



Short Communication

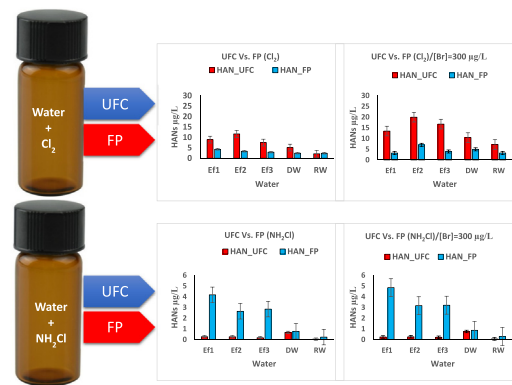
Estimation of haloacetonitriles formation in water: Uniform formation conditions versus formation potential tests

Amer Kanan^a, Tanju Karanfil^{b,*}^a Department of Environment and Earth Sciences, Faculty of Science and Technology, Al-Quds University, Palestine^b Department of Environmental Engineering and Earth Science, Clemson University, SC, USA

HIGHLIGHTS

- HANs formation from five different chlorinated water sources were higher under UFC than FP tests.
- Chlorination FP tests do not provide meaningful information for HAN precursors in water samples.
- UFC (or SDS) chlorination test should be used for a better estimation of HAN precursors in water.
- Higher HANs formed under FP test compared to UFC test during chloramination.
- Chloramination FP tests may be used for determining HAN precursors in water reactive to chloramine.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 17 May 2020

Received in revised form 12 July 2020

Accepted 13 July 2020

Available online xxx

Editor: Damia Barcelo

Keywords:

Disinfection by-products

Haloacetonitriles

Formation potential test

Uniform formation conditions test

Chlorination

Chloramination

ABSTRACT

To date, several studies have used formation potential (FP) tests to examine the presence of HAN precursors in water and wastewater. However, given the decomposition of HANs with time at elevated free chlorine levels, FP test results do not provide meaningful results. We conducted side-by-side FP and uniform formation condition (UFC) experiments to demonstrate that, in order to obtain practical, meaningful, and representative information about HANs formation and their precursors during chlorination, it is important to conduct experiments and report results under UFC [or simulated distribution system (SDS)] conditions.

The results confirmed higher HAN formation under UFC than FP tests during chlorination of the tested two surface water and three wastewater effluent samples, indicating HAN decomposition at high chlorine conditions of FP tests. In addition, the well reported ratio (~10%) of HAN/THM from previous studies was more consistent with the UFC results but was lower than 10% in the FP results. On the other hand, HAN formation during chloramination of the same samples were lower under the UFC than FP conditions. Furthermore, FP tests under both chlorination and chloramination resulted in lower bromine substitution factor.

We concluded that reporting results of HANs FP tests are not representative, and future studies should focus on UFC or distribution system specific (SDS) experiments for chlorination. However, chloramination FP tests may still provide some information about the HAN precursors in waters.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

Disinfection is ubiquitous in water and wastewater treatment for preventing waterborne diseases, while disinfectants tend to react with

* Corresponding author.

E-mail address: tkaranf@clemson.edu (T. Karanfil).

organic and inorganic precursors present in the water matrix forming unintended but potentially harmful by-products known as disinfection by-products (DBPs) (Karanfil et al., 2008; Richardson et al., 2007). Since their discovery in the 1970s (Bellar et al., 2015; Rook, 1974), selected DBPs in drinking water have been regulated around the world (Karanfil et al., 2008; U. S. EPA, 1998, 1979, 2010), and they have been intensively studied for all aspects and conditions of their formation, precursors, treatment, toxicity, and other health effects.

Two types of laboratory tests are commonly considered to evaluate the DBP formation in water samples (APHA et al., 2017; Summers et al., 1996). First, the formation potential test (FP) in which the disinfectant is added to water in excess amount for a prolonged (e.g., 7-day) contact time at pH 7.0 ± 0.2 in the presence of a buffer at 25 ± 2 °C (APHA et al., 2017). The FP test is conducted to determine indirectly the amount of DBP precursors in a sample (Stevens and Symons, 1977; Stuart et al., 2001). Due to high disinfectant dose and long contact time, FP tests result in significantly higher DBPs concentration as compared to their occurrence under practical water treatment and distribution conditions. The second test is the simulated distribution system (SDS) test in which water samples are disinfected to simulate specific operations of time, temperature, pH, and disinfectant dose similar to those in a specific distribution system (Koch et al., 1991; Summers et al., 1996). The SDS test has limitations making comparisons difficult between different systems with different disinfection conditions (e.g., residence time, pH) and seasonal variations (e.g., temperature) (Summers et al., 1996). To represent typical distribution systems conditions in the US, Summers et al. (1996) developed the uniform formation conditions (UFC) test, in which the free chlorine residual after the 24 h incubation is maintained 1.0 ± 0.4 mg/L at 20.0 ± 1.0 °C and pH 8.0 ± 0.2 (Summers et al., 1996). This test allows the comparison of different waters side by side under the same formation conditions.

