA has pursued to improve regulatory action.[11] However, with the sheer number of emerging contaminants the task should not be considered simple, straightforward, and undemanding. Chemicals which were once believed not to be a drinking water concern are now detectable. Also, the transformation of a chemical through environmental fate pathways is not known for every contaminant. Although the USPEA, under the safe drinking water act, asserted regulation of 25 additional contaminants every three years since 1991, regulation of less than 25 since then have occurred.[11-13] Regulation of emerging drinking water contaminants is difficult due to the multiple aspects that must be considered: occurrence level (maximum and average), carcinogenic and toxicity levels, and removal techniques available and feasibility within DWTPs.

The data collected from the Contaminant Candidate List (CCL) assist the USPEA in the proposal of emerging drinking water contaminants for evaluation under the Unregulated Contaminant Monitoring Program (UCMR) to determine their presence within drinking water.[14,15] In 2001, perchlorate was placed on the UCMR 1 for a national assessment by monitoring the occurrence between 2001-2005.[14] Perchlorate was detected in 16.7% of DWTPs analyzed which ranged from 4 – 420 μg/L, with an average of 9.9 μg/L.[16] Perchlorate concentrations within drinking water are dependent upon locational activities, transportation of contamination, and natural deposits. A removal technique applicable

within drinking water treatment for perchlorate is necessary, especially for DWTPs with high perchlorate concentrations due to natural deposits.[17-19] Particularly as perchlorate has been classified as a sodium-iodide symporter inhibiter, which has been linked to detrimental health effects of neurological development and energy homeostasis.[20-21]

In 2007, six N-nitrosamines were placed on the UCMR 2, including N-nitrosodimethylamine (NDMA), N-nitrosodiethylamine (NDEA), N-nitrosodi-n-butylamine (NDBA), N-nitrosodi-n-propylamine (NDPA), N-nitrosomethylethylamine (NMEA), and N-nitrosopyrrolidine (NPYR). EPA method 521 was utilized to monitor the occurrence between 2008 – 2012. Of the 1198 DWTPs sampled, 324 detected NDMA, 26 detected NDEA, 21 detected NPYR, 5 detected NDBA, and 3 detected NMEA. NDMA was the most prominent in number of detections as well as the concentration detected: 2 – 630 ng/L, with an average of 9 ng/L.[15] The DWTPs NDMA formation at these concentrations should be a concern due to their high carcinogenic nature.[10] However, due to currently non-regulatory status, N-nitrosamine formation within DWTPs has the potential to rise as MCA disinfection becomes increasingly utilized. The USEPA has placed NDMA, NDEA, NDPA, NPYR, and N-nitrosodiphenylamine (NDPhA) on the draft CCL4 list for further evaluation. A removal technique for N-nitrosamines is less applicable due to the formation is largely contributed to within the distribution system. Therefore, a strategy for minimization of formation should be targeted.

Nitrogenous DBPs (N-DBPs) as a whole are known to have high toxicity and halonitromethanes (HNMs), among N-nitrosamines, are no exception. HNMs cytotoxicity and genotoxicity is significantly greater than THMs and HAAs.[22] Although HNMs have not been placed on a USEPA CCL or UMCR list, research of HNM formation within

DWTPs has been underway.[23-25] Amongst the disinfection methods, ozone-chlorination yielded the highest formation of HNMs which could be attributed to the formation of low molecular weight precursors available after ozonation.[22-23] However, without coupled ozonation, chlorination formation of HNMs was greater than chloramination, prominently from the hydrophilic fraction of NOM.[24] Therefore, the reduction of HNM formation within DWTPs by removal of the precursors will be obstinate by drinking water treatment. Alternative treatment or removal methods should be investigated.

2. TRENDS, GOALS AND OBJECTIVES

2.1. TRENDS IN DRINKING WATER CONTAMINANT RESEARCH

Current research is focused on one of two broad categories: (1) alterative drinking water treatment to negate the formation of regulated and emerging contaminants or (2) removal of drinking water contaminants, either (a) contained within the source water or (b)after formation (DBPs). Prevention of DBP formation has proven to be most challenging, however, is the most practical in terms of treatment due difficulty or inefficiency of removal once formed. Research has found effective DBP removal of formed THMs and HAAs by air stripping and biodegradation by implementation of biological filtration, respectively.[26,27] Removal of certain DBP precursors can be achieved by enhanced treatment methods: enhanced coagulation/softening, activated carbon adsorption, anion exchange, and/or nanofiltration.[26] Yet, these techniques can be costly to implement, maintain, and operate. Alternatively, changing the primary or secondary disinfectant is an option, but it is not a complete solution.

2.2. GOALS AND OBJECTIVES

The primary goals of this research were (1) to find alternative treatment methods for the removal of emerging drinking water contaminants and (2) minimize the formation of DBPs. Upon determining alternative treatment methods for emerging contaminants,

many aspects were high priority: cost and ease of implementation; cost of usage, upkeep and maintenance; applicability within DWTPs; and efficiency.

With the USEPA UCMR 1 nationally observed perchlorate concentrations, a systematic investigation into the perchlorate concentrations across the state of Missouri was conducted on a seasonal basis. The study included DWTPs within Missouri where perchlorate was estimated to be high, such as agricultural areas and locations utilizing ordnance and explosives.[17,19,20,28,29] Perchlorate removal by alternative treatment methods were explored, especially for regions of the United States where natural deposits contribute to perchlorate contamination within drinking water. Due to the chemical properties and stability of perchlorate, removal from conventional DWTPs is recalcitrant. Perchlorate removal by means of adsorptive materials was explored.

In contrast, an alternative approach was taken for N-DBPs as adsorptive removal is not a practical approach due to the formation within the distribution system. The difficulty was determination of an alternative treatment method to target the minimization of N-DBPs, without formation of regulated DBPs, and maintain a low cost, efficient, and implementable alternative treatment method. Simply switching disinfectants (FC, MCA, ozone) would not be justified as previously discussed -- the formation of N-DBPs still result.[22-25] Therefore, a non-chlorine alternative disinfectant was explored.

Peracetic acid (PAA) as a disinfectant has been applied within several fields from medical to industrial. As a non-chlorine containing disinfectant, PAA has been recommended for FC resistant microorganisms due to the effectiveness of deactivating various bacteria, viruses, and pathogens.[30-32] Wastewater treatment within the United States, along with European DWTPs, have implemented PAA disinfection for these reasons.

Therefore, PAA evaluation of generated DBPs (regulated and nitrogenous) was investigated within drinking water. PAA disinfection formation potentials of THMs, HAAs, HNMs, bromate, and N-nitrosamines were studied.

PAPER

I. SIMULTANEOUS DETECTION OF PERCHLORATE AND BROMATE USING RAPID HIGH-PERFORMANCE ION EXCHANGE CHROMATOGRAPHY – TANDEM MASS SPECTROMETRY AND PERCHLORATE REMOVAL IN DRINKING WATER

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ABSTRACT

Perchlorate and bromate occurrence in drinking water causes health concerns due to their effects on thyroid function and carcinogenicity, respectively. The purpose of this study was three fold: 1) to advance a sensitive method for simultaneous rapid detection of perchlorate and bromate in drinking water system; 2) to systematically study the occurrence of these two contaminants in Missouri drinking water treatment systems; and 3) to examine effective sorbents for minimizing perchlorate in drinking water. A rapid high performance ion exchange chromatography – tandem mass spectrometry (HPIC-MS/MS) method was advanced for simultaneous detection of perchlorate and bromate in drinking water. The HPIC-MS/MS method was rapid, required no preconcentration of the water samples, and had detection limits for perchlorate and bromate of 0.04 μg/L and 0.01 μg/L, respectively. The method was applied to determine perchlorate and bromate concentrations in total of 23 selected Missouri drinking water treatment systems during differing seasons. The water systems selected include different source waters: ground water, lake water, river water, and ground water influenced by surface water. The concentrations of perchlorate and bromate were lower than or near to method detection limits in most of the drinking water samples monitored. The removal of perchlorate by various adsorbents was studied. A cationic organoclay (TC-99) exhibited effective removal of perchlorate from drinking water matrices.

KEYWORDS

High performance ion chromatography-mass spectrometry; perchlorate removal; bromate detection; TC-99 organoclay; drinking water disinfection byproduct

INTRODUCTION

Perchlorate (ClO_4^-) occurs naturally in some regions of the United States (e.g., in arid southwest), as well as being a component of commercial products such as solid rocket propellant, fireworks, pyrotechnics, ordnance, explosives, bleach, some fertilizers and air bag inflation systems (El Aribi et al. 2006, Greer et al. 2002, Rao et al. 2007, USEPA 2012, Blount et al. 2007, California Department of Public Health 2007). Perchlorate is highly soluble, mobile, and chemically inert in water and soil resulting in its ability to be transported vast distances in groundwater or rivers. In contrast, bromate (BrO_3^-) occurs in drinking water primarily as a disinfection byproduct; specifically, when bromide is present in source water, ozonation can lead to high levels of bromate under specific treatment conditions (International Agency for Research on Cancer 1999).

Perchlorate and bromate are both problematic inorganic drinking water contaminants which have been difficult to treat by conventional water treatment technology. Their toxicological potencies makes both of them a significant concern to the water industry and public health. Perchlorate blocks the sodium-iodide symporter (NIS) rendering it a NIS inhibitor and has been identified to be toxic to human neurological development and energy homeostasis (Blount et al. 2007). Bromate has been classified as a Group 2B carcinogen by the International Agency for Research on Cancer (International Agency for Research on Cancer 1999). Animal studies have demonstrated bromate's toxicity to the kidneys and to be a possible male reproductive toxicant. Oral consumption of bromate-contaminated drinking water by rats has been shown to be carcinogenic and has since been documented to be a potent carcinogen in humans. For these reason, the USEPA placed

bromate under the Stage 1 Disinfectants/Disinfection Byproducts Rule as a regulated contaminant at a maximum contaminant level (MCL) of 10 μg/L (USEPA 2013). In 2005, the USEPA set a reference concentration for perchlorate of 24.5 μg/L and currently project to set a drinking water standard by January 2016 (Wilson 2010, USEPA 2011, USEPA 2014).

Two separate USEPA standard methods are generally utilized to detect perchlorate (Method 331.0) and bromate (Method 557) (USEPA 2005, USEPA 2009). Method 331.0 is able to analyze perchlorate within source and drinking water utilizing liquid chromatography-electrospray ionization mass spectrometry. Method 557 is utilized for bromate detection in drinking water using ion chromatography-electrospray ionization tandem mass spectrometry. Currently there is no USEPA-approved method for simultaneous monitoring of perchlorate and bromate. As perchlorate is currently under determination of the regulatory limit, the USEPA Method 331.0 was expanded in this study for simultaneous detection of perchlorate and bromate.

During the USEPA Unregulated Contaminant Monitoring Regulation 1 (UCMR1) Program, perchlorate levels were monitored in public drinking water systems (PWS) across the United States including Missouri. Perchlorate was found in over 4% of public water systems nationally at the level of greater than or equal to 4 μg/L (USEPA 2011). Because Missouri state is an agricultural state which uses large amount of fertilizer, fireworks are allowed in the state, and military training station, further screening of perchlorate was

recommended. Therefore, total of 23 Missouri drinking water facilities were selected for seasonal perchlorate screening in the study.

Perchlorate, bromate, and bromide can occur in treated drinking water due to their generally inefficient removal during the treatment process or by unintended addition as a contaminant in hypochlorite disinfectant solutions (Pisarenko et al. 2010, Gandhi and Procter). Studies have shown perchlorate removal can be achieved by advanced treatment processes (i.e. reverse osmosis, ion exchange, and adsorption/ultrafiltration) (Water Research Foundation 2014, Xie et al. 2011). Agricultural waste, giant reed, modified with surface quaternary amine groups was shown to have fast kinetics of perchlorate removal from aqueous solutions. However, the pH range of adequate adsorption is not ideal for drinking water treatment process as removal was optimal at pH 3.5-7 and decreased with pH (Baidas et al. 2011). Therefore, further investigation of perchlorate removal by adsorptive materials needs to be studied.

In this study, the USEPA method for perchlorate analysis was modified for the rapid, direct, and simultaneous analysis of perchlorate and bromate using high performance ion exchange chromatography – tandem mass spectrometry (HPIC-MS/MS) without need for any preconcentration procedures. The method was applied to Missouri drinking water samples to determine the perchlorate and bromate prevalence and magnitude. Finally, preliminary adsorptive treatment options for perchlorate were studied for a variety of adsorbents.

MATERIALS AND METHODS

Chemicals

Sodium perchlorate and sodium bromate was purchased from Fisher Scientific (Pittsburg, PA, USA) and Sigma-Aldrich (Saint Louis, MO, USA), respectively. Ultrapure water was generated using a Milli-Q Advantage A10 and Millipore Elix water purification system (Millipore, MA, USA). The standard perchlorate and bromate stock solutions were prepared by dissolving the standards in ultrapure water. The isotope-labeled perchlorate ($Cl^{18}O_4^-$) internal standard was purchased from Cambridge Isotope Laboratories (Andover, MA, USA). The ion chromatography (IC) mobile phase was prepared by diluting 40 wt% methylamine (Sigma-Aldrich, Saint Louis, MO, USA) with ultrapure water to a concentration of 200 mM. The mobile phase was freshly prepared within every three days.

Powdered active carbons (PAC), Hydrodarco B, Hydrodarco 3000, Superdarco, and granular activated carbon (GAC) 830, were obtained from Norit (Marshall, TX, USA). Aquanuchar and WPH PACs were obtained from MWV Specialty Chemicals (North Charleston, SC, USA) and Calgon (Pittsburgh, PA, USA), respectively. Kaolin, Bentonite and Montmorillonite clays were obtained from Sigma Aldrich (Saint Louis, MO, USA). TC-99 (CAS 68911-87-5), an organoclay with surface alkyl quaternary ammonium groups, generally utilized for removing negatively-charged tannic and humic compounds, was obtained from Biomin, Inc. (Ferndale, MI, USA).

HPIC-MS/MS method

The high performance liquid chromatography system consisted of a Shimadzu (Columbia, MD, USA) degasser (DGU-30A3), pumps (LC-20 AD XR), auto sampler (SIL-20AC XR) and column oven (CTO-20A). An Ionpac AS21 ion exchange column (2×250mm) and an Ionpac AG21 guard column (2x50mm) were purchased from Dionex (Sunnyville, CA, USA). The mobile phase was 200 mM methylamine aqueous solution at a flow rate of 0.50 mL/min with isocratic elution. The sample injection volume was 50 μL. A 4000Q Trap mass spectrometer (AB SCIEX, Foster City, CA, USA) was used to detect and quantify perchlorate and bromate.

Isotope-labeled perchlorate was used as internal standard for perchlorate quantification and an external calibration method was used for bromate quantification. Multiple-reaction monitoring (MRM) mode was used with negative electrospray ionization. The quantification ion pair (m/z 98.7 ($^{35}Cl^{16}O_4^-$) / 82.9 ($^{35}Cl^{16}O_3^-$)) and confirmation ion pair (m/z 100.9 ($^{37}Cl^{16}O_4^-$) / 84.8 ($^{37}Cl^{16}O_3^-$)) were used to detect perchlorate. The isotope-labeled internal standard ion pair was m/z 106.9 ($^{35}Cl^{18}O_4^-$) / 89 ($^{35}Cl^{18}O_3^-$). For bromate detection, the quantification ion pair was m/z 126.8 ($^{79}Br^{16}O_3^-$) /110.9 ($^{79}Br^{16}O_2^-$) and confirmation ion pair was 128.8 ($^{81}Br^{16}O_3^-$) /112.9 ($^{81}Br^{16}O_2^-$). The ratio of $^{35}Cl^{16}O_4^-$/$^{37}Cl^{16}O_4^-$ and $^{79}Br^{16}O_3^-$/$^{81}Br^{16}O_3^-$ occur naturally at 3.086:1 and 1.00:0.980, respectively, as further confirmation of the analyte peaks.

Water sample collection and analysis

During the phase one of the study, a total of 18 drinking water treatment facilities across Missouri were selected for perchlorate occurrence study. The source water systems selected include groundwater (GW), surface water (SW) and groundwater influenced by surface water (GU) sources. Treatment facilities were selected based on their geographical location considered high risk for perchlorate contamination across the state of Missouri, along with different disinfection treatments of the source water, which included chlorination with gaseous chlorine and alkali hypochlorite solution, and chloramination (Table 4). In the state of Missouri, it is not mandatory for ground water facilities to disinfect source water. Paired source water and treated drinking water samples were collected during consecutive winter and summer seasons. All sample collections and filtrations followed the USEPA Standard Method 331.0 (USEPS 2005). To collect water samples, a sterile plastic bottle was utilized followed by filtration into a 125-mL sterile high-density polyethylene sample bottle (Fisher Scientific, Pittsburg, USA) using a Corning 26 mm surfactant free cellulose acetate (SFCA) 0.2 μm membrane filter (Fisher Scientific, Pittsburg, PA, USA). The water samples were placed in an iced cooler and transported to the laboratory within 24 hours, stored at 4°C and analyzed by HPIC-MS/MS within two weeks of sample storage limits (USEPA 2005, USEPA 2009) after the collection.

In order to test seasonal fluctuation of perchlorate concentration in more detail, phase two study was conducted by collecting and testing the water samples for four seasons (spring, summer, fall, and winter) in a year. In this phase of study, bromate was also simultaneously detected within five drinking water treatment systems with GW, SW, and GU source water.

The water sample collection and handling procedures were same with the phase one process. No ethylenediamine or other preservative was added into the samples during sample collection because no ozonation disinfection was used in the selected drinking water facilities, and typical realistic chlorination treatment of drinking water would not form significant bromate (Tynan et al 1993).

The quality control (QC) guidelines from the USEPA standard method were closely followed. The linear range of calibration for each compound, method detection limit, reproducibility, and spike recoveries of each compound in ultrapure water and in water sample matrices were all determined. During the analysis of water samples, at least one blank, two duplicated samples and one spiked sample were processed with each batch of samples. Ongoing QC standards were analyzed at the beginning of each batch, after every 10 samples and at the end of the batch. In any case of QC failure, the origin of the problem was identified and the samples were re-analyzed.

