Thai Environmental Engineering Journal Vol. 38 No. 2 (2024) : 47-55
www.eeat.or.th

The Effect of Bromide Ions on the Formation of Brominated Haloacetic Acids (Br-HAAs) in Tropical Rivers, Thailand

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Article History; *Received: 16 August 2024, Accepted: 16 August 2024, Published: 30 August 2024*

Abstract

With the presence of bromide ions in chlorination during water purification, hypobromous acid (HOBr) is formed, leading to the formation and distribution of brominated disinfection by-products (Br-DBPs) in tap water. Brominated haloacetic acids (HAAs) in tap water are known to be significantly harmful and toxic to human health. Bromide ions are naturally present in groundwater and surface water, primarily as affected by seawater intrusion. Conventional treatment methods face difficulty in completely eliminating bromide ions. This study investigated the concentration of bromide ions and the haloacetic acid formation potentials (HAAFPs) in three tropical river sources in Thailand: the Tha-Chin River, the Chao Phraya River, and the Mae Klong River. The bromide ion concentrations were 44.79, 41.34, and 18.22 µg/L, respectively. In these three rivers, chlorinated and brominated HAAs (trichloroacetic acid (TCAA), dichloroacetic acid (DCAA), bromodichloroacetic acid, and bromochloroacetic acid) were detected after chlorination. The sum of only DCAAFPs and TCAAFPs were significantly higher than the US EPA regulations of 60 µg/L for total HAA5 (the sum of monochloroacetic acid, monobromoacetic acid, DCAA, dibromoacetic acid, and TCAA). The DCAAFPs in the Chao Phraya River were relatively high, surpassing the WHO guidelines of 50 µg/L. This study also found that the Tha-Chin River had high levels of bromide ions and brominated HAAFPs, resulting from seawater intrusion from the estuary Gulf. These findings highlighted the formation of brominated HAAFPs, which were particularly significant in water sources with higher levels of bromide ions in the water.

Keywords : Bromide ion; disinfection by-products; dissolved organic matter; haloacetic acids; tropical river

Introduction

Chlorination, a commonly used method to eliminate pathogens in the water supply, leads to the formation of disinfection by-products (DBPs), which include carcinogenic trihalomethanes (THMs) and haloacetic acids (HAAs). HAAs are one of the DBPs that have been detected frequently in many regions [1-3]. Nine HAA species commonly occur: three chlorinated HAAs (i.e., monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA)), three brominated HAAs (i.e., monobromoacetic acid (MBAA), dibromoacetic acid (DBAA), tribromoacetic acid (TBAA)), and three chlorinated and brominated HAAs (i.e., bromochloroacetic acid (BCAA), bromodichloroacetic acid (BDCAA), and dibromochloroacetic acid (DBCAA)).

Many studies have shown bromine incorporation into DBPs (including THMs and HAAs) when bromide ion (Br^-) are present in source waters [4, 5]. The presence of Br^- changes the reaction pathways of chlorine and dissolved organic matter (DOM) [6, 7]. Br^- is oxidized by chlorine to produce hypobromous acid (HOBr). HOBr reacts more rapidly than hypochlorous acid (HOCl) with DOM, leading to the more formation of brominated DBPs [8, 9]. Brominated DBPs are generally known to be more mutagenic and toxic compared with chlorinated ones [10, 11]. Many studies show that Br^- concentrations in water can vary widely. In the US, the average concentration of Br^- in water supplies is around 62 μg/L, though in certain coastal regions, levels may exceed 500 μg/L [12]. Sohn et al. (2006) found that Br^- concentrations in surface and groundwater ranged from 7 to 312 μg/L, leading to variations of brominated THMs and HAAs [13]. In China, the Yangtze, Huangpu, Tai, and Qiantang Rivers have Br^- concentrations ranging from 100 to 720 μg/L, leading to the formation of brominated HAAs, such as BCAA and BDCAA [14].

