# Modifying the initial rates of disinfection by-product formation potentials

Angela B. Rodriguez<sup>a</sup>, Steven J. Duranceau<sup>b,\*</sup>

*a Hazen and Sawyer, 1000 N. Ashley Dr., Suite 1000, Tampa, Florida 33602, USA, Tel. +1 (813) 549-2122; email: arodriguez@hazenandsawyer.com* 

*b Civil, Environmental and Construction Engineering Department, University of Central Florida; 12800 Pegasus Drive, Eng. Bldg. 2, Suite 211, Orlando, Florida 32816, USA, Tel. +1 (407) 823-1440; email: steven.duranceau@ucf.edu*

Received 30 March 2021; Accepted 28 June 2021

## **abstract**

A novel disinfection by-product (DBP) control process focused on modifying the initial formation rate of these compounds to reduce 7-day formation concentrations when chlorine is used as a disinfectant has been developed and evaluated. The novel treatment process utilizes sulfate, ultraviolet irradiation, pH, and aeration to enhance the initial formation and subsequent removal of total trihalomethane (TTHM), while also suppressing the initial formation of haloacetic acids (HAAs). The novel treatment process was evaluated for four different surface waters that ranged between 9.8 and 135 mg/L calcium (as  $CaCO<sub>3</sub>$ ), 7.0 and 36 mg/L bicarbonate alkalinity (as  $CaCO<sub>3</sub>$ ), and 1.9 and 2.9 mg/L dissolved organic carbon representative of specific ultraviolet absorbance values between 1.7 and 3.3. It was determined that 7-day TTHM and HAA formation potential reductions ranged from 36% to 57% and 20% to 47%, respectively, for the four waters studied. The primary factor governing DBP control was found to be the initial contact time at an elevated pH. A linear relationship between compressing the TTHM and HAA formation time and each DBP's corresponding decrease in 7-day TTHM ultimate formation concentration was identified. The research reported in this study describes a novel approach to DBP control which could be evaluated by water purveyors to provide treatment for organic-laden surface water supplies through the incorporation of pH adjustment chemicals and a recirculating spray aeration system.

*Keywords:* Disinfection by-products; Formation rate; Surface water; Sulfate; Specific ultraviolet absorbance

## **1. Introduction**

Total trihalomethanes (TTHM) and haloacetic acids (HAA) are disinfection by-products (DBPs) regulated per the U.S. Environmental Protection Agency's Stage 2 disinfectants and disinfection by-products (D/DBP) Rule component of the Safe Drinking Water Act [1]. TTHM and HAAs are two groups of regulated DBPs produced as a result of chemical reactions that occur when a water source containing dissolved natural organic matter (NOM) is disinfected for potable water use. The type of disinfectant and NOM in water determines the type of DBP formed and parameters such as contact time, temperature, pH

and bromide content influence the rate and quantity of by-products formed in water systems [2–4].

The control of DBP formation in potable water systems can be categorized into three distinct strategies: change the disinfectant type; pre-formation control; or post-formation control. The research described herein presents a novel pre- and post-formation control approach based on the use of chlorine as the primary and secondary disinfectant type. Hence, details regarding changing disinfectants to control DBP formation are not discussed. For further information regarding changing disinfectant type, the reader is referred to others [5–8].

<sup>\*</sup> Corresponding author.

<sup>1944-3994/1944-3986 © 2021</sup> Desalination Publications. All rights reserved.

## *1.1. Pre-formation control*

Many unit process operations that target the removal or transformation of NOM to control DBP formation have been widely reported and utilized by water purveyors [2,9,10]. These approaches include precursor removal by coagulation, granular activated carbon, anion exchange, biofiltration, membrane filtration, and advanced oxidation processes [9–16].

Although research evaluating the enhancement or suppression of TTHM and HAA formation is less prevalent, several investigations have been performed over the years. For example, Liang and Singer [17] found that HAA formation was favored in low pH conditions while TTHM formation was favored in high pH conditions. In addition, the study found that coagulation can preferentially remove HAA precursors over THM precursors for the conditions studied and that HAA precursors are more aromatic in nature. Additionally, Obolensky and Singer [18] documented that temperature was the most significant variable in chloroform formation, and that pH had a strong positive influence on chloroform formation but an opposite influence on the formation of trichloroacetic acid. While the removal of TTHM by aeration and HAA through biological filtration has been shown to be viable treatment methods, current chlorinated by-product post-formation control technologies are limited by the DBP re-formation rate within the distribution system due to contact time. Another study showed that the formation of trihalomethanes (THMs) and haloacetic acids (HAAs) in chlorinated water distribution systems were positively correlated with residence time, chlorine dosage, water temperature, and bromide concentration during chlorine disinfection processes; additionally, the research confirmed the findings of others that elevated pH promoted THM formation while inhibiting HAA production [19]. Lemus-Pérez et al. [20] studied the effect of operating conditions such as biofilm age, water velocity, chlorine and pipeline length on biofilm-disinfectant interactions and showed that exopolymeric substances could contribute to DBP formation.