Characterization of TC-99 organoclay by X-ray diffraction

The organoclay, TC-99, was characterized to determine the composition of the clay. Approximately 1 gram of TC-99 was suspended into ultrapure water. The suspended sample was then thoroughly mixed and allowed to set for 10 minutes. From the dispersed sample, the X-ray diffraction (XRD) sample was taken from the top of the solution and transferred to a clean glass slide. The XRD sample was air dried overnight before analysis. A PANalytical X'Pert Multi-Purpose X-ray Diffractometer (Westborough MA, USA) equipped with a copper k-alpha source and PIXcel detector was utilized for the analyses.

Expansion of the clay was examined after placing the XRD sample within the glycolation chamber overnight.

RESULTS AND DISCUSSION

Method validation

Table 1 shows the optimized MS parameters for simultaneous perchlorate and bromate detection including ion source temperature, ion spray voltage, auxiliary gas, nebulizing gas, curtain gas, dwell time, entrance potential (EP), declustering potential (DP), collision energy (CE) and collision cell exit potential (CXP). A representative HPIC-MS/MS chromatogram obtained for simultaneous detection of perchlorate and bromate is shown in Figure 1. The retention times, calibration curve linear ranges, regression coefficient (R^2), method detection limits (MDL) and limit of quantification (LOQ) are shown in Table 2.

Table 1. Mass spectrometer operation conditions and parameters

Parameters	Perchlorate Ion Pairs			Bromate Ion Pairs	
	Quantification (98.7/82.9)	Confirmation (100.9/84.8)	Isotope-labeled (106.9/89.0)	Quantification (126.8/110.9)	Confirmation (128.8/112.9)
Ion source temp. (°C)	500	500	500	500	500
Ion spray voltage (V)	-4500	-4500	-4500	-4500	-4500
Auxiliary gas (psi)	30	30	30	30	30
Nebulizing gas (psi)	40	40	40	40	40
Curtain gas (psi)	25	25	25	25	25
Dwell time (ms)	150	150	150	150	150
EP (V)	-10	-10	-10	-10	-10
DP (V)	-5	-60	-10	-20	-50
CE (V)	-38	-36	-42	-30	-34
CXP (V)	-15	-3	-3	-7	-5

Table 2. Retention time, ion pairs, linear range, R^2, MDL and LOQ

Ion	Retention time	Quantification	Confirmation	Isotope-labeled Quantification	Linear range	R^2	MDL	LOQ
	(mins)	ion pair	ion pair	ion pair	(µg/L)		(µg/L)	(µg/L)
Perchlorate	7.65	98.7/82.9	100.9/84.8	106.9/89.0	0.20-700	0.9999	0.04	0.12
Bromate	2.2	126.8/110.9	128.8/112.9	N/A	0.20-700	0.9984	0.01	0.05

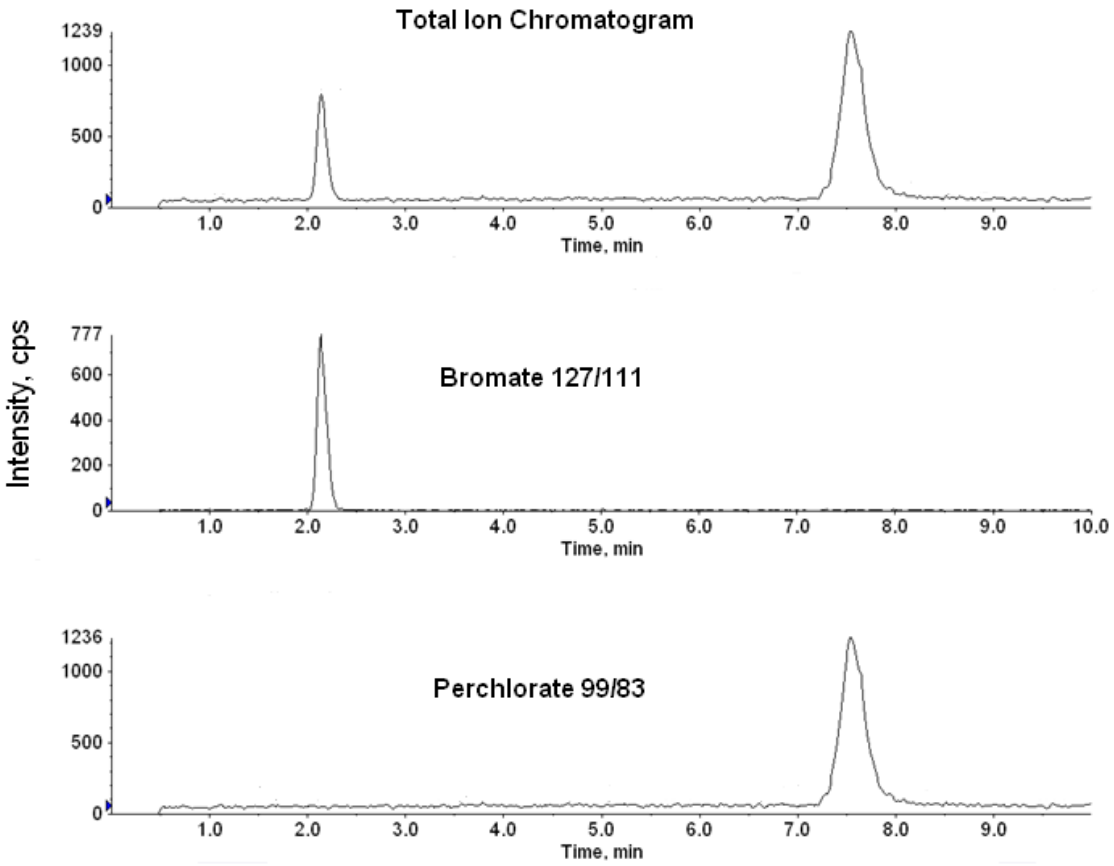

Figure 1. Representative UFIC-MS/MS chromatogram for simultaneous detection of perchlorate and bromate

The detection limits based on a signal-to-noise (S/N) ratio of 3 were 0.04 μg/L and 0.01 μg/L for perchlorate and bromate, respectively. The LOQ based on a S/N ratio of 10 were 0.12 μg/L and 0.05 μg/L for perchlorate and bromate, respectively. The MDLs for this method are higher than the MDLs of EPA Methods 331.0 and 557, might mainly due to different approaches in MDL determination. The EPA method detection limit was determined by fortification of the matrix with analyte at 2-5 times the noise level, and analyzing seven replicates over three days. The detection limit was then calculated by the equation of DL = S*t, where S is the standard deviation of the samples and t is the 99%

confidence level with n-1 degrees of freedom (USEPA 2005). The detection limit of bromate was also calculated as described for Method 331.0. Nevertheless, the MDLs of our method are low enough for application of perchlorate and bromate screening in drinking water based on the bromate regulatory limit of 10 μg/L and maximum reporting level of 6 μg/L of perchlorate which has been set by the state of California. The calibration curve resulted in linearity up to 700 μg/L for both perchlorate ($R^2 > 0.9999$) and bromate ($R^2 > 0.9984$). Reproducibility and recovery were determined by analyzing four consecutive analyses of perchlorate or bromate spiked into drinking water at relevant concentrations of 0.50 μg/L (low level), 2 μg/L (medium level) and 20 μg/L (high level). Precision and spike recovery results are shown in Table 3 for both tap water and surface water, containing native concentrations below the detection limits. Spike recoveries between 108.55-119.6% and 73.9-96.5% for perchlorate and bromate were obtained, respectively, for all concentration levels in all water matrices and with high precision (relative standard deviations (RSD) 0.78 - 8.39% and 1.12% - 4.90% for perchlorate and bromate, respectively). The EPA methods have defined acceptable recoveries of perchlorate and bromate to be 80-120% and 70-130%, respectively (USEPA 2005, USEPA 2009).

Table 3. Perchlorate and bromate spike recovery (n=4)

Compound	Low Level Spike (0.5 µg/L)				Medium Level Spike (2 µg/L)				High Level Spike (20 µg/L)			
	Tap Water		Surface Water		Tap Water		Surface Water		Tap Water		Surface Water	
	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)	Recovery (%)	RSD (%)
Perchlorate	108.68	8.39	108.55	7.31	114.28	2.49	110.91	2.66	117.76	0.78	119.61	1.76
Bromate	96.55	2.04	79.34	4.29	94.75	2.56	78.55	4.90	95.2	1.12	73.86	1.70

Perchlorate occurrence in Missouri drinking water systems

Source and treated drinking water samples were collected from 18 water treatment facilities across Missouri for two consecutive winter and summer seasons (January and July) for analysis. The perchlorate concentrations in the sampled Missouri drinking water systems ranged from below the MDL to 0.29 μg/L and 1.34 μg/L for winter and summer samples (Table 4). The RSD of duplicate samples ranged from 0.00 – 28.28%. Perchlorate spike recoveries obtained for the spiked samples ranged from 68.5 - 110.0% for both winter and summer samples.

The majority of the monitored drinking water samples contained perchlorate concentrations below, or near, the MDL. In contrast, during the summer the three highest perchlorate concentrations detected were 1.34 μg/L, 1.32 μg/L and 1.27 μg/L in treated water, significantly higher ($p<0.001$) than the corresponding source water sample indicating perchlorate was formed or introduced during the water treatment process. Each of these three high perchlorate water facilities utilized hypochlorination or chloramination for disinfection. Hypochlorination disinfection resulted in up to an 87% increase in perchlorate concentration in the treated water in comparison to the source water. Hypochlorite solutions utilized in drinking water disinfection have been known to contain and/or generate undesired disinfection byproducts such as perchlorate, bromate, chlorite and chlorate (Pisarenko et al. 2010). The difference in the winter and summer perchlorate concentrations was possibly related to the greater chlorine demand resulting in increased disinfectant dosages during the summer season. Facilities using gaseous chlorine (instead of

hypochlorite) had much lower perchlorate concentrations further implicating hypochlorite as a key source of the perchlorate.

Table 4. Perchlorate occurrence in Missouri drinking water systems

Facility ID	Water Source	Disinfection Method	Water Sample	Winter Season Perchlorate Concentration (µg/L)	Summer Season Perchlorate Concentration (µg/L)
A	GW	none	untreated	<MDL	<MDL
			duplicate	<MDL	0.17
B	GW	chlorination	untreated	<MDL	0.16
			treated	<MDL	0.20
C	GW	chloramines	untreated	0.11	0.12
			treated	0.10	0.13
D	GW	none	untreated	<MDL	0.18
			treated	<MDL	0.27
E	GW	hypochlorination	untreated	<MDL	0.17
			treated	<MDL	1.27
F	GW	chloramines	untreated	<MDL	0.13
			treated	<MDL	1.32
G.1	GW	hypochlorination	untreated	<MDL	0.24
			treated	<MDL	1.34
G.2	GW	hypochlorination	untreated	<MDL	0.11
			treated	<MDL	0.37
H	GW	gaseous chlorination	untreated	<MDL	0.23
			duplicate	<MDL	N/A
			treated	<MDL	0.11
			duplicate	<MDL	N/A
I	GW	hypochlorination	untreated	<MDL	0.23
			treated	<MDL	0.31
J	GW	none	untreated	<MDL	0.18
			duplicate	<MDL	0.21
K.1	SW	gaseous chlorination	untreated	0.29	0.16
			treated	0.28	0.25
K.2	GW	gaseous chlorination	untreated	<MDL	0.17
			treated	<MDL	0.11
L	GW	none	untreated	0.14	<MDL
			duplicate	0.14	0.19
M	GW	none	untreated	<MDL	<MDL
			duplicate	<MDL	<MDL
	SW	gaseous	untreated	<MDL	0.49

Table 4. Perchlorate occurrence in Missouri drinking water systems (cont.)

N		chlorination	treated	<MDL	0.14
			duplicate	<MDL	N/A
O	GW	gaseous chlorination	untreated	<MDL	0.13
			duplicate	N/A	<MDL
			treated	<MDL	<MDL
			duplicate	N/A	<MDL
P	GU	gaseous chlorination	untreated	0.23	0.12
			duplicate	N/A	0.18
			treated	0.25	0.18
			duplicate	N/A	0.20
Q	GW	gaseous chlorination	untreated	<MDL	0.13
			untreated	<MDL	0.25
			treated	<MDL	0.18
			duplicate	<MDL	N/A
R	GW	hypochlorination	untreated	<MDL	0.11
			treated	<MDL	<MDL

GW: ground water
SW: surface water
GU: ground water influenced by surface water

Simultaneous detection of perchlorate and bromate in Missouri drinking water systems

In the second phase of this study, perchlorate and bromate were simultaneously detected within five drinking water facilities for four quarterly sample collections. Samples were collected following the USEPA method for perchlorate analysis as previously described in this paper. The SFCA filter utilized for perchlorate analysis was tested for feasibility and confirmed suitable for bromate analysis. Spike recoveries were experimentally determined at 1, 5, and 10 μg/L bromate spiked in water samples. The spike recoveries within these facilities' samples for perchlorate and bromate were between 95 - 105% and 65% - 90%, respectively, with native concentrations shown in **Table 5**. Spike recoveries for bromate can be improved further by use of an internal standard if desired.

Bromate concentrations in the monitored Missouri drinking water facilities ranged from lower than the MDL to 2.57 μg/L (**Table 5**). The RSD for duplicate samples ranged from 0.00 – 18.13% .The bromate concentrations in SW systems (Facilities 2 and 3) those were disinfected by chlorination were below the MDL for both source and treated water. In the GW and GU systems (Facilities 1, 4, and 5, **Table 5**), bromate was only observed in the treated water, not in source water, indicating the bromate was formed during the water treatment process or introduced by the treatment chemicals during the water treatment. As bromate is generally formed by ozone oxidation and the drinking water treatment facilities did not utilize ozone, the most likely source of bromate was introduction during treatment. Pisarenko et al. (2010) also concluded that bromate can be generated within hypochlorite solutions during storage as bromine is oxidized and measured up to 2.6 μg/L of bromate in finished water from source water containing bromate below the detection limit. Therefore, the source of bromate within Facility 5 could be linked to the hypochlorite solution used for disinfection of the drinking water, and possibly supported by the seasonal decrease in bromate formation from March through September ($R^2 = 0.9610$).

Table 5. Perchlorate and bromate seasonal occurrence in Missouri drinking water systems

Facility ID	Water Source	Disinfection Method	Sample	1nd Collection		2nd Collection		3rd Collection		4th Collection	
				Fall		Winter		Spring		Summer	
				Perchlorate (µg/L)	Bromate (µg/L)	Perchlorate (µg/L)	Bromate (µg/L)	Perchlorate (µg/L)	Bromate (µg/L)	Perchlorate (µg/L)	Bromate (µg/L)
1	GU	gaseous chlorination	untreated	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
			untreated duplicate	<MDL	<MDL	N/A	N/A	<MDL	<MDL	<MDL	<MDL
			treated	<MDL	1.12	<MDL	1.22	<MDL	0.69	<MDL	0.57
			treated duplicate	N/A	N/A	<MDL	1.09	<MDL	0.65	<MDL	0.64
4	GW	gaseous chlorination	untreated	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
			untreated duplicate	<MDL	<MDL	N/A	N/A	<MDL	<MDL	<MDL	<MDL
			treated	<MDL	0.98	<MDL	<MDL	<MDL	0.73	<MDL	<MDL
			treated duplicate	<MDL	0.91	<MDL	<MDL	<MDL	0.67	<MDL	<MDL
5	GW	hypo-chlorination	untreated	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL
			untreated duplicate	<MDL	<MDL	N/A	N/A	<MDL	<MDL	<MDL	<MDL
			treated	0.21	1.43	<MDL	0.59	<MDL	2.26	0.28	2.20
			treated duplicate	0.23	1.32	<MDL	0.45	<MDL	2.57	0.28	2.05

GU: ground water influenced by surface water
GW: ground water

Perchlorate removal

Selection of adsorbents. In this study, carbon- and clay-based adsorbents were screened for their capability to remove perchlorate from drinking water. Due to the anionic nature of perchlorate, the adsorbents with more positive surface charge were anticipated to have greater adsorptive capacity based on electrostatic mechanistic considerations. Both PAC and GAC are used in many water treatment facilities in Missouri and elsewhere. In this study, four PACs and two GACs were tested. Two PACs (Norit HDB and Superdarco) and two GACs (Norit Hydrodarco 3000 and 830) were lignite coal-based carbons with point of zero charge (PZC) of approximately 10.6 such that the carbons have a net (though different magnitude) positive surface charge at each study pH level. The two other PACs (Calgon WPH and Meadwestvaco Aquanuchar) are bituminous-coal- and wood-based carbons, respectively, with PZCs of 6.1 and 4.9, respectively, resulting in a net positive charge at pH 4 and a net negative charge at pH 7 and 10 (Jain et al. 2004, Knappe 2014). Another powdered adsorbent studied was an organoclay (TC-99). X-ray diffraction analyses of TC-99 yielded four prominent diffraction peaks at the angles of incidence (2Θ) 12.35, 24.90, 37.75, and 51.08Å, corresponding to the basal spacing of kaolinite. Three other clays were also examined for comparison (i.e., Kaolin, Bentonite and Montmorillonite) each with a net negative surface charge due to isomorphic substitutions within their crystalline lattice.

As a preliminary study, 100 mg/L of each adsorbent was added to 5 mM phosphate buffered-water containing 10 μg/L perchlorate at pH 4, 7, and 10, respectively. Samples were placed in 15 mL centrifuge tubes and agitated in an orbital shaker for one hour (to

simulate short-term exposure in a treatment plant) and 24 hours (to approximate equilibrium). The screening results showed that little or no removal (less than 20%) was achieved for any of the PACs or GACs except for the lignite-coal-based carbons (HDB, Superdarco and Hydrodarco 3000) at the lowest study pH. This is consistent with the degree of cationic surface charge of the carbons and the solution pH. Furthermore, each of the lignite-based activated carbons achieved 56% to 76% removal at pH 4 where each were mostly cationic, and less than 20% at the higher pH levels. The screening results also showed, as expected based on their PZC, that the clays (Kaolin, Bentonite and Montmorillonite) provided no removal of perchlorate at any of the study pH levels. This is consistent with the electrostatic repulsion caused by the strong acid nature of perchlorate (such that it is always in the dissociated anionic form) and coupled with these clays' anionic nature across the studied pH range. However, the data demonstrated that the kaolinite-based organoclay, TC-99, had a high efficiency removal of perchlorate, presumably due to its cationic nature promoting electrostatic attraction of perchlorate across the studied pH range. Specifically, the concentrations of perchlorate after the TC-99 treatment were below the detection limits at pH 4, 7, and 10. Due to the high efficiency of perchlorate removal by TC-99, it was selected for further study.

