รายงานวิจัยฉบับสมบูรณ์

โครงการ การก่อตัวของสารพลอยได้กลุ่มคาร์บอนและไนโตรเจนจากการฆ่าเชื้อโรคของกลุ่มสารอินทรีย์ละลายน้ำ

Formation of Carbonaceous and Nitrogenous Disinfection by-products of Fractionated Dissolved Organic Matter

โดย

รองศาสตราจารย์ ดร. จรงค์พันธ์ มุสิกะวงศ์

มิถุนายน 2562

สัญญาเลขที่ RSA5980047

รายงานวิจัยฉบับสมบูรณ์

โครงการ การก่อตัวของสารพลอยได้กลุ่มคาร์บอนและไนโตรเจนจากการฆ่าเชื้อโรคของกลุ่มสารอินทรีย์ละลายน้ำ

Formation of carbonaceous and nitrogenous disinfection by-products of fractionated dissolved organic matter

โดย

รองศาสตราจารย์ ดร. จรงค์พันธ์ มุสิกะวงศ์

ภาควิชาวิศวกรรมโยธา คณะวิศวกรรมศาสตร์
มหาวิทยาลัยสงขลานครินทร์ วิทยาเขตหาดใหญ่

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัยและมหาวิทยาลัยสงขลานครินทร์
(ความเห็นในรายงานนี้เป็นของผู้วิจัย สกว. และมหาวิทยาลัยสงขลานครินทร์ ไม่จำเป็นต้องเห็นด้วยเสมอไป)

บทคัดย่อ

งานวิจัยนี้มีวัตถุประสงค์เพื่อประเมินโอกาสการก่อตัวของสารผลพลอยได้จากการฆ่าเชื้อโรค (disinfection by-products formation potential, DBPFP) ชนิดใหม่ในน้ำดิบจากระบบประปากรุงเทพมหานครและสิงห์บุรี น้ำจากแม่น้ำเจ้าพระยา และน้ำเสียชุมชนและน้ำทิ้งจากระบบบำบัดน้ำเสียชุมชนในจังหวัดอ่างทองและอยุธยา ประเทศไทย งานวิจัยนี้เก็บน้ำตัวอย่าง 3 ครั้งเพื่อทำการวิเคราะห์ค่า trihalomethane formation potential (THMFP) iodo-THMFP (I-THMFP) haloacetronitrile formation potential (HANFP) trichloronitromethane formation potential (TCNMFP) ตลอดจนได้วิเคราะห์ค่า DBPFP ของกลุ่มสารอินทรีย์ที่มีน้ำหนักโมเลกุล (molecular weight, MW) > 10 kDa 3 kDa < MW < 10 kDa 1 kDa < MW < 3 kDa และ MW < 1 kDa และ hydrophobic organic fraction (HPO) transphilic organic fraction (TPI) และ hydrophilic organic fraction (HPI) สารส้ม สารส้มร่วมกับถ่านกัมมันแบบผง (powder activated carbon, PAC) และสารส้มร่วมกับ magnetic ion exchange (MIEX) ถูกนำมาใช้เพื่อลดสารอินทรีย์ กลุ่มสารอินทรีย์ และ DBPFP นอกจากนี้ได้ศึกษาจลนศาสตร์การก่อตัวของสารผลพลอยได้จากการฆ่าเชื้อโรค (disinfection by-products, DBPs) ของน้ำดิบ น้ำดิบที่ผ่านการบำบัด และกลุ่มสารอินทรีย์ THMFP ของน้ำจากแม่น้ำ น้ำเสีย และน้ำทิ้ง มีค่าค่อนข้างสูง ค่าเฉลี่ย THMFP I-THMFP HANFP และ TCNMFP ของน้ำทิ้งจากระบบบำบัดน้ำเสียมีค่าสูงกว่าค่าดังกล่าวของน้ำดิบประมาณ 2 เท่า 3 ถึง 7 เท่า 1 ถึง 3 เท่า และ 6 ถึง 13 เท่า ตามลำดับ ดังนั้นควรมีการดำเนินการป้องกันและควบคุมน้ำทิ้งจากระบบบำบัดน้ำเสียที่จะปนเปื้อนสู่น้ำดิบ ค่าความเข้มข้นของ THMFP มีค่าสูงที่สุด HANFP มีค่า lethal concentration 50- weighted และ lowest cytotoxicity-weighted concentrations สูงที่สุดในกลุ่ม DBPs สารอินทรีย์กลุ่ม 1 kDa < MW < 3 kDa มีค่า THMFP/DOC I-THMFP/DOC HANFP/DOC และ TCNMFP/DOC สูง สารอินทรีย์กลุ่ม 3 kDa < MW < 10 kDa มีค่า I-THMFP/DOC HANFP/DOC และ TCNMFP/DOC สูง TPI มีค่า THMFP/DOC I-THMFP/DOC และ TCNMFP/DOC สูง ส่วน HPI และ HPO มีค่า HANFP/DOC และ TCNMFP/DOC สูง ตามลำดับ สารส้ม 80 และ 100 mg/L ควบคุมพีเอชที่ 7 เป็นสภาวะที่เหมาะสมในการโคแอกกูเลชันน้ำดิบและน้ำทิ้งตามลำดับ การเพิ่มประสิทธิภาพการโคแอกกูเลชันด้วยสารส้มโดย PAC มีสภาวะที่เหมาะสมที่สารส้มและ PAC 80 mg/L และ 40-80 mg/L และ 100 mg/L และ 80 – 100 mg/L สำหรับน้ำดิบและน้ำเสียตามลำดับ การเพิ่มประสิทธิภาพการโคแอกกูเลชันด้วยสารส้มโดย MIEX มีสภาวะที่เหมาะสมที่สารส้มและ MIEX 80 mg/L และ 2-4 mL/L และ 100 และ 4-6 mL/L สำหรับน้ำดิบและน้ำเสียตามลำดับ การเพิ่มประสิทธิภาพการโคแอกกูเลชันด้วยสารส้มโดย MIEX ลดค่าสารอินทรีย์ กลุ่มสารอินทรีย์ DBPFP และ กลุ่มชนิดสารอินทรีย์ได้ดีที่สุด Iodo-trihalomethanes (I-THMs) ของน้ำดิบไม่มีการก่อตัวเมื่อไอโอไดด์อยู่ในช่วง 0.5 ถึง 5 μg/L THMFP มีค่าเพิ่มสูงขึ้นเมื่อค่าโบรไมด์เพิ่มจาก 0.1 ถึง 1 mg/L และค่า THMFP มีแน้วโน้มลดลงเมื่อค่าโบรไมด์เพิ่มจาก 1 ถึง 10 mg/L ค่า I-THMFP ลดลงเมื่อค่าโบรไมด์เพิ่มจาก 0.1 ถึง 10 mg/L อัตราจลศาสตร์ของ THMFP เป็นไปตามปฏิกิริยาอันดับที่ศูนย์และหนึ่ง ค่าการก่อตัวของ THMs ของน้ำดิบมีแนวโน้มคงที่ระหว่าง 3 ถึง 72 ชั่วโมง อัตราจลศาสตร์รูปแบบสองขั้นตอนประกอบด้วยการก่อตัว (ปฏิกิริยาอันดับที่ศูนย์) ตามด้วยการสลาย(ปฏิกิริยาอันดับที่หนึ่ง) เป็นอัตราจลศาสตร์ของ THMFP ของน้ำที่ผ่านการบำบัด I-THMFP ของน้ำดิบ และ น้ำที่ผ่านการบำบัด และHANFP ของน้ำทิ้งจากระบบบำบัดน้ำเสีย ปฏิกิริยาอันดับที่ศูนย์เป็นอัตราจลศาสตร์ของการก่อตัวของสาร trihalomethanes (THMs) ของกลุ่มสารอินทรีย์ MW > 10 kDa 3 kDa < MW < 10 kDa 1 kDa < MW < 3 kDa และ MW < 1 kDa ปฏิกริยาอันดับที่ศูนย์เป็นอัตราจลศาสตร์ของการสลายของ BCIM ของกลุ่มสารอินทรีย์ MW < 1 kDa อัตราจลศาสตร์รูปแบบสองขั้นตอน ประกอบด้วยการก่อตัว (ปฏิกิริยาอันดับที่ศูนย์) ตามด้วยการสลาย (ปฏิกิริยาอันดับที่หนึ่ง) เป็นอัตราจลศาสตร์ของ HANFP การก่อตัวของสาร THMs ของ HPI และ TPI อธิบายได้โดยปฏิกิริยาอันดับที่ศูนย์ และ ปฏิกิริยาอันดับที่หนึ่ง ตามลำดับ อัตราจลศาสตร์ของ THMs ของ HPO ขึ้นอยู่กับแต่ละ THMs species. I-THMs ของ HPO และ TPI มีการก่อตัวด้วยปฏิกิริยาอันดับที่ศูนย์ตามด้วยปฏิกิริยาอันดับที่หนึ่ง I-THMs ของ HPI มีการสลายตามปฏิกิริยาอันดับที่ศูนย์ การก่อตัวของ haloacetronitrile อธิบายได้โดยปฏิกิริยาอันดับที่ศูนย์

Abstract

This research aimed at assessing emerging disinfection by-products formation potential (DBPFP) in raw water (RW) from the Bangkok and Sing Buri water treatment plants, water from Chao Phraya River, domestic wastewater (WW), and treated domestic wastewater from Ang Thong and Ayutthaya provinces in Thailand. Water samples were collected three times for determining trihalomethane formation potential (THMFP), iodo-THMFP (I-THMFP), haloacetronitrile formation potential (HANFP), trichloronitromethane formation potential (TCNMFP). DBPFPs of dissolved organic matter (DOM) fractions with molecular weight (MW) > 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa and hydrophobic organic fraction (HPO), transphilic organic fraction (TPI), and hydrophilic organic fraction (HPI) were investigated. The reductions of DOM, DOM fractions, and DBPFP by alum coagulation, alum coagulation with powder activated carbon (PAC), and alum coagulation with magnetic ion exchange (MIEX) were investigated. The kinetics of disinfection by-products formation of raw water, treated water, and DOM fractions were determined. High THMFP level of river water, WW, TWW and wastewater were detected. Considering average value, the THMFP, I-THMFP, HANFP, and TCNMFP of TWW were about two times, three to seven times, one to three times, and six to thirteen times higher than that of RW. The prevention and control methods must be established for the discharging of TWW to RW. The highest DBPs based on measured weight concentration was determined for THMFP. HANFP was found as the highest lethal concentration 50- weighted and lowest cytotoxicity-weighted concentrations of DBPs. DOM with 1 kDa < MW < 3 kDa has a high THMFP/DOC, I-THMFP/DOC, HANFP/DOC, and TCNMFP/DOC. DOM with 3 kDa < MW < 10 kDa has a high I-THMFP/DOC, HANFP/DOC, and TCNMFP/DOC. TPI has a high THMFP/DOC, I-THMFP/DOC, and TCNMFP/DOC. HPI and HPO have a high HANFP/DOC and TCNMFP/DOC, respectively. Alum coagulation at a dosage of 80 and 100 mg/L under control pH at 7 was the optimal condition for raw water and treated wastewater, respectively. The optimal condition of enhanced alum coagulation by PAC were determined at 80 and 40 – 80 and 100 and 80 – 100 (alum and PAC in mg/L) for raw water and treated wastewater, respectively. The optimal condition of enhanced alum coagulation by MIEX were found at 80 and 2-4 and 100 and 4-6 (alum in mg/L and MIEX in ml/L) raw water and treated wastewater, respectively. Enhanced alum coagulation by MIEX provided the best reduction of DOM, DOM fraction, DBPFP, and chemical classes of DOM. Iodo-trihalomethanes (I-THMs) of raw water did not form when the iodide increase from 0.5 to 5 μg/L. THMFP increased when Br- increased from 0.1 to 1 mg/L; then it decreased when Br- increased from 1 to 10 mg/L. The I-THMFP decreased by increasing Br^- from 0.1 to 10 mg/L. The kinetic rates of THMFP of raw water explained by zero-order and first-order reactions. THMFP formation from 3 to 72 h was considerably constant. A two-stage pattern including a formation (the zero-order kinetic) and degradation (the first-order kinetic) rate was determined for THMFP of treated water, I-THMFP of raw water and its treated water, and HANFP of raw water and treated wastewater. The zero-order kinetics of THM formation of DOM fractions with MW > 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa were assessed. The zero-order kinetic of BCIM degradation was determined for DOM with MW < 1 kDa. A zero-order kinetic of HAN formation followed first-order kinetic of HAN degradation were determined. THMs formation of HPI and TPI expressed by first-order kinetic and zero-order kinetics, respectively. The kinetic of THMs of HPO based on individual THMs species. I-THMs of HPO and TPI have a formation pattern (a zero- and first-order kinetic). I-THMs of HPI have a degradation pattern (zero-order kinetic). HANs formation of HPI could be expressed by a zero-order kinetic.

Executive Summary

1. Background and rationale

Water supply is essential for human life. Quality of water supply depends on the quality of raw water and the performance of the water treatment process on the removal of contaminants. In general, a water treatment plant (WTP) is located nearby water sources and far from the city. Concerning the outward expansion of cities and industries, river water as one of the sources of raw water are facing the more complex problem of contaminations from wastewater and treated wastewater discharges. This is because wastewater and treated wastewater could increase the level of dissolved organic matter (DOM) and bromide into the source of raw water. In some areas, levels of salinity in raw water are moderately high according to sea-level rise could increase the level of iodide. The wastewater and treated wastewater discharges and sea-level rise must be shortly inevitable for the WTP.

The reaction between DOM and chlorine causes the formation of carbonaceous and nitrogenous disinfection by-products (DBPs) (Rook, 1974). DOM in water composed of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) (Lee and Westerhoff, 2006). Trihalomethanes (THMs) is traditional carbonaceous DBPs (C-DBPs). THMs include chloroform, bromodichloromethane (BDCM), dibromochloro-methane (DBCM), and bromoform. The THMs standards of 80 and 100 µg/L in drinking water have been set by the United States Environmental Protection Agency (US. EPA, 1998) and European Union (EU) (EU, 1997), respectively. The World Health Organization (WHO) has set health-related guideline values of 200, 60, 100, and 100 µg/L for chloroform, BDCM, DBCM, and bromoform, respectively (WHO, 1996). The Metropolitan Waterworks Authority (MWA), Thailand, uses this guideline as the reference standard.

The reaction of between DOM and chlorine or chloramines can produce nitrogenous DBPs (N-DBPs) such as halonitromethanes (HNMs) and haloacetonitriles (HANs) such as trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN). WHO has set guideline values of 20 and 70 µg/L for DCAN and DBAN, respectively (WHO, 2008). HNMs consist of chloronitromethane, dichloronitro-methane, trichloronitromethane, bromochloronitromethane, bromodichloronitromethane, bromonitromethane, dibromonitromethane, dibromochloronitromethane, and tribromonitro-methane. HMNs were detected in low concentration in compared with that of THMs and haloacetic acids (HAAs). HMNs have not been regulated. However; cytotoxicity and genotoxicity caused by HNMs are comparable or even higher when compared with that of THMs and HAAs (Krasner et al., 2006; Richardson et al., 2007). Iodoform (triiodomethanes, TIM) can form during the oxidative treatment of this water in the presence of iodide. Fives iodated trihalomethanes (iodo-THMs) have been found in disinfected water: bromochloro-iodomethane (BCIM); chlorodiiodomethane (CDIM); dibromoiodomethane (DBIM); di-chloroiodomethane (DCIM); and bromidiiodomethane (BDIM) (Richardson et al., 2007; and Krasner et al., 2006). The cytotoxicity and genotoxicity of iodo-THMs in mammalian cells assays were higher than that of brominated and chlorinated analogues (Bichsel and Gunten, 2000; Cancho et al., 2000).

The formation of DBPs depends on the quantity and nature of DOM. DOC, ultraviolet absorbance at wavelength 254 nm (UV-254), specific ultraviolet absorption (SUVA), and DON have been used to determine quantities of DOM. The trihalomethane formation potential (THMFP, haloacetonitilre formation potential (HANFP), halonitromethane formation potential (HNMFP), and iodo-trihalomethane formation potential (I-THMFP) are used to determine complete reactions between DOM and chlorine for producing DBPs. For the nature of DOM, the resin fractionation technique can separate DOM into three fractions: hydrophobic organic fraction (HPO; transphilic organic fraction (TPI); and hydrophilic organic fraction (HPI) (Aiken and McKnight, 1992; Lee et al., 2004. The ultrafiltration (UF) membrane can fractionate DOM into several groups according to molecular weight (MW) cut-offs of 30, 10, 5, 3 and 1 kDa (Xu, et al., 2011. By conducting disinfection by-products formation potential (DBPFP) on DOM fractions the reactivity of DOM fractions on forming DBPs can be determined.

A three-dimensional fluorescent spectroscopy analysis, the use of fluorescent excitation-emission matrix, FEEM), has been used to classify DOM into tyrosine-like, tryptophan-like, and humic and fulvic acid-like substances (Chen et al., 2003; Musikavong et al., 2007). In terms of chemical classes, pyrolysis gas chromatography-mass spectrometer (GC/MS) has been used to identify the putative origin and chemical classes of DOM. (Musikavong and Wattanachira, 2013). The putative origin of DOM in water that could form DBPs can be determined by the pyrolysis GC/MS analysis. The study of the putative origin of DOM on the formation of HMNs, and I-THMs has been limited recently.

The water treatment process in Thailand uses coagulation, sedimentation, filtration, and chlorination. Poly aluminium chloride (PACl) and alum have been used as the coagulant. The filtration media is uniform sands. The principal focus of a WTP is to reduce turbidity and suspended solids. Concerning the complex problem of raw water contamination, sometimes the powder activated carbon (PAC) has been used after coagulation. To produce the safe water supply from C-DBPs and N-DBPs, the investigation of optimal condition for reduction of precursors of DBPs and the level DBPs are considerably important. The Bangkhen WTP is the largest plant in Thailand and uses raw water from the Chao Phraya River. The water supply of about 3.7 million m^3/day is produced and distributed to around six million people in Bangkok and nearby provinces.

Raw water of the Bangkhen WTP is drawn from the Chao Phraya River at Phathumthani Province and flows along the canal of the plant. The raw water of the Bangkhen WTP can be contaminated with the wastewater and treated wastewater from communities and industries at the upstream locations. Due to the sea level rise, sometimes, the level of salinity of raw water is moderately high. Iodide was detected in seawater, urine, and wastewater effluent (Gong and Zhang, 2013). When the Chao Phraya River is contaminated with seawater, urine, wastewater effluent, together with using chlorine as a disinfectant in the water treatment process, then this can cause the formation of C-DBPs and N-DBPs in the water supply.

The putative origins of DOM and the formation of THMs, I-THMs, HANs, and HNMs, of 1) wastewater, treated wastewater that has potentially discharge to the Chao Phraya River, 2) raw water of the Bangkhen WTP, 3) coagulated water by PACl, alum and another coagulant,

and 4) coagulated water by PACl or alum with PAC or magnetic ion exchange (MIEX) resin have never been reported. In addition, the study on the formation of THMs, I-THMs, HANs, and HNMs of raw water of the Bangkhen WTP under the variation of pH, iodide and bromide concentrations, reaction times, DOC, and DON have been limited and must be investigated. This information and knowledge can be a help to support the operation and control of the water treatment plant in Thailand.

2. Objectives

- To identify characteristics and structure of DOMs in water samples including raw water and coagulated water of the Bangkhen WTP, domestic wastewater, and treated wastewater by using resin fractionation, UF fractionation, pyrolysis GC/MS, and FEEM techniques.
- To determine the formations of THMs, I-THMs, HANs, and HNMs of water samples.
- To determine the formations of THMs, HANs, I-THMs, and HNMs of HPO, TPI, HPI, group of DOM fractions by the UF technique: molecular weight (MW) < 1 kDa fraction; 1 kDa < MW <3 kDa; 3 kDa < MW <10 kDa; and MW > 10 kDa of water samples.
- To determine the effect of iodide and bromide concentrations, DOC, DON, DOC/DON, and reaction time on the formation of THMs, HANs, I-THMs, and HNMs.

3. Research methodology

Raw waters from the Chao Phraya River were collected from the pumping station of Bangkhen WTP (BK WTP) at a downstream location (RW−1) and Singburi WTP (SB WTP) at an upstream location (RW−2). Water supply (WS) samples were collected from the water supply of Bangkhen WTP. Water samples from the river were obtained from the Siriraj sampling site, which is located downstream of the Chao Phraya River after the BK WTP. This sample stands for water with seawater, treated and untreated wastewater contamination**.** Domestic wastewater before (WW−1) and after treated wastewater (TWW−1) were collected from the WWTP in Ang Thong (AT) province. In addition, domestic wastewater before **(**WW−2**)** and treated wastewater **(**TWW−2**)** were obtained from the WWTP in Ayutthaya (AY) province. These two WWTPs are located in the upstream location of the Chao Phraya River. The wastewater and treated wastewater represent the sources of contamination from human activities**.** Water samples were collected in October 2016, May 2017, and February 2018 as the representative of the study during the rainy season, summer, and winter, respectively. The water supply samples were collected in October 2016 and May 2017. The experimental procedures are divided into three main experiments.