Ultraviolet (UV) irradiation is a technology that itself does not affect DBP formation potential directly but is often integrated into advanced oxidation processes to be effective [21]. Although UV irradiation does not affect DBP formation directly, it was reported however that UV can affect NOM characteristics, and thus indirectly affect DBP formation potential [22]. Also, it was found that typical disinfection doses of UV irradiation (40–186 mJ/cm2 ) did not influence DBP formation potential, although higher UV doses (1,000 mJ/cm2 ) increased TTHM formation potential by 30%–40% [23]. Other researchers have noted that UV irradiation can decrease protein/tryptophan-like and humic-like fluorescence in waters which are n-Nitrosodimethylamine and TTHM precursors, respectively [22,24]. A more recent study found that TTHM formation potential increased during UV irradiation followed by chlorine disinfection; as the UV irradiation dose increased, the DBP formation potential increased, and TTHM concentrations decreased with increasing pH [25].

Additionally, the effect of metal ions on TTHM and HAA formation has also been researched. In the presence of copper, magnesium, or calcium ions, TTHM formation potentials are increased with copper having the largest impact followed by magnesium and then calcium [26,27]. Zhang and Andrews [28] found that exposure to solid corrosion products can also increase disinfectant decay and HAA formation potential. A more recent study found that iron corrosion products, such as goethite, could interact with NOM to suppress the initial rate of formation for HAA and prolong the reaction times required for HAA formation [29]. This same study suggested that metal oxides could catalyze the reactions responsible for brominated DBPs. While this study also found that metal ions can increase DBP formation potential rates in synthetic waters, the phenomenon was not seen in experiments with natural waters [29]. Zhao et al. [30] had previously noted an increase in TTHM and a decrease in HAAs due to the catalytic effect of cupric ions in natural and synthetic waters; however, the effects of calcium, ferrous and ferric ions on DBP formation for natural water yielded no relationship.

Sulfate radical-based advanced oxidation processes represent a relatively new concept for refractory organics control [31,32]. As in the case of hydroxyl radical, the inorganic constituents of waters are believed to be competing scavengers of sulfate radicals [32]. A review of sulfate radical-based oxidation processes and their impacts on bromate formation can be found elsewhere [33,34]. Others suggested that that DBP alteration in a UV-persulfate process depended on the reactivity between the sulfate radical and organic nitrogen precursors [35]. Additionally, a method that is based on the UV-persulfate process was shown to be an effective method for degrading isopropyl alcohol in an aqueous solution [36]. Although the effectiveness as an advanced oxidation process for TTHM and HAA control through NOM transformation remains unclear, a sulfate-radical-based oxidation process concept does show promise for precursor control [37].

## *1.2. Post-formation control*

Post-formation control strategies target DBP physicochemical properties such as biodegradability (HAA) and volatilization (TTHM). For example, GAC can be used to remove TTHM directly from chlorinated water [38,39]. On the other hand, the control of TTHM concentrations in distribution systems through aeration has proven to be a popular strategy in the industry that is based on the semi-volatility of chloroform, bromoform, dichlorobromomethane and dibromochloromethane. Work completed by Cecchetti et al. [40] found that the efficiency of spray aeration systems for removing TTHM was primarily influenced by spray configuration (droplet size, travel distance, spray pattern) and magnitude (percent recycle) as opposed to temperature, spray angle, and TTHM species. The study also showed that spray aeration can remove brominated TTHM species, even though they have lower Henry's Law constants [40]. Smith and Duranceau [41] found that one pass aeration systems could control TTHM formation potentials in bromide-free waters and that nozzle type affected the efficiency of the system. Yoakum and Duranceau [42] expanded on those findings by showing that multiple-pass spray

and tray aeration could compress TTHM formation potential as well as remove bromide from water by volatilizing bromoform.