Perchlorate removal by TC-99. Studies were conducted for the removal of perchlorate at an initial perchlorate concentration of 10 μg/L with a contact time of 24 hours using the organoclay, TC-99. Concentrations of 0, 5, 10, 25, 50, 75, and 100 mg/L of TC-99 were studied at a pH of 6.6 or 8.6. Each sample was tested in triplicate. Blanks and control samples (with 10 μg/L perchlorate, and no TC-99) were conducted in parallel. The results

for perchlorate removal in different water matrices, including ultrapure, tap, and surface water are shown in **Figure 2**. The tap water was chlorinated ground water, which contained a free chlorine residual concentration of 0.20 mg/L. The tap and surface water contained 0.93 and 4.14 mg/L of dissolved organic carbon (DOC), respectively. The total hardness of the tap water averages 280 mg/L as $CaCO_3$.

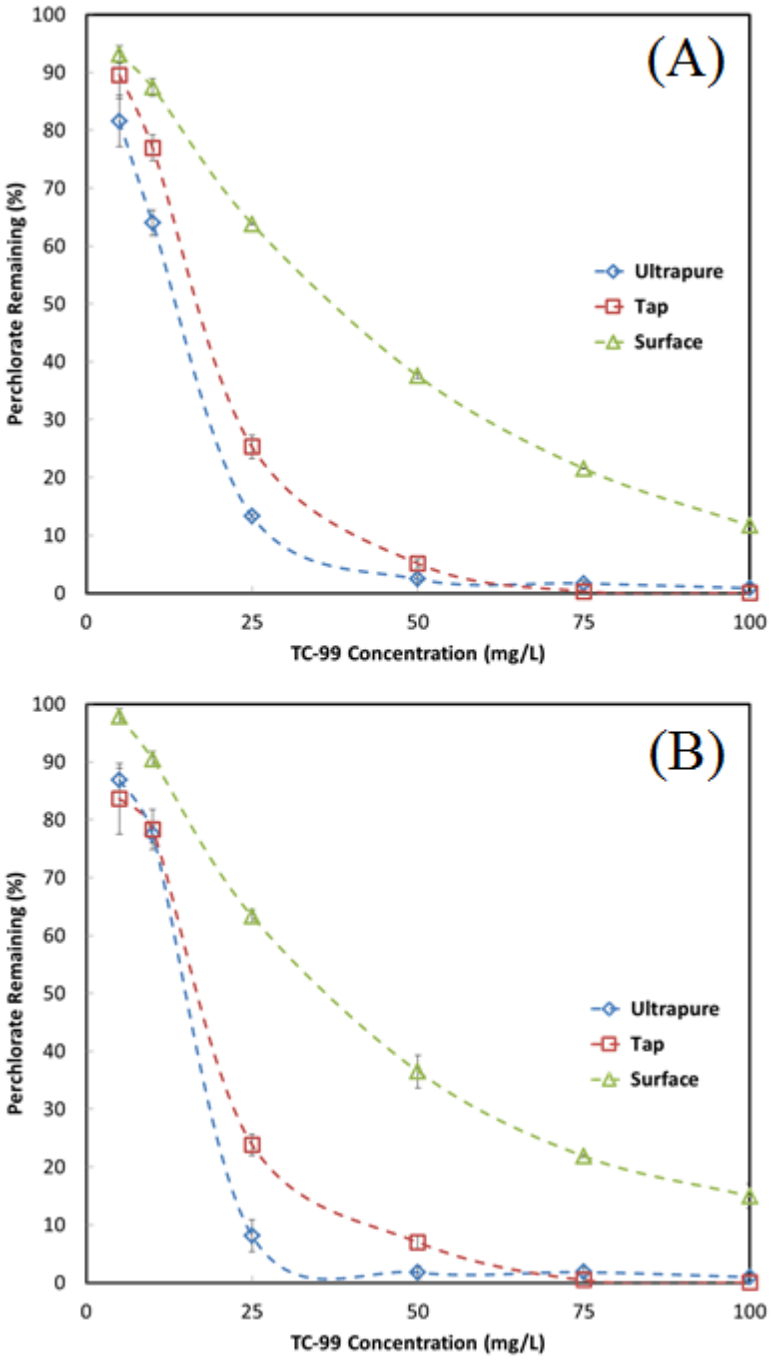

Figure 2. Removal of 10 µg/L perchlorate using TC-99 within ultrapure water, tap water, and surface water matrices at pH 6.6 (A) and pH 8.6 (B).

At pH 6.6, an intense decrease in the percent of perchlorate removal was observed from 10 mg/L to 25 mg/L of TC-99 after a 24 hour exposure time in ultrapure and tap water. However, a less drastic decrease occurred in surface water due conceivably to competitive sorption by the anionic natural organic matter (NOM) constituents in the water. Similar trends were also observed at pH 8.6. As TC-99 removed twice as much perchlorate from tap water than surface water, incorporation of the adsorbent would be most efficient after flocculation and sedimentation within the drinking water treatment process.

A kinetic study of perchlorate removal using TC-99 was conducted in a tap water matrix, at pH 8.6, in triplicate and with control samples. The exposure times studied included 0.5, 1, 2, 4, 12, and 24 hours with a TC-99 dosage of 25 mg/L. After a half hour 39.6% of the initial 10 μg/L perchlorate was removed by 25 mg/L TC-99 and within one hour only 34.0% perchlorate remained (**Figure 2**). After one hour, the perchlorate removal began to level off to approximately 70% within tap water. Therefore, the kinetics of perchlorate removal by using TC-99 is fast and equilibrium of removal occurs within three hours. Both of which are applicable for perchlorate removal during drinking water treatment.

SUMMARY

An HPIC-MS/MS method has been expanded and validated for simultaneous detection of perchlorate and bromate in water samples without sample preconcentration or other sample preparation, except filtration before analysis. The method is fast, robust and sensitive. The detection limits of perchlorate and bromate were 0.04 μg/L and 0.01 μg/L,

respectively, at a S/N ratio of 3. The method significantly reduces sample preparation, analysis time, and sample numbers in comparison with the methods which require detection of perchlorate and bromate individually. Water samples from 23 Missouri water facilities have been analyzed and the concentrations of perchlorate and bromate were majorly around or below the MDLs.

To remove perchlorate in the water systems which have high concentrations in the United States and other countries, an organoclay TC-99, has been identified to be effective. The study results have shown that TC-99 has higher removal efficiency for perchlorate than the commonly used adsorbents in water treatment facilities. The implications of the results are favorable as the kinetics of perchlorate removal is quick enough for the utilization of TC-99 within drinking water treatment facilities.

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CONFLICTS OF INTEREST

The authors declare that there are no conflicts of interest.

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II. ASSESSMENT OF DISINFECTION BYPRODUCT FORMATION BY PERACETIC ACID-BASED DISINFECTION FOR DRINKING WATER

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ABSTRACT

Peracetic acid (PAA) is a possible alternative disinfectant to free chlorine (FC) due to its high oxidation potentials, wide inactivation capability for a wide range of microorganisms, and non-toxic decomposition byproducts. However, its applicability in drinking water treatment needs to be evaluated for disinfection efficiency and disinfection byproduct (DBP) formation. In this study, PAA and FC were studied in parallel to compare disinfection efficiency and DBP formation potentials under different drinking water treatment conditions including pH, disinfectant dosage, and exposure time. Major United States Environmental Protection Agency (US EPA) regulated DBPs including trihalomethanes (THMs), haloacetic acids (HAAs), and bromate, as well as emerging drinking water contaminants including halonitromethanes (HNMs) and perchlorate, were monitored by ultra-fast liquid-chromatography tandem mass spectrometry (UFLC-MS/MS), gas-chromatography mass spectrometry (GC-MS), and solid phase micro-extraction (SPME) gas chromatography electron capture detection (GC-ECD) analysis. The experiment results demonstrated that PAA is an effective disinfectant and yielded minimal to undetectable concentrations of DBPs under all experimental conditions investigated.

HIGHLIGHTS

- Disinfection efficiency achieved by PAA and FC were analogous
- Source water disinfection was achieved within 5 minutes with 15 mg/L PAA
- FC disinfection yielded THMs and HAAs over regulatory limits
- PAA disinfection yielded minimal DBP formation across all conditions investigated

KEYWORDS

Peracetic acid disinfection, Drinking water disinfection byproduct (DBP), trihalomethanes (THMs), haloacetic acids (HAAs)

1. INTRODUCTION

The most common drinking water disinfectants are free chlorine (FC), chloramines, and ozone. Peracetic acid (PAA) has been utilized as a non-chlorine alternative disinfectant for medical supplies and sanitizing milk equipment; applied in the food and pulp industries; and to prevent biofilm formation.[1, 2] PAA has been introduced to water treatment in Europe and some waste water treatment plants within the United States.[3, 4] The strong oxidizing capability, short exposure time requirements, effectiveness against a wide range of microorganisms, and non-toxic decomposition byproducts makes PAA a great candidate for drinking water disinfection.[5-9]

FC and PAA are both effective at deactivating spores, yeasts, molds, fungi, bacteria, viruses, and pathogens. PAA has been proposed as an alternative, non-chlorinated disinfectant for microorganisms which have built FC resistance.[2, 5, 10] This study focused on the evaluation of PAA as an alternative drinking water disinfectant based on the formation of DBPs by PAA disinfection. A common method used to produce the PAA-based disinfectant is the reaction of hydrogen peroxide and acetic acid which yield, for example the commercially available Proxitane WW-12 (Solvay Chemicals, Inc., Houston, TX, USA), a quaternary equilibrium mixture of acetic acid, hydrogen peroxide, PAA, and water by the following equilibrium:

$$CH_3CO_2H\ (aq) + H_2O_2\ (aq) \leftrightarrow CH_3CO_3H\ (aq) + H_2O\ (l)$$

Proxitane WW-12 is currently used for some waste water treatment systems and was used for this study as the PAA source.

FC has an oxidation potential of 1.36 V, while PAA's is 1.81 V.[1] PAA in solution is present as peracetate ion, acetate ion, or hydroxyl radical dependent on the pH. The hydroxyl radical is theorized to be the driving force of PAA oxidation and has an oxidation potential of 2.8 V. Hydroxyl radical formation decreases as pH increases due to the decrease in spontaneous decomposition.[9] Therefore, the effectiveness of PAA would be affected by pH, yielding higher efficiencies at pH 7 than pH 8 – 9.[1] Drinking water treatment facilities source water typically range from 6.5 to 8.5, where PAA would be most effective.[11] In comparison, FC performs optimally between pH 5.5 – 7.5 due to hypochlorous acid

(HOCl) domination. At pH 7.6, pK_a of HOCl, the hypochlorite ion (OCl^-) will begin to be the dominant specie and generally has slower disinfection kinetics.[12] While FC is an effective disinfectant, there is generally rapid formation of regulated and emerging disinfection by-products (DBPs).

The United States Environmental Protection Agency (US EPA) regulated drinking water DBPs make up less than 2 percent of the identified DBPs and include five haloacetic acids (HAA), four trihalomethanes (THM), bromate, and chlorite.[13] The USEPA has regulated these DBPs with maximum contaminant levels (MCLs) of 60 μg/L, 80 μg/L, 10 μg/L, and 1 mg/L, respectively.[14] HNMs are a group of unregulated, emerging DBPs with higher cytotoxicity, genotoxicity, and mutagenicity than the US EPA regulated THMs and HAAs, though generally occur at lower concentrations.[15, 16] Perchlorate is known to be a sodium-iodide symporter inhibitor, while bromate is a regulated potent carcinogen.[17] California set a MCL of 6 μg/L for perchlorate in 2007 and USEPA is currently determining the regulatory level.[18]

The present study evaluated the formation of nine chlorinated and brominated HAAs: monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA), bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and chlorodibromoacetic acid (CDBAA); four THMs: trichloromethane (TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and tribromomethane (TBM); 6 halonitromethanes (HNMs): chloronitromethane (CNM), dichloronitromethane (DCNM), trichloronitromethane (TCNM), bromonitromethane (BNM), bromochloronitromethane (BDNM), and dibromonitromethane (DBNM);

perchlorate; and bromate. These regulated DBPs and emerging DBPs formations were monitored by ultra-fast liquid-chromatography tandem mass spectrometry (UFLC-MS/MS), gas-chromatography-mass spectrometry (GC-MS), and GC-ECD after disinfection by PAA or FC. Parallel DBP formations by PAA and FC were studied under different pH, disinfectant dosages, and exposure times.

2. MATERIALS AND METHODS

2.1. Chemicals and supplies

The nine HAA standards were purchased from Sigma-Aldrich (St. Louis, MO, USA). The ultrapure MilliQ (MQ) water was generated using a Milli-Q Advantage A10 and Millipore Elix water purification system (Millipore, MA, USA). The individual HAA stock solution preparation and storage were performed by following the Meng et al method.[19] The individual stock solution of each HAA was prepared in methanol at a concentration 1000 mg/L and stored at 4°C. A secondary standard solution mixture was prepared at a concentration of 10 mg/L containing each HAA in MQ water, and further diluted with MQ water to make calibration standard solutions. The LC-MS grade acetonitrile was purchased from Fisher Scientific (Pittsburg, PA, USA) and the MS grade acetic acid was from Sigma-Aldrich (St. Louis, MO, USA). The THM standards were purchased from Sigma-Aldrich (St. Louis, MO, USA). TCM, BDCM, DBCM, TBM stock solutions were prepared individually in MQ at 629, 870, 1620, and 960 mg/L, respectively. The THM stock solutions were combined to create a secondary standard solution mixture and further diluted with MQ. HNM standards BNM and TCNM were purchased from Sigma-Aldrich (Saint Louis, MO, USA). CNM, DCNM, BCNM, and DBNM were synthesized by Orchid Cellmark (New Westminster, Canada). CNM, DCNM, BNM, BCNM, DBNM,

and TCNM solid standards were dissolved in methyl tert-butyl ether (MTBE) (Fisher Scientific; Pittsburg, PA, USA) individually, each at a stock solution concentration of 1 mg/mL. Working standard solutions were prepared by combining the HNM stock solutions and diluted with MTBE. An internal standard of 1 mg/mL d_8-napthalene in MTBE was purchased from Sigma-Aldrich (Saint Louis, MO, USA) and utilized in analyzing HNM standards and samples. Sodium perchlorate and sodium bromate standards were purchased from Fisher Scientific (Pittsburg, PA, USA). Methylamine 40% (w/w) for perchlorate and bromate analysis was purchased from Sigma-Aldrich (St. Louis, MO, USA). The PAA disinfectant was provided by Solvay (Solvay Chemicals, Inc., Houston, TX, USA) and FC was purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Disinfection byproducts analysis

A method by Meng, et al. was modified to simultaneously analyze all nine HAAs by UFLC-MS/MS.[19] A Shimadzu UFLC system (Columbia, MD) consisted of a degasser (DGU-30A3), two pumps (LC-20 AD XR), an auto sampler (SIL-20AC XR), and a column oven (CTO-20A) was utilized. The method was modified to utilize a Phenomenex Synergi Max-RP (150×2.00 mm, 4 μm particle size) column. The samples were filtered through a SFCA 0.20 μm filter and then directly injected for UFLC-MS/MS analysis. Separation was achieved by a gradient elution of mobile phase (A) 0.1% acetic acid in ultrapure water and (B) 0.1% acetic acid in acetonitrile, at a flow rate of 0.50 mL/min with an initial mobile phase at 20% B for two minutes, increased to 80% B over four minutes and then held at 80% B for four minutes. The gradient was then decreased back to 20% B and equilibrated for seven minutes. A 4000Q Trap mass spectrometer (AB SCIEX, Foster City, CA) was used in multiple-reaction monitoring (MRM) mode with ESI-negative

ionization to quantitatively detect each HAA. Optimized MS parameters were: collision gas at medium (L/h), negative ion mode, 150 ms dwell time, -10 V entrance potential, 20 L/h curtain gas, -4500 V ion spray voltage, heater temperature at 500 °C, ion source gas 1 at 35 psi, and ion source gas 2 at 35 psi. Parameters for the individual HAAs were shown in Table 1.

Table 1. Haloacetic acid method mass spectrometer parameters

Compound	Q1 mass	Q3 mass	DP (V)	CE (V)	CXP (V)
MCAA	92.924	35	-20	-18	-3
DCAA	126.868	82.96	-35	-14	-3
TCAA	160.894	116.687	-20	-12	-5
MBAA	136.877	78.939	-35	-16	-3
DBAA	216.906	172.781	-35	-16	-9
TBAA	248.841	78.885	-25	-44	-11
BCAA	172.922	128.856	-25	-16	-7
BDCAA	206.884	162.4	-20	-10	-9
CDBAA	250.763	206.71	-20	-6	-19

A SPME-GC method was used to analyze THMs with modification of utilizing an automatic SPME sampler and electron capture detector.[20] The instrument was an Agilent 7890A GC with a micro-electron capture detector (GC-μECD) with a PAL autosampler for SPME injection. The published method SPME and GC separation conditions were utilized, with modified implementation of the autosampler instead of manual operation of SPME to improve reproducibility of analysis. THMs were separated by a Vocol GC column (10 m x 0.2 mm with 1.2 μm film, Supelco, Bellefonte, PA, USA). The GC was operated in splitless mode with the inlet and ECD detector temperature at 220°C and

250°C, respectively. A GC-MS method developed by Shi et al. was used for HNM detection, while a recently developed HPIC-MS/MS method simultaneously detected perchlorate and bromate.[17, 21]

2.3. Water sample characterization

Source water, ground water influenced by surface water, water was obtained from Missouri drinking water treatment facilities. Dissolved organic carbon (DOC), total nitrogen (TN), bromide, and ammonia were measured prior to disinfection treatments. During all experiments, residual PAA and FC were monitored. The DOC was measured with a Shimadzu TOC-L total organic carbon analyzer with total nitrogen measuring capability (Columbia, MD, USA). A Dionex DX-120 ion chromatography system with a conductivity detector was used to measure the bromide concentration. HACH test kits were utilized for detection of ammonia (TNT 830), PAA and FC were measured by HACH Diethyl-p-phenylenediamine (DPD) pillow test kits per manufacturer's instructions.