The first experiment is the identification of precursors of C-DBPs and N-DBPs and formation of C-DBPs and N-DBPs. The water samples including raw water, water supply, wastewater, treated wastewater, and river water for the first, second and third samplings were analyzed for their pH, turbidity, salinity, and alkalinity. Then, water samples, except water supply, were filtered using GF/F and analyzed for their DOC, DON, FEEM, bromide, iodide,

THMFP, HANFP, I-THMFP, and HNMFP. Raw water and treated wastewater were analyzed for their chemical classes (pyrolysis GC/MS). Water samples at the first and second samplings, except water supply, were fractionated using the resin fractionation technique into three fractions: HPO, TPI and HPI (Aiken and McKnight, 1992) and using a UF technique to obtain DOM into four groups: MW < 1kDa, 1 kDa < MW < 3 kDa, 3 kDa < MW < 10 kDa, and MW > 10 kDa (Xu, et al., 2011). These DOM fractions were analyzed for their DOC, FEEM, THMFP, HANFP, HMNFP, and I-THMFP. The weight measured concentration of water samples and their DOM fractions in terms of lethal concentration 50-weighted of DBPs, and lowest cytotoxicity-weighted concentrations of DBPs were evaluated.

For the second experiment, the reduction of precursors of C-DBPs and N-DBPs were carried out. The raw water of Bangkhen WTP (RW−1) at the first, second, and third samplings, treated wastewater (TWW− 1) from Ang Thong and Ayutthaya (AY) provinces, and (RW−1) nixed with TWW−1 (AY) (50% v/v) were used in the experiments. The water samples were coagulated by using five alum dosages of 5 –120 mg/L under controlled pH of 7. The optimal dosage for turbidity removal was determined. Then the supernatants were filtered through 0.7 µm GF/F filter and measured for their DOC and DON. The optimal dosage of DOC and DON removal was determined. The enhanced coagulations by PAC and MIEX were performed using alum dosage at optimal DOC and DON reductions on the variation dosage of PAC and MIEX between 10-120 mg/L and 0.5-6 mL/L respectively.

The coagulated water under the optimal turbidity reduction (CW−1), the coagulated water under the optimal DOC and DON reductions (CW−2), and the coagulated water under optimal condition of enhanced PAC or MIEX coagulation (CW−3), were analyzed for their DOC, DON, I-, Br-, FEEM, chemical classes, THMFP, HANFP, I-THMFP, and HNMFP. The CW−1, CW−2, and CW−3 were fractionated using resin and UF fractionation techniques. The HPO, TPI, HPI, and DOM of four groups: MW < 1kDa, 1 kDa < MW < 3 kDa, 3 kDa <MW < 10 kDa, and MW > 10 kDa of selected samples were measured for their DOC, FEEM, THMFP, HANFP, ITHMFP, and HNMFP.

In the third experiment, the effect of iodide and bromide concentrations, DOC, and DON of reaction on the formation of C-DBPs and N-DBPs was conducted. The variation parameters were iodide, bromide, DOC, DON, DOC/DON, and reaction times. The raw water samples (RW−1 and RW−2, BK), treated wastewater (TWW−1 (AT) and TWW−1 (AY)) were used for this experiment. For the formation of C-DBPFP and N-DPBFP analysis, treated wastewater (TWW−1, AY) was used to mix raw water of the WTP (RW−1, BK) to obtain water samples that have DOC (~3.2 to 5.6 mg/L), DON (~0.20 to 1.22 mg N/L), and DOC/DON (~5 to 29). The iodide and bromide were added into the raw water of the WTP (RW−1, BK) to obtain water samples that have iodide (~0.5 to 5 µg/L) and bromide (~0.1 to 10 mg/L). All water samples of each experiment were measured for their THMFP, HANFP, I-THMFP, and HNMFP. For the kinetic of precursors on the formation of DBPs analysis, the coagulated water from Bangkhen WTP was fractionated. The coagulated water, HPO, TPI, HPI and DOM with MW < 1 kDa, 1 kDa < MW < 3 kDa, 3 kDa < MW < 10 kDa, and MW > 10 kDa were carried out the DBPFP test at the reaction times from 3 to 72 hr.

4. Results and discussion

4.1 C-DBPFP and N-DBPFP in raw water, wastewater, and treated wastewater

The pH levels of water samples ranged from 7.0 to 8.2. The average value of turbidity of the water supply of 1.5 was determined. The salinity was not detected in the raw water at the upstream location. Salinity between 0.1 and 0.4 was detected in water samples. On average, DOCs of 3.8, 3.8, and 4.8 mg/L were detected in raw water of the Bangkhen WTP and Singburi WTP, and river water at the downstream location, respectively. DOC of 5.3 and 7.4 mg/L of wastewater and 7.0 and 4.8 mg/L of treated wastewater were detected from the domestic WWTPs in Ang Thong and Ayutthaya, respectively. DONs of 0.28, 0.19, and 0.25 mg N/L were detected in raw water of the Bangkhen WTP and Singburi WTP, and river water, respectively. DONs of 1.49 and 0.74 mg N/L of wastewater and 1.31 and 0.74 mg N/L of treated wastewater were detected from the domestic WWTPs in Ang Thong and Ayutthaya, respectively.

Average values of bromide of 36, 42, and 19 µg/L were detected in raw water of the Bangkhen WTP, and Singburi WTP, and river water, respectively. On average, bromide of 2,126 and 4,178 mg/L of wastewater and 2,652 and 1,827 mg/L of treated wastewater were detected from the domestic WWTPs in Ang Thong and Ayutthaya, respectively. Iodides of 10.1, 6.2, and 7.6 µg/L were detected in raw water of the Bangkhen WTP and Singburi WTP, and river water, respectively. Iodides of 308 and 48.6 µg/L of wastewater and 92.4 and 75.3 µg/L of treated wastewater were detected from the domestic WWTPs in Ang Thong and Ayutthaya, respectively. Two fluorescent peaks of tyrosine-like substance at 225 nm/290 nm and 245 nm/350 nm, three fluorescent peaks of tryptophan-like substances 230 nm/345 nm, 280 nm/360 nm, and 230 nm/420 nm and three fluorescent peaks of humic- and fulvic-like at 275 nm/410 nm, 330 nm/410 nm, 260 nm/450 nm were determined in water samples.

Considering the average value, THMFPs of raw water of the Bangkhen WTP and Singburi WTP, and river water were 180, 103, and 300 µg/L, respectively. THMFPs of 363 and 452 µg/L of wastewater and 408 and 427 µg/L of treated wastewater were detected from the domestic WWTPs in Ang Thong and Ayutthaya, respectively. Chloroform was the dominant THMFP species in all water samples followed by BDCM and DBCM, respectively. Bromoform mostly detected in treated wastewater. On average, I-THMFP of 3, 6, and 1 µg/L were detected in raw water of the Bangkhen WTP and Singburi WTP, and river water, respectively. I-THMFP of 22 and 19 µg/L of wastewater and 20 and 19 µg/L of treated wastewater were detected from the domestic WWTPs in Ang Thong and Ayutthaya, respectively. CDIM and DCIM were the dominant detected I-THMFP species.

Average values of HANFPs of 13, 29, and 12 µg/L were detected in raw water of the Bangkhen WTP and Singburi WTP, and river water, respectively. On average, HANFPs of 17 and 28 µg/L of wastewater and 18 and 21 µg/L of treated wastewater were detected from the domestic WWTPs in Ang Thong and Ayutthaya, respectively. Among four HANFP species, DCAN was the most abundant in water samples. BCAN and TCAN were the other HANFP species found in both wastewater and treated wastewater samples. DBAN was the dominant HANFP species in treated wastewater rather than in other water sources. Trichloronitromethane formation potential (TCNMFP) of 2, 3, and 2 µg/L were detected in

raw water of the Bangkhen WTP and Singburi WTP, and river water, respectively. TCNMFP of 10 and 20 µg/L of wastewater and 27 and 18 µg/L of treated wastewater were detected from the domestic WWTPs in Ang Thong and Ayutthaya, respectively.

Considering the average value, the THMFP of treated wastewater was about two times higher than that of raw water. Relatively high levels of I-THMFP were found in wastewater and treated wastewater. The I-THMFP of treated wastewater was three to seven times higher than that of raw water. The HANFP of treated wastewater was one to three times higher than that of raw water. High levels of TCNMFP were found in wastewater and treated wastewater. TCNMFP of treated wastewater was six to thirteen times higher than that of raw water. The discharge of treated wastewater to raw water must be prevented and controlled. A moderate correlation was obtained from the relationship between THMFP and DOC with R^2 of 0.8076 for raw water whereas a fair (R^2=0.6903) correlation was obtained from the relationship between THMFP and DOC for wastewater. A moderate correlation was observed for the relationship between TCNMFP and DOC with R^2 of 0.7901 of treated wastewater. For almost all water sources, poor correlations were found between DBPFP species and Br^- and DBPFP species and I^-.

With considering the average value, weight measured the concentration of DBPs of raw water from high to low was THMFP > HANFP > I–THMFP > TCNMFP. For other water sources, the rank order of these DBPs on a mass concentration basis was THMFP > HANFP > TCNMFP > I–THMFP. Regard to the value of the LC_{50}-weighted concentration of DBPs in water sources, the rank order was HANFP > THMFP >TCNMFP > I–THMFP in raw waters and river waters. For wastewater, the rank order for toxic risk was HANFP > THMFP > I–THMFP >TCNMFP. Treated wastewaters contained highly toxic HANFP, followed by I–THMFP, THMFP, and TCNMFP. Considering the value of the lowest cytotoxicity-weighted concentration of C–DBPs and N–DBPs, the rank order was HANFP > THMFP > I–THMFP in raw waters and river waters. For wastewaters and treated wastewaters, the rank order of these DBPs was HANFP > I–THMFP > THMFP. Considering measured weight concentration, THMFP was found as the highest DBPs. The highest lethal concentration 50-weighted and lowest cytotoxicity-weighted concentrations of DBPs were determined for HANFP.

4.2 Formation of C-DBPs and N-DBPs of fractionated DOM in raw water, wastewater, and treated wastewater

DOM with MW < 1 kDa was the dominant DOM fraction in all water samples. The ranges of percent distribution of DOC of DOM with MW < 1 kDa of raw water, wastewater, and treated wastewater were from 36 to 63, 15 to 48, and 49 to 60% by weight of total DOC, respectively. The DOM with MW > 10 kDa was found as the second dominant DOM. The percent distribution of DOM with MW > 10 kDa of raw water, wastewater, and treated wastewater ranged from 19 to 27, 24 to 29, and 11 to 25%, respectively. The order of the DOC distribution of raw water, wastewater, and treated wastewater could be express as follows: DOM with MW < 1 kDa, MW > 10 kDa, 3 kDa < MW < 10 kDa, and 1 kDa < MW < 3 kDa, respectively. The order of the DOC distribution of wastewater and treated wastewater was the

same as that of raw water. The wastewater and treated wastewater could be the DOM contamination sources to raw water.

The HPO was the dominant DOM fractions. The ranges of percent distribution of HPO in raw water, wastewater, and treated wastewater were from 22 to 50, 59 to 67, and 39 to 55% by weight of total DOC, respectively. HPI was the second significant DOM fraction. The ranges of percent distribution of HPI of raw water, wastewater, and treated wastewater ranged from 28 to 38, 23 to 30, and 33 to 43%, respectively. The TPI was found as minority DOM group. The coagulation process effectively removes DOM with high MW and HPO's character. HPO and DOM with MW > 10 kDa were found as the significant DOM and could be sufficiently removed by coagulation process. When the dominant DOM fraction in water primary contains low MW and HPI's character, the enhanced coagulation or advanced water treatment process such as PAC and MIEX resin should be considered as the optional for removal of dominant DOM fractions.

DOM with 1 kDa < MW < 3 kDa has a high THMFP/DOC. DOM with 3 kDa < MW < 10 kDa and MW > 10 kDa have a moderate THMFP/DOC. DOM with MW < 1 kDa had a low value of THMFP/DOC. Chloroform, BDCM, and DBCM were the THMFP species that detected in all DOM fractions. In the case of resin fractionation, the highest THMFP/DOC of DOM fractions of all water samples was determined for TPI, followed by HPO, the dominant DOM fraction. HPI has a less active in THMs formation. Chloroform was the main THMFP species. In term of DOC distribution, TPI had the lowest value of DOC; however, TPI had the highest value of THMFP/DOC. DOM in TPI might contain the active character for the THMs formation.

In the case of raw water, DOM with 1 kDa < MW < 3 kDa and 3 kDa < MW < 10 kDa has a high I-THMFP/DOC. DOM with MW > 10 kDa and MW < 1 kDa had a low value of I-THMFP/DOC. For wastewater and treated wastewater, DOM with MW < 1 kDa and 1 kDa < MW < 3 kDa were the active fraction on I-THMs formation. DOM with MW > 10 kDa and 3 kDa < MW < 10 kDa have a less active on I-THMs formation. CDIM, DCIM, and BDIM were the I-THMFP species that mostly detected in all DOM fractions. In the case of resin fractionation, the highest I-THMFP/DOC of DOM fractions of all water samples was determined for TPI, followed by HPO, the dominant DOM fraction. HPI has a less active in I-THMs formation. DOM in TPI might contain the active character for the I-THMs formation. DCIM, BDIM, and TIM were I-THMFP species detected.

DOM with 1 kDa < MW < 3 kDa and 3 kDa < MW < 10 kDa have an active character on the HANs formation, whereas DOM with MW > 10 kDa and MW < 1 kDa have a less active nature on the HANs formation. The detected HANs species in almost all fractions were TCAN, DCAN, and BCAN. In the case of resin fractionation, the high HANFP/DOC of DOM fractions of all water samples was determined for TPI and HPI, followed by HPO. TCAN and DCAN were the main species. DOM in TPI and HPI might contain the active character for the HANs formation.

The active DOM fraction on HNM formation was DOM with 1 kDa < MW < 3 kDa. DOM with 3 kDa < MW < 10 kDa of raw water and treated wastewater have an active character on the HANs formation, whereas DOM with MW < 1 kDa has a less active nature on the HANs

formation. In the case of resin fractionation, the high HNMFP/DOC of DOM fractions of all water samples was determined for HPO and TPI, followed by HPI. TCNM was the detected HNMFP species.

DOM with MW < 1 kDa has the high DBPs species/LC50 followed by the DOM with MW > 10 kDa. The DOM with 1 kDa < MW < 3 kDa has a moderate value of DBPs species/LC50. The DOM with 3 kDa < MW < 10 kDa has a low value of DBPs species/LC50. In the case of resin fractionation, the value of DBPs species/LC50 of HPI was higher than that of HPO and TPI. HANs were determined as the DBPs species of all DOM fractions with the highest LC50. The significant DOM with MW < 1 kDa has the high DBPs/Lowest Cytotox. Conc followed by the DOM with 1 kDa < MW < 3 kDa. The DOM with 3 kDa < MW < 10 kDa and MW > 10 kDa have a moderate or low value of DBPs/Lowest Cytotox. Conc. In the case of resin fractionation, the value of DBPs/Lowest Cytotox. Conc of HPI was higher than that of HPO and TPI. HANs were determined as the DBPs species of all DOM fractions with the highest of the lowest Cytotoxicity concentration.

4.3 Reduction of precursors of emerging DBPs by enhanced coagulation with PAC and MIEX resin

The DOC of BK raw water at the first (RW-1), second (RW-2), and third (RW-3) sampling, TWW (AT-1), TWW (AY-1), and BK raw water (RW-1) mixed TWW (AY-1) (50% v/v) were 4.6, 3.2, 3.7, 5.3, 5.6, and 5.1 mg/L, respectively. The DON, of RW-1, RW-2, RW-3, TWW (AT-1), TWW (AY-1), and RW mixed with TWW were 0.16, 0.44, 0.25, 0.20,.1.22, and 1.07 mg N/L, respectively.

For BK raw water, the optimal condition for DOC and DON reduction was determined at alum dosage at 80 mg/L under controlled pH 7. Under this condition, it could reduce DOC and DON by 29 and 60%, on average. The optimal condition for enhanced alum coagulation by PAC of RW-1, RW-2, and RW were 80 and 40, 80 and 80, and 80 and 80 (alum and PAC in mg/L), respectively. In the case of enhanced coagulation with MIEX, the optimal condition for RW-1, RW-2, and RW were 80 and 4, 80 and 2, and 80 and 4 (alum in mg/L and MIEX in mL/L), respectively. On average, the optimal condition of alum coagulation with PAC could reduce DOC and DON by 43 and 62%, respectively. The optimal condition of alum coagulation with MIEX could reduce DOC and DON by 51 and 77%, respectively.

In the case of TWW (AT-1), TWW (AY-2) and RW mixed with TWW (AY-1) the optimal condition for DOC and DON reduction was determined at under controlled pH 7and alum dosage at 100, 100, and 100 mg/L, respectively. Under this condition, it could reduce DOC and DON in treated wastewater and RW mixed with treated wastewater by 21 and 10%, and 24 and 76%, respectively. The optimal condition for enhanced alum coagulation by PAC of TWW (AT-1), TWW (AY-2) and RW mixed with TWW (AY-1) were 100 and 100, 100 and 100, and 100 and 80 (alum and PAC in mg/L), respectively. In the case of enhanced coagulation with MIEX, the optimal condition for TWW (AT-1), TWW (AY-2) and RW mixed with TWW (AY-1) were 100 and 6, 100 and 6, and 100 and 4 (alum in mg/L and MIEX in mL/L), respectively. The optimal condition of alum coagulation with PAC could reduce DOC and DON in treated wastewater and raw water mixed with treated wastewater by 40 and 20%

(on average) and 42 and 60% respectively. The optimal condition of alum coagulation with MIEX could reduce in treated wastewater and raw water mixed with treated wastewater by 50 and 37% (on average) and 71 and 32% respectively.

Under optimal condition for raw water, alum coagulation, alum coagulation with PAC, and alum coagulation with MIEX could reduce THMFP and HANFP by 9 and 39%, 22 and 45%, and 45 and 61%, respectively. The reduction of I-THMFP and HNMFP varied according to the sampling period. For treated wastewater and raw water mixed with treated wastewater, under optimal condition alum coagulation, alum coagulation with PAC, and alum coagulation with MIEX provides the successful reduction of THMFP. The I-THMFP, HANFP, and HNMFP mostly did not detect or detected in low level after treatment.

For raw water, at optimal condition, alum coagulation could reduce DOM with MW > 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa by 41, 21, 48, and 39%, respectively. Alum coagulation with PAC and alum coagulation with MIEX could reduce MW > 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa by 71, 41, 58, and 44% and 57, 47, 46, and 71%, respectively In the case of treated wastewater and raw water mixed with treated wastewater, alum coagulation could reduce DOM with MW > 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa by 27, 17, 21, and 30%, respectively. Alum coagulation with PAC and alum coagulation with MIEX could reduce MW> 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa by 35, 32, 39, and 45% and 55, 41, 61, and 45%, respectively

Considering the DOM fraction by resin fractionation of the raw water, coagulation with alum coagulation could remove DOC of HPO and HPI by 41 and 12% (on average), respectively, the DOC of TPI was not available. In the case of alum coagulation with PAC and alum coagulation with MIEX, the results of the DOM fraction did not conduct. For treated wastewater, when using alum coagulation with PAC, the reduction of DOC of HPO and HPI of 36 and 56% were obtained, respectively. TPI could not be removed.

Aliphatic hydrocarbon, phenolic, ether, alcohol, and organic nitrogen classes in raw water accounted for 34, 11, 10, 9, and 7% (on average), respectively. Other classes were determined in minority. Alum coagulation, alum coagulation with PAC, and alum coagulation with MIEX could reduce aliphatic hydrocarbon and organic nitrogen by 36 and 40%, 37 and 12%, and 33 and 35%, respectively. Only alum coagulation with MIEX could reduce phenol and alcohol by 22 and 21% (on average), respectively. Ether could not reduce by the coagulation and enhanced coagulation.

In the case of treated wastewater, ether, aliphatic hydrocarbon, and organic nitrogen were the major chemical classes and accounted for 37, 15, and 12% (on average), respectively. The other classes were determined as a minority. Alum coagulation, alum coagulation with PAC, and alum coagulation with MIEX could reduce ether and organic nitrogen by 22 and 72%, 32 and 34%, and 22 and 26%, respectively. Alum coagulation with PAC could slightly reduce aliphatic hydrocarbon by only 6%. For raw water mixed with treated wastewater, aliphatic hydrocarbon, organic nitrogen, aromatic hydrocarbon, and other compounds accounted for 17, 9, 8, and 6%, respectively. Alum coagulation, alum coagulation with PAC,

and alum coagulation with MIEX could reduce aromatic hydrocarbon by 52, 83, and 68%, respectively. Only coagulation with MIEX could reduce aliphatic hydrocarbon by 21%.