## *1.3. Identified knowledge gap – DBP formation control*

Previous research has shown that there are multiple ways to suppress DBP formation either through change of disinfectant, post-formation constituent removal (aeration for TTHM), water quality changes (pH), or NOM transformations (UV irradiation and sulfate radical oxidation). Yet previous research has either utilized synthetic waters to elucidate the effects of these techniques on DBP formation or investigated these techniques as standalone systems. The examination of the impact of incorporating sulfate, UV irradiation, pH, and aeration on DBP formation in surface waters has not been fully explored. The research reported in this paper examined the effect of each component utilizing a stepwise-cumulative experimental structure to study the incorporation of UV, pH adjustment and aeration for TTHM formation and HAA suppression in four surface water supplies.

## **2. Materials and methods**

## *2.1. Experimental set-up: DBP formation potential*

A bench-scale post-treatment process was designed and constructed for use in conducting the experiments and a picture of the set-up can be found in Fig. 1. The set-up consists of a 5-gallon Nalgene tank with a magnetic stir bar on top of a stir plate. The water (2-gallons) was recirculated at 1 gpm through the system utilizing a magnetic drive pump and flowmeter. Water re-entered the Nalgene tank either after passing through a spray nozzle or by flowing through a tube with the outlet beneath the water level inside the tank. A chemical addition port and pH meter port were drilled into the lid of the tank. A UV irradiation system (Vitapur VUV-S645B) was also incorporated into the unit, with the system operated in either on or off mode depending on treatment scheme.

Table 1 summarizes the post-treatment scenarios investigated using the bench-scale unit. The varying pH scheme investigated the effect of no pH adjustment, pH adjustment to 8.8, and pH adjustment to 10 during the first 3 h of contact time with chlorine along with 2 h of aeration on DBP formation potentials. The varying  $SO<sub>4</sub>$  scheme investigated the addition of 16.5, 50, 100 and 200 mg/L of sulfate on DBP formation potentials while using the previously established optimum pH for DBP control as identified in the varying pH experiments. The UV irradiation experiments investigated the effect of using UV before chlorine dosing or after chlorine dosing on DBP formation potentials while using the optimum initial incubation pH and sulfate concentration identified in previous experiments. The final process incorporated the addition of 50 mg/L of sulfate, 1-h of UV treatment pre-chlorine addition, 3-h incubation at pH 10 post-chlorine addition, and a 2-h post-incubation aeration step. This treatment process, referred to as the novel treatment process in this manuscript, was utilized on the four water sources investigated in this study to determine its applicability to surface waters of various starting qualities.

Two Hawaii and two Florida surface waters were utilized for this study. Table 2 presents basic water quality parameters for the four waters relied on for this evaluation that includes basic inorganic content (calcium and alkalinity) and organic content such as dissolved organic carbon (DOC), ultraviolet absorbance at 254 nm ( $UV_{254}$ ) and specific ultraviolet absorbance (SUVA). Since aromatic organics have a greater tendency to react with chlorine to create DBPs, a higher SUVA indicates there is a greater potential for the formation of by-products than a lower value.

While the Hawaii surface waters received the sulfate boost, the Florida surface waters did not as they already contained at least 50 mg/L of sulfate. The chlorine dose and



Fig. 1. Bench-scale DBP control process set-up.



Sequence or step	Baseline	Varying pH	Varying SO <sub>4</sub>	Pre-UV	Post-UV	Novel process
1.	Dose Cl <sub>2</sub>	pH Adj.	$SO4$ addition	$SOa$ addition	$SOa$ addition	50 mg/L $SO4$ addition
2.	pH Adj.	Dose Cl <sub>2</sub>	pH Adj.	UV irradiation 1 h	pH Adj.	UV irradiation 1 h
3.	Bottle & incubate	Incubate 3 h	Dose Cl <sub>2</sub>	pH Adj.	Dose Cl <sub>2</sub>	pH Adj. 10
4.		Aerate 2 h	Incubate 3 h	Dose Cl <sub>2</sub>	Incubate 3 h	Dose Cl <sub>2</sub>
5.		pH Adj.	Aerate 2 h	Incubate 3 h	UV irradiation 1 h	Incubate 3 h
6.		Bottle & incubate	pH Adj.	Aerate 2 h	pH Adj.	Aerate 2 h
7.			Bottle & incu- bate	pH Adj.	Dose Cl <sub>2</sub>	pH Adj.
8.				Bottle & incubate	Aerate 2 h	Bottle & incubate
9.					pH Adj.	
10.					Bottle & incubate	

Table 2 Water quality comparison for surface water supplies evaluated



post-aeration pH adjustment target were specific for each water and reflected typical full-scale conditions.

HAA samples were taken for each run, with duplicate runs conducted for each water.