In tropical areas like Thailand, higher temperatures, intensive rainfall, and various other conducive factors increase the concentration of DOM in water sources. Br^- naturally occur in groundwater and surface water due to seawater intrusion and discharges from agricultural areas and industries [15]. Conventional water treatment processes (i.e., coagulation, sedimentation, and rapid sand filtration) struggle to remove Br^-. Consequently, concentrations of carcinogenic brominated DBPs in tap water can increase. This study aimed to comprehensively investigate the relationship of the concentration of bromide ions and HAA formation potentials (FPs) in the three water sources used for water supply in Thailand (the Chao Phraya River, the Mae Klong River, and the Tha-Chin River). This study also focused on the relationship between Br^- concentrations and HAAFPs and various factors, including pH, temperature, and conductivity.

Methodology

Study Area

The sampling points of surface water from three rivers, including the Chao Phraya River (14°2'26.9"N, 100°33'21.0"E), the Mae Klong River (13°44'22.5"N 99°50'34.0"E), and the Tha-Chin River 13°55'45.1"N 100°12'01.9"E) (as shown in Figure 1) were investigated. Water samples from raw water sources were collected from a depth of 1.0 meter below the water surface and promptly stored in 10-liter bottles. The sampling was conducted on different dates, with the Mae Klong and Tha-Chin Rivers being sampled on 21 September 2023, and the Chao Phraya River on 1 October 2023. Each river was sampled only once at a single designated point. The collected water samples were prepared for dissolved organic carbon (DOC) analysis by filtering them through 0.7 μm cellulose acetate membrane filters (GF/F, Whatman) using a vacuum pump (N820, Labsort) within 24 h of collection [16].

Analytical Methods

1. Measurement of water quality parameters

The pH and temperature were determined using a pH meter (pHTestr30, EUTECH), and conductivity was measured using a conductivity meter (ECTestr11, Eutech). DOC was analyzed using a TOC analyzer (TOC-V, Shimadzu).

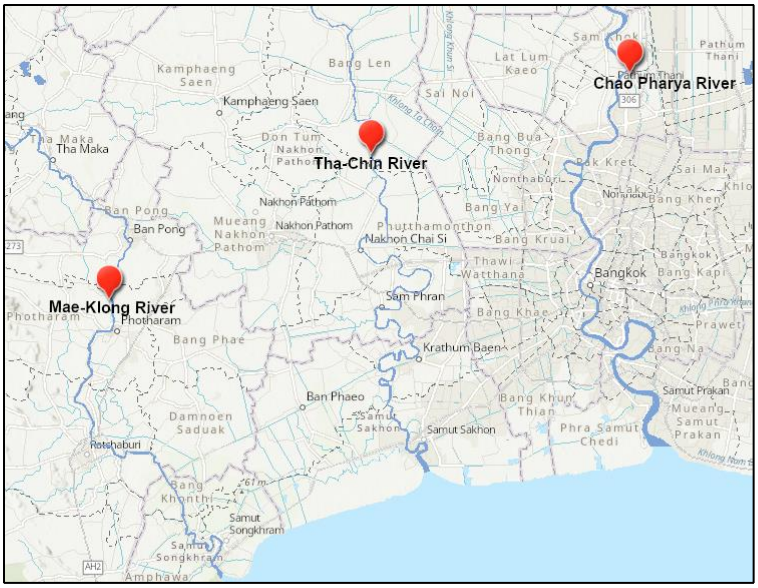

Figure 1 Sampling sites in tropical rivers in Thailand

2. Determination of bromide ion concentrations

Br^- concentrations were determined by LC-MS/MS (6500 QTARP, Sciex, Massachusetts, USA) equipped with an Acclaim Trinity P1 column (3 µm, 2.1×100 mm, Thermo Fisher Scientific). The mobile phases consisted of 200 mM ammonium acetate added with 0.5% acetic acid and acetonitrile. The gradient conditions of organic solvent are as follows: 96% (0-2.5 min), 86% (15.5 min), 5% (16-24.5 min), and 96% (25-34.5 min). The flow rate was maintained at 0.3 mL/min, and the injection volume was set at 10 µL. Quantification of Br^- concentration was performed using negative electrospray ionization (ESI) mode, with multiple reaction monitoring (Q1= *m/z* 79, Q3=*m/z* 79). Calibration curves were prepared using standard solutions containing bromide ions at concentrations of 1, 3, 10, 30, and 100 µg/L, with each calibration point run in triplicate to ensure accuracy and precision. Quality control samples were periodically analyzed to monitor the stability and consistency of the instrument throughout the analytical sequence.