4.4 Kinetics of DBPs formation from dissolved organic matter fractions and inorganic ions in the raw water

The formation potential of chloroform and BDCM decreased initially (I^- concentration 0.5 and 0.7 μg/L), then the chloroform and BDCM species tend with increasing I^- concentrations from 1 to 5 μg/L. Increase in iodide dosage from 0.5 to 0.7 μg/L slightly increased in the total HANFP. When the iodide concentration increased from 0.7 to 2 μg/L, the HANFP slightly decreased. The maximum HANFP of 10 μg/L was taken place in iodide dose of 5 μg/L. The I-THMs and TCNM did not form when the iodide dosage increases from 0.5 to 5 μg/L.

The total THMFP increased by increasing Br^- from 0.1 to 1 mg/L, while further increase in the Br^- to 10 mg/L did not increase in the total THMFP. The formation of bromoform species tends to increase with increasing Br^- from 0.1 to 1 mg/L, whereas chloroform decreased. DBCM and BDCM increased initially, but then they decreased. The formation potential of total I-THMs decreased by increasing Br^- from 0.1 to 10 mg/L. TIM formation potential and DCIM formation potential decreased by increasing the Br^- concentration. The level of BDIM formation potential was formed only in the highest Br^- of 10 mg/L. Increasing Br^- concentrations from 0.2 to 10 mg/L resulted in decreased total HANFP concentrations. While further increase in the Br^- level leads to an increase in the total HANFP. DBAN did not form at the initial Br^- of 0.1 mg/L. The DBANFP species exhibited high levels in the Br^- at 5 and 10 mg/L. BCAN increased initially but then decreased, and its maximum concentration occurred at Br^- of 0.2 mg/L. DCAN formation potential was measured at low concentration when the Br^- level was increased from 0.1 to 0.5 mg/L. TCNM did not form when the Br- dosage increase from 0.1 to 10 mg/L.

The kinetic rates of THMFP of raw water explained by zero-order and first-order reactions. THMFP formation from 3 to 72 h seems to be constant or slightly decreased. A two-stage pattern including a formation (the zero-order kinetic) and degradation (the first-order kinetic) rate was determined for THMFP of treated water, I-THMFP of raw water and its treated water, and HANFP of raw water and treated wastewater.

The zero-order kinetics of THM formation of DOM fraction with MW > 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa were assessed. The zero-order kinetic of BCIM degradation was determined for DOM with MW < 1 kDa. In the case of HAN, a zero-order kinetic of HAN formation followed first-order kinetic of HAN degradation were determined. THM formation of HPI and TPI expressed by a first-order kinetic and zero-order kinetic, respectively. The kinetic of THMs of HPO based on species. Chloroform and BDCM and DBCM have a formation (zero-order kinetic) and a formation (zero-order kinetic) followed by degradation (first-order kinetic), respectively. I-THMs of HPO and TPI had a formation pattern (a zero- and first-order kinetic). I-THMs of HPI has a degradation pattern (zero- order kinetic). HAN formation of HPI could be expressed by a zero-order kinetic.

CONTENT

Page

ABSTRACT (Thai)..... (1)
ABSTRACT (English)..... (2)
EXECUTIVE SUMMARY ..... (3)
CONTENTS..... (13)
LIST OF FIGURES ..... (19)
LIST OF TABLES..... (25)

CHAPTER I INTRODUCTION..... 1
1.1 Background and rational 1
1.2 Objectives 4
1.3 Scope of research 4

CHAPTER II THEORY AND LITERATURE REVIEW..... 7
2.1 Trihalomethanes (THMs)..... 7
2.2 Haloacetonitriles (HANs) 9
2.3 Iodo-trihalomethanes (I-THMs)..... 10
2.4 Halonitromethanes (HNMs)..... 13
2.5 Level of I-THMs and HNMs in seawater 16
2.6 Dissolved organic matter 17
2.6.1 Quantification and Characterization of DOM and DON 17
2.6.2 Dissolved organic nitrogen 18
2.7 Fractionation of DOM by Ultrafiltration 19
2.8 Polyaluminium chloride coagulation and enhanced coagulation by power activated carbon 19

CHAPTER III RESEARCH AND METHODOLOGY..... 23

CONTENS (cont.)

Page

3.1 Sampling and Sample collection....23
3.2 Experimental procedures....25
3.2.1 Experiment I The Identification of precursors of C-DBPs and N-DBPs and formation of C-DBPs and N-DBPs....25
3.2.2 Experiment II Reduction of precursors of C-DBPs and N-DBP....27
3.2.3 Experiment III The effect of pH, iodide and bromide concentrations, DOC, and DON of reaction on the formation of C-DBPs and N-DBPs....29
3.3 Reagents....30
3.4 Basic water parameter analysis....30
3.5 DOC UV-254, SUVA and DON analysis....31
3.6 Iodide and bromide analysis....31
3.7 FEEM analysis....32
3.8 Fractionation of DOM....32
3.8.1 Resin fractionation....32
3.8.2 Size fractionation....32
3.9 Pyrolysis GC/MS analysis....33
3.10 DBPs' formation potential (DBPFP)....34
3.11 Analysis of DBPFP....35
3.12 Coagulation experiment....35

CHAPTER IV CARBONACEOUS AND NITROGENOUS DISINFECTION PRODUCTS'FORMATION POTENTIAL IN RAW WATER, WASTEWATER, AND TREATED WASTWATER....37
4.1 Intoduction....37
4.2 Experimental procedure....40
4.3 Result and discussion....40
4.3.1 Basic water quality....40
4.3.2 Organic precursors....43

CONTENS (cont.)

Page

DOC as the precursor of C-DBPs....45
DON as the precursor of N-DBPs....45
DOC/DON ratio....47
4.3.3 The presence of bromide and iodide ions....47
4.3.4 Fluorescent organic matter....49
4.3.5 Formation potential of C-DBPs....52
THMs' formation....52
I-THMs formation....59
4.3.6 Formation potential of N–DBPs....60
HANs' formation....60
HNM formation....62
4.3.7 The relationship between DBPFP and DOC concentration, DBPFP and bromide, and DBPFP and iodide....63
4.3.8 Evaluation of cytotoxicity risk caused by C–DBPs and N–DBPs....68

CHAPTER V FORMATION OF CARBONACEOUS AND NITROGENOUS DISINFECTION BY PRODUCTS OF FRACTIONATED DISSOLVED ORGANIC MATTER IN RAW WATER, WASTEWATER, AND TREATED WASTEWATER....71
5.1 Introduction....71
5.2 Water samples and experimental procedure....73
5.3 Results and discussion....74
5.3.1 Mass distribution of the fractionated DOM....74
5.3.2 DBPFP of DOM fractions....76
THMFP....76
I-THMFP....80
HANFP....83
HNMFP....87

CONTENS (cont.)

Page

5.3.3 Toxicity of size fractionation....90
Size fractionation....90
Lethal concentration fifty (LC50)....90
Lowest cytotoxicity concentration (Lowest Cytotox. Conc.)....91
Resin fraction....93
Lethal concentration fifty (LC50)....93
Lowest cytotoxicity concentration (Lowest Cytotox. Conc.)....95

CHAPTER VI REDUCTION OF PRECIRSORS OF EMERGING DISINFECTION BY-PRODUCT BY ENHANCED COAGULATION WITH POWDER ACTIVATED CARBON AMD MAGNETIC ION ECHANGED....97
6.1 Introduction....97
6.2 Experimental procedure....100
6.3 Results and discussion....101
6.3.1 Water sample characteristic....101
6.3.2. Reduction of turbidity by alum coagulation....103
6.3.3. Reduction of DOC and DON by alum coagulation, and enhanced alum coagulation with PAC and MIEX....104
6.3.4. DBPFP species and their reduction at optimal coagulation; alum coagulation, enhanced alum coagulation by PAC, and enhanced coagulation by MIEX....115
a) Reduction of THMFP....115
b) Reduction of I-THMFP....121
c) Reduction of HANFP....124
d) Reduction of HNMFP....125
6.3.5 DOM fractions and their reductions....128
a) Reduction of DOC of each MW size fraction....128

CONTENS (cont.)

Page

b) Reduction of DOC of each organic resin fraction 131
6.3.6 DBPFPs of DOM fractions and their reduction 132
a) DBPFP/DOC of each organic fraction by ultrafiltration 132
THMFP/DOC reduction 132
Iodo-THMFP/DOC reduction 134
HANFP/DOC reduction 136
HNMFP/DOC reduction 138
b) DBPFP/DOC of each organic fraction by resin fraction 139
6.3.7. FEEM analysis of DOM fractions at optimal coagulation 140
a) FEEM of DOM fractions by resin fractionation 140
b) Reduction of HPO, HPI and TPI fractions 142
6.3.8. Chemical classes in coagulated water 143

CHAPTER VII KINETICS OF DBPS FORMATION FROM DISSOLVED ORGANIC MATTER FRACTIONS AND INORGANIC IONS IN THE RAW WATER 149
7.1 Introduction 149
7.2 Experimental procedure 150
7.3 Results and discussion 150
7.3.1 Water sample characteristic 150
7.3.2 Effect of iodide (I–) and bromide (Br–) content on the DBP formation potential (DBPFP) 151
(a) Influence of iodide content 151
(b) Influence of bromide content 153
7.3.3 Kinetics of THMs, I-THMs, HANs, and HNMs formation in raw water and coagulated water 155
7.3.4 Kinetics of DOM size fraction on the formation potential of THMs, I-THMs and HANs in raw water 161

CONTENS (cont.)

Page

7.3.5 Kinetic of HPO, TPI, and HPI on the formation of THMs, I-THMs and HANs in raw water.....166

CHAPTER VIII CONCLUSION.....173
Reference 181
Appendix.....195

LIST OF FIGURES

Figure **page**

2-1 Iodide reacts with monochloramine (NH2Cl), and hypochlorous acid…… 11
2-2 The potential of CHCl2I formation upon chlorinated the effluent of each unit (reaction conditions: pH = 7, time = 24 h, temperature = 25 □ C, Cl2 dose = 5 mg/L unit.....13
3-1 The location of sampling sites.....24
3-2 Identification of precursors of C-DBPs and N-DBPs and formation of C-DBPs and N-DBPs. 26
3-3 Reduction of precursors of C-DBPs and N-DBPs analysis.....28
3-4 The effect of precursors and reaction time on the formation of C-DBPs and N-DBPs 29
4-1 The FEEM peak positions at A, B, C, D, E, F, G and H for raw water from the Bangkhen WTP in this study. 49
4-2 THMFP, the ratio of THMFP to the WHO guideline and I□THMFP for raw water, river water, domestic wastewater, and treated wastewater s 53
4-3 HANFP and HNMFP for raw water, river water, domestic wastewater, and treated wastewater.....61
4-4 Relationship between DOC of raw water, domestic wastewater and treated wastewater samples and THMFP and TCNMFP.....65
4-5 Weight measured concentration (A), lethal concentration 50-weighted (B), and lowest cytotoxicity-weighted concentrations (C) of DBPs. 69
5-1. THMFP Species/DOC of DOM fractions in raw water, wastewater, and treated wastewater classified by ultrafiltration: (a) MW > 10 kDa; (b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa 77
5-2. THMFP-Species/DOC of DOM fractions in raw water, wastewater, and treated classified by resin fractionation: (a) HPO; (b) TPI; (c) HPI 79
5-3. I-THMFP-Species/DOC of DOM fractions in raw water, wastewater, and treated wastewater classified by ultrafiltration: (a) MW > 10 kDa; (b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa 81

LIST OF FIGURES

Figure **Page**

5-4. I-THMFP-Species/DOC of DOM fractions in raw water, wastewater, and treated wastewater classified by resin fractionation: (a) HPO; (b) TPI, (c) HPI ... 82
5-5. HANFP-Species/DOC of each organic size fraction in raw water supply, wastewater and treated wastewater (a) MW > 10 kDa; (b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa ... 84
5-6. HANFP-Species/DOC of each organic resin fraction in raw water supply, wastewater and treated wastewater (a) HPO; (b) TPI, (c) HPI ... 86
5-7 HNMFP-Species/DOC of each organic size fraction in raw water supply, wastewater and treated wastewater (a) MW > 10 kDa;n(b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa ... 88
5-8 HNMFP-Species/DOC of each organic resin fraction in raw water supply, wastewater and treated wastewater (a) HPO; (b) TPI, (c) HPI ... 89
5-9 DBPs/LC50 of DOM fractions in raw water, wastewater, and treated wastewater classified by ultrafiltration: (a) MW > 10 kDa; (b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa ... 91
5-10 DBPs/Lowest Cytotox. Conc. of DOM fractions in raw water, wastewater, and treated wastewater classified by ultrafiltration: (a) MW > 10 kDa; (b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa ... 93
5-11 DBPs/LC50 of DOM fractions in raw water, wastewater, and treated wastewater classified by resin: (a) HPO; (b) TPI; (c) HPI ... 94
5-12 DBPs/Lowest Cytotox. Conc. of DOM fractions in raw water, wastewater, and treated wastewater classified by resin: (a) HPO; (b) TPI; (c) HPI ... 95
6-1. Turbidity of the raw water (RW) of BK WTP, treated wastewaters (TWW) of AT, and AY, and the RW mixed with TWW (50% v/v) in the alum coagulation experiment ... 103
6-2. Residual of DOC and DON and the percentage of DOC and DON reduction by the alum coagulation (A), the enhanced alum coagulation (80 mg/L alum)

LIST OF FIGURES

Figure **Page**

with PAC (B), and MIEX (C) for raw water of the BK WTP at the first sampling. 106

6-3. Residual of DOC and DON and the percentage of DOC and DON reduction by the alum coagulation (A), the enhanced alum coagulation (80 mg/L alum) with PAC (B), and MIEX (C) for raw water of the BK WTP at the second sampling 107

6-4. Residual of DOC and DON and the percentage of DOC and DON reduction by the alum coagulation (A), the enhanced alum coagulation (80 mg/L alum) with PAC (B), and MIEX (C) for raw water of the BK WTP at the third sampling 110

6-5. Residual of DOC and DON and the percentage of DOC and DON reduction by the alum coagulation, the enhanced alum coagulation with PAC, and MIEX for treated wastewater (TWW) of the AT from the first sampling (A, B, C) and the AY from the first sampling (D, E, F). 111

6-6. Residual of DOC and DON and the percentage of DOC and DON reduction by the alum coagulation (A), the enhanced alum coagulation (100 mg/L alum) with PAC (B), and MIEX (C) for treated wastewater (TWW) of the AY WTP from the first sampling mixed with raw water of the BK WTP (50% v/v). 114

6-7. THMFP species, and the ratio of THMFP to the WHO guideline for raw water of the BK WTP and their treated waters. 116

6-8. THMFP species, and the ratio of THMFP to the WHO guideline for treated wastewater from AT and the AY from the first sampling (TWW AT-1 and TWW AY-1), and raw water of the BK WTP mixed with treated wastewater of the AY (RW BK1+TWW AY1) at 50% v/v and their treated waters. 120

6-9. I-THMFP of raw water, treated wastewater, raw water mixed with treated wastewater and their treated waters. 123

6-10. HANFP for raw water, treated wastewater, raw water mixed with treated wastewater and their treated waters 126

LIST OF FIGURES

Figure **Page**

6-11. TCNMFP for raw water, treated wastewater, raw water mixed with treated wastewater and their treated waters 127
6-12. THMFP/DOC of each organic size fraction for raw water, treated wastewater, raw water mixed with treated wastewater and their treated waters by alum, alum with PAC, and alum with MIEX. 133
6-13. I-THMFP/DOC of each organic size fraction for raw water, treated wastewater, raw water mixed with treated wastewater and their treated waters by alum, alum with PAC, and alum with MIE 135
6-14. HANFP/DOC of each organic size fraction for raw water, treated wastewater, raw water mixed with treated wastewater and their coagulated waters by alum, alum with PAC, and alum with MIEX 137
6-15. HNMFP/DOC of each organic size fraction for raw water and treated wastewater, and their coagulated waters by alum, alum with PAC, and alum with MIEX 138
6-16. DBPFP/DOC of HPO, HPI and TPI for raw water and treated wastewater, and their coagulated waters by alum, and alum with PAC..... 140
6-17. Fluorescence intensity of DOM size fractions for raw water, treated wastewater, raw water mixed with treated wastewater after coagulation by alum, alum with PAC, and alum with MIEX. 141
6-18. Fluorescence intensity of DOM resin fractions for raw water and treated wastewater, and their coagulated waters by alum, and alum with PAC..... 143
7-1 The influence of iodide ion on the formation potential of THMs of raw water. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L 152
7-2 The influence of iodide ion on the formation potential of HANs of raw water. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L)..... 153
7-4 The influence of bromide ion on the formation potential of I-THMs of raw water. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L)..... 154
7-5 The influence of bromide ion on the formation potential of HANs of raw water. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L)..... 155
7-6 The effect of retention time on the formation potential of (a) chloroform, (b) BDCM, and (c) DBCM species of THMFP of raw and treated water of the BK WTP from the

LIST OF FIGURES

Figure **Page**

first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L) 156
7-7 The effect of retention time on the formation potential of (a) DCIM and (b) TIM species of I-THMFP of raw water and treated water of the BK WTP from the first sampling (RW BK-1). (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L)..... 159
7-8 The effect of retention time on the formation potential of (a) TCAN, (b) DCAN, and (c) BCAN species of HANFP of raw water and treated water of the BK WTP from the first sampling (RW BK-1). (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L)..... 160
7-9 The effect of DOM size fraction and retention time on the formation potential of (a) chloroform, (b) BDCM, and (c) DBCM species of THMFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L 162
7-10 The effect of DOM size fraction of < 1 kDa and retention time on the formation potential of BCIM species of I-THMFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L)..... 164
7-11 The effect of DOM size fraction and retention time on the formation potential of TCAN, DCAN, and BCAN species of HANFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L)..... 165
7-12 The effect of DOM resin fraction and retention time on the formation potential of (a) chloroform, (b) BDCM, and (c) DBCM species of THMFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L)..... 167
7-13 The effect of DOM resin fraction and retention time on the formation potential of TIM and DCIM species of I-THMFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, Cl2 free Cl2 residual = 3-5 mg/L) 170

LIST OF FIGURES

Figure **Page**

7-14 The effect of HPI fraction and retention time on the formation potential of TCAN, DCAN, and BCAN species of HANFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl2 residual = 3-5 mg/L)..... 171

LIST OF TABLES

Table **Page**

2-1 Structure, formula and molecular weight of four THMs....8
2-2 Structure, formula and molecular weight of four HANs....9
2-3 Structure, formula and molecular weight, of six I-THMs....12
2-4 HNM Cytoxicity and Genotoxicity Ranking....14
2-5 Structure, formula and molecular weight of HNMs....15
3-1 The sampling sites....25
3-2 The water sample for experiment II....27
4-1 The pH, turbidity, salinity, alkalinity of raw water (RW), river water,domestic wastewater (WW), and treated wastewater (TWW) for the three sampling times....42
4-2 UV-254, SUVA, DOC, DON, and DOC/DON....44
4-3 Bromide (Br^-) and iodide (I^-) concentrations....48
4-4 Fluorescence intensity of water samples of the peaks of Excitation (Ex)/Emission (Em) wavelength....51
4-5 DBPFP of raw water (RW), river water, domestic wastewater (WW) and treated wastewater (TWW) for the three sampling times....55
4-6 Percent distribution of THMFP, I□THMFP, and HANFP species of raw water, river water, domestic wastewater and treated wastewater....56
4-7 Linear correlation coefficients (R2) between DBPFP and DOM surrogate parameters of raw water, domestic wastewater, and treated wastewater....63
4-8 Linear correlation coefficients (R2) between DBPFP species and the bromide ion (Br-) and iodide ion (I-) of raw water, domestic wastewater, and treated wastewater....66
5-1. DOC of DOM fractions and their percent distribution....75
6-1. Characteristics of raw water (RW), treated wastewater (TWW), and raw water mixed treated wastewater (RW+TWW) (50% v/v)....102
6-2. Concentrations and percent distributions of THMFP, I-THMFP, HANFP and HNMFP species in raw water, treated wastewater, and raw water mixed with

LIST OF TABLES (comt.)