#### *2.2. Equipment, reagents, and sample preparation*

Bulk water for the experiments for each of the four surface water supplies was collected at available treatment process sample taps prior to disinfection in 15-gallon blue Nalgene drums and stored at 4°C until use. The bench-top disinfection and pH adjustment processes were carried out using a sodium hypochlorite solution and a lime solution. Throughout the treatment and formation potential experiments, additional water quality parameters such as pH, temperature, conductivity, turbidity, and  $UV_{254}$  were monitored. Water quality analyses were conducted in accordance with sample preparation and methods outlined in Standard Methods for the Examination of Water and Wastewater [43]. The TTHM and HAA formation potentials were developed using 60, 125, and 250 mL amber glass bottles that were incubated at room temperature (approximately 25°C). Free chlorine residuals were monitored throughout the 7-day DBP formation potential test for each experiment. TTHM measurements during the treatment process (final process) were taken after 1 h of UV irradiation, 3 h of pH 10 incubation, and 2 h of aeration, and the following bottle incubation times  $-10$ , 24, 72, and 168 h. HAA measurements during the treatment process (final process) were taken after 1 h of UV irradiation, and the following bottle incubation times – 10, 24, 48, 96, and 168 h. Duplicate 7-day TTHM and

#### *2.3. Data analysis*

The DBP experimental data was analyzed using Microsoft® Excel to build formation potential models using logarithmic trendlines fitted to the collected water quality information. Statistical parameters used for analysis included average and relative percent difference for each water source investigated. Formation potential models were used to compare the calculated rates to each of the treatment scenario with each other and the baseline. The logarithmic trendlines were used to develop relationships that related the reductions in the 7-day DBP formation potentials to the changes in initial DBP formation rates. The 7-day DBP data was further analyzed to determine the effectiveness of the novel process at controlling DBP formation for the different surface waters investigated.

#### **3. Results and discussion**

The purpose of this study was to develop and assess a novel post-treatment DBP control process that would enhance stripping of formed TTHM while suppressing concomitant HAA formation. The method was established by analyzing the initial formation rate, aeration efficiency, post-treatment formation rate, and 7-day concentration for TTHM as well as the initial formation rate and 7-day concentration for HAA. The TTHM and HAA initial formation rates were associated with the first 3 h of contact time with chlorine. An "optimum" option for each treatment scheme was selected and incorporated into the subsequent treatment scenarios investigated. The novel post-treatment DBP control process was first developed using one of the Hawaii surface waters (Hawaii-A). Once the treatment process was confirmed, the experiments were repeated on an alternative Hawaiian water supply (Hawaii-B) and two additional Florida surface water supplies (Florida-A and Florida-B) of varying qualities. The goal was to evaluate the effectiveness of the developed treatment process on different surface waters to determine whether the process was a site-specific solution or a viable treatment alternative for surface waters in general.

## *3.1. Novel post-treatment DBP control process development*

Results for each process treatment scheme evaluated that was first developed using the Hawaiian-A water is summarized in Table 3. Under baseline conditions, the first Hawaiian surface water yielded TTHM and HAA formation potentials of 206 and 191 ppb, respectively. Subsequent treatment scenarios achieved a reduction in HAA 7-day

Table 3

			Hawaii-A formation results for each optimal treatment scenario
--	--	--	--

concentrations, with the most significant reduction occurring by elevating the pH to 10 during the first 3 h of contact time with chlorine. Although sulfate addition and UV irradiation did not significantly affect the 7-day formation concentration for TTHM, changes with the initial formation rate and aeration efficiency were noted. The most significant reduction in 7-day TTHM content was a result of elevating the pH to 10 for the first 3 h of chlorine contact. Treatment with the novel process increased 7-day chlorine consumption by 1.0 mg/L, most likely a result of an increase carbon demand due to more favorable reaction conditions, as has been described previously by [9]. The developed novel treatment process achieved a 7-day formation concentration reduction of 36% for TTHM and 39% for HAA (Fig. 2).

## *3.2. Novel post-treatment DBP control process assessment*

The developed novel treatment process was further assessed for its applicability as a general DBP control method for surface waters using three additional surface waters. The results of the experiments with the Hawaii-B water are summarized in Table 4. The treatment enhanced the initial TTHM formation by a factor of approximately 1.6 and suppressed initial HAA formation by a factor



N/A – Not applicable



**□Baseline ■Treatment** 

Fig. 2. Hawaii-A 7-day DBP formation potential results.