Although numerous DBPs have been identified in drinking waters, only 11 (four trihalomethanes, THM4, five haloacetic acids, HAA5, chlorite and bromate) are currently regulated by the US Environmental Protection Agency (EPA). Haloacetonitriles (HANs), which were reported in drinking water for the first time in 1975 (McKinney et al., 1976), are formed during chlorination/chloramination of natural organic matter (NOM) containing nitrogenous functional groups, such as amines, amino acids derived from proteins, and/or anthropogenic compounds (Yang et al., 2012). In addition, chloramination of NOM, which does not contain nitrogen, can also form HANs, where chloramine serves as the source of nitrogen (Chuang and Tung, 2015; Krasner et al., 2006; Ye et al., 2018; Yu and Reckhow, 2015). Although HANs typically occur at about $\sim 1/10$ of the level of the regulated THM4 (Krasner et al., 2006; Oliver, 1983), they are orders of magnitude more toxic than the regulated DBPs (Liu et al., 2018; Liviach et al., 2010; Muellner et al., 2007; Plewa et al., 2017). Studies have reported HANs driving the toxicity in water samples despite their orders of magnitude lower concentrations compared to regulated organic DBPs. As a DBP class, the HANs are more toxic than regulated carbon-based DBPs. Using CHO cell assays of chronic cytotoxicity and acute genotoxicity (DNA damaging and DNA strand breaks) of HANs showed that cytotoxic potency of dibromoacetonitrile (DBAN) and trichloroacetonitrile (TCAN) were 2.8 mM to 0.16 mM, respectively. Moreover, HANs induced acute genomic damage. Indeed, brominated haloacetonitriles are reported to exhibit more cytotoxic and genotoxic than their chlorinated analogs (Krasner et al., 2016; Muellner et al., 2007; Plewa et al., 2017). Therefore, understanding and investigation of HAN formation in water and wastewater effluents have received increase attention in recent years.

Several studies have shown that HANs can hydrolyze at an accelerating rate in a system of an alkaline pH combined with high free chlorine residual for prolonged contact time (Chen et al., 2017; Glezer et al., 1999; Huang et al., 2016; Peters et al., 1990; Reckhow et al., 2001; Yu and Reckhow, 2015). Furthermore, the high chlorine dose during the FP test outcompetes the bromine and results in an underestimation of

the bromine incorporation to brominated HANs (Symons et al., 1993) which are known to have higher toxicity (Liviach et al., 2010; Muellner et al., 2007; Plewa et al., 2017). On the other hand, there was no significant difference in HAN stability with or without the presence of chloramines at doses up to 4 mg/L (as Cl_2), indicating that chloramine does not react with HANs (Yu and Reckhow, 2015). Furthermore, the formation of dichloroacetonitrile (DCAN) showed a linear increase in concentration as the monochloramine dose increased from 2 to 20 mg/L as Cl_2 after 3 days of chloramination of NOM solutions (Yang et al., 2007). Therefore, HANs are much more stable in chloraminated waters than chlorinated waters. This is important for some disinfection scenarios where chlorine pre-disinfection or oxidation is performed prior to ammonia addition to convert chlorine to chloramine. In this case, HANs are formed during chlorination can persist after the addition of ammonia (chloraminated waters) (Hayes-Larson and Mitch, 2010).

To date, several studies have been conducted to examine HAN formation under the FP conditions (Ahmadi and Ramavandi, 2014; Bond et al., 2014b; Bougeard et al., 2010; Chen et al., 2017, 2018; Chu et al., 2017; Chuang and Tung, 2015; Ding et al., 2018; Huang et al., 2013, 2016, 2019; Kozari et al., 2020; Krasner et al., 2008; Kristiana et al., 2017; Li et al., 2017; Liu et al., 2020; Luo et al., 2020; Reckhow and Singer, 1984; Wang et al., 2018; Wei et al., 2017; Yang et al., 2012, 2017). Given the decomposition of HANs at elevated free chlorine levels, in this study we conducted side-by-side experiments to compare the HAN UFC and FP tests using five different water sources. In addition, we performed HAN UFC and FP tests under chloramination conditions and compared with the chlorination results, and the effect of bromide in terms of HAN speciation for both oxidants.

2. Experimental work

Three wastewater effluent grab samples (Ef1, Ef2, and Ef3) were collected from municipal wastewater treatment plants, while a treated surface water grab sample (DW) was obtained from a water treatment plant after conventional clarification processes (coagulation, flocculation, sedimentation). No oxidant was applied in water or wastewater treatment plants before the sample collection. A raw surface water grab sample (RW) was also obtained from a lake serving as a drinking water source.

Dissolved organic carbon (DOC) and dissolved nitrogen (DN) were measured using a high-temperature combustion TOC analyzer [Minimum reporting level (MRL) 0.1 mg/L]. Bromide (Br^-) and nitrate were measured using ion chromatography [MRL 10 $\mu\text{g/L}$] (Soyluoglu et al., 2020). Varian Carry 50 was used to measure the UV absorbance at wavelength 254 nm using a 1 cm cell according to SM 5910 method (APHA et al., 2017).