3. HAAFP in chlorination

The chlorination condition for HAAFPs was as follows: 10 mL of sample volume, initial chlorine dose (by sodium hypochlorite) at 30 or 50 mg Cl_2/L, the reaction time 24 h, pH 7 (maintained by 5 mM phosphate buffer), temperature 30 °C in a dark place. After 24 h of the reaction, residual free chlorine was measured using the DPD colorimetric method and quenched with ammonium chloride (50 mg N/L). HAA concentrations were determined by LC-MS/MS (6500 QTARP, Sciex) equipped with a reverse phase column (zorbax SB-Aq, 5 µm, 4.6×150 mm, Agilent technologies, CA, USA). The mobile phases consisted of methanol and 0.3% formic acid solution. The methanol gradient conditions are as follows: 1% (0-0.5 min), 50% (20 min), 99% (21-31 min), and 1% (32-35 min). Calibration curves were prepared using five levels of working standard solutions containing the nine HAA compounds at identical concentrations of 1, 3, 10, 50, 70, and 100 µg/L.

Results and Discussion

Water quality characteristics of rivers in tropical area in Thailand

The water quality of three tropical rivers in Thailand are shown in **Table 1**. The results showed that all rivers had a pH of 7.1-8.0, a temperature of 28.8-32.7 °C, and conductivity (EC) of 160–250 µS/cm. The Tha-Chin River had the highest conductivity value, followed by the Chao Phraya River. The lowest level was found in the Mae-Klong River. Br^- concentrations varied from 18.22 to 44.79 µg/L. The highest values of Br^- are in the Tha-Chin River, followed by the Chao Phraya

Table 1 River water quality characteristics (Br^-, and DOC are expressed as average ± standard deviation in triplicate.)

Source water	pH	Temp. (°C)	EC. (µS/cm)	Br^- (µg/L)	DOC (mg/L)
Chao Phraya River	7.1	31.5	210	41.34 ± 1.17	4.85 ± 0.44
Tha-Chin River	7.3	28.8	250	44.79 ± 5.72	3.41 ± 0.02
Mae-Klong River	8.0	32.7	160	18.22 ± 1.75	2.07 ± 0.06

River, and the lowest in the Mae-Klong River. Most freshwater systems typically exhibit Br^- concentrations ranging from 10 to 500 µg/L [15, 17], whereas seawater typically maintains a concentration of 65 mg/L [18]. In other studies, Br^- in the range of 20-63 µg/L was reported for the Bangphakong River [19], 26.2 µg/L in the China Wu River, and 54.01 µg/L in the Qiantang River [20]. The highest value of conductivity was in the Tha-Chin River, followed by the Chao Phraya River and the Mae-Klong River. The conductivity had a positive relationship with Br^- concentrations. As a result, seawater intrusion from the Gulf of Thailand estuary or human activities might contribute to the high conductivity of the Tha-chin River and Chao Phraya River.

The DOC concentrations are at 4.85 mg/L for the Chao Phraya River, 3.41 mg/L for the Tha-Chin River and 2.07 mg/L for the Mae-Klong River. The Chao Phraya River had the highest value among all the three rivers. The high DOCs in the waters indicated the presence of a wide range of organic substances, resulting from complex interactions between natural processes and human activities, including the decay of vegetation, the impacts of eutrophication, the occurrence of algal blooms, and the release of wastewater. Nevertheless, the Mae-Klong River had the lowest DOC because of limited urban development along the river's path. Other research investigated water sources in Thailand and reported that the concentrations of DOC in river waters were 2 to 12 mg/L [21, 22], showing that the DOCs in the rivers examined in our study were within the range observed in previous research conducted in Thailand.