Table **Page**

treated wastewater, and their treated water at the optimal dosages of alum, alum with PAC, and alum with MIEX coagulation. 118
6-3. DOC of DOM fractions and their percent distribution by ultrafiltration in raw water, treated wastewater and their treated water 128
6-4. DOC of DOM fractions and their percent distribution by resin fractionation in raw water, treated wastewater and their treated water 131
6-5 Summary of the prominent major fragments of each chemical class in the raw water of BK-1 and their reduction 144
6-6 Summary of the prominent major fragments of each chemical class and their reduction in the raw water of BK-2 145
6-7 Summary of the prominent major fragments of each chemical class and their reduction in the raw water mixed with treated wastewater (RW+TWW) 146
6-8 Summary of the prominent major fragments of each chemical class and their reduction in the treated wastewater of AT-1 147
6-9 Summary of the prominent major fragments of each chemical class and their reduction in the treated wastewater of AY-1 148
7-1 Characteristics of the water samples tested. 151
7-2 Specific formation and degradation rates of THMFP, I-THMFP, and HANFP after 72 h of incubation in raw and coagulated water of the BK-1. 158
7-3 Specific formation and degradation rates of THMFP, I-THMFP, and HANFP under 72 h of incubation in each DOM size fractions of the BK-1 raw water 163
7-4 Specific formation and degradation rates of THMFP, I-THMFP, and HANFP under 72 h of incubation in HPO, TPI and HPI fractions of the BK-1 raw water 168

Chapter I
Introduction

1.1 Background and rational

Water supply is essential for human life. Quality of water supply depends on the quality of raw water and performance of water treatment process on the removal of contaminants. In general, a water treatment plant is located nearby water sources and far from the city. This is done to preserve raw water from several sources of contamination. Concerning the expansion of cities and industries, the sources of the raw water such as river water are facing the more complex problem of contaminations from wastewater and treated wastewater discharges. Besides, in some areas, levels of salinity in raw water are moderately high because the sea level rise. This situation must be shortly inevitable for the water supply plant. The formation of carcinogenic disinfection by-products (DBPs) through the reaction between dissolved organic matter (DOM) and chlorine in the water treatment process was discovered by Rook (1974). Several pieces of research have to date focused on DOM characterization, formation of DBPs in the chlorination or chloramination of water supply/drinking water, the emerging DBPs, the removal of DBPs precursors and DBPs, and minimization of chlorination DBPs (Ratasuk et al., 2008; Matilainen et al., 2010, Matilainen and Sillanpaa, 2010; Matilainen et al., 2011).

DOM in water composed of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) (Lee and Westerhoff, 2006). DOM is the primary precursor of the formation of DBPs in the water supply. The reaction between DOC and chlorine can produce carbonaceous DBPs (C-DBPs) such as trihalomethanes (THMs). THMs consist of four compounds including trichloromethane (chloroform, TCM), bromodichloromethane (BDCM, dibromochloromethane (DBCM), and tribromomethane (bromoform, TBM). The THMs standard of 80 µg/L in drinking water has been set by the US. Environmental Protection agency (US.EPA, 1998). European Union (EU) set the standard of THMs in drinking water of 100 µg/L (EU, 1997). The World Health Organization (WHO) has set health-related guideline values of 200, 60, 100, and 100 µg/L for TCM, BDCM, DBCM, and TBM, respectively (WHO, 1996). This guideline is used as the reference standard by the Metropolitan Waterworks Authority (MWA), Thailand. In the presence of DON, the reaction of between DOM and chlorine or chloramines can produce nitrogenous DBPs (N-DBPs) such as *N*-nitrosodimethylamime (NDMA), halonitro-methanes (HNMs), and haloacetonitriles (HANs). The major HANs in drinking water compose of trichloroacetonitrile (TCAN),

dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN). WHO has set guideline values of 20 and 70 µg/L for DCAN and DBAN, respectively (WHO, 2011).

When bromide, iodide, and nitrite present in water, chlorine can react with DOM to form HNMs and others DBPs (Sadiq and Rodriguez, 2004; Hu et al., 2010). HNMs consist of chloronitromethane, dichloronitromethane, trichloronitromethane, bromochloronitro-methane, bromodichloronitromethane, bromonitromethane, dibromonitromethane, dibromochloronitromethane, and tribromonitromethane. HMNs were detected in low concentration in compared with that of THMs and haloacetic acids (HAAs). HMNs have not been regulated. However, cytotoxicity and genotoxicity caused by HNMs are comparable or even higher when compared with that of THMs and HAAs. (Krasner et al., 2006; Richardson et al., 2007)

Iodoform (triiodomethanes, TIM) can form during the oxidative treatment of this water in the presence of iodide. In addition, other fives iodated trihalomethanes (Iodo-THMs) have been found in disinfected water: bromochloroiodomethane (BCIM); chlorodiiodomethane (CDIM); dibromoiodomethane (DBIM); dichloroiodomethane (DCIM); and bromidiiodomethane (BDIM)(Richardson et al., 2007; and Krasner et al., 2006). The cytotoxicity and genotoxicity of iodo-THMs in mammalian cells assays were higher than that of brominated and chlorinated analogs (Bichsel and Gunten, 2000; Cancho et al., 2000).

The formation of C-DBPs and N-DBPs depends on the quantity and nature of DOM. Other parameters such as pH, temperature, iodide and bromide concentrations, reaction time, and chlorine and chloramine dosages affect formation of C-DBPs and N-NBPs. DOC, ultraviolet absorbance at wavelength 254 nm (UV-254), specific ultraviolet absorption (SUVA), and DON have been used to determine quantities of DOM. The trihalomethane formation potential (THMFP), haloacetonitilre formation potential (HANFP), halonitromethane formation potential (HNMFP), and iodo-trihalomethane formation potential (I-THMFP) are used to determine complete reactions between DOM and chlorine or chloramine for producing C-DBPs and N-DBPs.

For the specific group of DOM, the resin fractionation technique using DAX-8 and XAD-4 resin can separate DOM into three fractions: (i) hydrophobic organic fraction (HPO); (ii) transphilic organic fraction (TPI); and (iii) hydrophilic organic fraction (HPI) (Aiken and McKnight, 1992; Lee et al., 2004). The ultrafiltration (UF) membrane can be utilized to fractionate DOM into several groups according to molecular size cut-offs of 30, 10, 5, 3 and 1 kDa (Xu, et al., 2011). By conducting THMFP, HANFP, HNMFP, and I-THMFP on DOM

fractions by resin and UF techniques, the reactivity of DOM fractions on forming THMFP, HANFP, HNMFP, and I-THMFP can be determined. A three-dimensional fluorescent spectroscopy analysis, the use of fluorescent excitation-emission matrix, FEEM), has been used to classify DOM into tyrosine-like, tryptophan-like, and humic and fulvic acid-like substances. (Chen et al., 2003; Musikavong et al., 2007)

In terms of chemical classes, pyrolysis gas chromatography-mass spectrometer (GC/MS) has been used to identify the putative origin of DOM. It is one of the most advanced techniques that provide the information on pyrolysis fragments of chemical classes of DOM (Musikavong and Wattanachira, 2013). By analysis of pyrolysis GC/MS, the putative origin of DOM in a water sample that could form THMs, HANs, HMNs, and ITHMs can be determined. The study of the putative origin of DOM on the formation of HANs, HMNs, and I-THMs has been limited recently.

The conventional water treatment process in Thailand consists of coagulation, sedimentation, filtration, and chlorination. Poly aluminum chloride (PACl) and alum have been used commonly as the coagulant. Most of the filtration media are uniform sands. The principal focus of a water treatment plant is to reduce turbidity and suspended solids. With regards to the complex problem of raw water contamination, sometimes the powder activated carbon (PAC) has been used in the treatment process after coagulation. To produce the safe water supply from DBPs, the investigation of optimal condition for reduction of precursors of THMs, HANs, HNMs, and I-THMs and the level of THMs, HANs, HMNs, and I-THMs are considerably important. The Bangkhen water treatment plant (WTP) is the largest WTP in Thailand and use raw water from the Chao Phraya River. The water supply of about 3.7 million m^3/day is produced and distributed to around six million people in Bangkok and nearby provinces. To protect wastewater and treated wastewater discharge from domestics and industries in Bangkok area and to ensure that quantity of water is sufficient for production, raw water of the Bangkhen WTP is drawn from the Chao Phraya River at Phathumthani Province. Raw water flows along the canal of MWA to the plant.

Eventhough, the raw water supply of the Bangkhen WTP has a protection system, this raw water can be contaminated with the wastewater and treated wastewater from communities and industries at the upstream locations. In addition, due to the sea level rise: sometimes, the level of salinity of raw water is moderately high. It can cause unusual tastes to the water supply. According to a study of Gong and Zhang (2013), iodide was detected in seawater, urine, and wastewater effluent. When the Chao Phraya River is contaminated with seawater, urine, wastewater effluent, together with using chlorine as a disinfectant in the

water treatment process, then this can cause the formation of THMs, HANs, HNMs, and I-THMs in the water supply.

The quality of raw water and water supply of the Bangkhen WTP is essential. Levels of DOM fractions, THMFP, haloacetic acids formation potential (HAAFP) of raw water of the Bangkhen WTP was investigated (Panyapinyopol et al., 2005; Kanokkantapong el al., 2006). The level of DON in raw water of the Bangkhen WTP and its removal by poly aluminum chloride (PACl) coagulation was determined (Kumsuvan et al., 2014). The putative origins of DOM and the formation of THMs, HANs, HNMs, and I-THMs of 1) wastewater, treated wastewater that has potentially discharge to the Chao Phraya River, 2) raw water of the Bangkhen WTP, 3) coagulated water by PACl, alum and another coagulant, and 4) coagulated water by PACl or alum with PAC have never been reported. In addition, the study on the formation of THMs, HANs, HNMs, and ITHMs of raw water of the Bangkhen WTP under the variation of pH, iodide and bromide concentrations, reaction times, DOC, and DON have been limited.

1.2. Objectives

- To identify characteristics and structure of DOMs in raw water and coagulated water of the Bangkhen WTP, domestic wastewater, and treated wastewater by using resin fractionation, UF fractionation, pyrolysis GC/MS, and FEEM techniques.
- To determine the formations of THMs, HANs, I-THMs, and HNMs of raw water and coagulated water of the Bangkhen WTP, domestic wastewater, and treated wastewater.
- To determine the formations of THMs, HANs, I-THMs, and HNMs of HPO, TPI, HPI, group of DOM fractions by the UF technique: < 1kDa fraction; 1-3 kDa fraction; 3-10 kDa fraction; and > 10 kDa of raw water and coagulated water of the Bangkhen WTPs, domestic wastewater, and treated wastewater.
- To determine the effect of iodide and bromide concentrations, DOC, DON, DOC/DON, and reaction time on the formation of THMs, HANs, I-THMs, and HNMs.

1.3. Scope of research

- Raw water was collected three times from the Bangkhen WTP in the rainy season, summer and winter.

- Two domestic wastewater and two treated wastewater were collected three times at the upstream location of the raw water canal of the Bangkhen WTP.
- The alum was used as coagulants in coagulation experiments with dosages of 10 - 120 mg/L for alum and 1 – 5 mg/L for MIEX.
- The PAC and magnetic ion exchange (MIEX) was used for the enhanced alum coagulation experiments with dosages of 10-100 mg/L.
- A jar test apparatus was used for performing coagulation and enhanced coagulation experiments.
- UF membrane was used in this study. The membrane filtration was conducted with a dead-end UF unit at constant pressure.
- DAX-8 and XAD-4 resin were used in the fractionation experiment to separate HPO, TPI and HPI. The resin fractionation was performed following the method developed by Aiken and Mcknight (1992).
- Water samples for DON analysis were prepared in accordance with the method developed by Xu et al., (2010)
- Samples for analysis of THMs, HANs, I-THMs, and HNMs were extracted and analyzed in accordance with EPA Method 551.1 and 552.3.
- THMs, HANs, I-THMs, and HNMs were analyzed by gas chromatography with electron captor detector (GC/ECD).
- The chemical classes of DOM in water samples were carried out according to the study of Musikavong and Wattanachira (2013) and analyzed with pyrolysis GC/MS.
- The UF fractionation technique developed by Xu, et al., (2011) was modified to fractionate DOM into (i) < 1 kDa fraction (ii) 1-3 kDa fraction (iii) 3-10 kDa fraction, and (iv) >10 kDa fraction.

Chapter II
Theory and Literature Review

2.1 Trihalomethanes (THMs)

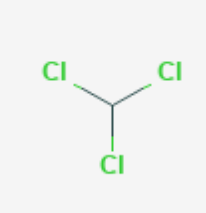
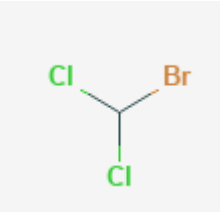
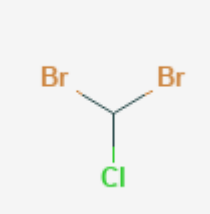
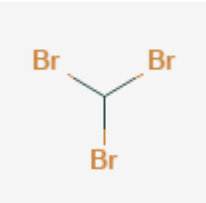
Trihalomethanes (THMs) consist of four compounds, including trichloromethane (chloroform, TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM) and tribromomethane (bromoform, TBM). The THMs standard of 80 µg/L in drinking water has been set by the United States Environmental Protection agency (US.EPA) (US.EPA, 1998). European Union (EU) set the standard of THMs in drinking water of 100 µg/L (EU, 1997). World Health Organization (WHO) has set health-related guideline values of 200, 60, 100, and 100 µg/L for TCM, BDCM, DBCM, and TBM, respectively (WHO, 1996). The sum of the ratio of THMs species/WHO guidelines must be lower than one. This guideline is used as the reference standard by the Metropolitan Waterworks Authority (MWA), Thailand.

Feungpean et al., (2014) determined the dissolved organic carbon (DOC) and THMs of the water supply in the Bangkok area of 624 samples. The range of DOC from 0.83 to 8.78 mg/L was detected. THMs ranged from 13 to 168 µg/L with an average value of 66 µg/L. Chloroform was the major THMs species. It accounted for 85% of total THMs. The total chlorine dose, free chlorine residual, and contact time affected to THMs formation. MWA has determined the THMs sum of ratio according to the WHO standard. The value of amount of THMs species ratio of water supply in summer 2014 was close to one. It indicated that raw water supply from the Bangkhen WTP contained the DBPs in the moderately high level.

Golea et al., (2017) investigated the linear relationship between THMs formation potential (THMFP) and haloacetic acids formation potential (HAAFP) and ultraviolet adsorption at wavelength 254 nm (UV-254), DOC, and hydrophobic organic fraction (HPO). Raw water and treated water from 30 surface water sites were collected over 18 – 30 months during January 2013 and June 2015. In the case of raw water, the strong correlations for THMs formation were observed for the relationship between THMFP and UV-254 (correlation coefficient, $R^2 = 0.82$), THMFP and HPO ($R^2 = 0.82$), and THMFP and DOC ($R^2 = 0.79$). The relationships between HAAFP and UV-254 ($R^2 = 0.74$), HAAFP and HPO ($R^2 = 0.77$), and HAAFP and DOC ($R^2 = 0.74$) were determined. For the treated water, the weak correlation was determined for all samples. The correlations for THMs formation were observed for the relationship between THMs and UV-254 ($R^2 = 0.52$), and HPO ($R^2 = 0.53$),

and THMFP and DOC (R^2 = 0.62). The relationships between HAAFP and UV-254 (R^2 = 0.39), HAAFP and HPO (R^2 = 0.44), and HAAFP and DOC (R^2 = 0.43) were determined. The weak correlation of disinfection by-products (DBPs) and dissolved organic matter (DOM) in treated water could cause by the reduction of HPO content and the reactive DOM with contributing to DBPs formation. Structure, formula and molecular weight of four THMs are presented in Table 2-1

Table 2-1 Structure, formula and molecular weight of four THMs

THMs	Structure	Formula	Molecular weight (g/mol)
TCM		$CHCl_3$	119.37
BDCM		$CHBrCl_2$	162.82
DBCM		$CHBr_2Cl$	208.28
TBM		$CHBr_3$	252.731

SOURCE: *http://pubchem.ncbi.nlm.nih.gov*

2.2 Haloacetonitriles (HANs)

The major haloacetronitriles (HANs) in drinking water compose of trichloro-acetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN) and dibromoacetonitrile (DBAN). The WHO has set guidelines values of 20 and 70 µg/L for DCAN and DBAN, respectively (WHO, 2011). High HANs values have been reported in water from three distribution system of water treatment plant (WTP) including Thapra, Kota, and Khon Kaen University WTPs in Khon Kaen Municipality, Khon Kean province, Thailand during November 2015 to December 2016. The Thapra and Kota WTP used chlorine as the disinfectant, whereas the Khon Kaen University WTP used chlorine dioxide. The maximum concentration of 30 µg/L was found. DCAN increased in summer 2016 and decreased in winter 2016. For the Kota distribution system, ranges of DCAN, TCAN, and DBAN were 0.14-10.9, 0.16-12.7, and < 0.1-4.5 µg/L respectively. This observation was similars to that of the Thapra distribution system, which HANs in the range of 5-20 µg/L were determined. For the Khon Kaen University WTP, DCAN, TCAN, and DBAN ranged from 0.06 to 5, 0.14 to 14, and 0.47 from 4 µg/L., respectively (Ratpakdi et al., 2019). The study of the level of HANs of raw water and water supply of the Bangkhen WTP is limited. Structure, formula and molecular weight of four HANs are presented in Table 2-2

Table 2-2 Structure, formula and molecular weight of four HANs

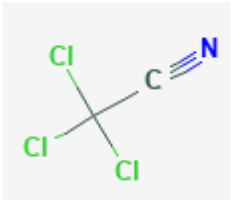
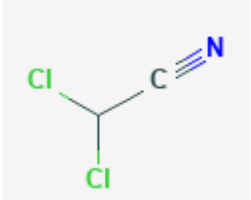
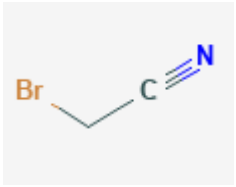
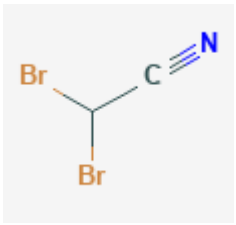
HANs	Structure	Formula	Molecular weight (g/mol)
TCAN		C_2Cl_3N	144.38
DCAN		C_2HCl_2N	109.94

Table 2-2 Structure, formula and molecular weight of four HANs (Cont.)

HANs	Structure	Formula	Molecular weight (g/mol)
BCAN		C_2H_2BrN	119.95
DBAN		C_2HBr_2N	198.84

SOURCE: *http://pubchem.ncbi.nlm.nih.gov*

2.3 Iodo-trihalomethanes (I-THMs)

Drinking water required to be disinfected during the water treatment process. Treated wastewater is subjected to disinfect prior to discharge to natural waterways. In the disinfection process, iodide can be oxidized by disinfectants to form hypoiodous acids (HOI) and I^-. Then HOI and I^- can react with DOM to form iodinated DBPs (Kransner et al., 2006). Iodide is rapidly oxidized to be HOI in the oxidation and disinfection process of chlorine, monochloramine, and ozone. Besides, HOI can form during oxidative in the water treatment and can be further oxidized to iodate ($IO3^-$) or react with DOM to form iodo-organic and compounds as DBPs. The example and equation of iodide react with monochloramine (NH_2Cl), and hypochlorous acid is listed and presented in Figure 2-1 (Ting et al., 2013).

Iodoform (triiodomethanes, TIM) can be formed during the oxidative treatment of water in the presence of iodide. Other fives iodated trihalomethanes (Iodo-THMs) have been found in disinfected water namely bromochloroiodomethane (BCIM), chlorodiiodomethane (CDIM), dibromoiodomethane (DBIM), dichloroiodomethane (DCIM), and bromo-diiodomethane (BDIM) (Richardson et al., 2007; and Krasner et al., 2006). Structure, formula and molecular weight of six I-THMs are presented in Table 2-3.

$$I^- + NH_2Cl + H^+ + H_2O \rightarrow HOI + NH_4^+ + Cl^-$$
$$HOI + NOM \rightarrow I - DBP_s \quad (1)$$

$$H_2O_2 + Cl^- \rightarrow HOCl + H_2O$$
$$HOCl + RNH_2 \text{ (taurine)} \rightarrow RNHCl + H_2O \quad (2)$$
$$RNHCl + I^- + H_2O \rightarrow RNH_2 + HOI + Cl^- \; HOI + NOM \rightarrow I - DBP_s$$

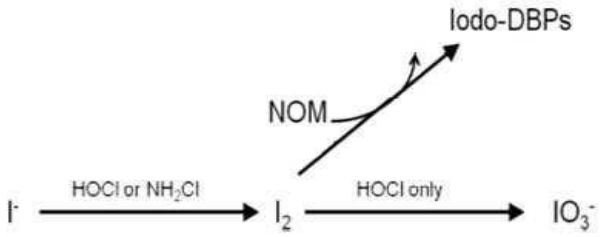
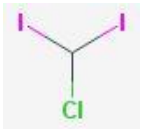
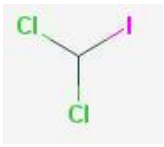
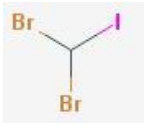
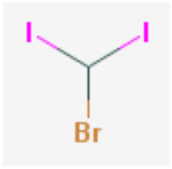
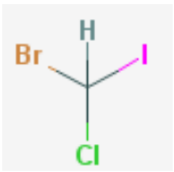


Figure 2-1 Iodide reacts with monochloramine (NH_2Cl), and hypochlorous acid (Ting et al., 2013).