2.4. Water disinfection treatments

The disinfection experiments were performed by varying treatment conditions including pH, disinfectant dosage, and exposure time. Source water was transferred into 125 mL amber glass bottles for each experiment. For the pH effect study, the source water was adjusted to pH 6, 7, 8, 9, and 10 using 5 mM phosphate buffer, and disinfected with 4 mg/L PAA or FC for 4 hours. For the disinfectant dosage study, the source water was adjusted to pH 8 and disinfected with PAA or FC at concentrations of 0.5, 1, 2, 4, 10, and 50 mg/L for 4 hours. Exposure time study utilized 15 mg/L PAA or FC disinfection at pH 8 for 5, 15, 30, 60, and 240 minutes. Negative controls of source water and MQ water were

performed for each experimental set without disinfection treatment. PAA and FC concentrations of each sample were monitored by HACH test kits and then the residual disinfectant was quenched with sodium thiosulfate. Each sample was divided for each group of analytes' analysis with respect to sample preparation and analysis method.

2.5. Disinfection efficiency evaluation

The disinfection efficiencies of PAA and FC were determined for heterotrophs using SimPlates test kit for Heterotrophic Plate Count (HPC) (IDEXX; Westbrook, ME, USA). Disinfection efficiency was evaluated for the ambient source water, along with each disinfected sample. The disinfected samples included those based on pH (6, 7, 8, 9, and 10), disinfectant dosage (0.5, 1, 2, 4, 10, and 50 mg/L disinfectant), and exposure time (5, 15, 30, 60, and 240 minutes). Each sample was evaluated after treatment was quenched with sodium thiosulfate. The manufacturer's instructions were followed to determine the most probable number (MPN).

3. RESULS AND DISCUSSION

3.1. Water characterization

Source water was collected from Missouri drinking water facilities. The dissolved organic carbon (DOC) and total nitrogen (TN) were measured at 4.54 mg/L DOC and 2.82 mg/L TN, respectively. DOC is a known precursor for some DBPs such as THMs, therefore, DOC is related to water quality and level of DBP formation.[22] To determine the brominated species of DBPs, the source water bromide concentration was adjusted to contain 120 μg/L Br^-. To simulate facilities struggling with high ammonia concentrations within their source water, ammonia was also adjusted to 1 – 1.2 mg/L ammonia-N. Source

water prior to disinfection contained 2.52 μg/L total HAAs (THAAs), 0.57 μg/L total THMs (TTHMs), and less than the method detection limits (<MDL) for total HNMs (THNMs), perchlorate, and bromate. The DBPs produced by the disinfection process were determined by subtracting the initial source water DBP concentration from the resulting disinfected sample DBP formation. Each DBP monitored was quantified and the total formation of each contaminant was calculated.

3.2. Disinfection efficiency

The disinfection efficiency was determined by the utilization of Simplate test kits. Source water was measured to have a MPN for heterotrophs of 112 before disinfection. Over the pH range monitored, source water was disinfected with 4 mg/L PAA for 4 hours which resulted in MPNs ≤ 2 (Table 3). The dosage study resulted in the reduction of source water MPN to ≤ 2 with 0.5 mg/L PAA after 4 hours (Table 6). The same results were reached with an exposure time as short as 5 minutes when disinfected with 15 mg/L of PAA or FC (Table 8). A representative SimPlate test results were shown in Figure 1. The source water (A) without disinfection had a MPN of 112, while both 4 mg/L PAA (B) and 4 mg/L FC (C) disinfections resulted in a MPN ≤ 2.

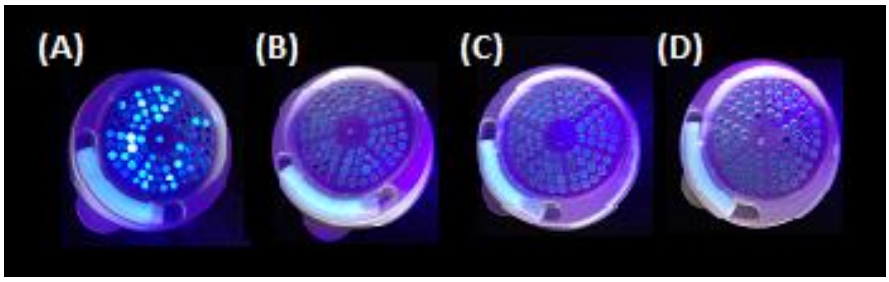

Figure 1. Disinfection efficiency by SimPlate evaluation. (A) Source water without disinfection, (B) MQ water without disinfection, (C) source water disinfected with 4 mg/L PAA , and (D) source water disinfected with 4 mg/L FC.

3.3. Free chlorine disinfection byproduct formation

FC DBP formation within drinking water has been extensively investigated, however, in this study the formations were also analyzed to determine the formation potential within the studied matrix. The FC DBP formations were used as a comparison for the PAA DBPs generated. FC experiments where run at pH 8 with (1) an extreme dosage of 50 mg/L FC for four hours and (2) differing exposure times (5, 15, 30, 60, 240 minutes) with an FC dosage of 15 mg/L. To achieve breakpoint chlorination, a residual concentration averaging 3.05 ± 0.41 mg/L FC was achieved for all exposure samples. The dosed and residual FC concentrations for 15 mg/L and 50 mg/L for a four hour exposure period at pH 8 are provided in **Table 2**.

Table 2. Free chlorine (FC) dosed and residual concentrations for source water (pH 8) after a four hour exposure period, with disinfection efficiency in terms of most probable number (MPN).

FC (mg/L)		Simplate
Dosed	Remained	MPN
Source water	---	112
15.00	2.48	<2
50.00	29.00	2

After four hours of extreme FC disinfection (50 mg/L) a residual of 29.00 mg/L FC was achieved and yielded significant formation of HAAs, THMs, HNMs, and bromate (**Table 3**). The formation of 74.81 μg/L THAAs and 96.13 μg/L TTHMs both exceeded the USEPA MCLs of 60 μg/L HAA-5 and 80 μg/L THM, respectively. HAA formation, in decreasing order, by FC was TCAA (23.31 μg/L), BDCAA (21.06 μg/L), DCAA (19.96μg/L), BCAA (4.54 μg/L), MCAA (2.66 μg/L), MBAA (1.59 μg/L), DBAA (1.1

7μg/L), and TBAA (0.52 μg/L). All THM species were observed under these conditions: 55.80 μg/L TCM, 24.98 μg/L BDCM, 14.00 μg/L DBCM, and 1.35 μg/L TBM. Under neutral or alkaline conditions, it is known that FC can form hypobromous acid, or hypobromite – pH dependent speciation. In alkaline conditions, the further decomposition of hypobromite is favored, which results in the formation of bromate.[23] This trend was observed within this study, where bromate formation was detected, but remained below the USEPA MCL (10 μg/L) at 5.82 μg/L. THNM formation was 12.68 μg/L exclusively contributed by BCNM. However, even at extreme FC dosage, perchlorate formation was not observed (<0.10 μg/L).

As the exposure time was increased from 5 – 240 minutes THAAs, TTHMs, and THNMs formations increased: 16.77 – 46.40 μg/L, 21.84 – 54.01, and 7.23 – 12.01 μg/L, respectively (Table 9). The trends in specie concentrations observed mimicked those of the extreme FC dosage for THAAS, TTHMs, and THNMs. With 15 mg/L FC disinfection, bromate formed in as quickly as 5 minutes and remained constant at 2.29 ± 0.06 μg/L throughout the monitored exposure times. However, the formation of bromate was dependent upon the initial FC dosage. With a higher dosage (50 mg/L FC) resulted in greater bromate formation (5.82 μg/L bromate), in comparison to lower FC dosage (15 mg/L FC, 2.29 μg/L bromate). Overall, THAAs, TTHMs, and bromate remained below the USEPA MCL, while perchlorate remained below the detection limit.

Table 3. Disinfection byproduct formations (μg/L) at pH 8 after a four hour exposure period when source water was disinfected with free chlorine (15 and 50 mg/L).

Disinfectant Dosage (mg/L)		15	50
HAA	MCAA	1.74	2.66
	DCAA	13.54	19.96
	TCAA	11.43	23.31
	MBAA	0.47	1.59
	DBAA	2.44	1.17
	TBAA	0.91	0.52
	BCAA	4.92	4.54
	BDCAA	10.95	21.06
	CDBAA	<10.00	<10.00
	THAAs	**46.40**	**74.81**
THM	TCM	26.74	55.80
	BDCM	17.22	24.98
	DBCM	9.01	14.00
	TBM	1.03	1.35
	TTHMs	**54.01**	**96.13**
HNM	CNM	<1.00	<1.00
	DCNM	<0.80	<0.80
	TCNM	<0.60	<0.60
	BNM	<0.80	<0.80
	BCNM	12.01	12.68
	DBNM	<8.00	<8.00
	THNMs	**12.01**	**12.68**
ClO_4^-		**<0.10**	**<0.10**
BrO_3^-		**2.25**	**5.82**

3.4. pH effects on disinfection byproduct formation

The pH range of source water of drinking water systems range typically between 6.5 – 8.5. Yet, the pH can range anywhere between 6 to 11 at different steps throughout treatment processes dependent upon the treatment utilized.[11] Therefore, the pH effects on PAA disinfection and DBP formation potentials were examined at pH 6, 7, 8, 9, and 10, with a

duplication at pH 7. A disinfectant dosage of 4 mg/L PAA was utilized to disinfect the source water for four hours. A comparison sample was run at pH 8 disinfected with 15 mg/L FC for four hours, which achieved breakpoint chlorination.

Table 4. Peracetic acid (PAA) dosed and residual concentrations for source water (pH 6 – 10) after a four hour exposure period, with disinfection efficiency in terms of most probable number (MPN). Relative standard deviation provided for samples run in duplicate (n=2) and denoted within parentheses.

	PAA (mg/L)		Simplate
pH	Dosed	Remained	MPN
ambient source water	---	---	112
6	4	3.12	2
7	4	3.40 (6.65)	<2
8	4	3.20	<2
9	4	2.80	<2
10	4	2.88	2

The residual concentrations of PAA were monitored immediately after the four hour exposure period (**Table 4**). The PAA residual concentrations ranged from 2.80 mg/L to 3.20 mg/L, with a maximum residual at pH 7 and decreased as the pH increased. The observed decreased residual with increased pH could be attributable to the increased decomposition rate.[24, 25] After a four hour exposure period each pH sample was analyzed for DBP formations. Each DBP monitored was quantified and the total concentration of each DBP group was calculated (**Table 5**), with PAA DBP illustrated in **Figure 2 A**.

After source water was disinfected by 4 mg/L PAA for four hours, the HAA concentrations remained near or below the detection limits across the pH range 6 – 10. MBAA formed near the detection limit at pH 9 (0.10 μg/L) and pH 10 (0.14 μg/L). Other pH conditions with PAA disinfection did not form any detectable HAAs (**Table 5**). TTHM concentrations after disinfection with PAA were 0.17 μg/L (pH 6) and 0.04 μg/L (pH 7), and below detection limits at a pH greater than 7. TCM was the major contributor to the TTHM concentrations, with slight formation of BDCM at pH 6. The maximum concentration of TCM formation occurred at pH 6 (0.14 μg/L) and decreased to below the detection limit (0.20 μg/L) at pH 8 and above. Previous studies have found FC disinfection to yield increased TTHM formation with an increase of pH 6 – 8, with TCM and BDCM being the most prevalent species.[13, 26-28] The results of this study also correspond with those previously, as TCM was the major contributing THM when pH 8 source water was disinfected with FC. However, the formation potential of TTHMs was significantly reduced with disinfection by PAA.

Table 5. Disinfection byproduct formations (μg/L) at pH 6 – 10 after a four hour exposure time when source water was disinfected with 4 mg/L Peracetic acid. Relative standard deviation provided for samples run in duplicate (n=2) and denoted within parentheses.

pH		6	7	8	9	10
HAA	MCAA	<0.25	<0.25	<0.25	<0.25	<0.25
	DCAA	<0.50	<0.50	<0.50	<0.50	<0.50
	TCAA	<5.00	<5.00	<5.00	<5.00	<5.00
	MBAA	<0.10	<0.10	<0.10	0.10	0.14
	DBAA	<0.25	<0.25	<0.25	<0.25	<0.25
	TBAA	<0.50	<0.50	<0.50	<0.50	<0.50
	BCAA	<0.50	<0.50	<0.50	<0.50	<0.50
	BDCAA	<5.00	<5.00	<5.00	<5.00	<5.00
	CDBAA	<10.00	<10.00	<10.00	<10.00	<10.00
	THAAs	**<MDL**	**<MDL**	**<MDL**	**0.10**	**0.14**
THM	TCM	0.14	0.04 (9.97)	<0.20	<0.20	<0.20
	BDCM	0.03	<0.05	<0.05	<0.05	<0.05
	DBCM	<0.20	<0.20	<0.20	<0.20	<0.20
	TBM	<0.05	<0.05	<0.05	<0.05	<0.05
	TTHMs	**0.17**	**0.04**	**<MDL**	**<MDL**	**<MDL**
HNM	CNM	<1.00	<1.00	<1.00	<1.00	<1.00
	DCNM	<0.80	<0.80	<0.80	<0.80	<0.80
	TCNM	<0.60	<0.60	<0.60	<0.60	<0.60
	BNM	<0.80	<0.80	<0.80	<0.80	<0.80
	BCNM	<1.00	<1.00	<1.00	<1.00	<1.00
	DBNM	<8.00	<8.00	<8.00	<8.00	<8.00
	THNMs	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**<MDL**
ClO_4^-		**<0.10**	**<0.10**	**<0.10**	**<0.10**	**<0.10**
BrO_3^-		**<0.05**	**<0.05**	**<0.05**	**<0.05**	**<0.05**

Previous studies demonstrated with increased pH (6 – 8), the formation of HNMs also increased.[13] Within source water disinfected by PAA the HNM concentrations remained below the detection limits; therefore, the pH effect of HNM formation by PAA disinfection was inconclusive. Although both disinfectants have oxidation potentials greater

than the oxidation potential required to oxidize chlorate ion to perchlorate ion (1.226 V), perchlorate concentrations below the detection limit (0.10 μg/L) across the pH range studied. In contrast, bromate – a well-known DBP of ozone treatment due to ozone's high oxidation potential (2.07 V) – formation occurred when source water was disinfected with FC, however, was not observed with PAA disinfection.[1, 12] PAA treatment bromate formation remained below the detection limit (0.05 μg/L) from pH 6 – 10.

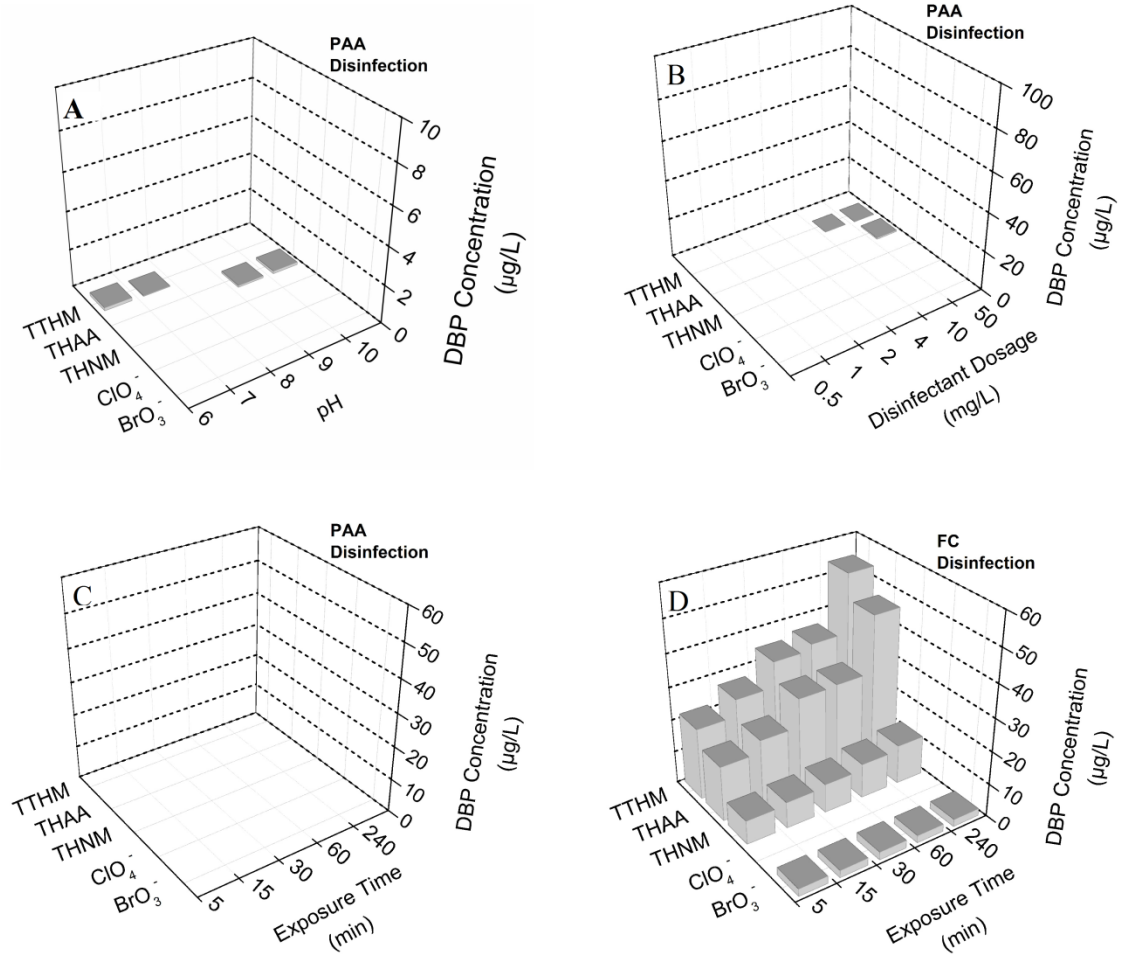

Figure 2. Total disinfection byproduct formation dependence. Dependence on source water (A) pH (pH 6 – 10) when disinfected with 4 mg/L PAA, (B) PAA disinfectant dosage concentration (0.5 – 50 mg/L), and exposure time (5 – 240 minutes) of (C) 15 mg/L PAA disinfection or (D) 15 mg/L FC disinfection. The DBPs monitored include total THM (TTHM: TCM, BDCM DBCM, and TBM), total HAA (THAA: MCAA, DCAA, TCAA, MBAA, DBAA, TBAA, BCAA, BDCAA, and CDBAA), total HNM (THNM: CNM, DCNM, TCNM, BNM, BCNM, and DBNM), perchlorate, and bromate.