Haloacetic acid formation potential

Figure 2A shows the HAAFPs of the samples collected during the rainy season. Focusing on chlorinated HAA species (i.e., MCAA, DCAA, and TCAA), high DCAAFPs and TCAAFPs in the three source waters were found, while MCAAFPs were not quantified (less than LOQ at < 3µg/L). TCAAFPs in source waters collected from the Chao Phraya, Tha-Chin rivers, and Mae Klong were 165 µg/L, 103 µg/L, and 52 µg/L, respectively. In addition, DCAAFPs were 69 µg/L, 47 µg/L, and 25 µg/L, respectively. The orders of FPs were the same for DOC. The DCAAFPs in the Chao Phraya River largely exceeded the WHO guideline values in tap water (i.e., 50 µg/L) [23], suggesting that appropriate treatment is necessary for drinking of tap water. TCAAFPs in the Chao Phraya River were close to the WHO guideline (i.e., 200 µg/L) and in all three rivers considerably larger than regulations developed by several countries such as Japan (i.e., 30 µg/L), which means that TCAA is also needed to control for drinking of safe tap water.

Considering the total FP concentration, all three rivers had high HAA5 levels significantly exceeding the US EPA and EU regulations (i.e., 60 µg/L) [24], also strongly indicating the risk of DBPs in the tap water.

Moving to brominated HAA species (i.e., MBAA, BCAA, DBAA, BDCAA, DBCAA, and TBAA), only BCAAFP and BDCAAFP were quantified in all three rivers in this study, while the others were less than LOQ (1 µg/L). BCAAFP of the river waters of the Chao Phraya, Tha-Chin, and Mae Klong rivers were 4.12 µg/L, 4.73 µg/L, and 1.72µg/L respectively. BDCAAFP were 15.33 µg/L, 13.01 µg/L, and 6.20 µg/L, respectively. The magnitude relationship among them is the same as for chlorinated HAAs. Although the FPs were much lower than those of DCAAFPs and TCAAFPs (approximately one-tenth), it is not negligible considering their higher toxicity than the chlorinated forms. Although no standard or guideline values have been established for individual brominated HAAs, the substances are subject to monitoring in public water systems in many countries like U.S and Japan. The results of this study are the first successful determination of the brominated HAAFPs in raw waters in Thailand and will be valuable data for future water supply operations.

In a previous study conducted in China, TCAAFP was 168 µg/L and DCAAFP 236 µg/L in the Qiantang River [20]. Similarly, in Büyükçekmece Lake in Turkey, the levels of HAA5 were 87.0 µg/L, TCAAFP 23.9 µg/L, and DCAAFP 51.2 µg/L, respectively [25]. Comparatively, our study revealed that the levels of TCAAFPs in river waters in Thai were higher than DCAAFPs, meaning that the composition of the DOM may be different. Subsequently, the treatability may be different from the other areas, and a comprehensive treatment approach may need to be considered for ensuring the safety and proper water quality in the water supply system in Thailand.

Figure 2B shows the concentrations of HAAFPs per DOC in the three samples. The Chao Phraya, Mae Klong and Tha-Chin rivers had TCAAFPs of 31.2, 24.4, and 26.5 µg/mg C, and DCAAFP concentrations of 13.1, 11.1 and 12.0 µg/mg C, respectively. No significant differences were found between rivers. Not much difference was also found for brominated HAAFP. Since trihaloacetic acid FPs were greater than dihaloacetic acid FPs, major precursors of HAAs were likely to have aromatic moieties.