We conducted UFC and FP tests under chlorination and chloramination conditions for these 5 water samples (3 wastewater effluents and 2 surface water samples). The UFC conditions for chlorination consisted of reaction time of 24 ± 1 h, temperature of 20.0 ± 1.0 °C, pH 7.8 ± 0.2 , and predetermined Cl_2 dose to maintain 1.0 ± 0.4 mg/L after 24 h, while FP conditions for chlorination were reaction time of 120 h, temperature of 20.0 ± 1.0 °C, pH 7.8 ± 0.2 , and 100 mg/L Cl_2 dose. To maintain the pH 7.8 ± 0.2 , the samples were buffered using 10 mM phosphate buffer. A chlorine demand test for each water sample was conducted prior to UFC tests to determine the Cl_2 dose to maintain 1.0 ± 0.4 mg/L after 24 h. For chloramination, the conditions were the same as in chlorination, but preformed monochloramine was spiked at 3 mg/L (as Cl_2), and 100 mg/L (as Cl_2) in the UFC and FP, respectively. For preformed monochloramine preparation, a stock chlorine solution (500 mg/L) adjusted to pH 9 was titrated slowly (drop by drop via a burette) to $(\text{NH}_4)_2\text{SO}_4$ solution (NH_3 , 500 mg/L) adjusted to pH 9, continuously stirred to achieve a $\text{Cl}_2:\text{NH}_3$ ratio of 3.5:1 by weight. The resulting solution monochloramine concentration was about 250 mg/L (as Cl_2) with no measurable free chlorine. To

Table 1
Selected water samples characteristics used in the study.

| Water Source | DOC (mg/L) | DN (mg/L) | Br ⁻ (μg/L) | SUVA ₂₅₄ (L/mg-m) | Nitrate (mg/L) |
|----------------------------|------------|-----------|------------------------|------------------------------|----------------|
| Ef1 (WW Effluent) | 12.5 | 7.2 | 140 | 1.3 | 15 |
| Ef2 (WW Effluent) | 5.1 | 14.5 | 92 | 2.3 | 80 |
| Ef3 (WW Effluent) | 5.5 | 8.5 | 50 | 2.2 | 34 |
| DW (Treated surface water) | 3.7 | 1.2 | 38 | 1.25 | <MRL |
| RW (Raw surface water) | 1.5 | 1.2 | 16 | 1.9 | <MRL |

MRL: Minimum Reporting Level.

examine the bromide effect, one set of the experiments was conducted at ambient Br⁻, while a second set was conducted by adjusting the Br⁻ to 300 μg/L in each sample. All UFC and FP tests were conducted in triplicates using 125 mL head space free amber glass bottles and were stored in the dark.

3. Haloacetonitriles and trihalomethanes measurements

At the end of contact time, fifty mL samples were transferred into 60 mL extraction vials to determine the four trihalomethanes (THM4) species [chloroform (CHCl₃), bromodichloromethane (CHCl₂Br), dibromochloromethane (CHClBr₂), and bromoform (CHBr₃)] and six haloacetonitriles (HAN6) species [chloroacetonitrile (CAN), dichloroacetonitrile (DCAN), bromoacetonitrile (BAN) Bromochloroacetonitrile (BCAN), trichloroacetonitrile (TCAN)] dibromoacetonitrile (DBAN). After that, 3 mL of methyl tert-butyl ether (MtBE) and 10 g of anhydrous sodium sulfate were added to the extraction vials. To dissolve the salts, the extraction vials were put on a shaker table at

300 rpm for 15 min. After 15 min, vials were placed on the bench for 15 min for phase separation. The MtBE phase was transferred to GC vials to analyze by GC-ECD. The MRL of HAN6 and THM4 species were 0.5 and 1 μg/L, respectively (Liu et al., 2018).

4. Results and discussion

4.1. Water characteristics

Selected characteristics of the water samples used in the study are provided in Table 1. The water samples covered a wide range of DOC content (1.5 to 12.5 mg/L), while SUVA₂₅₄ of the samples had a narrow range (1.25 to 2.3 (L/mg-m)). The low SUVA₂₅₄ of the wastewater effluent is consistent with the typical effluent wastewater organic properties that are rich in hydrophilic and non-aromatic organic matter (soluble microbial products), whereas the treated water and raw source water organic matter were low in aromatic character indicating a more hydrophilic nature. DN of the waters ranged from 1.2 to 14.5 mg/L. The wastewater effluents had higher DOC and DN than the drinking water samples. The ambient Br⁻ level of the samples ranged from 16 to 140 μg/L.

4.2. HAN6 formation

The concentrations of HANs under FP and UFC tests for the five water samples are presented in Fig. 1. The results showed higher HAN concentrations under UFC than FP conditions for all samples both at ambient and spiked Br⁻ levels, when chlorine (Cl₂) is the oxidant. This reflects the effect of the HAN instability and degradation