3.5. Disinfection byproduct formation under different disinfectant dosages

Drinking water treatment facilities require different concentrations of disinfectant to be added to the source water due to the differing matrices. The concentration dependence of DBP formation in the source water was studied at 0.5, 1, 2, 4, 10, and 50 mg/L PAA at pH

8 and exposed for 4 hours, with a duplicate at 2 mg/L. These results were compared to 15 and 50 mg/L FC dosage under the same conditions. The residual disinfectant concentrations were measured immediately after the 4 hour exposure period. As expected, the PAA residual increased as the PAA dosage was increased, ranging from 0.16 – 32.25 mg/L PAA (0.50 – 50 mg/L dosage) (**Table 6**). Although both disinfectants achieved disinfection within 5 minutes (MPN ≤ 2), PAA disinfection reacted less with the matrix than FC, reflected within the DBP formations (**Table 7**). During FC disinfection, a large amount of FC was consumed by the formation of the excessive DBPs formation observed: 12.52 and 21.00 mg/L FC upon disinfection by 15 and 50 mg/L FC, respectively. PAA disinfection did not yield the same residual trend as FC due to the lack of DBP formation observed (**Table 7**). However, higher PAA consumption was observed at higher dosage concentrations due to spontaneous decomposition, noted by Yuan et al.[29] In comparison, FC disinfection yielded significantly more DBPs than PAA disinfection (**Figure 2 B**). The results indicated that even at very high PAA dosages, DBPs formation were below, or near, the detection limits, while FC DBP formation increased with increased initial FC dosage.

Table 6. Peracetic acid (PAA) dosed and residual concentrations for source water after a four hour exposure time to determine disinfectant dosage dependence. Relative standard deviation provided for samples run in duplicate (n=2) and denoted within parentheses.

PAA (mg/L)		Simplate
Dosed	Remained	MPN
Source water	---	112
0.50	0.16	<2
1.00	0.83	<2
2.00	1.63 (2.60)	<2
4.00	3.32	<2
10.00	8.51	<2
50.00	35.25	<2

Source water disinfection with PAA yielded slight HAA formation within a few samples: 0.04 μg/L MCAA at 0.5 mg/L PAA and 0.68 μg/L MBAA at 50 mg/L PAA. The MBAA formation at 50 mg/L PAA is most likely attributed to the 120 μg/L bromide concentration in the source water. As the FC dose was increased from 15 mg/L to 50 mg/L, the measured HAA formations also increased. At 15 and 50 mg/L, all HAA species are observed at detectable concentrations with the exception of CDBAA. THAA formation increased from 46.40 μg/L (15 mg/L FC) to 74.81 μg/L (50 mg/L FC). THAA formation at 50 mg/L FC was over the MCL of HAA-5; however, the regulated 5 HAAs formed (48.69 μg/L HAA-5) were not over the MCL. The TTHMs measured in this study are composed of the four US EPA regulated THMs (80 μg/L). Below a FC concentration of 10 mg/L the TTHM formation remained below the regulatory limit. However, at a FC concentration of 50 mg/L the TTHM formation exceeded the regulation. This study's results agreed with those observed within the drinking water treatment facilities worked with – the TTHMs formed greater than the MCL but the HAA-5 concentrations remained below the MCL. However, minimal THAAs or TTHMs were observed above the detection limits even when disinfected with 50 mg/L PAA.

Table 7. Disinfection byproduct formations (µg/L) for disinfectant dosage dependence when source water was disinfected for four hours with peracetic acid dosages of 0.5 – 50 mg/L.

Disinfectant Dosage (mg/L)		0.5	1	2	4	10	50
HAA	MCAA	0.04	<0.25	<0.25	<0.25	<0.25	<0.25
	DCAA	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
	TCAA	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00
	MBAA	<0.10	<0.10	<0.10	<0.10	<0.10	0.68
	DBAA	<0.25	<0.25	<0.25	<0.25	<0.25	<0.25
	TBAA	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
	BCAA	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50
	BDCAA	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00
	CDBAA	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
	THAAs	**0.04**	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**0.68**
THM	TCM	<0.20	<0.20	0.01	<0.20	0.01	0.05
	BDCM	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	DBCM	<0.20	<0.20	<0.20	<0.20	<0.20	<0.20
	TBM	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
	TTHMs	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**0.01**	**0.05**
HNM	CNM	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
	DCNM	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80
	TCNM	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
	BNM	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80
	BCNM	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
	DBNM	<8.00	<8.00	<8.00	<8.00	<8.00	<8.00
	THNMs	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**<MDL**
	ClO_4^-	**<0.10**	**<0.10**	**<0.10**	**<0.10**	**<0.10**	**<0.10**
	BrO_3^-	**<0.05**	**<0.05**	**<0.05**	**<0.05**	**<0.05**	**<0.05**

When source water was disinfected with PAA, TCM was the only THM specie detected at slightly above method detection limit, concentrations ranged from 0.01 μg/L TCM (2 mg/L PAA) to 0.05 μg/L TCM (50 mg/L PAA). However, When source water as disinfected by FC, TTHM formations increased from 54.01 μg/L (15 mg/L FC) to 96.13 μg/L (50 mg/L FC) with increasing FC dosage. A previous study stated when the FC to total organic carbon ratio (FC:TOC) is less than one the THM formation is most dependent upon FC dosage, and when the FC:TOC is greater than one there is minimal dependence upon the dosage.[30] In this study the measured DOC concentration was 4.54 mg/L in the source water. Therefore, the FC:TOC switches over from FC to TOC dependence over 5 mg/L FC, however, breakpoint chlorination was not achieved until 15 mg/L FC. As the FC:TOC switched to TOC dependence, an increased formation of multi-brominated THMs was also observed which was expected with 120 μg/L bromide present within the source water. Previous literature stated THM formation potentials shift toward brominated species with higher bromide concentrations, with the trend more pronounced in finished water – due to the FC:TOC.[30, 31] The same study concluded that the bromide effect is not observed in HNM formation by FC disinfection.[31] This study yielded similar results, as BCNM was the only detected HNM at 12.01 μg/L (15 mg/L FC) and 12.68 μg/L (50 mg/L). HNM formations remained below detection limits when source water was disinfected with PAA, even at an extreme dosage of 50 mg/L PAA.

The perchlorate concentrations remained below the detection limit (0.10 μg/L) in all samples disinfected by both PAA and FC, demonstration that the formation was not dependent upon the disinfectant dosage. Bromate formation remained below the detection limit (0.05 μg/L) for all PAA disinfection dosages. However, as the FC dosage was

increased, increased bromate formation was observed: 2.25 μg/L bromate with 15 mg/L FC to 5.82 μg/L bromate with 50 mg/L FC. These results indicated bromate formation is dependent upon the initial dosage of FC.

3.6. Disinfection byproduct formation with different exposure times

Water facilities need to utilize different exposure times for disinfectants based on dosage due to different source water matrices and facility design to achieve the required log removal. Exposure times of 5, 15, 30, 60, and 240 minutes were evaluated in this study with 15 mg/L PAA or FC disinfection at pH 8, with a duplication at 60 minutes. The PAA residual concentrations decreased minimally with increased exposure time due to minimal reaction with the matrix: 14.40 mg/L PAA (5 minutes) to 12.69 mg/L PAA (240 minutes) (Table 8). The FC residual was consumed considerable quicker as only 3.54 mg/L FC remained after 5 minutes disinfection, with 2.48 mg/L FC remaining after 240 minutes. These results were expected as the FC DBP formations were observed within 5 minutes, which consumed the FC dosed and generated DBPs at higher concentrations than those observed for PAA after 240 minutes.

Table 8. Peracetic acid (PAA) dosed and residual concentrations for source water disinfected with 15 mg/L PAA for exposure times of 5 – 240 minutes. Relative standard deviation provided for samples run in duplicate (n=2) and denoted within parentheses.

Exposure Time		PAA		FC	
(mins)	Dosed (mg/L)	Remained (mg/L)	Simplate MPN	Remained (mg/L)	Simplate MPN
source water	---	---	112	---	112
5	15.00	14.40	<2	3.54	<2
15	15.00	14.40	<2	3.44	<2
30	15.00	14.10	<2	3.20	<2
60	15.00	13.24 (0.53)	<2	2.82 (2.00)	<2
240	15.00	12.69	<2	2.48	<2

PAA DBP formations remained below detection limits within 5 – 240 minutes (**Figure 2 C**); while THAA, TTHM, and THNM formation increased with increased exposure time when source water was disinfected with 15 mg/L FC (**Figure 2 D**). FC formed 16.77 µg/L THAAs within 5 minutes and increased to 46.40 µg/L THAAs after 240 minutes. The concentrations of individual HAAs are provided in **Table 9**. DCAA, TCAA, and BDCAA were the dominate HAAs formed by FC disinfection. Almost half (42.4%) of the THAAs were brominated HAAs (Br-HAAs), which was higher than most observed Br-HAA in drinking water due to the higher concentration of bromide in the source water used for this study.

PAA disinfection exposure of 5 – 240 minutes yielded no detectable THMs. In contrast, disinfection of source water with 15 mg/L FC yielded increased THM formations with increased exposure time (**Table 9**). FC disinfected samples yield increased TTHMs from 21.84 – 54.01 µg/L at 5 – 240 minutes. TCM was the dominant specie increasing from

16.67 μg/L (5 minutes) to 26.74 μg/L (240 minutes). BDCM, DBCM, and TBM concentrations also increased with exposure time. The total Br containing THMs (Br-THMs) were 50.48% of TTHMs formed after 240 minutes. The proportion of Br-THMs formed were higher than those typical formed during low bromide containing source water disinfection. However, at 120 μg/L bromide concentration, 15 mg/L PAA disinfection did not generate any Br-DBPs after four hours.

PAA disinfection exposure up to 240 minutes did not yield HNMs at detectable concentrations. However, BCNM concentrations formed with disinfection by 15 mg/L FC increased with exposure time from 7.23 – 12.03 μg/L (5 – 240 minutes). These results also demonstrate the kinetics of BCNM formation is fast with FC disinfection. Previous studies have shown the dominant species formed within source water disinfected with FC, containing an average bromide concentration of 60 μg/L, are TCNM, DCNM, and BCNM.[31]

Table 9. Disinfection byproduct formations (µg/L) for exposure time dependence when source water was disinfected with 15 mg/L peracetic acid (PAA) or free chlorine (FC) for 5 – 240 minutes. Relative standard deviation provided for samples run in duplicate (n=2) and denoted within parentheses.

Exposure Time (mins)		PAA					FC				
		5	15	30	60	240	5	15	30	60	240
HAA	MCAA	<0.25	<0.25	<0.25	<0.25	<0.25	1.17	1.53	1.76	1.62 (29.52)	1.74
	DCAA	<0.50	<0.50	<0.50	<0.50	<0.50	7.26	7.83	8.77	9.81 (3.69)	13.54
	TCAA	<5.00	<5.00	<5.00	<5.00	<5.00	6.38	7.67	7.61	8.39 (3.14)	11.43
	MBAA	<0.10	<0.10	<0.10	<0.10	<0.10	0.23	0.38	0.50	0.41 (7.37)	0.47
	DBAA	<0.25	<0.25	<0.25	<0.25	<0.25	0.33	0.59	1.18	1.48 (1.07)	2.44
	TBAA	<0.50	<0.50	<0.50	<0.50	<0.50	<0.50	0.54	0.86	0.96 (10.26)	0.91
	BCAA	<0.50	<0.50	<0.50	<0.50	<0.50	1.40	1.93	2.56	3.19 (1.33)	4.92
	BDCAA	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	<5.00	5.73	6.91	10.95
	CDBAA	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00	<10.00
	THAAs	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**16.77**	**20.46**	**28.96**	**29.31**	**46.40**
THM	TCM	<0.20	<0.20	<0.20	<0.20	<0.20	16.67	18.26	21.19	20.08 (4.25)	26.74
	BDCM	<0.05	<0.05	<0.05	<0.05	<0.05	3.58	5.24	7.88	9.32 (2.74)	17.22
	DBCM	<0.20	<0.20	<0.20	<0.20	<0.20	1.44	3.02	5.03	6.28 (3.12)	9.01
	TBM	<0.05	<0.05	<0.05	<0.05	<0.05	0.16	0.35	0.40	0.55 (1.24)	1.03
	TTHMs	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**21.84**	**26.88**	**34.50**	**36.24**	**54.01**
HNM	CNM	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00	<1.00
	DCNM	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80
	TCNM	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60	<0.60
	BNM	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80	<0.80
	BCNM	<1.00	<1.00	<1.00	<1.00	<1.00	7.23	8.03	8.84	10.58 (3.88)	12.01
	DBNM	<8.00	<8.00	<8.00	<8.00	<8.00	<8.00	<8.00	<8.00	<8.00	<8.00
	THNMs	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**<MDL**	**7.23**	**8.03**	**8.84**	**10.58**	**12.01**
	ClO_4^-	**<0.10**	**<0.10**	**<0.10**	**<0.10**	**<0.10**	**<0.10**	**<0.10**	**<0.10**	**<0.10**	**<0.10**
	BrO_3^-	**<0.05**	**<0.05**	**<0.05**	**<0.05**	**<0.05**	**2.27**	**2.27**	**2.39**	**2.27 (2.15)**	**2.25**

When the source water was disinfected with PAA, bromate formation occurred below the detection limits for all monitored exposure times. However, bromate was observed within a consistent range between 2.25 to 2.39 μg/L, and formed in as quickly as 5 minutes (15 mg/L FC disinfectant dosage). These results reconfirm the significance of FC initial dosage on DBP formation. Bromate formation is more dependent on the initial dosage of FC rather than the exposure time. Therefore, to achieve the same contact time (CT) within a drinking water facility and reduce the formation potential of bromate, the CT would ideally be met by lower FC dosages and increased exposure time. The formation kinetics of bromate was quick, and the bromate concentrations once formed were stable, as previously predicted.[23] Perchlorate concentrations remained below the detection limits for PAA and FC disinfection of the source water across all exposure times.

4. CONCLUSIONS

The disinfection efficiency of PAA and FC were equivalent within the typical pH range of source water. Disinfection of the source water by PAA was achieved within 5 minutes (15 mg/L PAA disinfectant dosage), and with as little as 0.50 mg/L PAA dosage (4 hour exposure time). With high disinfectant dosages or longer exposure times, PAA disinfection overall yielded non-detectable formation of DBPs, while under the same conditions FC disinfection yielded HAAs, THMs, HNMs, and bromate. The dosage of FC was found to have a significant role in DBP formation compared to the dependence on time; yet, PAA did not portray the same trend. Overall, drinking water disinfection by PAA yielded significantly less monitored DBPs than FC under the same conditions: pH, disinfectant dosage, and exposure time. These results indicate that PAA could be a potential alternative disinfectant for drinking water treatment, especially for small drinking water facilities

struggling to meet drinking water regulations. However, further investigation of other DBPs, such as N-nitrosamines, should also be conducted, in addition to characterization of PAA within the distribution system. Preliminary experiments performed within surface water yielded similar formations upon PAA or FC disinfection – significantly less DBP formation by PAA disinfection in comparison to FC.

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III. FORMATION OF EIGHT N-NITROSAMINES IN THE ABSENCE AND PRESENCE OF SEVEN N-NITROSAMINE PRECURSORS IN DISINFECTED DRINKING WATER

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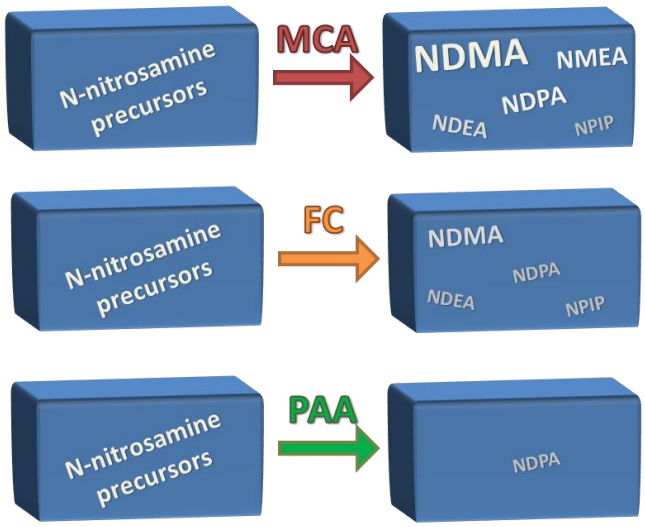
ABSTRACT



Eight N-nitrosamine formations (NFs) were investigated in the presence of seven N-nitrosamine precursors (precursors) when drinking water was disinfected with monochloramine (MCA), free chlorine (FC) or peracetic acid (PAA) and based on: (1) disinfectant, (2) disinfectant dosage, (3) exposure time and (4) pH. The general trends of NF for MCA with precursors present were: (A) NF increased with increased MCA residuals; (B) N-nitrosodimethylamine (NDMA) formation increased with exposure time (while other observed N-nitrosamine species decreased after three days); and (C) NDMA and N-nitrosopiperidine (NPIP) formations were greatest at pH 8 (while other N-nitrosamines decreased with increased pH). NFs were further investigated by comparing the disinfectants: MCA, FC, and PAA. Compared with MCA, FC disinfection resulted in lower NFs, while PAA disinfection NFs were below detection limits, with the exception of N-nitrosodi-n-propylamine (NDPA). When PAA primary disinfection occurred prior to MCA or FC secondary disinfection, the results paralleled those without PAA primary disinfection: NFs increased with increased MCA residuals and decreased with increased FC residuals. However, NDMA formation was increased by 95.3% when compared to FC disinfection. Precursors were also monitored for all experiments, with MCA yielding the greatest depletion of dimethylamine (DMA) and resulting in the greatest NDMA formation.