The potential of $CHCl_2I$ formation upon the chlorinating effluent of each unit of a water treatment plant is presented in Figure 2-2. The formation of I-THMs in water of each unit remained higher than that of the source water. This could be because of the different characteristics of organic precursors in each unit of the water treatment plant. However, the concentration of $CHCl_2I$ (20.91 µg/L) produced during the biological pretreatment was higher than that of other unit (Wei et al., 2013).

Table 2-3 Structure, formula and molecular weight, of six I-THMs

I-THMs	Structure	Formula	Molecular weight (g/mol)
TIM		CHI_3	393.73
CDIM		$CHCl\text{-}I_2$	302.28
DCIM		$CHCl_2I$	210.83
DBIM		$CHBr_2I$	299.73
BDIM		$CHBrI_2$	346.73
BCIM		CHBrClI	255.28

SOURCE: *http://pubchem.ncbi.nlm.nih.gov*

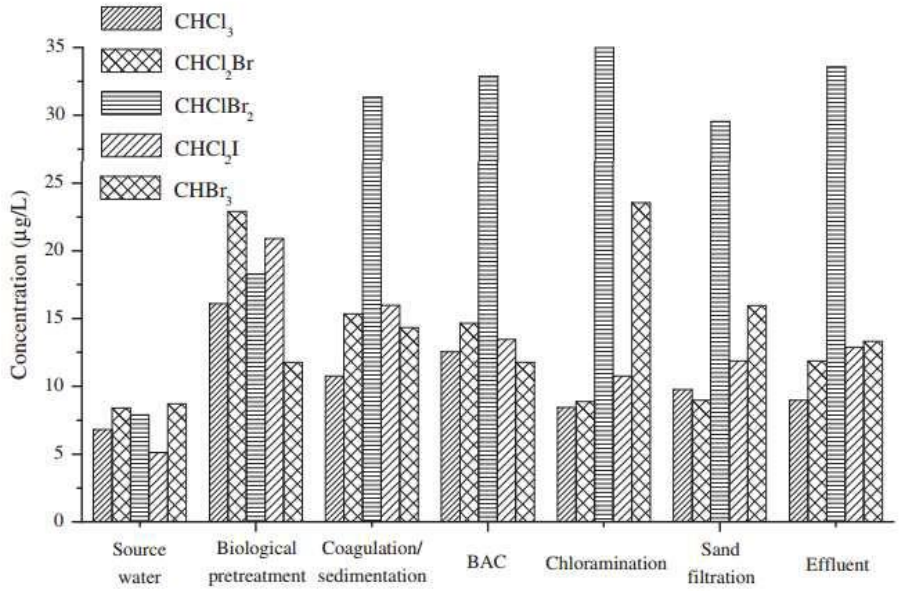


Figure 2-2 The potential of $CHCl_2I$ formation upon chlorinated the effluent of each unit (reaction conditions: pH = 7, time = 24 h, temperature = 25 ° C, Cl_2 dose = 5 mg/L unit (Wei et al., 2013

Levels of six I-THMs of water from 65 water treatments systems in winter and summer in Canada were surveyed. The water treatment systems in the survey consisted of large, medium, and small systems. Sources water, treated water, and three samplings along the distribution system were collected. Ranged of the total I-THMs from 0.02 to 21.7 µg/L was determined. Iodoform was detected as the highest concentration among six I-THMs species. Under winter condition, one or more I-THMs were detected at 31 out of 65 WTSs, whereas that at 46 out of 65 WTSs in summer conditions were found (Tugulea et al., 2018).

2.4 Halonitromethanes (HNMs)

Halonitromethanes (HNMs) consist of chloronitromethane, dichloronitromethane, trichloronitromethane, bromochloronitromethane, bromodichloronitromethane, bromo-nitromethane, dibromonitromethane, dibromochloronitromethane, and tribromonitromethane. HNMs are the cytotoxic and genotoxic N-DBPs. HNMs was found after the chlorination, ozone chloramination, and chloralmination of water. Hydrophilic organic fraction (HPI0 was found to be the major precursors of HNMs. Unfortunately; HPI was difficult to remove by the conventional coagulation process. The fractionation of DOM into HPO, transphilic organic fraction (TPI), HPI fraction are used to represent the significance of HNMs formation. (Jia et

al., 2009) The cytotoxicity and genotoxicity ranking of HNMs is tabulated in Table 2-2. (Plewa et al., 2004). The structure, formula, and molecular weight of HNMs is presented in Table 2-5.

Table 2-4 HNM Cytoxicity and Genotoxicity Ranking (Plewa et al., 2004)

Compounds	Cytotoxicity Ranking	Genotoxicity Ranking
Chloronitromethane	8	9
Dichloronitromethane	7	8
Trichloronitromethane	9	4
Bromochloronitromethane	6	7
Bromodichloronitromethane	5	2
Bromonitromethane	3	5
Dibromonitromethane	1	1
Dibromochloronitromethane	2	6
Tribromonitromethane	9	3

Table 2-5 Structure, formula and molecular weight of HNMs.

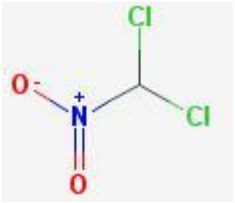
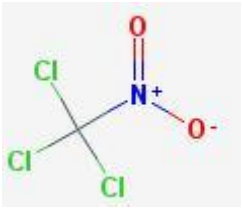
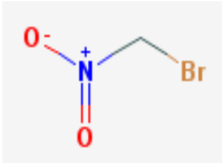
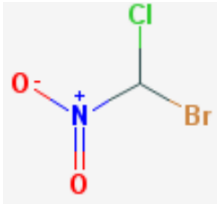
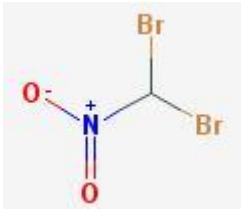
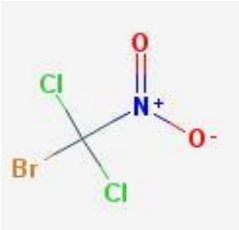
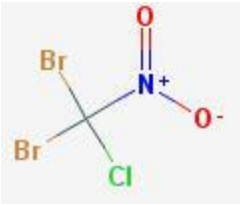
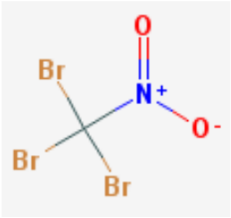
HNMs	Structure	Formula	Molecular weight [g/mol]
CNM		CH_2ClNO_2	95.48
DCNM		$CHCl2NO_2$	129.93
TCNM		CCl_3NO_2	164.37
BNM		CH_2BrNO_2	139.93
BCNM		$CHBrClNO_2$	174.38
DBNM		$CHBr_2NO_2$	218.83

Table 2-5. Structure, formula and molecular weight of HNMs. (Cont.)

HNMs	Structure	Formula	Molecular weight [g/mol]
BDCNM		$CBrCl_2NO_2$	208.82
DBCNM		CBr_2ClNO_2	253.27
TBNM		CBr_3NO_2	297.72

SOURCE: *http://pubchem.ncbi.nlm.nih.gov*

2.5 Level of I-THMs and HNMs in seawater

Many factors affect the formations of DBPs, including pH, temperature, disinfection, concentration, bromide concentration, nitrite concentration, reaction time, and precursor properties. The Chao Phraya River has been contaminated with sea water. Therefore, the information of the DBPs of sea water is important for the design of this study. The range of I-THMs of feed water of desalination plants in Red sea coast, Saudi Arabia (Le Roux et al., 2015) was 1.90-2.57 µg/L. For the seawater at Aquaria, undisclosed, HNMs ranged from 14.6 to 16.5 µg/L. (Shi et al., 2013)

2.6 Dissolved organic matter

Dissolved organic matter (DOM) is defined as the complex matrix of organic material present in natural waters. The term "*organic*" is used to describe general compounds that contain carbon (C) and one or more of the following elements: hydrogen (H), nitrogen (N), and oxygen (O). DOM is a dominant reactant in and product of biogeochemical processes in which the material serves as a carbon and energy source for biota and controls levels of dissolved oxygen, nitrogen, phosphorus, sulfur, various trace metals, and acidity (Leenheer and Croue, 2003). DOM in water composed of DOC and dissolved organic nitrogen (DON) (Lee and Westerhoff, 2006). DON has been considered as primary NDMA precursors (Aydin et al., 2012). DOC, UV-254, and specific ultraviolet adsorption (SUVA) are the secondary precursor of NDMA (Roux et al., 2011; Yoon et al., 2011).

2.6.1 Quantification and Characterization of DOM and DON

With regard to the heterogeneous character of DOM, there are two approaches for identifying the composition of DOM. DOM has been commonly quantified by using surrogate, nonspecific parameters such as DOC, UV- 254 (USEPA, 1999). For a more complicated approach, resin fractionation can be used to isolate bulks of DOM into DOM fractions that are chemically similar (AWWA, 1993).

DOM can be characterized on the basis of its apparent molecular weight (AMW) by using UF membrane. Amy et al. (1987) describe the procedure using a series of hydrophilic ultrafiltration membranes. That approach yielded a series of corresponding permeated for analysis with the following AMW ranges: < 0.5 kDaltons (kDa), < 1 kDa, < 3 kDa, < 5 kDa, < 10 Da, < 30 kDa.

Three-dimensional fluorescent spectroscopy (fluorescent excitation-emission matrix, FEEM) provides information on the putative origin of fluorescent organic matter in water. It could identify the matter as a tyrosine-like substance, tryotophan-like substance, humic acid and fulvic acid-like substances, and so on (Coble 1996; Nakajima et al. 2002; Chen et al. 2003; and Sierra et al., 2005). Methods that have been used to quantify and characterize DOM were modified and used to analyze DON as NDMA precursors.

Pyrolysis gas chromatography mass spectrometer (GC/MS) is the technique that could identify the chemical classes of DOM in the water. The chemical classes of DOM in water defined as aliphatic hydrocarbon, aromatic hydrocarbon, organic nitrogen, phenolic

compound, aldehydes and ketones, ester and alcohol, carboxylic acids, and unknown (Musikavong and Wattanachira, 2013).

2.6.2 Dissolved organic nitrogen

Four species of nitrogen are found in the secondary and tertiary treated wastewater effluents: (i) organic nitrogen, (ii) ammonium ion (NH_4^+), (iii) nitrate (NO_3^-), and (iv) nitrite (NO_2^-). Organic nitrogen consists of DON and particulate organic nitrogen (PON). DON plays an important role as precursors of many N-DBPs during the water treatment process. A study found that N-DBPs have higher teratogenic, mutagenic, and carcinogenic capability than carbon-containing disinfection by-products (C-DBPs), such as trihalomethanes (THMs) (Plewa et al., 2008).

Even by present-day analytical techniques, there are no analytical methods that can directly measure DON in water. DON was calculated from the difference between the total dissolved nitrogen (TDN) and inorganic nitrogen (DIN) (the summation amount of ammonia, nitrite and nitrate). According to the different methods for the analysis of TDN and inorganic, sometimes DIN concentration was higher than TDN. DON values, therefore, could not be determined. To deal with this situation, pre-treatment techniques such as dialysis (Lee and Westerhff, 2005) and membrane filtration (Xu et. al., 2010) were developed for DON analysis. Due to the complex analysis, the information of DON level in groundwater, reservoir waters, raw water supply, and water supply in Thailand, therefore, is limited.

DON cannot be measured directly but can be calculated by the following equation

$$DON = TN - NO_3^- - NO_2^- - NH_4^+$$

Where DON is a concentration of DON, TN is a concentration of total nitrogen, NO_3^- is a concentration of nitrate, NO_2^- is a concentration of nitrite, and NH_4^+ is a concentration of ammonium ion.

Na Phatthalung et al., (2014) studied the presence of organic carbon and organic nitrogen in groundwater, raw water supply, and water supply in the U-Tapao River Basin (UTRB), Thailand. DOC was found in groundwater, reservoir waters, raw water from the canal, and water supply in the UTRB. The amount of DOC in water from high to low was raw water supply, water supply, reservoir water, and groundwater. DON was not detected in

groundwater. The range of DON in reservoir waters, raw water supplies, and water supplies were from 0.02 to 0.08, from 0.04 to 0.88, and from 0.01 to 1.37 mg N/L, respectively. Fluorescent peaks of organic nitrogen, tryptophan like substances, in raw water supplies were detected at $230nm_{Ex}/345nm_{Em}$ and $280nm_{Ex}/355nm_{Em,}$ whereas that of humic and fulvic acids-like substances were found at $230nm_{Ex}/420nm_{Em}$, $275nm_{Ex}/410nm_{Em}$ and $330nm_{Ex}/410nm_{Em}$.

2.7 Fractionation of DOM by Ultrafiltration

Mitch and Sedlak (2004) utilized ultrafiltration with the pore size of 0.2, 0.45, and 0.7 µm to separate the water for determining NDMA precursors. Water samples were separated into three groups according to MW of 3,000 MW, 10,000 MW, and 30,000 MW for measuring NDMA precursors. It was found that the water after pass through 0.2, 0.45, and 0.7 µm contained the NDMA precursors of about 500 ng/L. Water samples at MW of 3,000 MW, 10,000 MW, and 30,000 MW had NDMA precursors of about 700 ng/L.

Xu et al., (2011) conducted the research on the measurement of DON in a drinking water treatment plant: size fraction, fate, and relation to water quality parameters. The UF membranes were used to fractionate DOM according to molecular size cut-offs into six groups: < 1kDa fraction, 1-3 kDa fraction, 3-5 kDa fraction, 5-10 kDa fraction, 10-30 kDa fraction, >30 kDa fraction. The < 1kDa fraction primary composed of the composition of DON, DOC, and UV-254 and it also was the major precursors of NDMA in raw water.

Wang et al., (2013) studied the effects of organic fractions on the formation and control of NDMA precursors during conventional water treatment processes. They fractionated DOM in water by using UF into three groups: < 1kDa fraction, 1-3 kDa fraction, and > 3 kDa fraction. It was found that the < 1kDa fraction had the highest NDMA-FP formation of 40 ng NDMA/mg C followed by 1-3 kDa fraction of 12 ng NDMA/mg C, and > 3 kDa fraction of 8 ng NDMA/mg C.

2.8 Polyaluminium chloride coagulation and enhanced coagulation by power activated carbon

DOM in raw water from reservoirs and canals as precursors to THMs formation was identified. Water samples were collected from two reservoirs, the U-Tapao canal (upstream and midstream) and the raw water in the rainy season and summer. In the reservoir and canal, aliphatic hydrocarbon and organic nitrogen were the major chemical classes. The optimal

dosage of PACl coagulation was 40 mg/L at pH 7. It reduced UV-254 to 57% and DOC to 64% (Musikavong and Wattanachira, 2013).

Raw water from the U-tapao, Songkla province were collected. The DOC of raw water in the rainy and summer season was 5.1 and 5.5 mg/L, respectively. In the rainy season, the coagulation with PACl reduced DOC of HPI and DOC of HPO at approximately 53% and 50%, respectively. In the summer season, the coagulation with PACl reduced DOC of HPI and DOC of HPO by 65% and 61%, respectively. (Srimuang et al, 2014).

The PACl coagulation, flocculation, sedimentation and filtration processes of 3 WTPs in the UTRB reduce DOC and UV-254 by 21-43% and 29-80%, respectively. They did not remove DON in almost all cases. The reduction of the summation of fluorescent intensity of humic and fulvic acids-like substances had a similar trend with the reduction of DOC (Na Phatthalung et al., 2014)

Zhou et al., (2014) studied the influence of HPO, TPI, and HPI on ultrafiltration membrane fouling. For the polysthersulfone, the irreversible fouling potential from high to low was HPO>TPI>charge hydrophilic>neutral hydrophilic. The reduction of effluent organic matter (EfOM) and background natural organic matter (NOM) by using different molecular weight cut-offs membranes was determined. The anthropogenic polysaccharide and protein-like substances that composed of polysaccharides, proteins, and colloids in EfOM could be mainly removed by UF membrane with the 100 kDa membrane. When the membrane's molecular size cut-offs were decreased, the humic substances in dissolved organic matter could be more easily removed compared with that in EfOM. The polysaccharides associated with the colloidal fraction and the humic substances could be classified as the main potential foulants for UF membranes processing wastewater EfOM. The molecular weight size cut-offs of the membrane and the molecular size of the main foulants were the critical parameter that could cause the cake filtrations or pore blocking of EfOM or NOM in the ultrafiltration process (Guo, 2014)

Tongchang et al., (2018) conducted the enhanced coagulation of DON. Three raw water sources in Thailand included the Banglen (BL) water treatment plant (WTP) and Bangkhen (BK) WTP in central Thailand and Hatyai (HY) WTP in southern Thailand. The DON (mg N/L) and the dissolved organic carbon (DOC)/DON ratio of 0.34 and 21, 0.24 and 18, and 1.12 and 3 were detected for the raw waters from BL, BK, and HY WTPs, respectively. The optimal coagulation conditions were obtained at PACl dosages of 150, 80, and 40 mg/L at pH 7 for the raw waters from BL, BK, and HY WTPs, respectively. Under

such conditions, it could reduce DON by 50, 42, and 42% respectively. The DON reduction of 71, 67, and 29% in the raw waters from BL , BK, and HY WTPs, respectively, could be conducted by using by PACl and PAC (both in mg/L) at 150 and 20, 80 and 20, and 40 and 60 mg/L, respectively. The moderately and fair correlations between the reductions in fluorescence intensities of tryptophan-like substances and DON reduction were determined.

The study of the removal of organic substances and disinfection precursors in the wastewater treatment system in China was conducted. Two pilot-scale experiments using an iron-carbon micro-electrolysis (ICME) combined with up-flow biological aerated filter (UBAF) process were employed in the experiment. The ICME pretreatment removed 15.6% of DOM and could increase the removal rate of the subsequent UBAF process. The UABF process could remove 31% of THMs precursor and 20% dichloroacetonitrile precursor (Chen et al., 2018).

Chapter III
Research Methodology

The experimental procedure of this research was divided into three parts. The first part was the identification of precursors of carbonaceous disinfection by-products (C-DBPs) and nitrogenous DBPs (N-DBPs) and formation of C-DBPs and N-DBPs. The second part was the reduction of precursors of C-DBPs and N-DBPs. The final part was the effect of iodide and bromide concentrations, DOM fractions, and reaction times on the formation of C-DBPs and N-DBPs.

3.1 Sampling sites and sample collection

The raw water from two water treatment plants (WTP), river water at a downstream location of the Chao Phraya River, and wastewater and treated wastewater from two domestic wastewater treatment plants (WWTP) were collected three times from each source water. Water supply samples (WS−1 and WS−2) were collected from the water supply of Bangkhen WTP at the first and second sampling. The location of sampling sites is illustrated in Figure 3-1. Water samples were collected in October 2016, May 2017, and February 2018 (Table 3-1) as the representative of the study on emerging C-DBPs' and N-DBPs' formation during the rainy season, summer, and winter, respectively.

Raw waters from the Chao Phraya River were collected from the pumping station of Bangkhen WTP (BK WTP) at a downstream location (RW−1) and Singburi WTP (SB WTP) at an upstream location (RW−2). Water samples from the river were obtained from the Siriraj sampling site, which is located downstream of the Chao Phraya River after the BK WTP. This sample stands for water with seawater, treated and untreated wastewater contamination.

Domestic wastewater before (WW−1) and after treated wastewater (TWW−1) were collected from the WWTP in Ang Thong (AT) province. In addition, domestic wastewater before (WW−2) and treated wastewater (TWW−2) were obtained from the WWTP in Ayutthaya (AY) province. These two WWTPs are located in the upstream location of the Chao Phraya River. The wastewater and treated wastewater represent the sources of contamination from human activities. All samples were stored at a temperature of 4 °C until analysis.