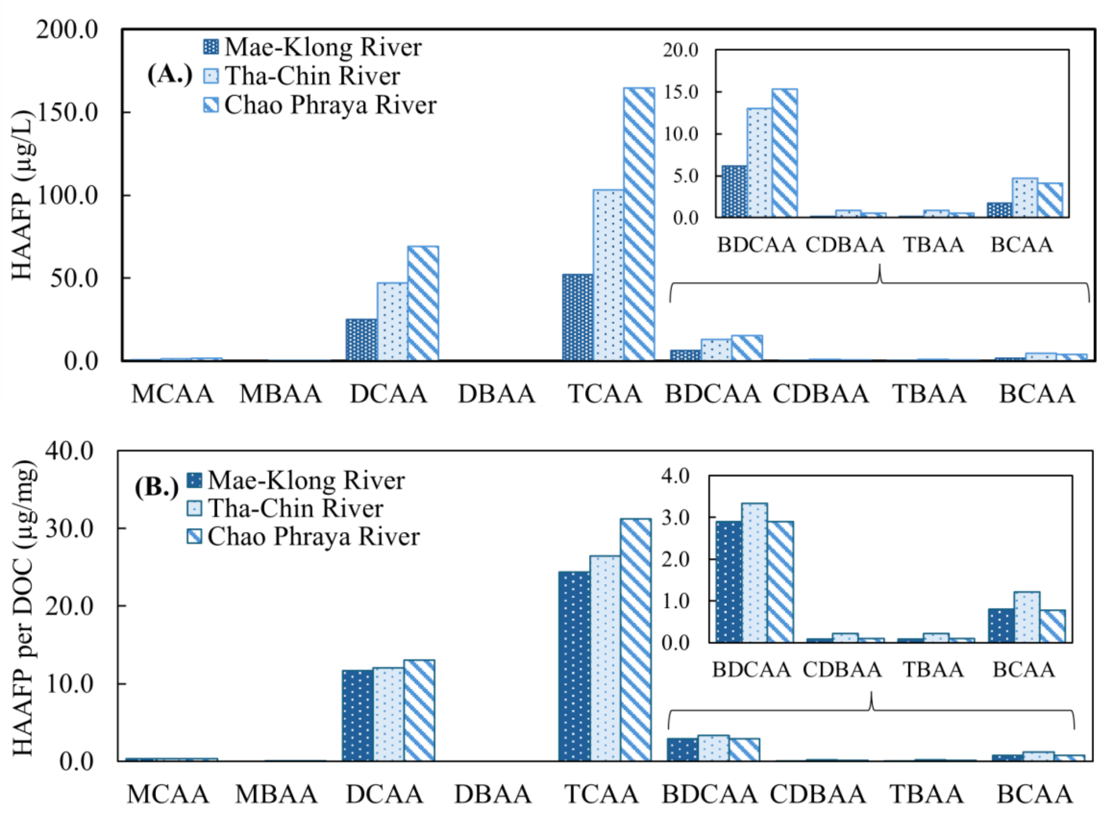

Figure 2 (A) HAAFPs and (B) HAAFPs per DOC of the river waters

Figure 3A illustrates the correlation between the sum of HAAFP per DOC and DOC levels in the Chao Phraya River, Mae- Klong River and Tha-chin River. Figure 3B depicts the correlation between the values of brominated HAAFP/DOC and the concentration of bromide ions. The Tha-Chin River displays a notable presence of brominated HAAFP, characterized by elevated levels of bromide ions. Consequently, after chlorination, the Br^- levels exhibited an increasing proportion of brominated HAA compared to chlorinated HAAFP. These results suggest that the concentration of DOC and Br^- have an impact on the increase in the HAAFP. The presence of Br^- specifically causes a shift in the distribution of HAAs towards more brominated species, leading to an increase of brominated HAAs [25].