INTRODUCTION

To decrease the formation of disinfection byproducts (DBP), such as trihalomethanes (THMs) and haloacetic acids (HAAs), and to meet drinking water regulations, many drinking water treatment plants (DWTPs) have switched or are looking to switch their disinfectant from free chlorine (FC) to monochloramine (MCA).[1] MCA disinfection is advantageous from a compliance standpoint due to lower formation of regulated DBPs in comparison to FC.[2, 3] However, MCA disinfection has been shown to enhance the formation of nitrogenous DBPs (N-DBPs). Specifically, in the presence of low molecular weight, hydrophilic dissolved organic matter, MCA disinfection of water has significant potential to form N-nitrosamines.[4-6]

N-nitrosamines are an unregulated group of compounds which are known to be carcinogenic.[3, 7, 8] The United States Environmental Protection Agency (USEPA) has determined N-nitrosodimethlyamine (NDMA) to have an associated cancer risk at a level of 0.7 ng/L in drinking water.[3, 9] Therefore, the USEPA has placed NDMA, along with N-nitrosodiethylamine (NDEA), N-nitrosodi-n-butylamine (NDBA), N-nitrosodi-n-propylamine (NDPA), N-nitrosomethylethylamine (NMEA), and N-nitrosopyrrolidine (NPYR), on the Unregulated Contaminant Monitoring Rule 2.[10] NDMA, NDEA, NDPA, N-nitrosodiphenylamine (NDPhA), and NPYR were placed on the USEPA Contaminant Candidate List 3 for further investigation within drinking water from 2008-2010, and drafted into the CCL4 in 2015.[11] California has set a state action level of 10 ng/L NDMA within drinking water.[12]

NDMA formation in wastewater has been widely studied and three major pathways have been reported: unsymmetrical 1,1-dimethylhydrazine (UDMH), chlorinated UDMH, and nitrosation.[4, 13-15] Studies have also stated nitrite, ammonia, and bromide can increase NDMA formation with nitrite assisting in nitrosation and the formation of the reactive specie bromamine in the presence of both ammonia and bromide.[4, 16-18] However, a comprehensive study of N-nitrosamine formation in drinking water in the presence of N-nitrosamine precursors has not been investigated for MCA, FC, and peracetic acid (PAA) disinfectant. This study focused on a comprehensive formation study of eight N-nitrosamines within drinking water: NDMA, NDEA, NDPA, NDBA, NMEA, NPYR, N-nitrosopiperidine (NPIP), and N-nitrosomorpholine (NMOR). Many secondary, tertiary, and quaternary amines contained in cationic polymers, shampoos, pharmaceuticals, and ion exchange resins are possible N-nitrosamine precursors.[16, 19] The seven N-nitrosamine precursors (precursors) utilized in this study have been linked to N-nitrosamine formation: dimethylamine (DMA), diethylamine (DEA), ethylmethylamine (EMA), trimethylamine (TMA), dipropylamine (DPA), 3-(Dimethylaminomethyl) indole (DMAI), and 4-dimethylaminopyridine (DMAP).[20] Previous drinking water research focused only on NDMA formation, transformation of a specific precursor, or effects of several conventional oxidants such MCA, FC, or ozone.[9, 18, 21-23] A comprehensive formation study of N-nitrosamines in drinking water with major representative precursors and various disinfectants have not been reported, particularly PAA.

The removal of NDMA is difficult by conventional treatment processes due to its physiochemical properties coupled with the continued formation within the distribution system.[24, 25] Therefore, prevention of N-nitrosamine exposure should focus on the limitation

of NFs by either reducing the N-nitrosamine precursors or minimization of N-nitrosamine formation during chemical treatment. This study focuses on three disinfectants (MCA, FC, and PAA) and their NFs in the presence and absence of N-nitrosamine precursors.

PAA is a commonly used disinfectant for ballast water, drinking water in Europe, and wastewater treatment within the United States.[26-29] West et al. demonstrated that PAA disinfection of drinking water formed minimal THMs, HAAs, halonitromethanes (HNMs), and bromate compared to FC disinfection.[30] PAA has the potential to be utilized as a drinking water disinfectant due to its strong oxidizing capability, and wide range of micro-organism deactivation.[30-34] Due to its non-toxic decomposition products and minimal DBP formation, PAA may be used as a more environmental friendly drinking water disinfectant. However, the formation of N-nitrosamines by PAA disinfection has not been studied and should be investigated. The high toxicity of N-nitrosamines necessitates a further understanding of NFs in drinking water. Furthermore, it will provide an understanding for the breadth of concern for N-nitrosamine formation on a larger scale. NFs were systematically investigated in the presence and absence of N-nitrosamine precursors when drinking water was disinfected with MCA, FC, PAA. In addition, utilization of PAA primary disinfection prior to FC or MCA secondary disinfection influence on NFs was also evaluated.

EXPERIMENTAL

Reagents and materials. Acetone (pesticide grade), methanol (optima grade), and methylene chloride (optima grade) were purchased from Fisher Scientific (Pittsburg, PA, USA). Water samples were dechlorinated using sodium thiosulfate (Fisher Scientific,

Pittsburg, PA, USA). Sodium hypochlorite solution (Sigma-Aldrich, Saint Louis, MO, USA), ammonium chloride (Fisher Scientific, Pittsburg, PA, USA), and PAA (Proxitane WW-12, Solvay Chemicals, Houston, TX, USA) were used for disinfection. MCA was prepared according to United States Patent # US 7,045,659 B2.[35] Hach test kits (Loveland, CO, USA) were utilized for detection of MCA, FC, and PAA. Supelco Supelclean coconut charcoal SPE cartridges (Sigma Aldrich, Saint Louis, MO, USA) were used to extract the water sample for analysis of N-nitrosamines. N-nitrosamine standards of 5000 mg/L NDMA, NDEA, NDPA, NDBA, NMOR, and NPIP; 1000 mg/L NMEA solutions; and pure (99.9%) NPYR were purchased from Sigma-Aldrich (Saint Louis, MO, USA). Individual standards were diluted to 1000 mg/L stock solutions with methylene chloride and combined to prepare a 1 mg/L working solution mixture. N-nitrosamine precursors standards, DMA (40 wt.% in H_2O), TMA (25 wt.% in H_2O), DMAI (99%), DMAP, EMA (97%), DEA (≥99.5%), and DPA (99%) were obtained from Sigma-Aldrich (St. Louis, MO). Stock solutions of each precursor were prepared at 1000 mg/L in ultrapure water and then combined to prepare a 1 mg/L working solution mixture. Isotope-labeled N-nitrosamine standards were purchased from CDN Isotopes (Pointe-Claire, Quebec, Canada) and Cambridge Isotope Laboratories (Andover, MA, USA) which included: NDMA-d6, NDEA-d10, NMEA-d3, NDBA-d18, NPIP-d10, NPYR-d8, NMOR-d8, and NDPA-d14. Standards were serially diluted to a concentration of 1000 mg/L with methylene chloride. NDPA-d14 standard was purchased as a 1000 mg/L standard in methylene chloride. A working internal standard solution mixture of 1 mg/L in methylene chloride was prepared from the 1000 mg/L standards.

Experimental water matrix. Water was collected in amber glass bottles from a DWTP which utilizes surface water (lake) as source water. The DWTP utilized conventional treatment process: chlorine dioxide pre-oxidation, coagulation, flocculation, sedimentation, filtration (sand and granular activated carbon), and MCA secondary disinfection (**Figure 1**). The waters used in the experiments were designated W2 (for water collected after filtration, but prior to the addition of FC before the clear well) and W3 (for finished drinking water immediately after ammonia was added to form MCA). W2 and W3 were collected, remained unquenched, and were transported to the laboratory (EPA method 521) where NF testing immediately begun.[36]

Water characterization. Conductivity, turbidity, total chlorine, free ammonia, and pH were measured on-site during the water collection using an Accumet portable conductivity meter (Fisher Scientific, Pittsburg, PA, USA), Orbeco portable turbidimeter (Sarasota, FL, USA), HACH Diethyl-p-phenylenediamine (DPD) pillow test kit (Loveland, CO, USA), and Accumet pH meter (Fisher Scientific, Pittsburg, PA, USA), respectively. Additional water was collected, transported, and analyzed according to their respective analytical method protocol for further characterization immediately upon arrival to the laboratory.[37] Specifically, the UV absorbance at wavelength 254 nm (UV_{254}) was measured using a Cary 50 spectrometer (Sparta, NJ, USA). Dissolved organic carbon (DOC) and total nitrogen (TN) content of the water were measured with a Shimadzu TOC-L TOC analyzer (Columbia, MD, USA). Major anions were analyzed by ion chromatography (IC) (Dionex model DX-120 IC, AG4A guard column, 4x250mm Dionex AS9-HC column, and conductivity detector, Sunnyvale, CA, USA).[38] Seven precursors were monitored using a HPLC-MS/MS method developed in our laboratory.[20] Sampled water did not contain

detectable levels of precursors or N-nitrosamines. Therefore, in all experiments, samples with precursors added were run concurrently to evaluate their impact on NF.

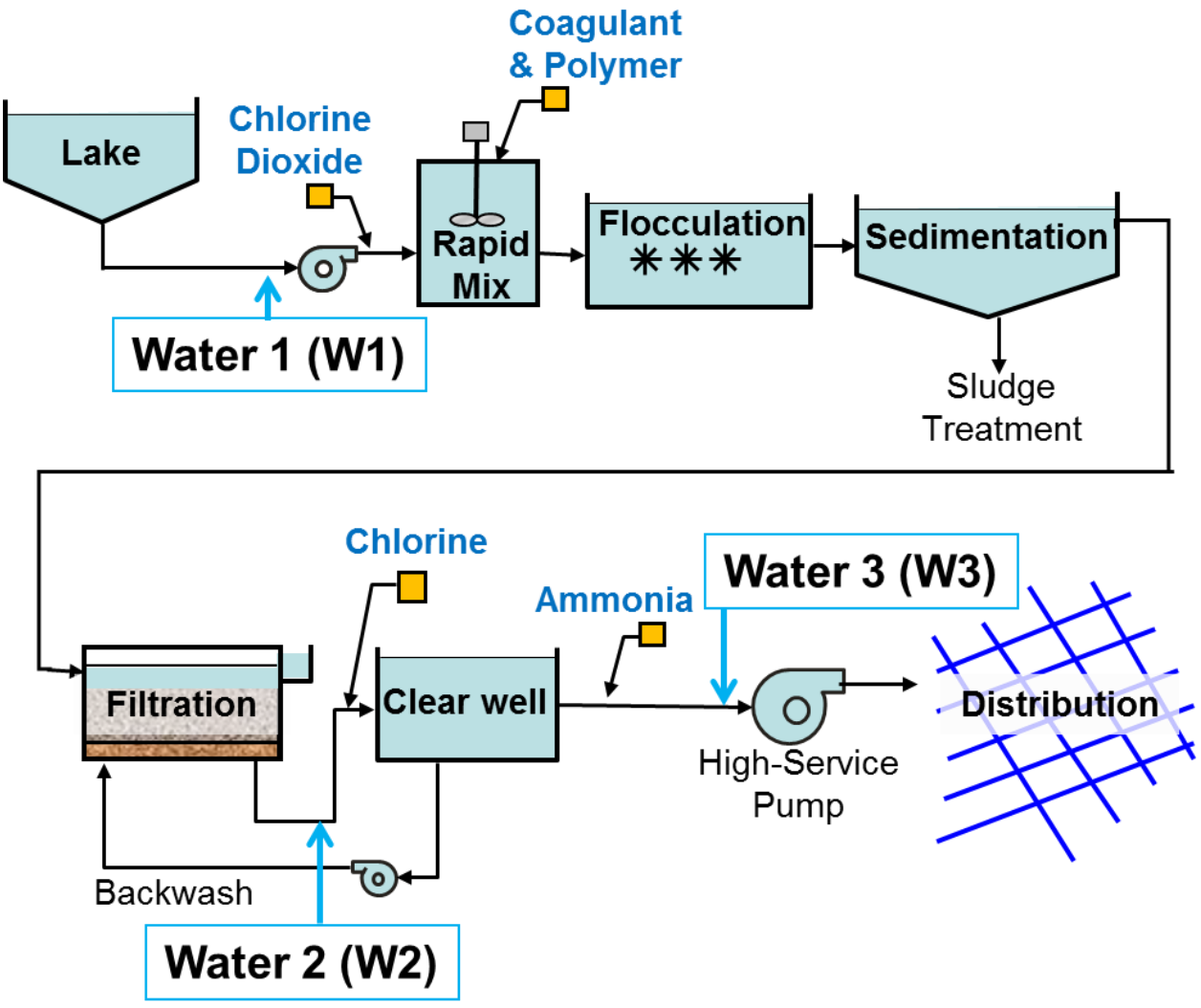


Figure 1. Drinking water treatment facility schematic and sampling sites.

Sample preparation and extraction. EPA Method 521 was followed for water sample storage, preparation, and extraction of N-nitrosamines.[36] Deuterated N-nitrosamine internal standards were added to each sample for isotope dilution to account for loss of analytes throughout sample extraction, elution, and evaporation. Glass wool was used to support 6.9 grams of anhydrous sodium sulfate within each glass drying cartridge, both purchased from Fisher Scientific (Pittsburg, PA, USA). The samples were then placed into a Zymark TurboVap LV evaporator (Charlotte, NC, USA) and were evaporated to 1 mL at 28°C under a gentle stream of nitrogen.

Instrumentation. The analytical method by McDonald et al. was adapted and validated for this study using an Agilent 6890 series GC with an Agilent 5973 network mass selective detector.[39] Using splitless mode, 2 μL of sample was injected and separated by an Agilent HP-5ms column (30 m × 250 μm ID, 0.25 μm film thickness) initially set to 42°C for 2 minutes, then ramped 10°C/min to 80°C, 15°C/min to 180°C, 35°C/min to 260°C and held for 5 minutes, and finally ramped to 280°C and held for 7 minutes. The flow rate of the carrier gas (helium) was 1.2 mL/min. The MS quad and MS source temperatures were set at 150°C and 240°C, respectively, and the electron ionization voltage was 70 eV. Selected ion monitoring (SIM) mode was used for quantification. Parent and product ion masses of each N-nitrosamine, along with the respective retention times, are provided in **Table S1.**

N-nitrosamine formation experiments. The initial pH and disinfectant concentration was measured prior to the start of each formation experiment. All samples were stored in the dark at room temperature in 500 mL amber glass bottles, without headspace, for the specified exposure period. As the collected water contained N-nitrosamine precursor

concentrations below the detection limits, another set of samples was prepared under the same conditions spiked with 100 μg/L of each precursor and conducted in parallel. After the specified exposure period, the pH and residual disinfectant concentration for each sample was measured. The sample was then quenched and prepared for analysis of N-nitrosamines and N-nitrosamine precursors.

The NF by MCA disinfection of the water matrix was determined by evaluation the exposure time and matrix pH. Exposure times of 4 hours, 1, 3, and 7 days of MCA disinfection of W3 were assessed with the residual MCA from the DWTP to determine the reaction and formation kinetics of N-nitrosamine precursors and N-nitrosamines, respectively. The pH dependence was also evaluated with adjustment by hydrochloric acid or sodium hydroxide to nominally pH 7 or 9, or remained unadjusted at an ambient pH of approximately 8. Each pH sample was prepared individually in W3 before transferred to the 500 mL amber glass bottle for an exposure period of 7 days.

NF dependence on disinfectants MCA, FC, and PAA was tested in W2 for a seven day exposure period. Simultaneously, samples were prepared in ultrapure water to determine the natural organic matter and matrix contributions to NFs. PAA was also evaluated as a primary disinfection of W2 prior to a seven day exposure by MCA or FC secondary disinfection.

Disinfectant dependence on N-Nitrosamine precursor depletion. To determine the disinfectant dependence on the depletion of precursors, the precursor concentrations were monitored in each matrix and after disinfection using a HPLC-MS/MS method.[20] The method detection limits of DMA (1.00 μg/L), EMA (5.00 μg/L), TMA (0.50 μg/L), DEA (1.00 μg/L), DPA (0.20 μg/L), DMAI (0.05 μg/L), and DMAP (0.02 μg/L) were validated in the DWTP water utilized. As the precursor concentrations in W2 and W3 were below the detection limits, spiked samples (100 μg/L of each precursor) were conducted in parallel. Immediately after quenching each sample, the precursor concentrations were monitored to evaluate individual precursor depletion by each disinfectant.

RESULTS AND DISCUSSION

Water characterization. To fully characterize the collected water samples, numerous water parameters were monitored. During water collection, pH, conductivity, turbidity, total chlorine, and free ammonia were analyzed on-site. UV_{254}, DOC, TN, total bromine, and major anions were also measured immediately upon return to the laboratory. W2 & W3 water pH ranged between 7.5 – 8.0 and had a conductivity of 281 – 290 μS/cm. The average turbidity of the source water (Water 1) was 11.71 NTU, with a final turbidity after rapid filtration of 0.04 NTU (W2 and W3).

The total chlorine was near the detection limit (0.13 mg/L Cl_2) throughout the treatment plant until chlorine was added after W2 to form MCA in the finished water (W3, 2.55 mg/L MCA-Cl_2). The natural free ammonia concentration was below the detection limit until W3 (0.10 mg/L NH_3-N) as ammonia was added after the clear well to form MCA. The total nitrogen (TN) of W2 and W3 was measured at 287 and 786 μg/L, respectively.

The UV_{254} and DOC decreased throughout the treatment process as expected, with lowest concentrations detected in W3 (0.053 UV_{254} and 2.622 mg/L DOC) as anticipated.

The major anions monitored included fluoride, chloride, nitrate, nitrite, sulfate, and bromide. Nitrite and bromide concentrations were below the detection limits of 0.02 and 0.06 mg/L, respectively. Fluoride, chloride, nitrate, and sulfate concentrations of W2 and W3 were 0.69 and 0.67 mg/L F, 11.25 and 12.57 mg/L Cl^-, 0.23 mg/L NO_3^- (remained constant), and 25.09 and 30.14 mg/L SO_4^{2-}, respectively.

PAA stability and feasibility. PAA was evaluated within W2 to determine whether pH would influence the stability and overall feasibility of PAA for drinking water disinfection. First, the PAA demand was determined by the addition of 5.0, 6.0, and 7.0 mg/L PAA to ambient W2. After an exposure of seven days, the matrix consumption of 6.66 mg/L PAA was determined. Next, the pH influence was determined by adjusting ultrapure and W2 to pH 7.03 ± .01, 7.82 ± 0.10, and 8.97 ± 0.00. Each sample was disinfected with 7.28 mg/L PAA. In ultrapure water, the residual PAA concentration was 5.57 ± 0.13 mg/L across the measured pH range indicating the PAA residual concentration was not pH dependent. However, for W2, the pH significantly influenced the residual PAA concentration. The average residual concentrations within W2 at pH 7, 8, and 9 were 2.93 ± 0.88, 0.62 ± 0.05, and 0.14 ± 0.05 mg/L PAA, respectively. The resulting trend of decreased residual PAA concentration with an increase in pH could be due to the decreased stability of PAA in an alkaline pH range, increased consumption of PAA by other matrix components which is pH dependent, or spontaneous decomposition of PAA.[40, 41] Therefore, alkaline matrices may require a higher dosage of PAA.