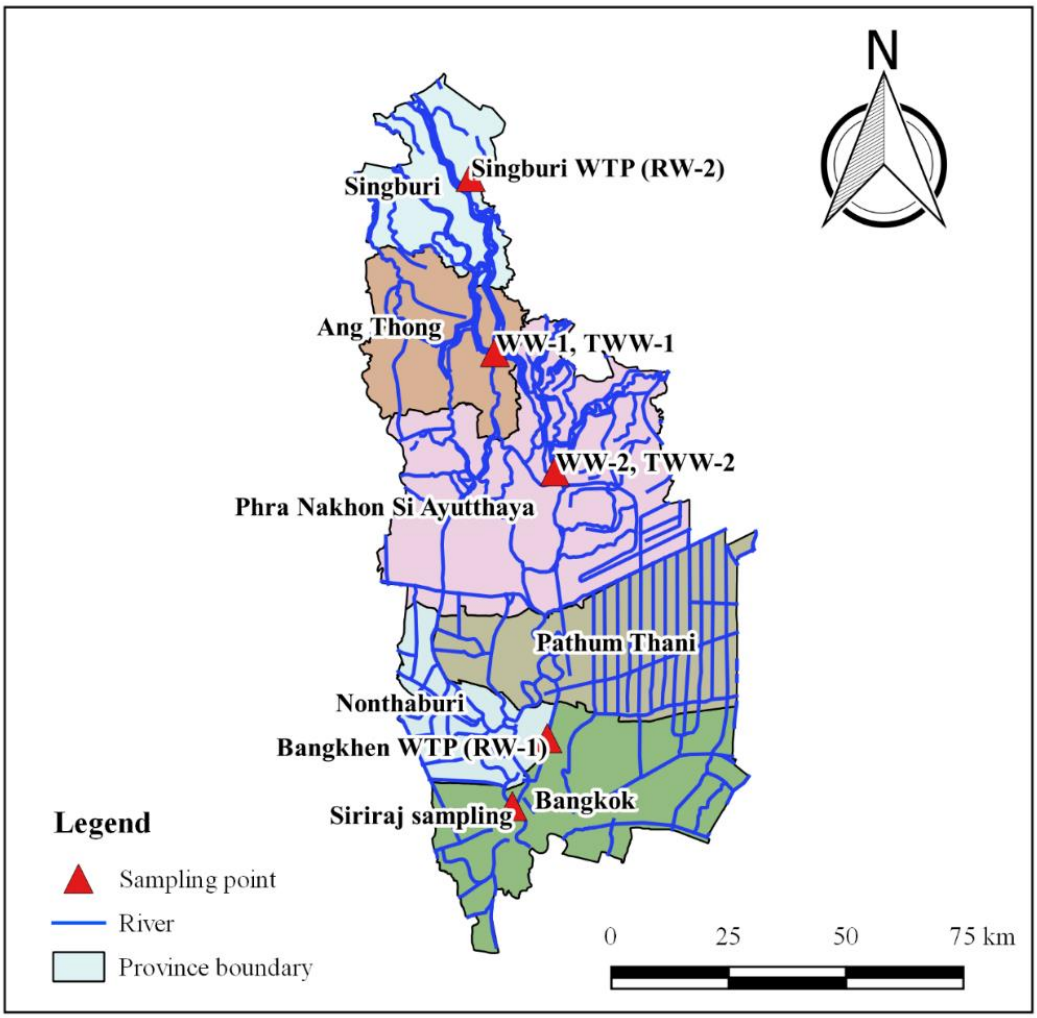


Figure 3-1 The location of sampling sites. (Na Patthalung and Musikavong, 2019)

Table 3-1 The sampling sites

Sampling	**1st** (October 2016)	**2nd** (April 2017)	**3rd** (February 2018)
Raw water (Bangkhen WTP, RW−1)	✓	✓	✓
Water supply (Bangkhen WTP)	✓	✓	×
Raw water supply (Singburi WTP, RW −2)	✓	✓	✓
Domestic Wastewater (WW)			
WWTP in Angthong (WW−1)	✓	✓	✓
WWTP in Ayutthaya (WW−2)	✓	✓	✓
Treated wastewater (TW)			
WWTP in Angthong (TWW−1)	✓	✓	✓
WWTP in Ayutthaya (TWW−2)	✓	✓	✓
River water			
Downstream: Siriraj sampling site	✓	✓	✓

3.2 Experimental procedures

3.2.1 Experiment I The identification of precursors of C-DBPs and N-DBPs and formation of C-DBPs and N-DBPs.

The water samples in this experiment including raw water, wastewater, treated wastewater, and river water for the first, second and third sampling (see Table 3-1) were analyzed for basic water parameters, carcinogenic substances and their precursors. The water supply at the first and second sampling was measured for their basic parameter only. The experiments for water samples in the rainy season (first sampling) and summer season (second sampling) were conducted using the conventional procedure as presented in Figure 3-2.

- Basic parameter analysis: Water samples were measured for their pH, turbidity, salinity, and alkalinity.
- Precursors and carcinogenic substances analysis: Water samples were filtered using GF/F and analyzed for their dissolved organic carbon (DOC), dissolved organic nitrogen (DON), fluorescent excitation-emission matrix (FEEM),

bromide, iodide, except water supply and river water, trihalomethanes (THMs), haloacetronitriles (HANs), iodo-trihalomethanes (I-THMs), halonitromethanes (HNMs), trihalomethanes formation potential (THMFP), haloacetronitrile formation potential (HANFP), iodo-trihalomethane formation potential (I-THMFP), and halonitromethane formation potential (HNMFP)

- Fractionation analysis: Water samples were fractionated using the resin fractionation technique into three fractions: HPO, TPI and HPI and using a UF technique to obtain DOM into four groups: molecular weight (MW) < 1kDa, 1 < MW <3 kDa, 3 < MW <10 kDa, and MW > 10 kDa. Then, these DOM fractions were analyzed for their DOC, FEEM, THMFP, HANFP, HMNFP, and I-THMFP.
- The weight measured concentration of water samples and their DOM fractions in terms of lethal concentration 50-weighted of DBPs, and lowest cytotoxicity-weighted concentrations of DBPs were evaluated.

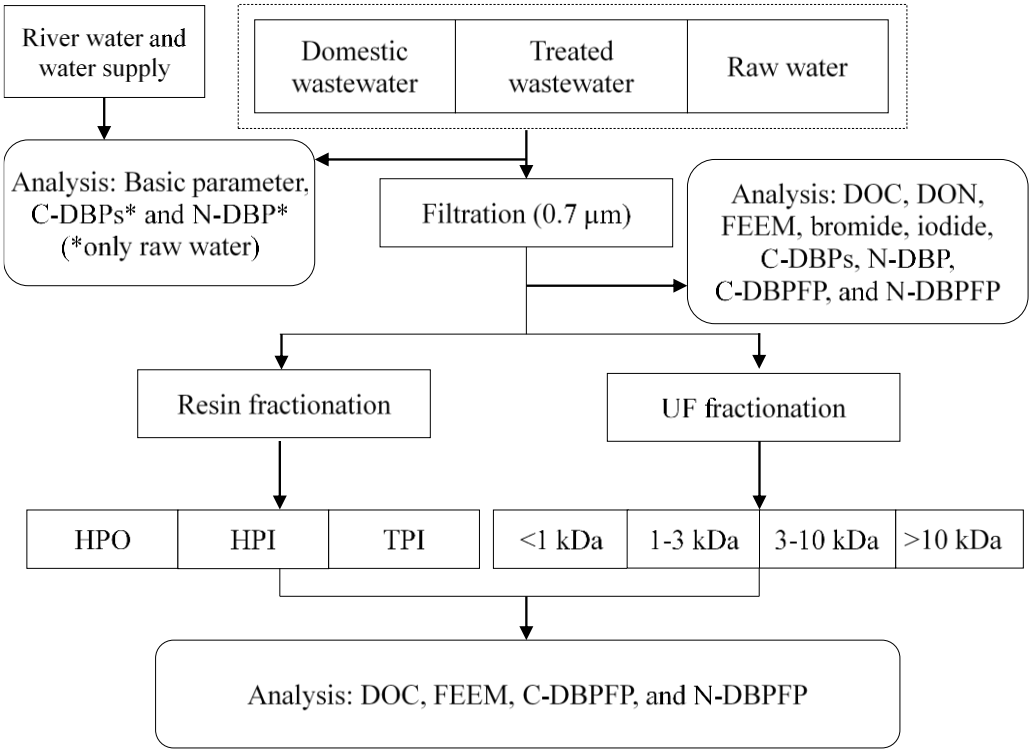


Figure 3-2. Identification of precursors of C-DBPs and N-DBPs and formation of C-DBPs and N-DBPs

3.2.2 Experiment II Reduction of precursors of C-DBPs and N-DBPs

The alum was used as the coagulant in the experiment. The enhanced coagulation experiment was conducted by using powder activated carbon (PAC) and magnetic ion exchange (MIEX). The water samples for coagulation and enhanced coagulation consisted of raw water of the Bangkhen WTP in rainy season (RW−1), summer season (RW−2), and winter season (RW−3), the RW−1 mixed with TWW−2 (AY) at a mixing ratio of 50:50 (volume by volume, v/v). In addition, 100% of treated wastewater (TWW−1 (AT) and TWW−1, (AY)) was chosen for the coagulation treatment. This was assumed that treated wastewater, as indirect potable water reuse, must be discharged to the natural waterways and the water from this source is used as raw water for the water treatment plant.

Table 3-2 The water sample for experiment II.

Water sample	**1st**	**2nd**	**3rd**
Raw water (RW−1, BK)	✓	✓	✓
Treated wastewater (TWW−1, AT)	✓	-	-
Treated wastewater (TWW− 1, AY)	✓	-	-
RW−1 (BK) + TWW−1 (AY), 50% v/v	✓	-	-

The experiments of each water sample were conducted using the conventional procedure as presented in Figure 3-3. Water samples were measured for their turbidity, DOC, ultraviolet adsorption at wavelength 254 nm (UV-254), specific ultraviolet adsorption (SUVA), DON, FEEM, chemical classes, THMs, HANs, HNMs, I-THMs, THMFP, HANFP, I-THMFP and HNMFP. Each water sample was conducted in 1 L jars using the conventional procedure. The water samples were coagulated by using five alum dosages of ~ 5 – 120 mg/L under controlled pH of 7. The water samples were rapidly mixed at 100 rpm for one min, followed by a slow mixing at 30 rpm for 30 min, and settling for one h. The supernatant was collected and measured for their turbidity. The optimal dosage for turbidity removal was determined. Then the supernatants were filtered through 0.7 µm GF/F filter and measured for their DOC and DON. The optimal dosage of DOC and DON removal was determined. The enhanced coagulations by powder activated carbon (PAC) and magnetic ion exchange (MIEX) were performed using alum dosage at optimal DOC and DON reductions on the variation dosage of PAC and MIEX between 10-120 mg/L and 0.5-5 mL/L respectively.

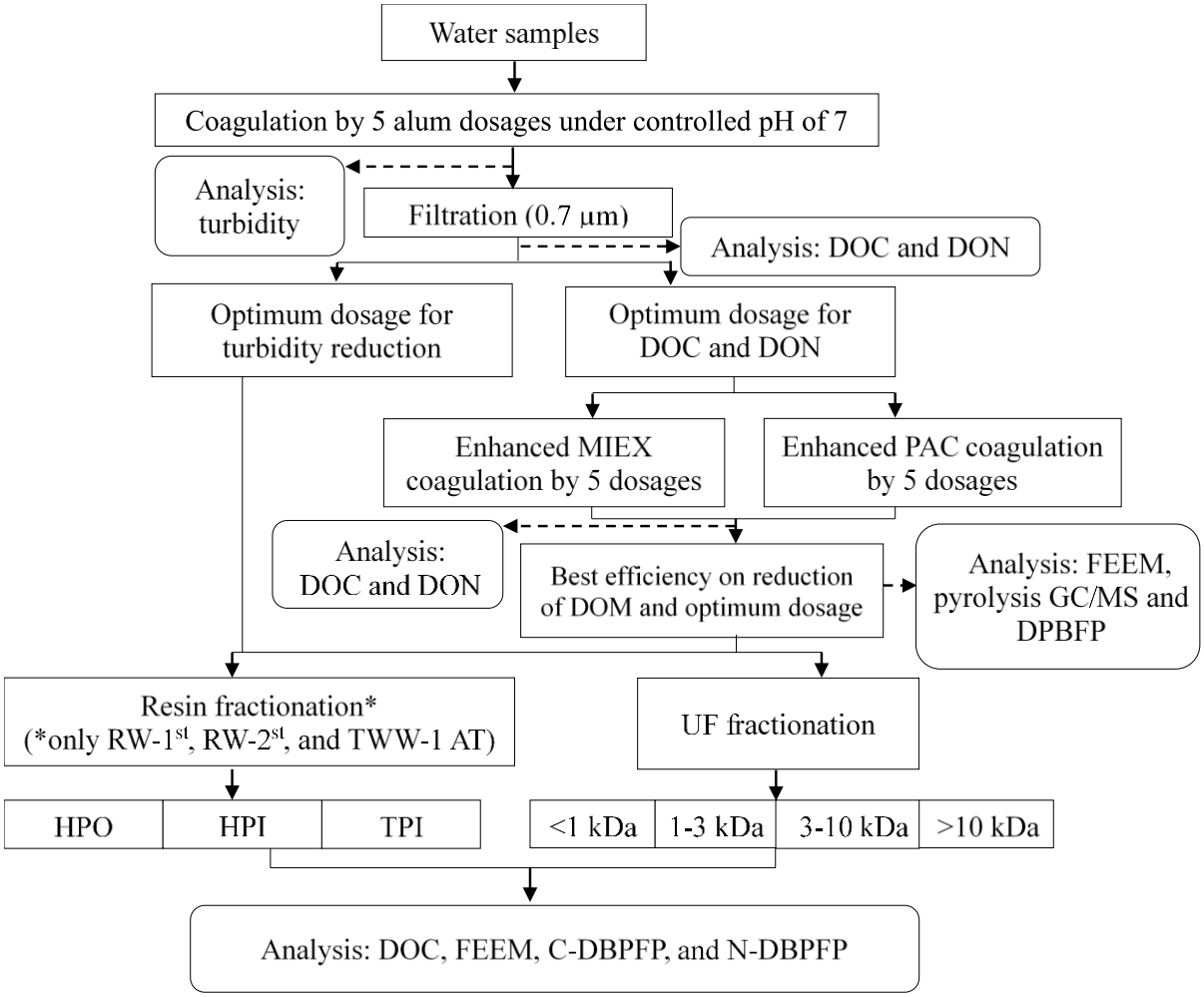


Figure 3-3. Reduction of precursors of C-DBPs and N-DBPs analysis.

The coagulated water under the optimal turbidity reduction (CW−1), the coagulated water under the optimal DOC and DON reductions (CW−2), and the coagulated water under optimal condition of enhanced PAC or MIEX coagulation (CW−3), were analyzed for their DOC, DON, FEEM, chemical classes, THMFP, HANFP, I-THMFP, and HNMFP. The CW−1, CW−2, and CW−3 were fractionated using resin and UF fractionation techniques. The hydrophobic organic fraction (HPO), transphibic organic fraction (TPI), hydrophilic organic fraction (HPI), and DOM of four groups: < 1 kDa, 1-3 kDa, 3-10 kDa, and > 10 kDa were measured for their DOC, FEEM, THMFP, HANFP, ITHMFP, and HNMFP.

3.2.3 Experiment III The effect of iodide, bromide, DOC, and DON concentrations, and DOM fractions of reaction time on the formation of C-DBPs and N-DBPs

In this experiment, the variation parameters were iodide, bromide, DOC, DON, DOC/ DON, and reaction times. The raw water samples (RW−1 and RW−2, BK), treated wastewater (TWW−1 (AT) and TWW−1 (AY)), and the RW−1 mixed with TWW−2 (AY) at a mixing ratio of 50:50 (volume by volume, v/v) were used for determined the influence of DOC, DON, DOC/DON on the THMFP, I-THMFP, HANFP and HNMFP. From the results of the experiment in part I, the levels of DOC, DON, bromide, and iodide, THMFP, HANFP, I-THMFP, and HNMFP of each water sample were determined. Experiments of each water samples were conducted using the conventional procedure as presented in Figure 3-4.

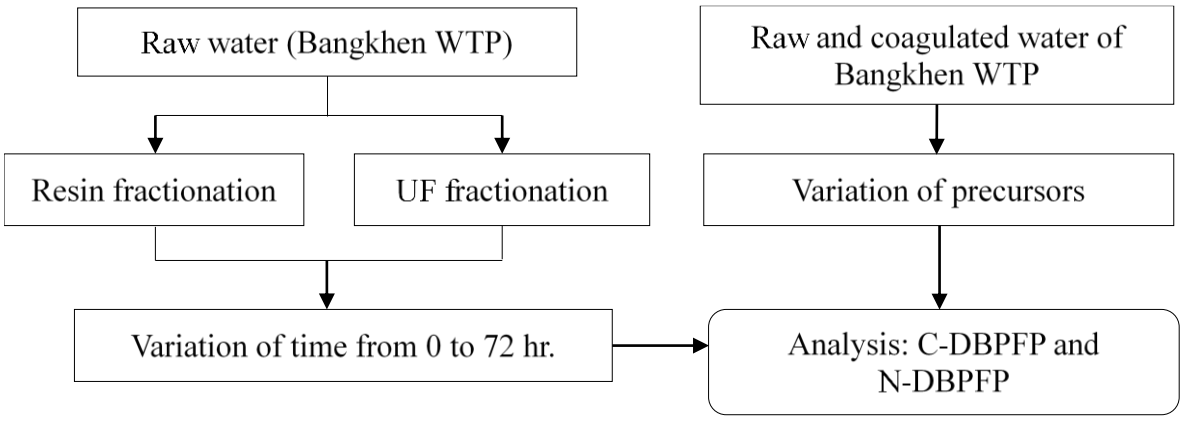


Figure 3-4. The effect of precursors and reaction time on the formation of C-DBPs and N-DBPs.

For the formation of C-DBPFP and N-DPBFP analysis, raw waters, treated wastewaters, and the RW−1 mixed with TWW−2 (AY) were selected as water samples that have DOC, DON, and DOC/DON follow by:

- Variation of five DOC values from ~3.2 to 5.6 mg/L
- Variation of five DON values from ~0.20 to 1.22 mg/L
- Variation of five DOC/DON values from ~5 to 29

The iodide and bromide were added into the raw water of the WTP (RW−1, BK) to obtain water samples that have iodide and bromide follow by:

- Variation of iodide concentrations from 0.5 to 5 µg/L
- Variation of bromide concentrations from 0.1 to 10 mg/L

All water samples of each experiment were measured for their THMFP, HANFP, I-THMFP, and HNMFP.

For the kinetic of precursors on formation of C-DPBFP and N-DPBFP analysis, the raw and coagulated waters from Bangkhen WTP were used in this experiment. Also, the raw water from Bangkhen WTP was fractionated in order to determine the kinetics of DBPs of each DOM fractions. The samples before and after fractionation were analyzed for kinetic of precursors on formation follows:

- Raw and coagulated water with variations of reaction times from 0 to 72 hr.
- HPO with variations of reaction times from 0 to 72 hr.
- TPI with variations of reaction times from 0 to 72 hr
- HPI with variations of reaction times from 0 to 72 hr
- DOM < 1 kDa with variations of reaction times from 0 to 72 hr
- DOM 1-3 kDa with variations of reaction times from 0 to 72 hr
- DOM 3-10 kDa with variations of reaction times from 0 to 72 hr
- DOM > 10 kDa with variations of reaction times from 0 to 72 hr

3.3 Reagents

A standard THM mixture (chloroform ($CHCl_3$), BDCM ($CHBrCl_2$), DBCM ($CHBr_2Cl$), and bromoform ($CHBr_3$)) containing 1,000 µg/mL of each compound in methanol was purchased from Supelco (Bellefonte, PA, USA). Separate neat standards for I-THMs analysis, including DCIM ($CHCl_2I$), BCIM (CHBrClI), BDIM ($CHBrI_2$), and CDIM ($CHClI_2$), were purchased from CanSyn Chem. Corp. (New Westminster, Canada), and TIM was purchased from Supelco (Bellefonte, PA, USA). Separate standard solutions for four HANs species, namely TCAN (CCl_3CN), DCAN (Cl_2CHCN), BCAN ($C_2HBrClN$), and DBAN (C_2HBr_2N) and one HNM species (TCNM or chloropicrin; CCl_3NO_2) were purchased from AccuStandard (New Haven, USA). The 4-bromofluorobenzene (1,000 lg/mL in methanol, purity >97.5%) as the internal standard solution was purchased from Supelco (Bellefonte, PA, USA).

3.4 Basic water parameter analysis

Water samples were measured for their pH, turbidity, salinity, and alkalinity. The pH, turbidity and salinity of water samples were direct measured by pH meter (HACH Sessions 1 with ± 0.01 pH unit accuracy), turbidity meter (HACH, Model 2100) and conductivity meter,

respectively. Alkalinity was determined by titration according to the Standard Method 2320 B. Concentrations of ammonia, nitrate, and nitrite were measured with a Hatch DR 2700 Portable Spectrophotometer.Ammonia was analyzed following the Standard Methods 8038 (Nessler Method) and 10031 (Salicylate Method). Nitrite (NO_2^-) was measured using the diazotization method (Hach Method 8507), and nitrate **(**NO_3^-) was analyzed using the cadmium reduction method (Hach Method 8192).

3.5 DOC UV-254, SUVA and DON analysis

The water samples for analyzing their DOC, UV-254, SUVA, and DON were filtered by a precombusted (550°C, 2 h) 0.7 μm filter before measurement. The filtered water samples were acidified with sulfuric acid (H_2SO_4) to pH ~2 for preservation and stored at 4°C until analysis.