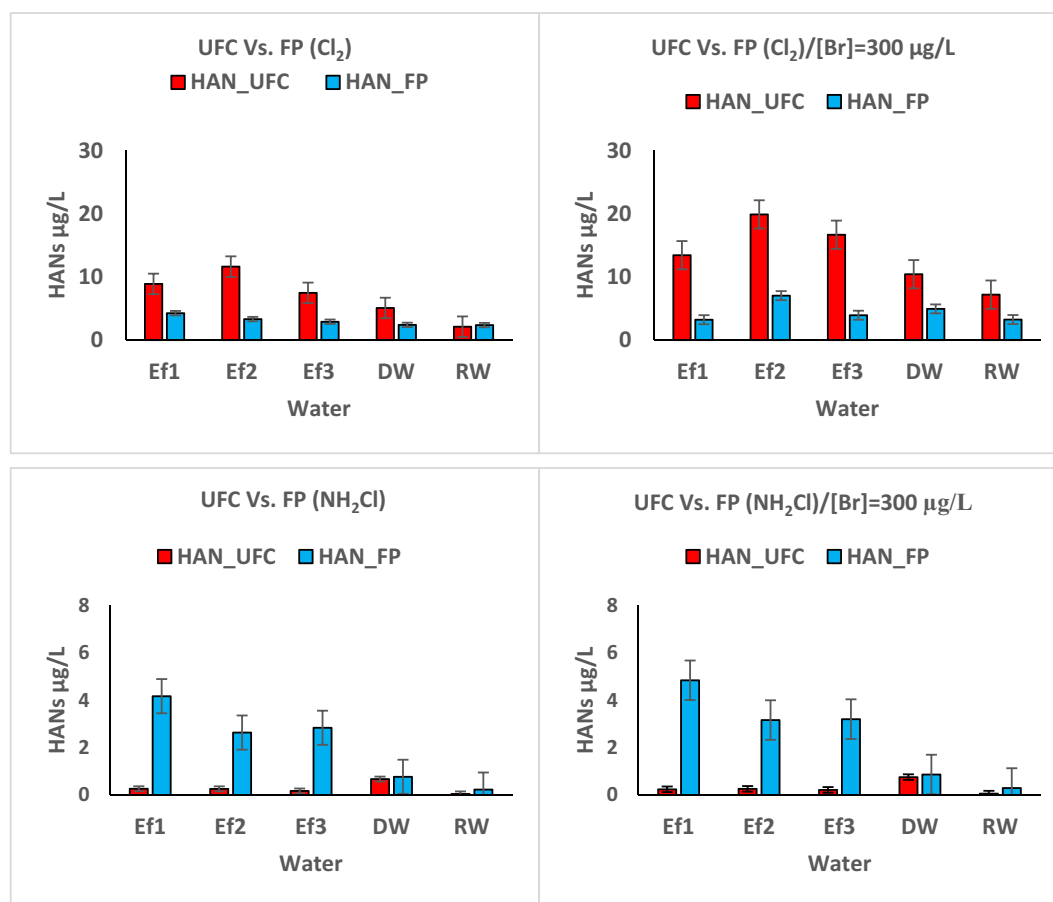


Fig. 1. Formation of HANs from chlor(am)ination of 5 different waters under uniform formation conditions (UFC) and formation potential (FP) at ambient and spiked Br⁻ (300 μg/L). Ef1, Ef2, and Ef3 are wastewater effluent water samples, DW and RW are treated and raw surface water samples, respectively. The error bars are standard deviation of triplicates.

via hydrolysis under different pH conditions and higher chlorine levels for long contact time (Yu and Reckhow, 2015; Bond et al., 2014a; Chen et al., 2017; Ding et al., 2018; Glezer et al., 1999; Huang et al., 2016; Reckhow et al., 2001; Szczuka et al., 2017; Yang et al., 2007). Different approaches (e.g., formula based on DOC, a constant excess chlorine dose (e.g., 10–100 mg/L), Cl_2 :precursor ratio) are used to determine the chlorine doses during FP tests. Regardless, all approaches aim maintaining an excess level of chlorine residual during the experiments. Different HAN species exhibit different degradation depending on the chlorine levels and pH. Collectively, the observation in the literature and the data presented in this paper show the difficulty of obtaining meaningful insights and comparing the work in different studies investigating chlorine reactive HAN precursors through chlorination FP tests.

In contrast to HANs, the formation of THMs during the same tests was higher under FP than UFC conditions during chlorination, confirming that FP tests inform about the chlorine reactive precursors of THM in water samples. The median of the mass ratio of HAN/THM produced under UFC conditions was ~10% (data not shown) which was consistent with ratios reported in previous HANs occurrence studies (Bond et al., 2011; Mitch et al., 2009; Oliver, 1983). On the other hand, under the FP conditions the median of the mass ratio of HAN/THM was ~1%. These results clearly show that FP tests are not suitable to determine HAN precursors in water samples during chlorination. Nevertheless, several studies and publications have reported HANs FP during chlorination without considering their stability.

In the case of chloramination, higher HAN FP concentrations were measured compared to UFC concentrations (Fig. 1) which can be explained by HAN stability in the presence of chloramine (Yang et al., 2007) and the contribution of nitrogen from chloramines in the formation of HANs, as has been shown in previous studies that both chloramines and dissolved organic nitrogen can serve as nitrogen source to form HANs (Chuang and Tung, 2015; Krasner et al., 2006; Ye et al., 2018; Yu and Reckhow, 2015). Therefore, FP tests during chloramination may still be representative in determining the HAN precursor levels in water samples reactive to chloramines. The three wastewater effluent samples, either under chlorination or chloramination, produced more HAN than the two surface waters. Similar trends were observed in previous studies (Gan et al., 2013; Jutaporn et al., 2020), which can be attributed to the higher DOC and DN content of the 3 wastewater effluents (Table 1); mainly the hydrophilic neutral and base fraction and small size fractions of wastewater effluent organic matter were attributed to HAN formation (Kozari et al., 2020; Ye et al., 2018). The median of the mass ratio of HAN/THM produced from the five waters tested was ~17. While under FP conditions, the median of the mass ratio of HAN/THM was ~25. This increase in the mass ratio of HAN/THM is due to the formation of fewer THMs during chloramination.