Effects of MCA exposure time on N-nitrosamine formation. To simulate a DWTF operating with MCA as residual disinfectant, the NF dependence on exposure time was studied. Under ambient conditions the initial pH was 8.00 ± 0.04 and concentration of 2.47 ± 0.05 MCA-Cl_2. After the designated exposure period, the final pH and residual MCA concentrations were measured. The final pH and residual concentration after 7 days without precursors present were 7.92 ±0.01 and 2.24 ± 0.22 mg/L MCA-Cl_2, respectively. With precursors present the pH was 8.06 ± 0.05 and MCA residual concentration of 1.98 ± 0.30 mg/L (MCA-Cl_2). Without precursors present the NFs remained below the detection limits for exposure times ranging from 4 hours to 7 days. The one exception was the formation of 8.93 ng/L NPYR at 7 days, also observed in previous studies formed from dissolved organic matter (DOM).[42] However, with the presence of precursors, the formation in ambient W3 was observed for NDMA, NMEA, NDEA, NDPA, and NPIP (**Figure S1**). NPYR was no longer observed above its detection limit which could be attributed to the observed N-nitrosamines formation pathways dominated kinetically over the formation pathway of NPYR. NDMA formation occurred rapidly and reached a concentration of 417 ng/L within 4 hours. As sufficient MCA and precursors were present, the NDMA concentration continued to increase over the 7 day exposure period and formed 1,042 ng/L. Similarly, the formation of other N-nitrosamines, NMEA, NDEA, NDPA, and NPIP, increased from 4 hours to 3 days, with a slight decrease from day 3 to day 7 observed. The decrease could be explained by degradation or further reactions of these N-nitrosamines. The formation of other N-nitrosamines, NPYR, NMOR, NDBA, were not observed even when precursors were present, most likely due to the kinetically favored pathways of the other formed N-nitrosamines.

Effects of matrix pH on N-nitrosamine formation. The pH dependence of a DWTP was simulated for MCA disinfection. The ambient conditions of W3 were measured at a pH of 8.03 ± 0.03 and an initial MCA concentration of 2.51 ± 0.00 mg/L (MCA-Cl_2). The pH of W3 was adjusted to pH 7.00 ± 0.00 and 8.97 ± 0.01. After seven days of exposure, the final pH and MCA residual concentration of each sample were measured. The residual MCA concentrations without precursors present were 1.04 mg/L MCA-Cl_2 (pH 7), 1.95 mg/L MCA-Cl_2 (pH 8), and 2.12 mg/L MCA-Cl_2 (pH 9). W3 with precursors present had slightly lower residual MCA concentrations: 0.95 mg/L MCA-Cl_2 (pH 7), 1.66 mg/L MCA-Cl_2 (pH 8), and 1.72 mg/L MCA-Cl_2 (pH 9). W3 without any precursors present had NFs below the detection limits, except for NPYR where the formation observed decreased with an increase in pH: 10.48 (pH 7), 8.93 (pH 8), and 7.74 ng/L NPYR (pH 9).Again, the samples with precursors present did not form NPYR, NMOR, or NDBA at concentrations above the detection limits, while NDMA, NMEA, NDEA, NDPA, and NPIP were all observed (**Figure S2**). NDMA was formed at the highest concentration at concentrations of 935 ng/L, 945 ng/L, and 1,042 ng/L at pH 9, 7, and 8, respectively after 7 days. The enhanced formation of NDMA at pH 8 observed in drinking water, which was also observed in wastewater, is attributable to the oxidation of UDMH.[18] The next highest formations were NMEA (89.52 ng/L, pH 7), NDEA (75.56 ng/L, pH 7), NDPA (26.76 ng/L, pH 7), and NPIP (4.85 ng/L, pH 8). NMEA, NDEA, and NDPA maximum formations occurred at pH 7 and decreased as pH increased (18.19 ng/L NMEA, 18.40 ng/L NDEA, and 9.04 ng/L NDPA at pH 9). In contrast, NPIP exhibited a slight increase at pH 8 (4.84 ng/L) in comparison to pH 7 (2.28 ng/L) or pH 9 (2.86 ng/L).

Effects of disinfectant on N-nitrosamine formation in ultrapure water. To determine the matrix effect on NFs, FC and MCA disinfection experiments were conducted in ultrapure water and exposed for seven days. FC and MCA were dosed to obtain a final disinfectant residual of 0.73 and 1.74 mg/L FC-Cl_2 and 1.64 and 2.59 mg/L MCA-Cl_2. Samples without and with precursors spiked were run in parallel. Without precursors, NFs remained below detection limits. However, when precursors were present ultrapure water had the potential to form N-nitrosamines (**Table 1**). Results are consistent with published works on NF pathways (UMDH and chlorinated UMDH), without nitrosation of the matrix.[4, 13, 14] Further investigation of NFs revealed less NDMA formation by FC disinfection in W2 than ultrapure water. This is perhaps due to the other competing formation pathways available through nitrosation for NDEA, NDPA, and NPIP available within W2 which were not accessible in ultrapure water. Within the ultrapure water, these pathways are inaccessible, therefore, only NDMA formed and at a significant concentration.

Table 1. Peracetic acid, free chlorine, and monochloramine disinfection N-nitrosamine formation with 100 µg/L of each N-nitrosamine precursors present in ultrapure water and water after rapid filtration (W2).

Matrix	Disinfectant	Disinfectant Residual (mg/L)	NDMA (ng/L)	NMEA (ng/L)	NDEA (ng/L)	NPYR (ng/L)	NMOR (ng/L)	NDPA (ng/L)	NPIP (ng/L)	NDBA (ng/L)
Ultrapure	Free Chlorine	0.73	16.34	<7.50	<1.50	<5.00	<2.50	<2.50	<1.50	<7.50
		1.74	11.43	<7.50	<1.50	<5.00	<2.50	<2.50	<1.50	<7.50
	Monochloramine	1.64	107.09	<7.50	6.44	<5.00	<2.50	4.61	<1.50	<7.50
		2.59	249.09	<7.50	7.43	<5.00	<2.50	<2.50	<1.50	<7.50
Water 2	Peracetic Acid	5.14	<1.50	<7.50	<1.50	<5.00	<2.50	7.76	<1.50	<7.50
		7.63	<1.50	<7.50	<1.50	<5.00	<2.50	7.95	<1.50	<7.50
	Free Chlorine	0.14	10.05	<7.50	<1.50	<5.00	<2.50	<2.50	5.68	<7.50
		0.62	7.49	<7.50	4.54	<5.00	<2.50	3.06	2.86	<7.50
		1.98	5.55	<7.50	<1.50	<5.00	<2.50	<2.50	<1.50	<7.50
	Monochloramine	1.13	758.87	57.31	41.53	<5.00	<2.50	18.88	1.63	<7.50
		2.58	1180.31	61.53	48.69	<5.00	<2.50	24.36	4.60	<7.50

Effects of different disinfectants on N-nitrosamine formation in natural water matrix. Three disinfectants were utilized in W2 to determine the NFs of each, and evaluate whether individual implementation would minimize N-nitrosamine formation. The disinfectant dependences were examined at the conditions which would achieve maximum NFs: ambient pH and exposure time of seven days. PAA, FC or MCA was added as a disinfectant to ambient water (pH 7.64 ± 0.11). The disinfectants were dosed to result in approximately 5 and 9 mg/L PAA, 0.5 and 1.5 mg/L FC-Cl_2 or 1.5 and 2.5 mg/L MCA-Cl_2 residual concentrations after seven days.

MCA and FC disinfection. FC residuals were 0.62 and 1.24 mg/L FC-Cl_2 without precursors and 0.62 and 1.98 mg/L FC-Cl_2 with precursors. The MCA residuals without and with precursors were 1.51 and 2.85 mg/L MCA-Cl_2 and 1.13 and 2.58 mg/L MCA-Cl_2, respectively.

NF for samples without precursors present resulted in concentrations below the detection limits for both FC and MCA as expected. When precursors were present, the NFs exhibited two distinct trends for MCA and FC. When MCA was utilized for disinfection, the following N-nitrosamines were observed: NDMA>NMEA>NDEA>NDPA>NPIP (Table 1). NDMA had the highest formation and increased concentration from 759 to 1,180 ng/L when the MCA residual increased from 1.13 to 2.58 mg/L MCA-Cl_2, respectively. NMEA, NDEA, NDPA, and NPIP exhibited a similar trend as NDMA: the formation increased with increased MCA residual concentration when precursors were present. However, the actual formation was much lower compared to NDMA at the

highest MCA residual: 61.53 ng/L NMEA, 48.69 ng/L NDEA, 24.36 ng/L NDEA, and 4.60 ng/L NDPA (Table 1).

FC disinfection in W2 with precursors present yielded NDMA, NDEA, NDPA, and NPIP at detectable concentrations (Table 1). However, contrary to the increased trend of NF with increased MCA residual concentration, NDMA and NPIP decreased as the FC residual concentration increased. This may be attributed to the rapid degradation of the N-nitrosamine precursors during FC treatment (Table S5). Additionally, less than 1% NDMA formed with FC disinfection in comparison toMCA disinfection. These results suggest in the presence of precursors in source water, FC should be added first, followed by the addition of ammonia to form MCA for residual disinfection in the distribution system to minimize the N-nitrosamine formation. These finding agree with Bond and Templeton's results.[15] Thus, DWTPs with precursors present in the source water should either consider using (1) FC disinfection or (2) FC pre-oxidization of the water followed by the addition of ammonia to form MCA within finished water.

PAA disinfection. Previous studies have demonstrated a dosage of 5 – 10mg/L PAA (with nominally a 10 minute contact time) was required to achieve a 3-log removal of fecal coliform, while a 4-log removal of fecal coliform, total coliform, and E. *coli* was achieved with 15 mg/L PAA (with nominally a 36 minute contact time).[43,44] Therefore PAA disinfection of W2 was investigated at these dosages of PAA to estimate the NFs: 9.72 and 14.98 mg/L PAA without precursors and 9.79 and 15.23 mg/L PAA with precursors. After 7 days, the pH of samples were 6.92 ± 0.10 with residual PAA concentrations of 5.14 and 9.10 mg/L and 5.35 and 7.60 mg/L PAA without and with precursors, respectively. In

ambient W2, without precursors present, NFs remained below detection limits. Similar results were obtained when 100 μg/L precursors were spiked into W2 and disinfected by PAA, except for slight formation of NDPA: 7.76 and 7.95 ng/L NDPA formed at residual PAA concentrations of 5.14 and 7.63 mg/L, respectively. Results implicate the potential of PAA to serve as a drinking water disinfectant without significant NFs, even at high dosages. FC and MCA both yielded NDMA concentrations over the USEPA 0.7 ng/L risk level and the California state action level of 10 ng/L within drinking water.[3, 12] PAA disinfection, however, did not form NDMA even during these extreme conditions. Furthermore, according to a previous study, PAA also minimized formation of other toxic disinfection byproducts such as THMs and HAAs.[30] As a result, PAA as a drinking water disinfectant would reduce concerns for the majority of current regulated DBPs and emerging DBPs in drinking water. However, more extensive studies on PAA in water distribution system need to be conducted.

Effect of PAA primary disinfection followed by FC or MCA secondary disinfection on N-nitrosamine formation. Further experiments were conducted to determine whether the same NF reduction would occur with W2 PAA primary disinfection followed by FC or MCA secondary disinfection. The implications would be minimization of not only NFs, but also reduction of regulated THMs and HAAs, by reducing the contact time with FC or MCA secondary disinfection.[29] PAA disinfection was utilized at an average clear well exposure period (5 hours) for the facility under W2 ambient conditions. The initial dosage of PAA was 0.75 mg/L with residual concentrations of 0.61 ± 0.02 mg/L PAA after 5 hours. The samples without precursors had an initial pH of 7.70 and final pH of 7.58 ± 0.09. The samples with precursors present had an initial pH of 7.74 and final pH of 7.71 ±

0.11. The initial concentrations of FC and MCA with and without precursors were 5.00 and 6.00 mg/L FC-Cl_2 and 3.00 and 4.00 mg/L MCA-Cl_2, respectively. The final disinfectant concentrations were 0.76 and 1.44 mg/L FC-Cl_2 and 1.61 and 2.37 mg/L MCA-Cl_2 without precursors present, and 0.10 and 0.49 mg/L FC-Cl_2, and 1.49 and 2.36 mg/L MCA-Cl_2 with precursors present.

PAA primary disinfection of W2 without precursors addition did not yield N-nitrosamines at detectable concentrations. The NFs for PAA primary disinfection followed by FC or MCA secondary disinfection with precursors present are shown in Table 2. Samples with precursors present exhibited approximately the same NFs as samples which were not disinfected with PAA prior to FC or MCA secondary disinfection. The formation of NDMA was 1,180 ng/L (2.58 mg/L MCA-Cl_2 residual) and 1,115 ng/L (2.36 mg/L MCA-Cl_2), without and with PAA primary disinfection, respectively. However, when PAA primary disinfection was followed by FC secondary disinfection, the NFs increased. The formation concentration of NDMA increased from 10.05 ng/L (FC disinfection) to 213.35 ng/L (PAA primary disinfection followed by FC secondary disinfection) with residual concentrations of 0.14 and 0.10 mg/L FC-Cl_2, respectively. This trend could be attributed to the PAA oxidation increasing the available lower molecular weight DOM which is then available to react with FC. Though, the same overall trend for FC was observed with or without PAA primary disinfection – when the FC residual concentration increased, the NF decreased. This may be due to the reaction kinetics of FC with the natural organic matter which may favor formation of other DBPs in preference to N-nitrosamines. Further comprehensive and simultaneous detection studies of regulated and unregulated DBPs to determine the secondary disinfection formations should be considered.

Table 2. N-nitrosamine formation with peracetic acid primary disinfection followed by free chlorine or monochloramine secondary disinfection with 100 µg/L of each N-nitrosamine precursors present in water after rapid filtration (W2).

Disinfectant	Disinfectant Residual (mg/L)	NDMA (ng/L)	NMEA (ng/L)	NDEA (ng/L)	NPYR (ng/L)	NMOR (ng/L)	NDPA (ng/L)	NPIP (ng/L)	NDBA (ng/L)
Free Chlorine	0.10	213.35	<7.50	14.52	<5.00	<2.50	52.93	4.51	<7.50
	0.49	137.97	<7.50	7.57	5.80	<2.50	23.41	1.88	<7.50
Monochloramine	1.49	667.29	40.67	23.89	7.76	<2.50	67.30	2.05	<7.50
	2.36	1114.73	53.43	35.08	<5.00	<2.50	75.93	1.83	<7.50

Without precursors present, the disinfectant utilized did not influence the NFs within these studied samples, but was disinfectant dependent with precursors present. PAA had previously been shown to reduce the formations of other DBPs.[30] In this work, PAA disinfection minimized NFs compared to FC or MCA disinfection. Although, PAA primary disinfection in combination with FC or MCA secondary disinfection did not reduce NFs when precursors were present, PAA may be beneficial when precursors are not present to help minimize N-nitrosamine and other DBPs formed due to FC or MCA disinfection.

Disinfectant dependence on N-Nitrosamine precursor depletion. As the formation pathways of N-nitrosamines have not been well studied within drinking water, seven N-nitrosamine precursors (precursors) were monitored to evaluate the depletion in correlation with NFs for each disinfectant. Previous work has demonstrated that N-nitrosamine formation by MCA disinfection occurs through the fewest intermediate steps by means of tertiary amines, followed by quaternary and secondary amines, and DMA as the major contributing precursor to NDMA formation.[9] In this study, three tertiary amines (TMA, DMAI, and DMAP) and four secondary amines (DMA, EMA, DEA, and DPA) were monitored by MCA, FC, and PAA disinfection.

The precursor data for each experiment investigated was provided in the supporting information. DMAI and DMAP had the greatest depletion and quickest kinetics (<MDL remaining within 1 day, **Table S2**) for all MCA disinfection within W2 and W3. However, DMAI and DMAP were not completely depleted by MCA disinfection within ultrapure water after a seven day reaction period, with 4% and 14% remaining, respectively (**Table**

S3). Indicating the matrix is also contributing to the depletion of these two precursors, in addition to increasing depletions of DMA, DEA, and DPA as much as 10 – 20% at a MCA residual concentration of 2.58 mg/L-Cl_2 after seven days (Table S5). The N-nitrosamines observed by MCA disinfection were NDMA, NDEA, and NDPA in ultrapure water, while NDMA, NMEA, NDEA, NDPA, and NPIP were observed in W2 (Table 1). The increased depletion in precursors resulted in increased species of N-nitrosamines observed and the pathways available allowed for the formation of NMEA and NDPA, which were not observed in ultrapure water. In more alkaline W3, enhanced depletion of DMA, EMA, TMA, DEA, AND DPA were observed ranging from 2.7 – 11.7% (Table S4) when comparing pH 7 to pH 9. Minimal precursor depletion enhancement is observed from pH 8 to pH 9, thus, the slight increase in NFs at pH 8 would be attributable to increased stability of MCA.

An interesting trend specific to FC disinfection, observed in both ultrapure and W3, was the depletion of TMA to below detection limits, along with DMAI and DMAP (Table S5). In ultrapure water, NDMA was the only observed N-nitrosamine formed by FC disinfection, while NDMA, NDEA, and NDPA, NPIP were observed in W2 (Table 1). Although lower concentrations of observed N-nitrosamines were formed by FC disinfection (1.98 mg/L FC residual) in W2, the depletion of EMA, TMA, DEA, and DPA were enhanced in comparison to MCA disinfection (2.58 mg/L MCA residual) by 40.4, 100.0, 33.2, and 46.5%, respectively. However, the depletion of DMA by FC disinfection was 21.8% less than MCA disinfection, which would explain the significantly less formation of NDMA by FC.