DOC concentrations in water samples were determined by a combustion method (Standard Method 5310D) (APHA, 1998) on a total organic carbon analyzer (TOC-V CSN, Shimadzu, Japan). The DOC is usually represented as a complex mixture of aromatic and aliphatic carbon-rich compounds of natural DOM in water (Sinsabaugh and Findlay, 2003).

UV-254 was measured by the Standard Method 5910B using a Genesys 10S UV/VIS spectrophotometer (Thermo Electron Corp. Madison, WI, USA). UV-254 can be used as a quantitative indicator of the DOM with aromatic rings in the water (Hong et al., 2013). SUVA was calculated using the UV-254 absorbance normalized to the mg/ L DOC concentration. The SUVA is a useful surrogate for DOC aromaticity in the natural organic matter of water (Weishaar et al., 2003).

DON concentrations in water samples were calculated directly by subtracting the concentrations of dissolved inorganic nitrogen (DIN) species (NH_4^+, NO_3^-, NO_2^-) from the total dissolved nitrogen (TDN) concentration. High DIN levels could become a concentration error of DON in the water sample. To reduce the DON measurement error, pretreating the water sample before TDN and DIN analysis was performed using nanofiltration (NF).

3.6 Iodide and bromide analysis

Iodide concentration in water samples was determined using the Standard Method 4500-I^- B. (leuco crystal violet method) for the high concentration of iodide (50 to 6,000 μg/L) and the Standard Method 4500-I^- C. (catalytic reduction method) for low concentration of iodide (< 80 μg/L). Bromide concentration in water samples was analyzed by ion

chromatography with an Alltech liquid chromatograph equipped with an Allsep anion column (100 mm length x 4.6 mm ID x 7 µm particle diameter, USA). Each sample was analyzed in duplicate.

3.7 FEEM analysis

The water samples for analyzing their FEEM were filtered by a precombusted (550°C, 2 h) 0.7 µm filter before measurement. The FEEMs of the samples were measured using a spectrofluorometer (JASCO FP-8200, Japan). Three-dimensional spectra were obtained by measuring the excitation and emission spectra at wavelengths from 220 nm to 600 nm (with 5 nm intervals). The FEEM of the Milli-Q water was determined and subtracted from the FEEM for each sample to remove most of the Raman scattering peaks. The photomultiplier tube voltage was maintained at 600 V and the scanning speed was set at 1200 nm/min. The FEEMs were corrected and the fluorescence intensities were converted into quinine sulphate units (QSU) as shown elsewhere (Zepp et al., 2004).

3.8 Fractionation of DOM

3.8.1 Resin fractionation

Water samples were fractionated using the resin fractionation technique into three HPO, TPI, and HPI. The filtered water with a pH of 2 was passed through DAX-8 resin followed by XAD-4 resin in accordance with the method developed by Leenheer et al. (1981) and Aiken et al. (1992). Effluent from the XAD-4 resin was collected, and this was referred to as the HPI fraction. The fraction referred to as HPO was retained by DAX-8 resin and eluted with 0.1 N NaOH in the reverse direction. The XAD-4 resin retained organic compounds comprising the TPI fraction, and these were also eluted with 0.1 N NaOH in the reverse direction. The pH of all the three fractions was adjusted to pH 7 with sodium hydroxide (NaOH) or sulfuric acid (H_2SO_4), and each fraction was adjusted to the initial sample volume prior to the measurement of DOC. All DOM fractions were stored at 4°C in a cold room prior to analyzing for their DOC, THMFP, HANFP, HMNFP, and I-THMFP.

3.8.2 Size fractionation

UF technique was used to fractionate the molecular size of DOM into four groups: > 10 kDa, 3-10 kDa, 1-3 kDa, and < 1kDa, using YM10, YM3, and YM1 Da Ultracel regenerated cellulose membrane (Millipore Corp, Bedford, USA) with decreasing molecular

weight cut-off (MWCO) of 10, 3 and 1 kDa. Before each run, the apparatus was cleaned and the membranes were thoroughly rinsed with several times with Milli-Q water to remove glycerin which was added by the producers to the membrane. Sequential filtration was performed with stirred 200 mL UF cells. The nitrogen pressure was maintained at 40 psi. The initial sample volume was 200 mL for all samples. Starting with the YM10 membrane. The filtration was stopped when the volume of retentate decreased to 50 mL. Permeate was collected for subsequent ultrafiltration. Organic-free deionized water was added to the cell to bring the volume back to 200 mL, and filtration was continued until the volume decreased to 50 mL again. This flushing process was repeated twice further to remove compounds with MW lower than the membrane cutoff. Then the retentate was collected, and the volume was diluted to the initial loading volume with deionized water. This ultrafiltration method resulted in four fractions with nominal molecular weights of > 10, 3-10, 1-3, and < 1 kDa. Each fraction was analyzed for their DOC, THMFP, HANFP, HMNFP, and I-THMFP.

3.9 Pyrolysis GC/MS analysis

The chemical class of DOM was characterized by a pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS, 7890 B GC-5977A MSD, Agilent, USA). Before sample injection, the prefrozen of water sample was conducted at −80°C for at least 24 h. Then they were placed in a freeze-drying unit at -85°C and 0.035 bars to obtain a uniform dry powder. To produce the sufficient amount of uniform power for GC/MS analysis, the freeze-drying process was repeated several times. Duplication was measured by Py-GC/MS for each sample.

About one milligram of uniform powder of all water samples was weighed into the buckets which attached to a sample holder in the quartz tube of the Py-GC/MS. The pyrolysis temperature was 700°C and held for 10 seconds. The pyrolyzer (Multi-Short Pyrolyzer EGA/PY-3030 D, Frontier, Japan) was attached to the injection port of the Agilent GC-MS. The Rtx-VMS column (30 m length x 0.25 mm diameter x 1.4 μm film thickness, maximum usable temperature: 240°C, Restek) was used for separation with helium as the carrier gas. The GC oven temperature was initially held at 40°C, followed by a rate of 2°C/min to 80°C, 3°C/min to 140°C, 5°C/min to 220°C, and a final ramp was 220°C, hold for 30 min.

The interpretation of the pyrochromatograms was conducted in accordance with Musikavong et al. (2009). In the first step, peaks in DOM pyrogram of all water samples in terms of "fragments" were identified by mass spectral correlation to the Wiley 10th with

National Institute of Standard and Technology 2014 (NIST 2014) mass spectral library. Only high-quality peak matching percentage of fragment > 85% between measured and library mass spectra are reported. Less than 85% of matched fragments was defined as an unknown fragment.

In the second step, it was to group fragments into similar chemical classes by a semi-quantitative technique. The identified fragments of samples were categorized into broad chemical classes including aliphatic hydrocarbon (AL); aromatic hydrocarbon (AR); organic nitrogen (ON); phenolic compound (PN); aldehydes (AH) and ketones (KT); ester (ES) and alcohol (AC); carboxylic acids (CA); and unknown (UN). The relative ratio of the area between fragments and one normalizing fragment (relative ratio = area of pyrolysis fragment/ area of the normalizing fragment) , was utilized to achieve a fingerprint of the pyrolysis (Page et al., 2002). Benzene was utilized as the normalization fragment.

3.10 DBPs' formation potential (DBPFP)

The water samples were filtered using GF/F (Whatman GF/F, 0.7 µm) and analyzed for their DBPFP. The DBPs analyzed in this study included four THM species (chloroform, BDCM, DBCM, and bromoform); five I–THM species (TIM, DCIM, BCIM, BDIM, and CDIM); four HAN species (TCAN, DCAN, BCAN, and DBAN); and one HNM species (TCNM). The DBPs formation potential test was conducted under controlled conditions including pH, temperature, and free chlorine residual to determine the highest DBPs' formation.

It must be noted that the DBPs' formation potential could not be used to represent the DBPs levels of water samples in their natural environment. The highest formation potential of THMs was measured according to the 7–day chlorine test procedure (the Standard Methods 5710B) (APHA, 1998). For I–THMs, HANs, and HNM, the highest formation potential of DBPs occurred during a 24–h chlorination reaction period with a hypochlorite reagent as determined in previous studies (Pantelki and Voutsa, 2018; Zhang et al., 2016; Bougeard et al., 2010; Song et al., 2010). In summary, the formation potential experiments for I–THMs, HANs, and HNM were conducted with a 24–h incubation period, but 7-day incubation for THMs.

Briefly, a water sample was neutralized by a phosphate buffer (pH 7.0 ± 0.2) prior to chlorination using a Cl_2 sodium hypochlorite solution in amber bottles with a screw cap. The samples were then incubated in the dark at 25 ± 2°C. Samples had a remaining free chlorine

residual of 3–5 mg/L as Cl_2 after the incubation period. Free residual chlorine was measured using the Standard Method 4500-Cl G. (DPD colorimetric method) with a Hach spectrophotometer. Each chlorinated sample was quenched with sodium thiosulfate after the end of the reaction. It was reported that sodium thiosulfate could have an effect on HANs degradation (Urbansky, 1999). In this work, the extraction process was shortly carried out after dechlorination of water samples to prevent HAN degradation.

3.11 Analysis of DBPFP

The DBPs were extracted with methyl tert-butyl ether (MTBE); purity 99.9% with 4-bromofluorobenzene as an internal standard following US EPA Method 551.1 (Munch and Hauman, 1995). The extraction conditions were based on a previously reported procedure with some modifications (Song et al., 2010). Briefly, 35 mL of water samples were analyzed by liquid-liquid extraction using MTBE (2 mL) with 4-bromofluorobenzene as the internal standard (50 µg/L).

All extracts were analyzed using a gas chromatograph (GC) with a micro-electron capture detector (Agilent 6890N). The analytical column was HP-5ms (5% diphenyl/95% dimethyl polysiloxane as stationary phase, 30 m length, 0.32 mm inside diameter × 0.25 mm film thickness). The injection was conducted in the split mode of 1 µL with a split ratio of 5:1 at 225°C with helium carrier gas at a flow rate of 10 mL/min. The GC oven temperature was 35°C for 8 min and ramped to 50°C at 5°C/min and held for 5 min, then ramped at 25°C/min to 180°C and held for 1 min. The detector temperature was maintained at 260°C. Nitrogen at 60 mL/min was used as the make-up gas. Duplication was carried out for DBPFP analysis.

3.12 Coagulation experiment

The alum was used as the coagulant in the experiment. The enhanced coagulation experiment was conducted by using PAC and MIEX. The water samples for coagulation and enhanced coagulation consisted of raw water (RW) of the Bangkhen WTP from the first and second sampling.

The PAC was supplied by Carbokarn Co., Ltd. (Bangkok, Thailand). PAC is a coconut shell based powdered activated carbon, Grade HRO M325-60. The PAC particle size is smaller than 325 mesh (0.045 mm) with a minimum iodine number of 950 mg/g. A minimum density of PAC is 0.5 g/cc. The activated carbon had surface areas as high 1000

m^2/g. The maximum moisture and ash contents of PAC are 10% and 8 % w/w, respectively. The pH of PAC is between 9 and 11.

The MIEX was supplied by IXOM Watercare (Centennial, CO, USA). MIEX is a macroporous strong base resin with quaternary ammonia functional groups, in the chloride form and made of polyacrylic matrix. Its total exchange capacity is 0.42 meq/mL. The presence of high amounts of iron oxide in its structure gives magnetic properties to the resin (Singer and Bilyk, 2002), allowing the resin beads to agglomerate and separate from the suspending solution by gravity, settling at relatively high overflow rates (Cornelissen et al., 2008; Singer and Bilyk, 2002). The MIEX resin particles (diameter ~ 180 μm) are 2-5 times smaller than traditional ion exchange resins. The MIEX resin can be applied to raw water in the form of a slurry.

Chapter IV

Carbonaceous and nitrogenous disinfection-products' formation potential in raw water, wastewater, and treated wastewater

4.1 Introduction

Dissolved organic matter (DOM) in source water mostly originates from ecological impacts and human activities at the specific location. A conventional water treatment process including coagulation, sedimentation, and filtration slightly removes DOM. A certain amount of DOM, therefore, can pass through a conventional process. Disinfection by chlorine is commonly employed after the conventional water treatment process. A reaction between DOM and chlorine can cause potentially harmful substances, also known as disinfection by-products (DBPs). DBPs in water are undesirable because of their toxicity to water consumers (Butterworth, 2005). Health risks may arise from the consumption of water contaminated with DOM and its DBPs. Currently, the investigation of DBPs' formation from different types of water sources is very important.

A surrogate parameter for DOM is dissolved organic carbon (DOC), which reacts with chlorine resulting in the formation of carbonaceous DBPs (C-DBPs). Trihalomethanes (THMs) are the most dominant species in chlorinated waters (Krasner et al., 2006) and traditionally used as a surrogate parameter for C-DBPs (Shanks et al., 2013). Four THMs species are often measured namely chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform. The United States Environmental Protection Agency (US EPA) has classified chloroform, BDCM, and bromoform as probable human carcinogens, while DBCM is classified as a possible human carcinogen (US EPA, 2011).

Levels of THMs are regulated by many environmental protection agencies worldwide. The European Community has set a limit for maximum THMs concentration to 100 μg/L (EECD, 1998) in drinking water, and the US EPA has set a regulation level for THMs in drinking water of 80 μg/L (US EPA, 2006). The World Health Organization (WHO) has regulated the health-related guideline values for bromoform (100 μg/L), DBCM (100 μg/L), BDCM (60 μg/L), and chloroform (300 μg/L) in drinking water (WHO, 2006). Also, the WHO suggested that the sum of the ratios of the THM concentrations to its respective guideline value should not exceed one (WHO, 2006). In Thailand, the levels of THMs in the water supply are regulated based on the WHO guideline values.

Recently, researchers have identified many emerging DBPs in water. These emerging DBPs may have greater toxicity than the regulated chloro- and bromo-THMs. Iodo-trihalomethanes (I-THMs) is an emerging class of C-DBPs that have higher cytotoxicity than THMs, except chlorodiiodomethane (CDIM) (Richardson et al., 2008). I-THMs can be formed in the disinfected water from raw water, sea water intrusion with bromide or iodide concentration (Tugulea et al., 2018). Five common I-THMs species, namely iodoform or triiodomethane (TIM), dichloroiodomethane (DCIM), bromochloroiodomethane (BCIM), bromodiiodomethane (BDIM), and CDIM have been identified in drinking water (Krasner et al., 2006; Richardson et al., 2008). The I-THMs have also been detected in treated wastewater effluents (Gong and Zhang, 2015). The increase in iodide concentration in source water may enhance the formation of I-THMs during disinfection (Zhang et al., 2015). Currently, the guideline value for I-THMs in drinking water is not currently regulated by the WHO.

Nitrogenous DBPs (N-DBPs) are one group of DBPs that are more toxic to human health than regulated C-DBPs (Muellner et al., 2007). N-DBPs may form in water from water sources with a high level of dissolved organic nitrogen (DON), especially when water sources are polluted by wastewater and algae organic matter (Lee and Westerhoff, 2006). Haloacetonitriles (HANs), N-nitrosamines, halonitromethanes (HNMs), and haloacetamides are emerging N-DBPs that have been recently reported (Krasner et al., 2006; Richardson et al., 2008). Among N-DBPs, HANs have been frequently reported and studied. Research on other N-DBPs in drinking waters is infrequently carried out. Previous studies have suggested that four HANs species, namely trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN) were often detected after chlorination of bromide-containing water (Chen and Westerhoff, 2010). WHO recommends drinking water guideline values for DCAN of 20 μg/L and DBAN of 70 μg/L (WHO, 2008). HNMs have been reported as extremely cytotoxic and genotoxic compared with regulated C-DBPs (Plewa et al., 2004). Chloropicrin or trichloronitromethane (TCNM) was primarily found as HNM species in drinking water and produced water from drinking water treatment plants during chlorination/chloramination (Jia et al., 2016). The regulation for emerging HNMs has not been promulgated. Currently, there is no regulation or guideline values for I-THMs as well as HANs and HNMs in water supply in Thailand. A well-managed water treatment plant for reducing the N-DBPs' formation is of critical importance.

Bangkok, the capital city of Thailand, has a registered population of about 8 million people. The Bangkhen water treatment plant (WTP), the largest WTP in Thailand, provides a

water supply of about 3.7 million m^3 per day to the majority of Bangkok's population and the vicinity of Bangkok. The Chao Phraya River is the major source of raw water for the Bangkhen WTP and other WTPs. The Chao Phraya River is located in Chao Phraya watershed. Approximately 69% of the total area in the Chao Phraya watershed is utilized for agricultural activities including paddy fields (60% of the total area), field crop (30%), perennial and fruit trees (5%), and other agriculture areas (5%). Other areas are community areas and buildings (15%), forests (10%), water (3%) and others (3%) (LDD, 2017). The Chao Phraya River has been markedly polluted by wastewater and treated wastewater discharge from domestic properties, industries, and agricultural activities which are located at an upstream location.

The iodide concentration in seawater varied from sub-μg/L and up to 60 μg/L levels (Ito et al., 2003; Chandramouleeswaran et al., 1998). Due to the sea level rise sometimes, the raw water from the Chao Phraya River is also exposed to high levels of iodide contamination from sea water. When raw water from the Chao Phraya River that is polluted by sea water, wastewater, and treated wastewater react with chlorine in the water treatment process, emerging C-DBPs and N-DBPs can be formed in the water supply. Emerging C-DBPs' and N-DBPs' formation has been a concern. To date, few studies have focused on the occurrence of I-THMs and HNMs in water. In addition, the study on the emerging DBPs' formation of raw water, wastewater, treated wastewater in Thailand is not thoroughly investigated. This work is aimed at investigating the formation potentials of four THMs (chloroform, BDCM, DBCM, and bromoform), five I-THMs (TIM, DCIM, BCIM, BDIM, and CDIM), four HANs (TCAN, DCAN, BCAN, and DBAN) and one HNM (TCNM) in raw water of Bangkhen WTP. The weight measured the concentration of DBPs, lethal concentration 50-weighted, and lowest cytotoxicity-weighted concentrations of DBPs of raw water were determined.

In addition, the raw water of one WTP from the Chao Phraya River from an upstream location was investigated for their DBPs' formation and toxicity. Wastewater and treated wastewater from two domestic wastewater treatment plants (WWTP) were also studied as the sources of discharged DOM. The water sample at a downstream location of the Chao Phraya River was selected as the water that was polluted by sea water. The obtained results could provide a better understanding of the formation of emerging C-DBPs and N-DBPs in the water supply that could cause a health effect. In addition, the results can be used by policy makers to establish the plan for controlling the level of DOM discharged and DBPs' formation in the water supply.

4.2 Experimental procedure

The identification of precursors of C-DBPs and N-DBPs and formation of C-DBPs and N-DBPs of water samples were determined. The water samples including raw water, water supply, wastewater, treated wastewater, and river water for the first, second and third samplings were analyzed for their pH, turbidity, salinity, and alkalinity. Then, water samples, except water supply, were filtered using GF/F and analyzed for their DOC, DON, FEEM, bromide, iodide, THMFP, HANFP, I-THMFP, and HNMFP. Water samples at the first and second samplings, except water supply, were fractionated using the resin fractionation technique into three fractions: HPO, TPI and HPI and using a UF technique to obtain DOM into four groups: MW < 1 kDa, 1 kDa < MW < 3 kDa, 3 kDa < MW < 10 kDa, and MW > 10 kDa. These DOM fractions were analyzed for their DOC, FEEM, THMFP, HANFP, HMNFP, and I-THMFP. The weight measured concentration of water samples and their DOM fractions in terms of lethal concentration 50-weighted of DBPs, and lowest cytotoxicity-weighted concentrations of DBPs were evaluated.

4.3 Results and discussion

4.3.1 Basic water quality

In this work, the raw water from two water treatment plant (WTP), river water at a downstream location of the Chao Phraya River, and wastewater and treated wastewater from two domestic WWTPs were collected three times from each source waters. Water samples were collected in October 2016, May 2017, and February 2018 as the representative of emerging C-DBPs' and N-DBPs' formation during the rainy season, summer, and winter, respectively. Raw waters from the Chao Phraya River were collected from the pumping station of Bangkhen WTP (BK WTP) at a downstream location (RW−1) and Singburi WTP (SB WTP) at an upstream location (RW−2). Water supply samples (WS−1 and WS−2) were collected from the water supply of Bangkhen WTP at the first and second sampling. Water samples from the river were obtained from the Siriraj sampling site, which is located downstream of the Chao Phraya River after the BK WTP. This sample stands for water with seawater, treated and untreated wastewater contamination. Domestic wastewater before (WW−1) and after treated wastewater (TWW−1) were collected from the WWTP in Ang Thong (AT) province. In addition, domestic wastewater before (WW−2) and treated wastewater (TWW−2) were obtained from the WWTP in Ayutthaya (AY) province. These two WWTPs are located in the upstream location of the Chao Phraya River. The wastewater and treated wastewater represent the sources of

contamination from human activities. All samples were stored at a temperature of 4 °C until analysis.

pH, turbidity, salinity, and alkalinity of raw water, water supply, river water, domestic wastewater, and treated wastewater samples are presented in Table 4-1. The pH levels of all water samples ranged from 7.0 to 8.2, which were nearly neutral. The pH of water supply was in the range of water supply standard of Metropolitan Waterworks Authority (MWA) from 6.5 to 8.5.