4.3. Bromine incorporation to HANs should be examined under UFC conditions

The Br-HANs measured during the FP tests in the presence of Cl_2 and NH_2Cl produced lower Br-HANs than those measured under UFC test. Bromine substitution factor (BSF) is used as a measure of bromine substitution among different DBP classes. BSF is the ratio of the molar concentration bromine in a given DBP class to the total molar concentration of chlorine and bromine in that DBP class (vary from 0 to 1) (Hua et al., 2006; Hua and Reckhow, 2012).

$$BSF = \frac{Br-DBP}{Cl-DBP + Br-DBP}$$

Calculated BSF of HANs, as shown in Fig. 2 are generally higher for the UFC than the FP test under both chlorination and chloramination.

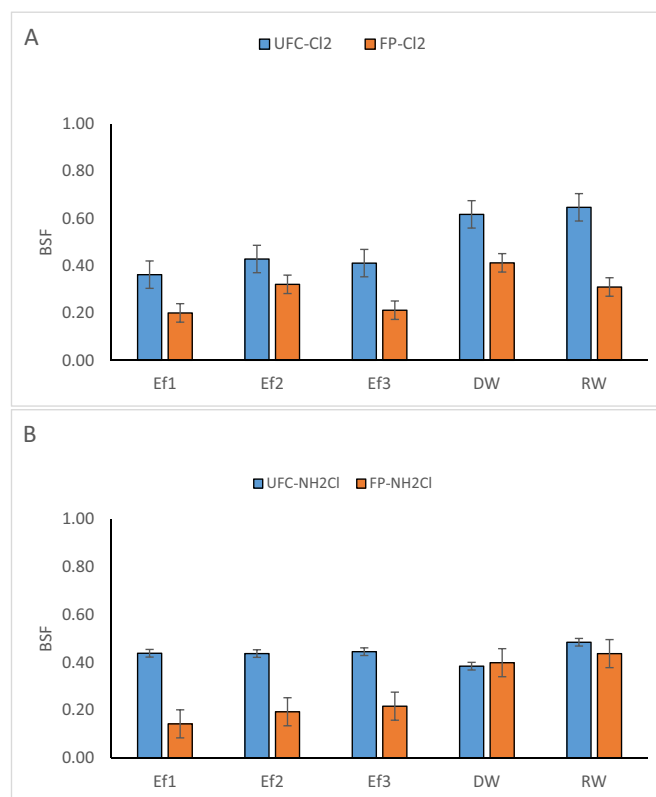


Fig. 2. Bromide substitution factor (BSF) of HANs under chlorination (A) and under chloramination (B) in the uniform formation conditions (UFC) and formation potential (FP) tests. Ef1, Ef2, and Ef3 are wastewater effluent water samples, DW and RW are treated and raw surface water samples, respectively. The error bars are standard deviation of triplicates.

This relates to the higher Cl_2/Br^- ratio, which leads to the oxidation of bromide and hindrance of Br^- incorporation (Symons et al., 1993). Thus, FP tests under chlorination and chloramination do not provide practically representative information about bromine speciation in water samples.

5. Conclusions and recommendations

HANs formation from five different chlorinated water sources were higher under UFC than FP tests due to HAN instability and degradation at higher chlorine levels for long contact times. Therefore, the UFC (or SDS) rather FP tests chlorination tests should be used for a better estimation of formation and presence of HAN precursors in water sources. On the other hand, chlorination FP tests still provide information about the chlorine reactive precursors of THM and HAA. In the case of chloramination, higher HANs formed under FP test compared to UFC test, and the FP test results can still be used for determining HAN precursors in water samples reactive to chloramine. FP tests both for chlorination and chloramination do not provide practically useful information about HAN speciation due to high oxidant levels. Considering increasing interest in HAN formation, this work highlights and call attention to these distinctions to produce useful information in the literature.

CRedit authorship contribution statement

Amer Kanan: Conceptualization, Methodology, Investigation, Writing - review & editing, Writing - original draft. **Tanju Karanfil:** Conceptualization, Methodology, Writing - review & editing, Writing - original draft, Supervision.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgment

Authors are grateful for Fulbright Scholar Program funding Dr. Amer Kanan's visit at Clemson University.