250

of about 2.0. The treatment successfully reduced TTHM concentrations via aeration to approximately 10 ppb and reduced the post-aeration formation potential rate. Treatment with the novel process, however, did not affect the 7-day chlorine consumption for this specific water that contained a greater amount of alkalinity and calcium than Hawaii-A. The developed novel post-treatment DBP control process achieved a 7-day concentration reduction of 40% for TTHM and 25% for HAA (Fig. 3).

A significant background concentration of HAA (~50 ppb) was identified to be present in the Florida-A water, theorized to be due to the pre-chlorination practice for plant algal growth control. To better assess the treatment process's impact on DBP formation control, the background HAA level was removed prior to data analysis by treating the baseline value as a new "0" datum. The experimental results for the Florida-A water have been summarized in Table 5. The treatment enhanced initial TTHM formation by a factor of approximately 1.8 and suppressed initial HAA formation by a factor of about 1.6. The treatment successfully reduced TTHM concentrations via aeration to approximately 10 ppb and reduced the post-aeration

Table 4





N/A – Not applicable



Baseline Treatment

Fig. 3. Hawaii-B 7-day DBP formation potential results.

# Table 5

Florida-A formation results for the novel treatment scenario



N/A – Not applicable

formation potential rate. Treatment with the novel process increased 7-day chlorine consumption by 1.0 mg/L. The developed novel treatment process achieved a 7-day formation concentration reduction of 57% for TTHM and 47% for HAA (Fig. 4).

Although the Florida-B water also employs pre-chlorination for algal growth control, no significant background level of HAA was found. The experimental results for the Florida-B water have been summarized in Table 6. The treatment enhanced initial TTHM formation by a factor of approximately 2.2 and suppressed initial HAA formation by a factor of about 1.5. The treatment successfully reduced TTHM concentrations via aeration to approximately 10 ppb and reduced the post-aeration formation potential rate. Treatment with the novel process decreased 7-day chlorine consumption by 1.0 mg/L, unlike what was found for the low alkalinity, low-hardness Hawaii-A water. The developed novel post-treatment DBP control process achieved a 7-day formation concentration reduction of 41% for TTHM and 20% for HAA (Fig. 5).

#### *3.3. Initial formation rate analysis*

The novel treatment process was found to reduce both 7-day TTHM and HAA formation concentrations by at least 20% for the four surface waters evaluated. Formation potential data for each surface water was analyzed to determine the percentage of DBP formed within the first 24 h and the subsequent 144 h of the 7-day incubation period for baseline and treatment conditions. Regardless of water type, 65%–75% of TTHM formation and 58%–77% of HAA formation occurred within the first 24 h of incubation for the baseline scenario. This non-linear formation would be expected; however, the shift in rate was revealed to change to some degree, depending on the water tested. Treatment with the new process shifted the formation of TTHM and HAA within the first 24 h to 43%–49% and 77%–98%, respectively. The shift in TTHM indicated that the treatment was able to reduce the fraction of rapidly reacting organics through the enhanced formation and subsequent TTHM stripping, leaving what is believed to be more recalcitrant organics remaining which would be expected to slow down overall formation rates, as has been suggested by [9]. The shift in HAA formation demonstrated that if adequate control and levels are achieved within the first 24 h, then compliance could be possible in a distribution system that has less than a 7-day water age. Additional study would have to be performed for any specific water supply to determine if the novel process would provide an alternative treatment opportunity considering site-specific regulatory needs.



Fig. 4. Florida-A 7-day DBP formation potential results.

# Table 6





N/A – Not applicable



**Baseline Treatment** 

Fig. 5. Florida-B 7-day DBP formation potential results.



Fig. 6. TTHM formation compression relationship.

Fig. 6 presents an observed and apparent overall linear relationship between TTHM formation time compression and decrease in 7-day TTHM concentration with 89% certainty's. TTHM formation time compression refers to the enhancement of the initial TTHM formation rate by the novel treatment process. TTHM formation time compression was calculated by measuring the peak pre-aeration novel treatment process TTHM concentration (in this case *t* = 3 h), determining the time required for the baseline process to achieve the same TTHM concentration (e.g., *t* = 8 h), and calculating the difference in the times (how much faster the TTHM concentration was achieved due to treatment). Additional studies varying formation time compression could help identify an optimum formation compression time for adequate TTHM control.