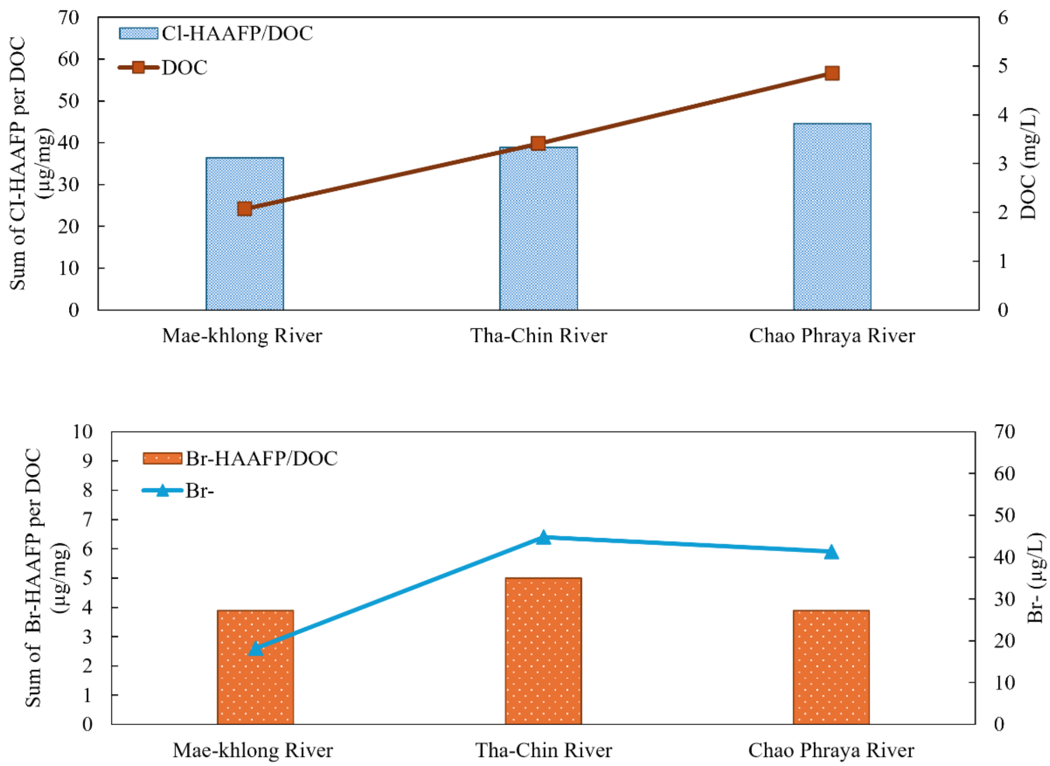

Figure 3 Relationships between (A) the sum of HAAFPs per DOC and DOC, (B) the sum of only brominated HAAs and Br^- concentrations

HAAFP percentage occurring in three tropical rivers in Thailand

Figure 4 displays the distribution percentage of HAAFPs in the three rivers: the Chao Phraya, Tha-Chin, and Mae Klong rivers. The patterns of HAAFPs were similar across all rivers, with TCAAFP and DCAAFP predominantly comprising over 90% of all HAAFPs. The identified HAAFP types included TCAAFP, DCAAFP, BDCAAFP, and BCAAFP. TCAAFP was the most prevalent, accounting for approximately 60%–64% across the three rivers, with the highest proportion found in the Chao Phraya River. DCAAFP comprises 27%–29% of the total, with the highest proportion observed in the Mae-Klong River. BDCAAFP accounts for 6%–7.6% and is most commonly found in the Tha-Chin River, while BCAAFP constitutes 1.6%–2.7%. Additionally, other HAAFP types are present in minute amounts, including MCAA (0.6%–0.8%), CDBAAFP (0.21%–0.50%), TBAAFP (0.21%–0.50%), MBAAFP (0.06%–0.14%), and DBAA (< detection limit).