References

- Ahmadi, M., Ramavandi, B., 2014. The formation potential of haloacetonitriles in the dez river water, Iran. *Environ. Technol. (United Kingdom)* 35, 2347–2355. <https://doi.org/10.1080/09593330.2014.903301>.
- APHA, AWAA, WEF, 2017. Standard methods for the examination of water and wastewater, American public health association. American Public Health Association, Washington, 23rd ed APHA <https://doi.org/10.2105/SMWW.2882.007>.
- Bellar, T.A.A., Lichtenberg, J.J., Kroner, R.C., 2015. The occurrence of organohalides in chlorinated drinking. *Am. Water Work. Assoc.* 66, 703–706.
- Bond, T., Huang, J., Templeton, M.R., Graham, N., 2011. Occurrence and control of nitrogenous disinfection by-products in drinking water – a review. *Water Res.* <https://doi.org/10.1016/j.watres.2011.05.034>.
- Bond, T., Huang, J., Graham, N.J.D., Templeton, M.R., 2014a. Examining the interrelationship between DOC, bromide and chlorine dose on DBP formation in drinking water – a case study. *Sci. Total Environ.* 470–471, 469–479. <https://doi.org/10.1016/j.scitotenv.2013.09.106>.
- Bond, T., Mokhtar Kamal, N.H., Bonnisseau, T., Templeton, M.R., 2014b. Disinfection by-product formation from the chlorination and chloramination of amines. *J. Hazard. Mater.* 278, 288–296. <https://doi.org/10.1016/j.jhazmat.2014.05.100>.
- Bougeard, C.M.M., Goslan, E.H., Jefferson, B., Parsons, S.A., 2010. Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine. *Water Res.* 44, 729–740. <https://doi.org/10.1016/j.watres.2009.10.008>.
- Chen, W., Liu, Z., Tao, H., Xu, H., Gu, Y., Chen, Z., Yu, J., 2017. Factors affecting the formation of nitrogenous disinfection by-products during chlorination of aspartic acid in drinking water. *Sci. Total Environ.* 575, 519–524. <https://doi.org/10.1016/j.scitotenv.2016.09.010>.
- Chen, S., Deng, J., Li, L., Gao, N., 2018. Evaluation of disinfection by-product formation during chlor(am)ination from algal organic matter after UV irradiation. *Environ. Sci. Pollut. Res.* 25, 5994–6002. <https://doi.org/10.1007/s11356-017-0918-x>.
- Chu, W., Yao, D., Deng, Y., Sui, M., Gao, N., 2017. Production of trihalomethanes, haloacetaldehydes and haloacetonitriles during chlorination of microcystin-LR and impacts of pre-oxidation on their formation. *J. Hazard. Mater.* 327, 153–160. <https://doi.org/10.1016/j.jhazmat.2016.12.058>.
- Chuang, Y.H., Tung, H.H., 2015. Formation of trichloronitromethane and dichloroacetonitrile in natural waters: precursor characterization, kinetics and interpretation. *J. Hazard. Mater.* 283, 218–226. <https://doi.org/10.1016/j.jhazmat.2014.09.026>.
- Ding, S., Chu, W., Bond, T., Wang, Q., Gao, N., Xu, B., Du, E., 2018. Formation and estimated toxicity of trihalomethanes, haloacetonitriles, and haloacetamides from the chlor(am)ination of acetaminophen. *J. Hazard. Mater.* 341, 112–119. <https://doi.org/10.1016/j.jhazmat.2017.07.049>.
- Gan, X., Karanfil, T., Kaplan Bekaroglu, S.S., Shan, J., 2013. The control of N-DBP and C-DBP precursors with MIEOX®. *Water Res.* 47, 1344–1352. <https://doi.org/10.1016/j.watres.2012.11.049>.
- Glezer, V., Harris, B., Tal, N., Iosefzon, B., Lev, O., 1999. Hydrolysis of haloacetonitriles: linear free energy relationship. Kinetics and products. *Water Res.* 33, 1938–1948. [https://doi.org/10.1016/S0043-1354\(98\)00361-3](https://doi.org/10.1016/S0043-1354(98)00361-3).
- Hayes-Larson, E.L., Mitch, W.A., 2010. Influence of the method of reagent addition on dichloroacetonitrile formation during chloramination. *Environ. Sci. Technol.* 44, 700–706. <https://doi.org/10.1021/es9025112>.
- Hua, G., Reckhow, D.A., 2012. Evaluation of bromine substitution factors of DBPs during chlorination and chloramination. *Water Res.* 46, 4208–4216. <https://doi.org/10.1016/j.watres.2012.05.031>.
- Hua, G., Reckhow, D.A., Kim, J., 2006. Effect of bromide and iodide ions on the formation and speciation of disinfection byproducts during chlorination. *Environ. Sci. Technol.* <https://doi.org/10.1021/es0519278>.
- Huang, H., Wu, Q.Y., Tang, X., Jiang, R., Hu, H.Y., 2013. Formation of haloacetonitriles and haloacetamides during chlorination of pure culture bacteria. *Chemosphere* 92, 375–381. <https://doi.org/10.1016/j.chemosphere.2013.01.031>.
- Huang, H., Wu, Q.Y., Tang, X., Jiang, R., Hu, H.Y., 2016. Formation of haloacetonitriles and haloacetamides and their precursors during chlorination of secondary effluents. *Chemosphere* 144, 297–303. <https://doi.org/10.1016/j.chemosphere.2015.08.082>.
- Huang, H., Shao, K.L., Duan, S.Y., Zhong, C.Y., 2019. Effect of copper corrosion products on the formation and speciation of haloacetamides and haloacetonitriles during chlorination. *Sep. Purif. Technol.* 211, 467–473. <https://doi.org/10.1016/j.seppur.2018.10.025>.
- Jutaporn, P., Armstrong, M.D., Coronell, O., 2020. Assessment of C-DBP and N-DBP formation potential and its reduction by MIEOX® DOC and MIEOX® GOLD resins using fluorescence spectroscopy and parallel factor analysis. *Water Res.* 172, 115460. <https://doi.org/10.1016/j.watres.2019.115460>.
- Karanfil, T., Krasner, S.W., Westerhoff, P., Xie, Y., 2008. Recent advances in disinfection by-product formation, occurrence, control, health effects, and regulations. *ACS Symp. Ser.* 995, 2–19. <https://doi.org/10.1021/bk-2008-0995.ch001>.
- Koch, B., Krasner, S.W., Scimmenti, M.J., Schimpff, W.K., 1991. Predicting the formation of DBPs by the simulated distribution system. *J. Am. Water Work. Assoc.* 83, 62–70. <https://doi.org/10.1002/j.1551-8833.1991.tb07233.x>.
- Kozari, A., Paloglou, A., Voutsas, D., 2020. Formation potential of emerging disinfection by-products during ozonation and chlorination of sewage effluents. *Sci. Total Environ.* 700, 134449. <https://doi.org/10.1016/j.scitotenv.2019.134449>.