Fig. 7 presents an observed overall linear relationship between initial HAA formation rate reduction and decrease in 7-day HAA concentration. Initial HAA formation rate reduction refers to the suppression of the HAA formation rate by the novel treatment process within the first 3 h of elevated pH chlorine contact time. The initial HAA formation rate reduction value was calculated by subtracting the HAA formation rate during the first 3 h of contact time of the baseline (e.g.,  $r = 20.0$  ppb/h) from the novel treatment process (e.g., *r* = 15.0 ppb/h). Additional studies varying the duration of the elevated pH chlorine contact time could help identify an ideal suppression duration for adequate HAA control.

#### **4. Conclusions**

TTHM and HAA are two types of regulated DBPs that are commonly associated with chlorine disinfection. Traditional methods for controlling the formation of these compounds may include the removal of organic matter through GAC or membranes, removal of TTHM via aeration, and removal of HAA via biodegradation. This study focused on developing and evaluating a novel treatment



Fig. 7. HAA formation rate suppression relationship.

process which utilized sulfate, UV irradiation, pH, and aeration to suppress HAA formation while enhancing TTHM formation and subsequent stripping of TTHM to compress 7-day DBP formation potentials for four differing quality surface waters. The process utilized 50 mg/L of sulfate addition, 1 h of UV irradiation, 3 h of pH 10 incubation and 2 h of air stripping followed by room temperature incubation to assess the process's effect on 7-day TTHM and HAA formation potentials. For the Hawaii-A water, the process was able to reduce TTHM by 36% and HAA by 39%. For the Hawaii-B water, the process was able to reduce TTHM by 40% and HAA by 25%. For the Florida-A water, the process was able to reduce TTHM by 57% and HAA by 47%. Finally, for the Florida-B water the process was able to reduce TTHM by 41% and HAA by 20%.

Findings suggest that the two most significant steps in the process in terms of DBP control were the 3 h of pH 10 incubation and 2 h of aeration. Analysis of the formation curve data indicate that if DBP control could be achieved within the first 24 h, continued control should also be possible over a 7-day water age. The process could be modified to include increased aeration time, or additional aeration cycles to reduce 7-day TTHM formation concentrations. Additional technologies that focus on organic removal, longer elevated pH incubation time, or a combination of both may be considered to further reduce 7-day HAA concentrations. Nevertheless, implementation of the pH and aeration process could provide an optional treatment regime with ng minimal infrastructure modifications within an existing WTP process (chemical addition location(s) and aeration system) as compared to incorporation of technologies such as GAC or membranes.

## **Acknowledgments**

This research would have not been possible without the support and commitment of the dedicated individuals and organizations involved. We would like to express our sincere gratitude to the County of Maui Department of Water Supply (DWS) for funding this work (Project No. 16208098). We would also like to gratefully acknowledge the

assistance and efforts of the Lake Manatee water treatment plant staff, Dyal water treatment plant staff, and the UCF Drinking Water Research Group. Specifically, we would like to thank James Landgraf, Carlyn Higgins, Daniel Whalen, and Daniel Cardona for their assistance with bulk water sampling and data collection. This research is also based upon work supported by the National Science Foundation Graduate Research Fellowship under Grant No. 1144246. Any opinion, findings, and conclusions or recommendations expressed in this material are those of the authors(s) and do not necessarily reflect the views of the National Science Foundation, the state of Florida's Board of Governors, nor of the funding agency supporting this work.

## **References**

- [1] Federal Register, Part II Environmental Protection Agency 40 CFR Parts 9, 141, and 142 National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection By-products Rule, Final Rule (Vol. 7, No. 2), Wednesday, January 4, 2006, Washington, D.C., 2016.
- [2] D.A. Reckhow, P.C. Singer, Chlorination by-products in drinking waters: from formation potentials to finished water concentrations, J. Am. Water Works Assn., 82 (1990) 173–180.
- [3] S.D. Richardson, M.J. Plewa, E.D. Wagner, R. Schoeny, D. Demarini, Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research, Mutat. Res., 636 (2007) 178–242.
- [4] G.H. Hua, D.A. Reckhow, DBP formation during chlorination and chloramination: effect of reaction time, ph, dosage, and temperature, J. Am. Water Works Assn., 100 (2008) 85-95
- [5] S. Batterman, L. Zhang, S.Q. Wang, Quenching of chlorination disinfection by-product formation in drinking water by hydrogen peroxide, Water Res., 34 (2000) 1652–1658.
- [6] S.D. Richardson, C. Postigo, Drinking Water Disinfection By-products, D. Barceló, Ed., Emerging Organic Contaminants and Human Health, The Handbook of Environmental Chemistry, Vol. 20, Springer, Berlin, Heidelberg, 2012, pp. 93–137.
- [7] L. Yang, C. Schmalz, J. Zhou, C. Zwiener, V. Chang, L. Ge, P.W. Wan, An insight of disinfection by-product (DBP) formation by alternative disinfectants for swimming pool disinfection under tropical conditions, Water Res., 101 (2016) 535–546.
- [8] R.A. Li, J.A. McDonald, A. Sathasivan, S.J. Khan, Disinfectant residual stability leading to disinfectant decay and by-product

formation in drinking water distribution systems: a systematic review, Water Res., 153 (2019) 335–348.