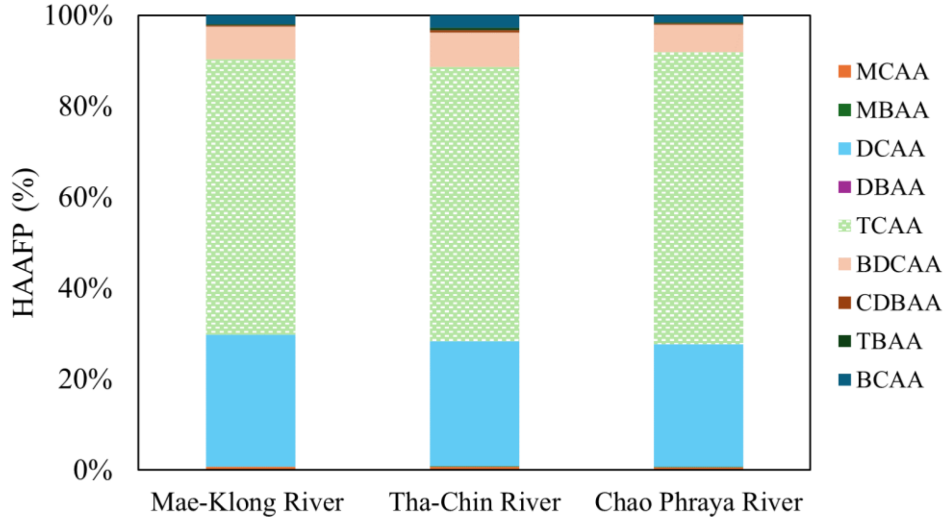

Figure 4 The percentage of HAAFP in tropical rivers in Thailand

Conclusion

A significant finding is the presence of Br^{-} in tropical rivers in Thailand, with concentrations detected in the Tha-Chin (44.79 µg/L), Chao Phraya (41.34 µg/L) and Mae-Klong rivers (18.22 µg/L). The bromide ion concentrations of these rivers were influenced by seawater intrusion from the Gulf of Thailand.

The occurrence of TCAAFP, DCAAFP, BDCAAFP and BCAAFP were identified in these rivers, with HAA5 (the sum of chlorinated HAAs, MBAA and DBAA were not detected.) levels significantly exceeding the US EPA and EU regulations (60 µg/L). DCAAFPs in the Chao Phraya River exceeded WHO guideline values (50 µg/L), indicating treatment is necessary for drinking tap water. TCAAFPs in the Chao Phraya River were close to WHO guidelines (200 µg/L) but in all three rivers greatly exceeded the regulations in Japan's regulations (30 µg/L), which means that TCAA is also needed to monitor for safe tap water. The HAAFP distribution in the Chao Phraya, Tha-Chin, and Mae Klong rivers shows TCAAFP (60%–64%) and DCAAFP (27%–29%) as the most prevalent, with minor contributions from BDCAAFP, BCAAFP. The presence of Br^{-} in river samples, notably in the Tha-Chin River, correlated with increased levels of brominated HAAFP (BDCAAFP, BCAAFP), indicating a positive correlation between Br^{-} levels and HAAFP formation.

Consequently, using chlorine in the water treatment process in the presence of Br^{-} can lead to the formation of brominated HAAFP, posing potential health risks. Therefore, the significant formation of brominated HAAFP is considerable in water sources with increased bromide levels. To build upon these findings, further research should extend the duration of data collection and incorporate information on rainfall amounts at each sampling site. Precipitation significantly impacts seawater intrusion and Br^{-} concentrations. A thorough understanding of these dynamics is essential for a comprehensive analysis of their influence on water quality. This approach will elucidate the relationship between environmental conditions and the formation of DBPs, ultimately leading to more efficient water treatment strategies.

Acknowledgement

The authors are grateful to the On-Site Laboratory Initiative of the Graduate School of Global Environmental Studies at Kyoto University for additional funding. Additionally, this study was financially supported by JSPS KAKENHI (Grant Numbers JP23K04088).

References

[1] Krasner, S.W., Westerhoff, P., Chen, Z., Amy, G., and Croué, J.P. 2006. Occurrence of a new generation of disinfection byproducts. Environmental Science & Technology, 40(23): 7175-7185.

[2] Richardson, S.D., Plewa, M.J., Wagner, E.D., Schoeny, R., and DeMarini, D.M. 2007. Occurrence, genotoxicity, and carcinogenicity of regulated and emerging disinfection by-products in drinking water: A review and roadmap for research. Mutation Research, 636 (1-2): 178-242.

[3] Park, K.-Y., Kim, J., Lee, Y., and Shin, H. 2019. Natural organic matter removal from algal-rich water and disinfection by-products formation potential reduction by powdered activated carbon adsorption. Journal of Environmental Management, 235: 310-318.

[4] Liang, L. and Singer, P.C. 2003. Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. Environmental Science & Technology, 37(13): 2920-2928.

[5] Ersan, M.S., Wols, B., Harmsen, D., and Medema, G. 2019. The interplay between natural organic matter and bromide on bromine substitution. Science of the Total Environment, 646: 1172-1181.

[6] Kumar, K. and Margerum, D.W. 1987. Kinetics and mechanism of general-acid-assisted oxidation of bromide by hypochlorite and hypochlorous acid. Inorganic Chemistry, 26(16): 2706-2711.