- Krasner, S.W., Weinberg, H.S., Richardson, S.D., Pastor, S.J., Chinn, R., Scimmenti, M.J., Onstad, G.D., Thurston, A.D., 2006. Occurrence of a new generation of disinfection byproducts. *Environ. Sci. Technol.* 40, 7175–7185. <https://doi.org/10.1021/es060353j>.
- Krasner, S.W., Westerhoff, P.K., Chen, B., Amy, G., Nam, S.-N., Chowdhury, Z.K., Sinha, S., Rittmann, B.E., 2008. Contribution of Wastewater to DBP Formation.
- Krasner, S.W., Lee, T.C.F., Westerhoff, P., Fischer, N., Hanigan, D., Karanfil, T., Beita-Sandif, W., Taylor-Edmonds, L., Andrews, R.C., 2016. Granular activated carbon treatment may result in higher predicted genotoxicity in the presence of bromide. *Environ. Sci. Technol.* 50, 9583–9591. <https://doi.org/10.1021/acs.est.6b02508>.
- Kristiana, I., Liew, D., Henderson, R.K., Joll, C.A., Linge, K.L., 2017. Formation and control of nitrogenous DBPs from Western Australian source waters: investigating the impacts of high nitrogen and bromide concentrations. *J. Environ. Sci.* 58, 102–115. <https://doi.org/10.1016/j.jes.2017.06.028>.
- Li, C., Gao, N., Chu, W., Bond, T., Wei, X., 2017. Comparison of THMs and HANs formation potential from the chlorination of free and combined histidine and glycine. *Chem. Eng. J.* 307, 487–495. <https://doi.org/10.1016/j.cej.2016.08.110>.
- Liu, C., Ersan, M.S., Plewa, M.J., Amy, G., Karanfil, T., 2018. Formation of regulated and unregulated disinfection byproducts during chlorination of algal organic matter extracted from freshwater and marine algae. *Water Res.* 142, 313–324. <https://doi.org/10.1016/j.watres.2018.05.051>.
- Liu, Z., Lin, Y.L., Chu, W.H., Xu, B., Zhang, T.Y., Hu, C.Y., Cao, T.C., Gao, N.Y., Dong, C. Di, 2020. Comparison of different disinfection processes for controlling disinfection by-product formation in rainwater. *J. Hazard. Mater.* 385, 121618. <https://doi.org/10.1016/j.jhazmat.2019.12.1618>.
- Liviac, D., Wagner, E.D., Mitch, W.A., Altonji, M.J., Plewa, M.J., 2010. Genotoxicity of water concentrates from recreational pools after various disinfection methods. *Environ. Sci. Technol.* 44, 3527–3532. <https://doi.org/10.1021/es903593w>.
- Luo, Y., Feng, L., Liu, Y., Zhang, L., 2020. Disinfection by-products formation and acute toxicity variation of hospital wastewater under different disinfection processes. *Sep. Purif. Technol.* 238, 116405. <https://doi.org/10.1016/j.seppur.2019.116405>.
- McKinney, J., Mauer, R., Haas, J., Thomas, R., 1976. Possible factors in the drinking water of laboratory animals causing reproductive failure. In: Keith, L.H. (Ed.), *Identif. Anal. Org. Pollut. Water*. vol. 1976. Ann Arbor Sci. Publ. Ann Arbor, MI, pp. 417–432.
- Mitch, W.A., Krasner, S.W., Paul, W., Dotsen, A., 2009. Occurrence and Formation of Nitrogenous Disinfection by-Products. Water Research Foundation & Environmental Protection Agency (EPA).
- Muellner, M.G., Wagner, E.D., Mccalla, K., Richardson, S.D., Woo, Y.T., Plewa, M.J., 2007. Haloacetonitriles vs. regulated haloacetic acids: are nitrogen-containing DBFs more toxic? *Environ. Sci. Technol.* 41, 645–651. <https://doi.org/10.1021/es0617441>.
- Oliver, B.G., 1983. Dihaloacetonitriles in drinking water: algae and fulvic acid as precursors. *Environ. Sci. Technol.* 17, 80–83. <https://doi.org/10.1021/es00108a003>.
- Peters, R.J.B., de Leer, E.W.B., de Galan, L., 1990. Chlorination of cyanoethanoic acid in aqueous medium. *Environ. Sci. Technol.* 24, 81–86. <https://doi.org/10.1021/es00071a008>.
- Plewa, M.J., Wagner, E.D., Richardson, S.D., 2017. TIC-Tox: a preliminary discussion on identifying the forcing agents of DBP-mediated toxicity of disinfected water. *J. Environ. Sci.* 58, 208–216. <https://doi.org/10.1016/j.jes.2017.04.014>.
- Reckhow, D.A., Singer, P.C., 1984. Mechanisms of organic halide formation during fulvic acid chlorination and implication with respect to preozonation. In: Robert, L.J., Richard, J.B., William, P.D., Sidney, K., Morris, H., R.J., Jacobs, Vivian A. (Eds.), *Water Chlorination Chemistry, Environmental Impact and Health Effects*. Lewis Publisher, INC, Williamsburg, Virginia, pp. 1229–1257.
- Reckhow, D.A., MacNeill, A.L., Platt, T.L., MacNeill, A.L., McClellan, J.N., 2001. Formation and degradation of dichloroacetonitrile in drinking waters. *J. Water Supply Res. Technol.* - AQUA 50, 1–13. <https://doi.org/10.2166/aqua.2001.0001>.
- Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., DeMarini, D.M., 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: a review and roadmap for research. *Mutat. Res. - Rev. Mutat. Res.* <https://doi.org/10.1016/j.mrrev.2007.09.001>.
- Rook, J.J., 1974. Haloforms in drinking water. *Am. Water Work. Assoc.* 68, 168–172.
- Soyluoglu, M., Ersan, M.S., Ateia, M., Karanfil, T., 2020. Removal of bromide from natural waters: bromide-selective vs. conventional ion exchange resins. *Chemosphere* 238. <https://doi.org/10.1016/j.chemosphere.2019.124583>.
- Stevens, A.A., Symons, J.M., 1977. Measurement of trihalomethanes and precursor concentration changes. *J. Am. Water Work. Assoc.* 69, 546–555. <https://doi.org/10.1002/j.1551-8833.1977.tb06815.x>.
- Stuart, M.E., Goody, D.C., Kinniburgh, D.G., Klinck, B.A., 2001. Trihalomethane formation potential: a tool for detecting non-specific organic groundwater contamination. *Urban Water* 3, 173–184. [https://doi.org/10.1016/S1462-0758\(01\)00039-5](https://doi.org/10.1016/S1462-0758(01)00039-5).
- Summers, R.S., Hooper, S.M., Shukairy, H.M., Solarik, G., Summers, R.S., Hooper, S.M., Owen, D., 1996. Assessing DBP yield: uniform formation conditions. *Am. Water Work. Assoc.* 88, 80–93.
- Symons, J.M., Krasner, S.W., Simms, L.A., Scimmenti, M., 1993. Measurement of THM and precursor concentrations revisited: the effect of bromide ion. *J. Am. Water Work. Assoc.* 85, 51–62. <https://doi.org/10.1002/j.1551-8833.1993.tb05921.x>.
- Szczuka, A., Parker, K.M., Harvey, C., Hayes, E., Vengosh, A., Mitch, W.A., 2017. Regulated and unregulated halogenated disinfection byproduct formation from