- P.C. Singer, Formation and control of disinfection by-products in drinking water, J. Environ. Eng., 120 (1994) 727–744.
- [10] T. Bond, E.H. Goslan, S.A. Parsons, B. Jefferson, Treatment of disinfection by-product precursors, Environ. Technol., 32 (2011) 1–25.
- [11] S.J. Randtke, In: S.J. Singer, Ed., Formation and Control of Disinfection By-Products in Drinking Water, Disinfection Byproduct Precursor Removal by Coagulation and Precipitate Softening, American Water Works Association, Denver, CO, pp. 237–258.
- [12] N. Lee, S. Sinha, G. Amy, M. Bourke, Evaluation of Magnetic Ion Exchange Resin Treatment for Preferential Removal of NOM Fractions, American Water Works Association – Water Quality Technology Conference, Seattle, Washington, November 10–14, 2002.
- [13] T.H. Boyer, P.C. Singer, Bench-scale testing of a magnetic ion exchange resin for removal of disinfection by-product precursors, Water Res., 39 (2005) 1265–1276.
- [14] V. Uyak, K. Ozdemir, I. Toroz, Seasonal variations of disinfection by-product precursors profile and their removal through surface water treatment plants, Sci. Total Environ., 390 (2008) 417–424.
- [15] N. Ates, L. Yilmaz, M. Kitis, Y. Ulka, Removal of disinfection by-product precursors by UF and NF membranes in low-SUVA waters, J. Membr. Sci., 328 (2009) 104–112.
- [16] Y. Sun, B. Angelotti, M. Brooks, B. Dowbiggin, P.J. Evans, B. Devins, Z.W. Wang, A pilot-scale investigation of disinfection by-product precursors and trace organic removal mechanisms in ozone-biologically activated carbon treatment for potable reuse, Chemosphere, 210 (2018) 539–549.
- [17] L. Liang, P.C. Singer, Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water, Environ. Sci. Technol., 37 (2003) 2920–2928.
- [18] A. Obolensky, P.C. Singer, Development and interpretation of disinfection by-product formation models using the information collection rule database, Environ. Sci. Technol., 42 (2008) 5654–5660.
- [19] K.J. Zhang, C.G. Qiu, A.H. Cai, J. Deng, X.Y. Li, Factors affecting the formation of DBPs by chlorine disinfection in water distribution system, Desal. Water Treat., 205 (2020) 91–102.
- [20] M.F. Lemus-Pérez, M. Rodríguez Susa, The effect of operational conditions on the disinfection by-products formation potential of exopolymeric substances from biofilms in drinking water, Sci. Total Environ., 748 (2020) 141148, doi: 10.1016/j. scitotenv.2020.141148.
- [21] D.A. Reckhow, K.G. Linden, J. Kim, H. Shemer, G. Makdissy, Effect of UV treatment on DBP formation, J. Am. Water Works Assn., 102 (2010) 100–105.
- [22] B.A. Lyon, R.M. Cory, H.S. Weinberg, Changes in dissolved organic matter fluorescence and disinfection by-product formation from UV and subsequent chlorination/ chloramination, J. Hazard. Mater., 264 (2014) 411–419.
- [23] B.A. Lyon, A.D. Dotson, K. Linden, H. Weinberg, The effect of inorganic precursors on disinfection by-product formation during UV-chlorine/chloramine drinking water treatment, Water Res., 46 (2012) 4653–4664.
- [24] L. Yang, D. Kim, H. Uzun, T. Karanfil, J. Hur, Assessing trihalomethanes (THMs) and n-Nitrosodimethylamine (NDMA) formation potentials in drinking water treatment plants using fluorescence spectroscopy and parallel factor analysis, Chemosphere, 121 (2015) 84–91.
- [25] Z.-B. Guo, Y.-L. Lin, B. Xu, C.-Y. Hu, H. Huang, T.-Y. Zhang, N.-Y. Gao, Factors affecting THM, HAN and HNM formation during UV-chlor(am)ination of drinking water, Chem. Eng. J., 306 (2016) 1180–1188.