Although PAA disinfection yielded a single observable N-nitrosamine (NDPA, 7.85 ± 0.13 ng/L), it yielded the greatest overall depletion of all precursors compared to FC or MCA: 22 – 40% depletion of DMA, DPA, EMA, and DEA (increasing depletion) and 89% depletion for TMA (5.35 mg/L residual PAA) (Table S5). When PAA primary disinfection was followed with FC secondary disinfection the formation of these observed N-nitrosamines were increased, with NDMA formation enhancement of 95.3%. These results were observed as the depletion of EMA, DEA, and DPA were increased by 16.5, 21.9, 21.3%, respectively, in comparison to FC disinfection (0.62 and 0.49 mg/L residuals) (Table S5 & Table S6). The enhanced NFs were considered to be a result of increased available low molecular weight DOM made available by the PAA primary disinfection prior to FC secondary disinfection.

To determine the specific precursor to N-nitrosamine formation pathways, further studies are required. However, the results of this study concluded that the PAA disinfection minimized NFs, presumably by rapid degradation of N-nitrosamine precursors. In comparison to FC and MCA disinfection, PAA disinfection had the highest precursor depletion and lowest NFs – with tertiary amines having the greatest depletion. The PAA kinetics of precursor depletion, along with individual precursor to N-nitrosamine conversion, should be further investigated.

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SECTION

3. CONCLUSIONS

As USEPA drinking water regulations continue to become more rigorous and more contaminants are constantly under review, research on toxicity, occurrence, formation, and removal endeavor to keep pace. With the perchlorate regulatory level currently under review by the USEPA, research of perchlorate treatment methods and DWTP treatment methods are necessary.[29] The potential health reduction by regulation action of perchlorate was examined for the state of Missouri. A systematic occurrence screening for DWTPs considered potentially higher risk were sampled on a seasonal basis.

The concentrations observed for source water was near or below the detection limits for winter and summer season. Which allows for the conclusion that concerns for perchlorate contamination of Missouri drinking water from such sources as agricultural, ordinance, and explosives is negligible. However, as perchlorate was observed within treated water at higher levels during the summer season, concerns for other regions which may struggle with perchlorate compliance should consider possible additional perchlorate contributions from disinfectant addition. The potential to minimize perchlorate contamination from disinfectants have been found by controlling the disinfectant storage time and conditions.[33]

For source water containing perchlorate, the DWTPs studied did not demonstrate perchlorate removal by conventional treatment processes. Removal experiments under drinking water conditions for multiple activated carbons (powdered and granular) and clays did not result in effective removal of perchlorate. Conversely, an organoclay (TC-99)

yielded higher removal efficiencies than the common DWTP adsorbents. The kinetics were found to be rapid with 59.4% removal of 10 μg/L perchlorate from tap water within 30 minutes with 25 mg/L TC-99. Higher dosages of TC-99 were found to remove over 90% of 10 μg/L perchlorate. These results are advantageous for DWTPs which may struggle to comply upon issuance of the USEPA perchlorate regulation due to perchlorate contamination within the source water.

PAA results demonstrate the potential for drinking water disinfection without the generation of regulated DBPs, unregulated DBPs, and emerging contaminants. The disinfection efficiency of PAA was equivalent to FC within the source water studied. Further studies revealed the quick kinetics of source water disinfection by PAA.

In comparison to FC, the THM, HAA, HNM, and bromate formation by PAA disinfection was significantly less in source water containing high levels of ammonia and bromide. At extreme dosage conditions (50 mg/L), FC formed THM and HAA concentrations over the USEPA TTHM MCL and just below the USEPA HAA-5 MCL. Formation of HNMs and bromate were also observed by FC disinfection. In contrast, when an extreme disinfectant dosage of PAA was applied, the formations of these contaminants were near or below the detection limits. Not only did PAA disinfection form less DBPs, but the consumption of PAA was also found to be much lower than FC disinfection due to the FC interaction with the ammonia to undergo breakpoint chlorination. Furthermore, PAA disinfected source water containing high bromide concentrations did not result in the same increased trend of DBPs as FC.

PAA, MCA and FC were also evaluated in parallel experiments to determine the N-nitrosamine formation. N-nitrosamine formations by MCA disinfection with N-nitrosamine precursors present were found to exceed 1 μg/L NDMA with increased

exposure time and MCA dosage. FC disinfection also yielded formation of N-nitrosamines, yet, the N-nitrosamine concentrations decreased with increased FC residual. In contrast, PAA disinfection of source water was determined to form N-nitrosamines at or below the detection limits, even within the presence of N-nitrosamine precursors.

N-nitrosamine formation by PAA primary disinfection followed by FC or MCA secondary disinfection was also evaluated. The trends for N-nitrosamines formed mirrored those from FC or MCA disinfection. However, PAA primary disinfection followed by FC secondary disinfection yielded increased N-nitrosamine formation potentials in comparison to FC disinfection. Overall, the combined results demonstrate the prospect of PAA as a drinking water disinfection, not only to reduce regulated, but also unregulated DBPs.

4. RECOMMENDATIONS FOR FUTURE RESEARCH

4.1. PERCHLORATE REMOVAL

As TC-99 has been demonstrated to efficiently remove perchlorate from drinking water, development of an applicable treatment unit/component would be the next step toward implementation. Due to the small particle size of TC-99, the adsorbent should be secured by another material to prevent possible exposure. With higher removal efficiency obtained within tap water, the most beneficial implementation would be achieved after filtration. However, consideration of the disinfectant influence on perchlorate removal and desorption from TC-99 would also be essential. Although low FC concentrations (0.20 mg/L) allowed for efficient removal, higher FC concentrations utilized at the DWTP should be evaluated. After development and confirmation of these elements, a pilot scale test should be carried out at a DWTP within a region with native perchlorate deposits contributing to the contamination of drinking water to determine the removal performance. Consideration of other chemicals within drinking water which are naturally occurring or added after treatment, such as fluoride, should also be considered for TC-99 adsorption.

4.2. PERACETIC ACID DISINFECTION

Further PAA research is needed to determine drinking water matrix influence on DBP formation potentials. The studies performed focused on high ammonia and bromide source water. However, determination of other matrix components, such as DOC, influence on PAA DBP formations should be further investigated. Furthermore, although

these studies have concluded that PAA DBP formations were below those of MCA and FC disinfection, analysis of (1) other possible byproducts of PAA disinfection and (2) PAA disinfection within the distribution system need to be evaluated. One major aspect that needs to be evaluated is the PAA influence on biofilm growth within the distribution system. Even though PAA decomposition by-products are small molecular weight hydrocarbons available for biodegradation and has the potential to promote biofilm formation within the distribution system, it is not hypothesized for this to occur with sufficient residual as PAA is utilized in oil and gas operations to inhibit bacterial growth.[34] The conditions mimic that of a distribution system: aqueous, shielded from light, lower dissolved oxygen, and long holding times. However, an in-depth distribution system study would be the next step toward possible implementation of PAA within DWTPs. After determination of the PAA influence on biolfilms within drinking water distribution systems, a pilot scale test should be considered for three water types: ground water, ground water influenced by surface water, and surface water.

APPENDIX

SUPPORTING INFORMATION:

FORMATION OF EIGHT N-NITROSAMINES IN THE
ABSENCE AND PRESENCE OF SEVEN N-NITROSAMINE PRECURSORS
IN DISINFECTED DRINKING WATER

Table S1. N-Nitrosamine GC-MS parent and production ion masses and retention times

Nitrosamine	Parent Ion (m/z)	Product Ion (m/z)	Retention Time (minutes)
NDMA	74	42	3.6
NDMA-D6	80	46	3.6
NMEA	88	42	4.8
NMEA-D3	91	45	4.8
NDEA	102	84	5.9
NDEA-D10	112	94	5.9
NPYR	100	41	8.4
NPYR-D8	108	46	8.4
NMOR	116	56	8.4
NMOR-D8	124	62	8.4
NDPA	130	70	8.5
NDPA-D14	144	78	8.5
NPIP	114	42	8.9
NPIP-D10	124	46	8.9
NDBA	84	158	10.6
NDBA-D18	94	46	10.6

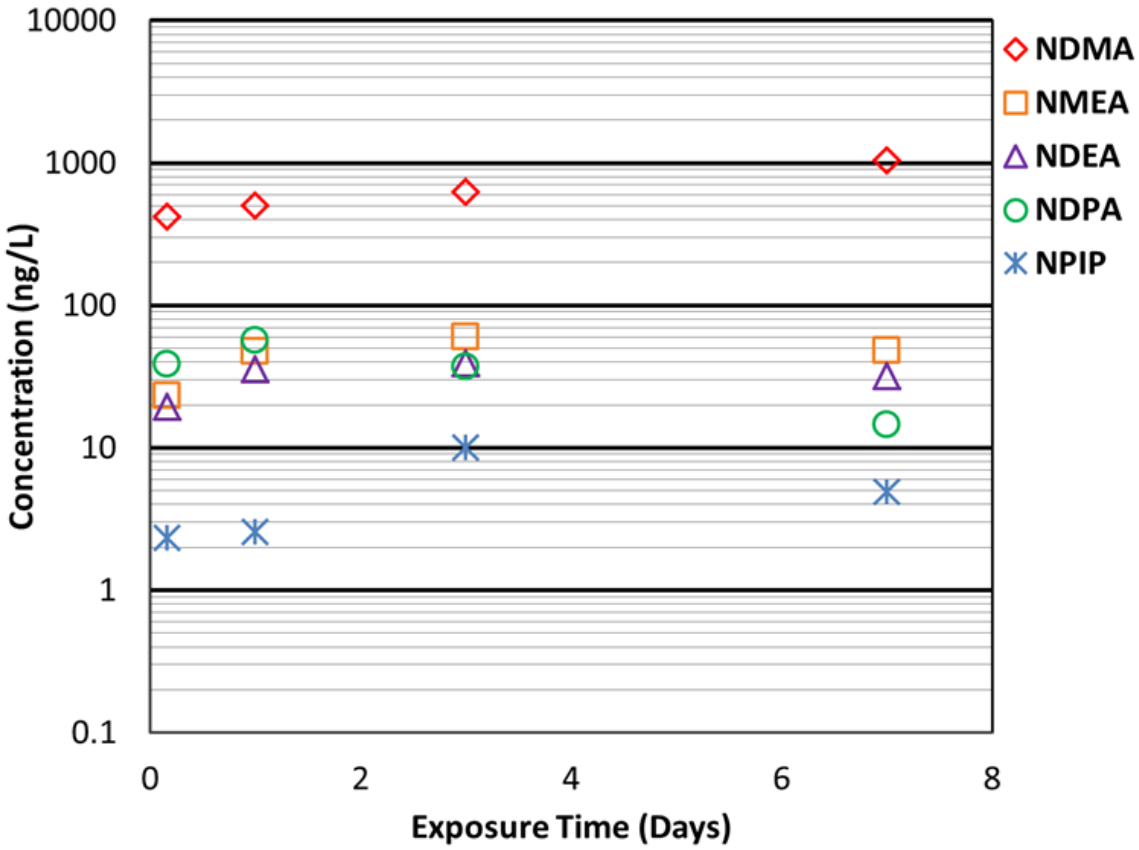

Figure S1. N-nitrosamine formation at different exposure times by MCA disinfection when 100 µg/L N-nitrosamine precursors are present in finished water (W3). N-nitrosamines not shown (NPYR, NMOR, NDBA) were below the detection limits.

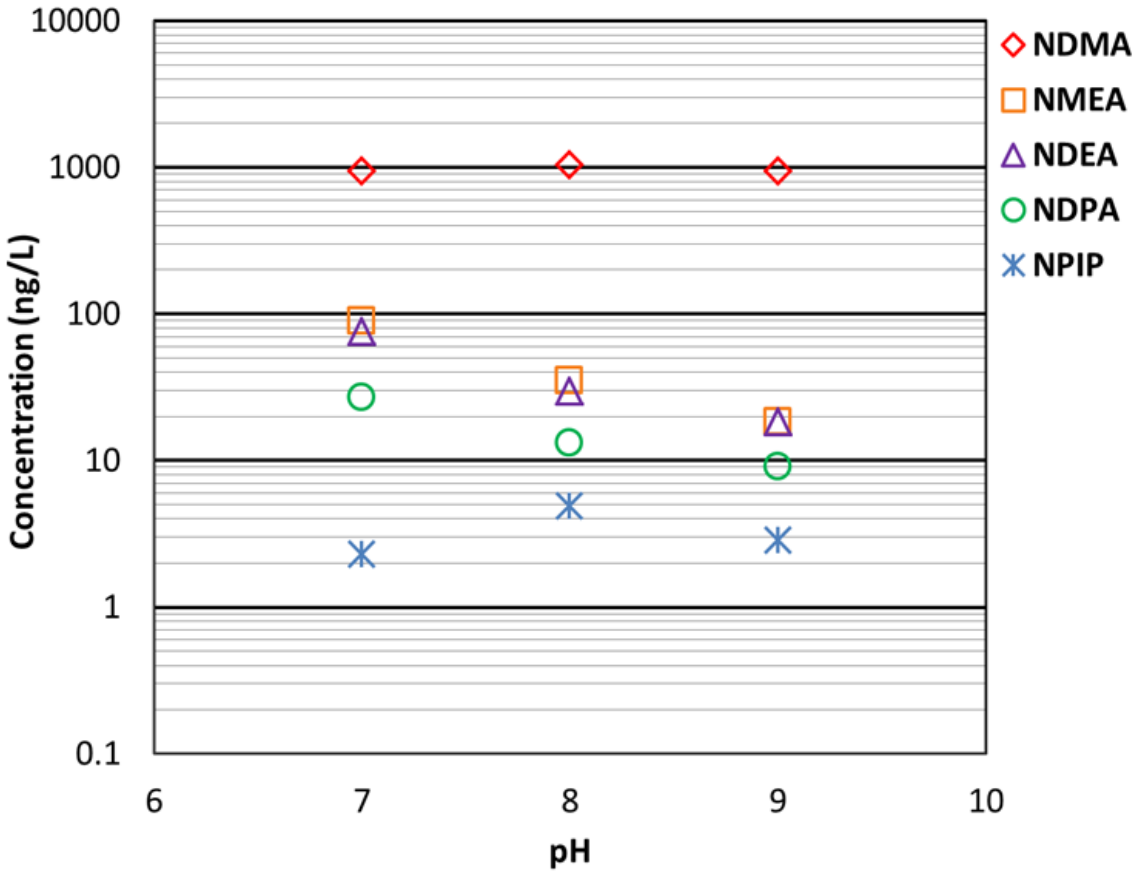

Figure S2. N-nitrosamine formation by MCA disinfection at different pHs when 100 µg/L N-nitrosamine precursors are present in finished water (W3). N-nitrosamines not shown (NPYR, NMOR, NDBA) were below the detection limits.

Table S2. Chloramine (MCA) exposure time dependence: N-nitrosamine precursor concentrations after 4 hrs, 1, 3, and 7 days. Precursors (100 µg/L) were added to ambient finished drinking water (W3) and reacted for the specified exposure time.

Exposure Time (Days)	Disinfectant Residual (mg/L)	Disinfectant Consumed (mg/L)	Remaining Precursor Concentration (%)						
			DMA (ng/L)	EMA (ng/L)	TMA (ng/L)	DEA (ng/L)	DPA (ng/L)	DMAI (ng/L)	DMAP (ng/L)
0.17	2.35	0.06	67.10	71.38	102.32	90.86	96.28	44.18	<MDL
1.00	2.08	0.33	68.43	72.07	107.12	89.44	99.11	<MDL	<MDL
3.00	1.84	0.57	76.34	74.13	102.59	90.20	94.61	<MDL	<MDL
7.00	1.66	0.85	66.59	78.69	83.63	86.58	99.10	<MDL	<MDL

Table S3. Free chlorine (FC) or chloramine (MCA) disinfection: N-nitrosamine precursor concentrations after 7 day exposure time in ultrapure water. Precursors (100 µg/L) were added to ultrapure water and reacted for seven days.

Disinfectant	Disinfectant Residual (mg/L)	Disinfectant Consumed (mg/L)	Remaining Precursor Concentration (%)						
			DMA (ng/L)	EMA (ng/L)	TMA (ng/L)	DEA (ng/L)	DPA (ng/L)	DMAI (ng/L)	DMAP (ng/L)
FC	0.73	1.11	118.20	69.14	<MDL	73.95	64.22	<MDL	<MDL
	1.74	1.12	111.92	67.57	<MDL	68.09	55.86	<MDL	<MDL
MCA	1.64	0.22	89.43	86.19	88.39	93.72	100.21	6.62	37.34
	2.59	0.24	85.42	80.27	89.31	98.26	95.63	4.19	13.68

Table S4. Chloramine (MCA) pH dependence: N-nitrosamine precursor concentrations after seven days. Precursors (100 µg/L) were added to finished drinking water (W3) at pH 7, 8, and 9 and reacted for seven days.

pH	MCA Residual	Disinfectant Consumed	Remaining Precursor Concentration (%)						
			DMA	EMA	TMA	DEA	DPA	DMAI	DMAP
	(mg/L)		(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
7	1.66	0.85	74.13	79.52	94.72	89.02	101.80	<MDL	<MDL
8	0.95	1.42	66.84	78.99	83.95	86.91	99.48	<MDL	<MDL
9	1.72	0.66	66.59	78.69	83.63	86.58	99.10	<MDL	<MDL

Table S5. Peracetic acid (PAA), free chlorine (FC) and chloramines (MCA) disinfection: N-nitrosamine precursor concentrations after seven day exposure time. Precursors (100 µg/L) were added to ambient filtered water (W2) and reacted for seven days.

Disinfectant	Disinfectant Residual	Disinfectant Consumed	Remaining Precursor Concentration (%)						
			DMA	EMA	TMA	DEA	DPA	DMAI	DMAP
	(mg/L)		(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)	(ng/L)
PAA	5.35	4.37	73.50	67.05	10.90	60.08	67.14	<MDL	<MDL
	9.10	5.88	71.08	64.67	7.39	56.96	66.56	<MDL	<MDL
FC	0.14	0.85	101.78	82.12	<MDL	78.39	78.11	<MDL	3.00
	0.62	1.20	98.46	81.06	<MDL	77.94	76.93	<MDL	<MDL
	1.98	1.12	87.43	48.45	<MDL	53.42	45.74	<MDL	<MDL
MCA	1.13	0.38	71.29	84.88	105.53	78.43	86.31	<MDL	<MDL
	2.58	0.34	68.35	81.29	107.87	79.98	85.48	<MDL	<MDL

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VITA

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