- chlorination of saline groundwater. *Water Res.* 122, 633–644. <https://doi.org/10.1016/j.watres.2017.06.028>.
- U. S. EPA, 1979. National Interim Primary Drinking Water Regulations; control of trihalomethanes in drinking water; final rule. *Fed. Regist.* 44 (44231), 68624–68707.
- U. S. EPA, 1998. National Primary Drinking Water Regulations: disinfectants and disinfection byproducts: 40 CFR 9, 141, 142. *Fed. Regist.* 63, 69390–69476.
- U. S. EPA, 2010. EPA 816-F-10-080 Comprehensive Disinfectants and Disinfection Byproducts Rules (Stage 1 and Stage 2): Quick Reference Guide [WWW Document]. U. S. Environ. Prot. Agency (doi:EPA 816-F-10-080).
- Wang, A.Q., Lin, Y.L., Xu, B., Hu, C.Y., Zhang, M.S., Xia, S.J., Zhang, T.Y., Chu, W.H., Gao, N.Y., 2018. Degradation of acrylamide during chlorination as a precursor of haloacetonitriles and haloacetamides. *Sci. Total Environ.* 615, 38–46. <https://doi.org/10.1016/j.scitotenv.2017.09.141>.
- Wei, X., Gao, N., Li, C., 2017. Evaluation and reduction of THMs, DCAN and TCNM formation potential from chlorination and chloramination of verapamil. *J. Environ. Chem. Eng.* 5, 4397–4405. <https://doi.org/10.1016/j.jece.2017.08.025>.
- Yang, X., Shang, C., Westerhoff, P., 2007. Factors affecting formation of haloacetonitriles, haloketones, chloropicrin and cyanogen halides during chloramination. *Water Res.* 41, 1193–1200. <https://doi.org/10.1016/j.watres.2006.12.004>.
- Yang, X., Shen, Q., Guo, W., Peng, J., Liang, Y., 2012. Precursors and nitrogen origins of trichloronitromethane and dichloroacetonitrile during chlorination/chloramination. *Chemosphere* 88, 25–32. <https://doi.org/10.1016/j.chemosphere.2012.02.035>.
- Yang, Z., Sun, Y.X., Ye, T., Shi, N., Tang, F., Hu, H.Y., 2017. Characterization of trihalomethane, haloacetic acid, and haloacetonitrile precursors in a seawater reverse osmosis system. *Sci. Total Environ.* 576, 391–397. <https://doi.org/10.1016/j.scitotenv.2016.10.139>.
- Ye, Z., Liu, W., Sun, W., Nie, X., Ao, X., 2018. Role of ammonia on haloacetonitriles and halonitromethanes formation during ultraviolet irradiation followed by chlorination/chloramination. *Chem. Eng. J.* 337, 275–281. <https://doi.org/10.1016/j.cej.2017.12.073>.
- Yu, Y., Reckhow, D.A., 2015. Kinetic analysis of haloacetonitrile stability in drinking waters. *Environ. Sci. Technol.* 49, 11028–11036. <https://doi.org/10.1021/acs.est.5b02772>.