- [26] J. Fu, J. Qu, R. Lie, Z. Qiang, H. Liu, X. Zhao, Cu(II) catalyzed THM formation during water chlorination and monochloramination: a comparison study, J. Hazard. Mater., 170 (2009) 58–65.
- [27] S. Navalon, M. Alvaro, H. Garcia,  $Ca^{2+}$  and  $Mg^{2+}$  present in hard waters enhance trihalomethane formation, J. Hazard. Mater., 169 (2009) 901–906.
- [28] H. Zhang, S.A. Andrews, Catalysis of copper corrosion products on chlorine decay and HAA formation in simulated distribution systems, Water Res., 46 (2012) 2665–2673.
- [29] V.K. Sharma, X. Yang, L. Cizmas, T.J. McDonald, R. Luque, C.M. Sayes, D.D. Dionysiou, Impact of metal ions, metal oxides, and nanoparticles on the formation of disinfection by-products during chlorination, Chem. Eng. J., 317 (2017) 777–792.
- [30] Y. Zhao, H.W. Yang, S.T. Liu, S. Tang, X.M. Wang, Y.F. Xie, Effects of metal ions on disinfection by-product formation during chlorination of natural organic matter and surrogates, Chemosphere, 144 (2016) 1074–1082.
- [31] Y. Deng, C.M. Ezyske, Sulfate radical-advanced oxidation process (SR-AOP) for simultaneous removal of refractory organic contaminants and ammonia in landfill leachate, Water Res., 45 (2011) 6189-6194.
- [32] Y. Guan, J. Ma, X.C. Li, J.Y. Fang, L.W, Chen, Influence of pH on the formation of sulfate and hydroxyl radicals in the UV/ peroxymonosulfate system, Environ. Sci. Technol., 45 (2011) 9308−9314.
- [33] C.T. Guan, J. Jian, S.Y. Pang, Y. Zhou, Y. Gao, J. Li, Z. Wang, Formation and control of bromate in sulfate radical-based oxidation processes for the treatment of waters containing bromide: a critical review, Water Res., 176 (2020) 115725, doi: 10.1016/j.watres.2020.115725.
- [34] Z. Wang, N. An, Y. Shao, N. Gao, E. Du, B. Xu, Experimental and simulation investigations of UV/persulfate treatment in presence of bromide: effects on degradation kinetics, formation of brominated disinfection by-products and bromate, Sep. Purif. Technol., 242 (2020) 116767, doi: 10.1016/j.seppur.2020.116767.
- [35] Z. Hua, X. Kong, S. Hou, S. Zou, X. Xu, H. Huang, J. Fang, DBP alteration from NOM and model compounds after UV/ persulfate treatment with post chlorination, Water Res., 158 (2019) 237–245.
- [36] C.C. Lin, C.Q. Tsai, Degradation of isopropyl alcohol using UV and persulfate in a large reactor, Sep. Purif. Technol., 209 (2019) 88–93.
- [37] W.-D. Oh, Z. Dong, T.-T. Lim, Generation of sulfate radical through heterogeneous catalysis for organic contaminants removal: current development, challenges and prospects, Appl. Catal., 194 (2016) 169-201.
- [38] M. Uchida, T. Nakamura, N. Kawasaki, S. Kitayama, S. Tanada, Adsorption removal of chloroform and bromoform by activated carbon fiber, Toxicol. Environ. Chem., 63 (2008) 227–231.
- [39] T. Nakamura, N. Kawasaaki, S. Tanada, K. Kawabata, M. Imaki, Chloroform adsorption by activated carbon, Toxicol. Environ. Chem., 57 (1996) 187–192.
- [40] A.R. Cecchetti, H. Roakes, M.R. Collins, Influence of selected variables on trihalomethane removals by spray aeration, J. Am. Water Works Assn., 106 (2014) E242–E252.
- [41] C.T. Smith, S.J. Duranceau, Trihalomethane formation downstream of spray aerators treating disinfected groundwater, J. Am. Water Works Assn., 108 (2016) E99–E108.
- [42] B.A. Yoakum, S.J. Duranceau, Using existing cascade tray aeration infrastructure to strip total trihalomethanes, J. Am. Water Works Assn., 10 (2018) E2–E12.
- [43] R.B. Baird, A.D. Eaton, E.W. Rice, Standard Methods for the Examination of Water and Wastewater, 23rd ed., American Public Health Association, American Water Works Association, and Water Environment Federation, Denver, CO, 2017.