[7] Liu, Y., Yu, L., Huang, J., and Wang, Y. 2022. Formation of regulated and unregulated disinfection byproducts during chlorination and chloramination: Roles of dissolved organic matter type, bromide, and iodide. Journal of Environmental Sciences, 117: 151-160.

[8] Cowman, G.A. and Singer, P.C. 1995. Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances. Environmental Science & Technology, 30(1): 16-24.

[9] Alsulaili, A.D. 2009. Impact of bromide, NOM, and pre-chlorination on haloamine formation, speciation, and decay during chloramination. Water Research, 43(5): 1432-1440.

[10] Heller-Grossman, L., Heller, M., and D. S. M. Barak. 1993. Formation and distribution of haloacetic acids, THM, and TOX in chlorination of bromide-rich lake water. Water Research, 27(8): 1323-1331.

[11] Westerhoff, P., Chao, P., and Mash, H. 2004. Reactivity of natural organic matter with aqueous chlorine and bromine. Water Research, 38(6): 1502-1513.

[12] Siddiqui, M.S., Amy, G.L., and Rice, R.G. 1995. Bromate ion formation: a critical review. Journal - American Water Works Association, 87(10): 58-70.

[13] Sohn, J., Amy, G., and Yoon, Y. 2006. Bromide ion incorporation into brominated disinfection by-products. Water, Air, and Soil Pollution, 174(1-4): 265-277.

[14] Liu, S., Zhang, Y., Wang, Y., and Chen, Y. 2011. Seasonal variation effects on the formation of trihalomethane during chlorination of water from Yangtze River and associated cancer risk assessment. Journal of Environmental Sciences (China), 23(9): 1503-1511.

[15] Kampioti, A.A. and Stephanou, E.G. 2002. The impact of bromide on the formation of neutral and acidic disinfection by-products (DBPs) in Mediterranean chlorinated drinking water. Water Research, 36(10): 2596-2606.

[16] Tada, Y., Nakagawa, T., Matsumoto, S., and Sakurai, K. 2023. High formation of trichloroacetic acid from high molecular weight and ultra-hydrophilic components in freshwater raphidophytes upon chlorination. Science of the Total Environment, 879: 163000.

[17] Cowman, G.A. and Singer, P.C. 1995. Effect of bromide ion on haloacetic acid speciation resulting from chlorination and chloramination of aquatic humic substances. Environmental Science & Technology, 30(1): 16-24.

[18] Kharkar, D., Turekian, K.K., and Bertine, K.J. 1968. Stream supply of dissolved silver, molybdenum, antimony, selenium, chromium, cobalt, rubidium, and cesium to the oceans. Geochimica et Cosmochimica Acta, 32(3): 285-298.

[19] Marhaba, T.F., Murthy, S.K., and Parulekar, S.J. 2006. Trihalomethanes formation potential of shrimp farm effluents. Journal of Hazardous Materials, 136(2): 151-163.

[20] Zheng, L., Xu, Z., Huang, Y., and Zhang, H. 2020. Precursors for brominated haloacetic acids during chlorination and a new useful indicator for bromine substitution factor. Science of the Total Environment, 698: 134250.

[21] Volk, C., Hübner, U., and Koch, C. 2002. Monitoring dissolved organic carbon in surface and drinking waters. Journal of Environmental Monitoring, 4(1): 43-47.

[22] Wang, Y., Small, M.J., and VanBriesen, J.M. 2017. Assessing the risk associated with increasing bromide in drinking water sources in the Monongahela River, Pennsylvania. Journal of Environmental Engineering, 143(3): 04016089.

[23] World Health Organization. 2011. WHO Guidelines for Drinking-Water Quality, 4th edition. Geneva: World Health Organization.

[24] U.S. Environmental Protection Agency. 2010. Stage 2 Disinfectants and Disinfection By-Products Rule: A Quick Reference Guide for Schedule 1 Systems. EPA 815-K-09-003.

[25] Uyak, V. and Toroz, I. 2007. Investigation of bromide ion effects on disinfection by-products formation and speciation in an Istanbul water supply. Journal of Hazardous Materials, 149(2): 445-451.