Turbidity values of raw water of the Bangkhen WTP ranged from 11 to 54 NTU with an average of 33±21.5 NTU. Slightly low turbidity in the range from 17 to 35 NTU with the average value of 25±9.2 NTU was observed in the upstream raw water at Singburi WTP. Turbidity of raw water from the downstream river water was between 2-31 NTU with an average value of 19±15.3 NTU. Turbidity values of water supply from Bangkhen WTP ranged from 1 to 2 NTU with an average of 1.5 NTU. The average value of turbidity was slightly higher than the standard pH MWA of 1 NTU.

Salinity represents the amount of salt in water, where salt can be in contaminated in the water at several forms. Salinity levels of raw water from the Bangkhen WTP, the downstream river water, and the upstream river water were in the range from 0.1 to 0.3, 0.1 to 0.2 g/L and not detected, respectively. This indicated that the salinity level of water source in the Chao Phraya River on downstream location was relatives high.

Table 4-1. The pH, turbidity, salinity, alkalinity of raw water (RW), river water, domestic wastewater (WW), and treated wastewater (TWW) for the three sampling times.

		BK WTP		SB WTP	River	AT		AY	
Parameter		RW-1	WS-1	RW-2	at downstream	WW-1	TWW-1	WW-2	TWW-2
pH	1st	7.8	7.5	7.9	7.6	8.2	7.9	7.7	7.8
	2nd	7.5	7.0	7.0	7.2	7.4	7.8	7.3	7.4
	3rd	7.3	-	7.1	7.0	7.0	8.0	7.0	7.1
	Ave.± SD	7.5±0.3	7.2	7.3±0.5	7.3±0.3	7.5±0.6	7.9±0.1	7.3±0.4	7.4±0.4
Turbidity (NTU)	1st	34	2	23	25	7	7	18	5
	2nd	54	1	35	31	45	10	8	6
	3rd	11	-	17	2	8	4	14	4
	Ave.± SD	33±21.5	1.5	25±9.2	19±15.3	20±21.7	7±3.0	13±5.0	5±1.0
Salinity	1st	0.3	0.2	ND	0.1	0.3	ND	0.1	0.2
	2nd	0.1	0.1	ND	0.1	0.1	0.4	0.3	0.2
	3rd	0.1	-	ND	0.2	0.2	0.3	0.2	0.2
	Ave.± SD	0.2±0.1	0.15	-	0.1±0.06	0.2±0.1	0.35	0.2±0.1	0.2±0
Alkalinity (mg/L as $CaCO_3$)	1st	80	55	70	80	202	130	145	140
	2nd	78	57	20	77	115	111	119	71
	3rd	85	-	70	63	123	105	166	100
	Ave.± SD	81±3.6	56	53±28.9	73±9.1	146±48.1	115±13.1	143±23.5	104±34.6

Remark: BK WTP = Bangkhen Water Treatment Plant, SB WTP = Sing Buri Water Treatment Plant, AT = Ang Thong, AY = Ayutthaya

(Na Patthalung and Musikavong, 2019)

The salinity of finished water of the Bangkhen WTP was determined at 0.1–0.2 g/L. In Thailand, the desirable salinity level of raw water supply for potable water production must be below 0.25 g/L. The results from a previous study indicated that the salinity, especially the bromide concentration, in water sources had the most significant impact on DBP formation (THMs and HAAs) in chlorinated freshwaters (Shah et al., 2015). The alkalinity of raw water the Bangkhen WTP and Singburi WTP were detected in from 78 to 85 and 20 to 70 mg/L as $CaCO_3$, respectively. Slightly high alkalinity values from 115 to 202 and 71 to 140 mg/L as $CaCO_3$ were found in wastewater and treated wastewater.

4.3.2 Organic precursors

RW−1, RW−2, and river water had similar range of UV-254 values: 0.12–0.14 cm^{-1} for RW-1, 0.09–0.16 cm^{-1} for RW-2, and 0. 11–0.19 cm^{-1} for river water at the downstream location. UV-254 values of WW−1 and WW−2 ranged from 0.07 to 0. 93 cm^{-1} and 0.18 to 0.34 cm^{-1}, respectively (Table 4-2). For treated wastewater, UV−254 of 0.12–0.16 cm^{-1} for TWW−1 and 0. 10–0.17 cm^{-1} for TWW−2 were determined. UV-254 in wastewater varied according to the sampling period. In almost every case, the UV-254 in wastewater is higher than that of raw water and river water.

SUVA of DOM ranges from 1.0 to 6.0 L/(mg·m) in surface waters (Hansen et al., 2016) which was related to aromatic carbon content in DOM (Weishaar et al., 2003). Ranges of SUVA of 3.0–4.1 L/(mg·m) for raw water and 2.7–3.7 L/(mg·m) for river water were similar. The seasonal variations can affect the quality of raw water and river water. According to the standard deviation (SD) values, the changes of season had little effect on the pH, UV-254, and SUVA of raw water and river water. The ranges of SUVA value of 2.2−12.7 L/(mg·m) for wastewater and 1.8–2.7 L/(mg·m) for treated wastewater were determined. In almost all cases, the SUVA of wastewater and treated wastewater was lower than that of raw water and river water, except WW−1 and WW−2 at the first sampling. When the SUVA was higher than 2 L/(mg·m), coagulation was suitable for reducing SUVA (US EPA, 1999). The raw water, river water, and wastewater (WW−1 and WW−2) at the first sampling had a high possibility of using coagulation for reducing DOM. Because of the low SUVA value of some wastewater samples and all treated wastewater samples, coagulation may not be suitable for reducing DOM.

Table 4-2. UV-254, SUVA, DOC, DON, and DOC/DON

Samples	UV-254 (cm^{-1})				SUVA (L/mg-m)				DOC (mg C/L)				DON (mg N/L)				DOC/DON			
	1st	2nd	3rd	Ave.± SD	1st	2nd	3rd	Ave.± SD	1st	2nd	3rd	Ave.± SD	1st	2nd	3rd	Ave.± SD	1st	2nd	3rd	Ave.± SD
Raw water																				
RW–1	0.14	0.13	0.12	0.13±0.01	3.0	4.1	3.2	3.4±0.6	4.6	3.2	3.7	3.8±0.7	0.16	0.44	0.25	0.28±0.14	29	7	15	17±11
RW–2	0.16	0.14	0.09	0.13±0.04	3.3	3.5	3.9	3.6±0.3	4.8	4.1	2.4	3.8±1.2	0.18	0.28	0.12	0.19±0.08	27	15	20	21±6
River water	0.19	0.11	0.15	0.15±0.04	3.7	2.7	2.9	3.1±0.5	5.1	3.9	5.4	4.8±0.8	0.09	0.32	0.33	0.25±0.14	57	12	16	28±25
Water Supply	0.05	0.05	NA	0.05	1.4	1.7	NA	1.6	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Wastewater																				
WW–1	0.93	0.12	0.07	0.37±0.48	12.7	2.2	2.4	5.8±6.0	7.3	5.6	3.0	5.3±2.2	2.62	1.39	0.47	1.49±1.08	3	4	6	4±2
WW–2	0.34	0.19	0.18	0.24±0.09	4.6	2.7	2.3	3.2±1.2	7.4	7.0	7.9	7.4±0.5	0.39	1.21	0.63	0.74±0.42	19	6	13	13±7
Treated wastewater																				
TWW–1	0.12	0.13	0.16	0.14±0.02	2.3	2.0	2.3	2.2±0.2	5.3	6.8	7.0	6.4±0.9	0.20	2.58	1.16	1.31±1.20	27	3	6	12±13
TWW–2	0.10	0.17	0.12	0.13±0.04	1.8	2.7	2.6	2.4±0.5	5.6	6.3	4.8	5.6±0.8	1.22	0.65	0.36	0.74±0.44	5	10	13	9±4

Remark: SD = standard deviation; NA is not available (Na Patthalung and Musikavong, 2019)

DOC as the precursor of C-DBPs

DOC is used as a surrogate parameter for a complex mixture of aromatic and aliphatic carbons in water. DOC is considered as the precursor of THMs' formation (Musikavong et al., 2016). In Table 4-2, DOC in the RW−1 and RW−2 ranged from 3.2 to 4.6 mg C/L and 2.4 to 4.8 mg C/L, respectively. These ranges are rather low compared with DOC of river water at the downstream location (3.9 to 5.4 mg C/L). Regarding the standard deviation of DOC (Table 4-2), it appears that seasonal variations have a minor effect on the DOC of raw and river water samples.

A relatively high range of DOC from 7.0 to 7.9 mg C/L was detected in WW−2, while DOC of WW−1 ranged from 3.0 to 7.3 mg C/L. For treated wastewater, ranges of DOC of TWW−2 and TWW−1 were from 4.8 to 6.3 mg C/L and 5.3 to 7.0 mg C/L, respectively. Treated wastewater is one of the major discharged DOM to a raw water source. The average value of DOC of treated wastewater was 1.5 to 1.7 times higher than that of raw water. When more treated wastewater is discharged into a raw water stream, more DOC must be removed by water treatment plants to reduce the possibility of C–DBPs' formation.

In comparison with the previous study, DOC can vary according to types of water. DOC in raw water of RW−1 of the BK WTP from a previous study was determined at 4.2 mg C/L, (Tongchang et al., 2018) which was similar to the detected DOC in this current study. River waters contained more organic carbon and generally had DOC in the range from 2 to 12 mg C/L (Volk et al., 2002; Wang et al., 2019). DOC in the domestic wastewater in Nanjing, China ranged from 18.2 to 24.6 mg C/L, with an average of 20.3 mg C/L (Liu et al., 2018). DOC in the wastewater after primary treatment and the final effluent from the Nine Springs WWTP in Madison, Wisconsin, USA were determined as 28.4 and 8.5 mg C/L, respectively (Maizel and Remucal, 2017). The range of DOC in domestic wastewater and the treated wastewater from the municipal WWTPs at the Chao Phraya River was lower than those of domestic wastewater in the USA and China.

DON as the precursor of N–DBPs

High DON levels in water may cause a problem of algal growth and anthropogenic nitrogen. In addition, DON in water had a probability of contributing to the formation of emerging N–DBPs (Dotson et al., 2009; Plewa and Wanger, 2009). DON from 0.16 to 0.44 mg N/L and 0.12 to 0.28 mg N/L were detected in RW−1 and RW−2, respectively (Table 4-2). The range of DON in the river water was 0.09 to 0.33 mg N/L and was comparable to that of

RW−1 and RW−2. During summer, high DON in raw water (the second sampling) was found compared to during the rainy season and winter. The highest DON level in the river water (the third sampling) at downstream was found during winter. These observations showed the effect of seasonal variations on the nature of DON in raw water and river water.

The WW−1 and WW−2 had high ranges of DON 0.47 to 2.62 mg N/L and 0.39 to 1.21 mg N/L, respectively. For treated wastewater, ranges of DON of TWW−1 and TWW−2 were from 0.2 to 2.58 mg N/L and 0.36 to 1.22 mg N/L, respectively. Water with a low DON is easier to manage in comparison to water with a high DON. A high amount of DON precursors in water tends to increase the risk of N−DBPs' formation and could lead to the formation of several toxic N−DBP species (Lee and Westerhoff, 2006). The average value of DON in treated wastewater was three to seven times higher than that of raw water. The water treatment plant that uses raw water contaminated with treated wastewater or wastewater must seriously consider and remove DON prior to chlorination for prevention of N−DBPs' formation. Investigations on advanced water treatment technologies such as adsorptions, advanced oxidation processes, and membrane filtrations for removing DOC and DON from raw water contaminated with treated wastewater must be conducted and employed for operating and controlling water treatment plants.

DON in raw water and wastewater is a major precursor of N−DBPs. These include HANs, HNMs, cyanogen chloride (CNCl), and NDMA (Lee and Westerhoff, 2006; Plewa and Wagner, 2009). The DON in surface waters (e.g., wastewater discharge, river, raw water) ranged from < 0.1 to > 10 mg N/L with the median at about 0.3 mg/L (Dotson et al., 2008; Westerhoff and Mash, 2002; Xu et al., 2011). DONs from 0.37 to 0.70 mg N/L have been detected in the raw water of a Kinmen Tai Lake WTP in Taiwan (Chang and Wang, 2013). In the United States, an average DON of 0.19 mg N/L was detected in the raw waters from 28 WTPs (Lee and Westerhoff, 2006). DONs from 0.2 to 0.4 mg N/L were determined in the raw waters from the Huron River, the Salt River, and the Harwood reservoir for WTPs in Virginia, USA (Lee and Westerhoff, 2008). A relatively high DON level of 0.53 mg N/L has been measured from the raw water of the Pinghu WTP, China (Zhang et al., 2015). According to the DON in surface water from the literature data and obtained result in this current work, ranges of DON in surface water were from 0.09 to 0.53 mg N/L.

Average DON concentration of 6.13 mg/L in influent wastewater from two municipal WWTPs in Beijing, China was reported (Huo et al., 2013). The DON of treated wastewater in municipal WWTPs ranged from 0.23 to 1.33 mg N/L (Chang and Wang, 2013; Huo et al.,

2013). The high DON levels in treated wastewater were determined because treated wastewater may contain mostly recalcitrant nitrogenous substances. With regard to the results obtained from this work and previous studies, it can be concluded that the ranges of the levels of DON in domestic wastewater and treated wastewater were from 0.39 to 6.13 mg N/L and 0.20 to 2.58 mg N/L, respectively.

DOC/DON ratio

A DOC/DON ratio can be used as an indicator of N–DBP formation (Chu et al., 2013). A low DOC/DON value probably provides high N–DBP formation such as NDMA and HNMs (Karanfil et al., 2011; Wang et al., 2013). In addition, a low DOC/DON ratio typically represents the nature of autochthonous natural organic matter (NOM), while a high DOC/DON ratio indicates the presence of allochthonous NOM (Aiken and Cotsaris, 1995). RW–1, RW–2, and river water had DOC/DON ratios ranging from 7 to 29, 15 to 27, and 12 to 57, respectively. The variations of DOC/DON ratio in raw water and river water are caused by the variations of DON (Table 4-2). The variation of DOC/DON ratios may be caused by the variation in the seasonal factor that correlated with algal growth and the generation of soluble microbial products such as tryptophan, tyrosine, and protein in water (Fan et al., 2012).

DOC/DON ratios of WW–1 and WW–2 ranged from 3 to 6 and 6 to 19, respectively. For treated wastewater, ranges of DOC/DON ratios of TWW–1 from 3 to 27 and TWW–2 from 5 to 13 were detected, respectively. When the DOC/DON ratio was lower than 20, it had a tendency to form high N–DBPs (Dotson et al., 2009). The DOC/DON ratio typically varied from 8 to 11 mg C/mg N in WWTP effluents (Dotson et al., 2008). In natural waters, the DOC/DON ratios are generally high within the range of 10 to 21 (Xu et al., 2011; Lee and Westerhoff, 2006). With reference to the DOC/DON ratio in this study and previous works, wastewater and treated wastewater had a greater probability of forming N–DBPs than raw water and river water.

4.3.3 The presence of bromide and iodide ions

The levels of bromide (Br^-) and iodide (I^-) in the water samples are presented in Table 4-3. Br^- from 16 to 48 µg/L and < 10 to 51 µg/L were detected in RW–1 and RW–2, respectively (Table 4-3). The range of Br^- in the river water was < 10 to 27 µg/L and was lower than that of RW–1 and RW–2. Br^- from 785 to 4,273 µg/L and 2,150 to 7,844 µg/L were detected in WW–1 and WW–2, respectively (Table 4-3). The range of Br^- in the treated

wastewater was < 10 to 5,050 µg/L and < 10 to 3,630 µg/L in TWW–1 and TWW–2, respectively. In almost all cases, the levels of Br^- treated wastewater were extremely higher than that of raw water and river water

I^- from < 0.1 to 16.9 µg/L and < 0.1 to 8.3 µg/L were detected in RW–1 and RW–2, respectively (Table 4-3). The range of I^- in the river water was 0.2 to 19.5 µg/L and was comparable to that of RW–1 and RW–2. I^- from 1.2 to 846 µg/L and < 0.1 to 56.2 µg/L were detected in WW–1 and WW–2, respectively. The range of I^- in the treated wastewater was 0.9 to 270 µg/L and 0.2 to 224 µg/L in TWW–1 and TWW–2, respectively. In almost all cases, the levels of I^- in treated wastewater were relatively higher than that of raw water and river water.

Table 4-3 Bromide (Br^-) and iodide (I^-) concentrations.

Samples	Br^- (µg/L)				I^- (µg/L)			
	1st	2nd	3rd	Ave.± SD	1st	2nd	3rd	Ave.± SD
Raw water								
RW–1	48	43	16	36±17	3.2	16.9	< 0.1	10.1
RW-2	51	32	< 10	42	4.1	8.3	< 0.1	6.2
River water	27	10	< 10	19	3.1	19.5	0.2	7.6±10.4
Wastewater								
WW–1	1,320	785	4,273	2,126±1,879	846	76.8	1.2	308±467
WW–2	2,540	2,150	7,844	4,178±3,181	41	56.2	< 0.1	48.6
Treated wastewater								
TWW–1	5,050	254	< 10	2,652	270	6.3	0.9	92.4±154
TWW–2	3,630	23	< 10	1,827	224	1.7	0.2	75.3±129

(Na Pattalung and Musikavong, 2019)

According to the results obtained in this work, the main discharged source of Br^- and I^- into the river water could originate from the wastewater and treated wastewater. To minimize the formation of brominated and iodinated DBPs, when the river water is utilized as raw water and is contaminated with high Br^- and I^- level from the upstream discharged, the water treatment plant needs to install advanced treatment technologies to remove Br^- and I^-. The other option is to minimize the level of Br^- and I^- in treated wastewater from the WWTP nearby the raw water sources by a tertiary treatment process prior discharging treated wastewater.

4.3.4 Fluorescent organic matter

The presence of fluorescent organic matter is attributable to the variety of compounds that are soluble microbial products, including aromatic proteins, polycarboxylate types, humic acid and polyaromatic-type humic acid in natural water and effluent wastewater (Chen et al., 2003; Yu et al., 2015). The leading components such as fluorescent peaks of tyrosine, tryptophan, and humic and fulvic-like substances in water have been identified in other studies (Chen et al., 2003). These groups of fluorescent organic matter have been shown to be precursors of DBPs. Aromatic compounds tend to have significant fluorescence intensities greater than those of aliphatic compounds (Sun et al., 2008).

The FEEM peak positions for raw water sample from the Bangkhen WTP are shown as example in Figure 4-1. Based on the literature data (Chen et al., 2003; Coble, 1996), the putative fluorescent organic matter in this study was classified into four substance groups: tyrosine-like, tyrosine- and protein- like, tryptophan-like, and humic- and fulvic-like substances. The positions of the eight major fluorescence peaks of raw water, river water, wastewater and treated wastewater were detected as follows: 225 nm_{Ex}/290 nm_{Em}(peak A) for tyrosine; 245 nm_{Ex}/305 nm_{Em}(peak B) for tyrosine- and protein- like, 230 nm_{Ex}/345 nm_{Em} (peak C); 280 nm_{Ex}/360 nm_{Em}(peak D) and 230 nm_{Ex}/420 nm_{Em} (peak E) for tryptophan-like substances; 275 nm_{Ex}/410 nm_{Em} (peak F), 330 nm_{Ex}/410 nm_{Em} (peak G) and 260 nm_{Ex}/450 nm_{Em} (peak H) for humic- and fulvic acid-like substances.

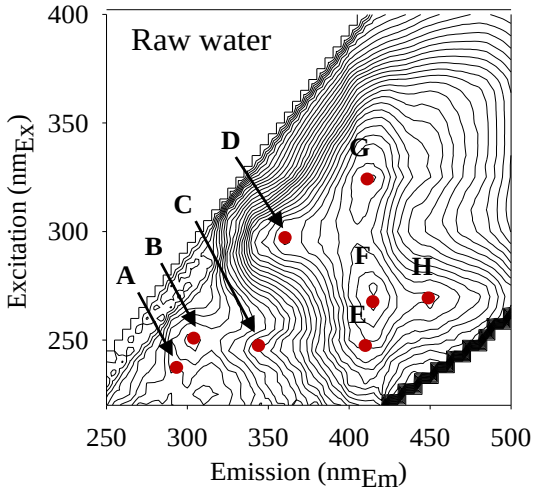


Figure 4-1. The FEEM peak positions at A, B, C, D, E, F, G and H for raw water from the Bangkhen WTP in this study.

The fluorescence intensities (in the QSU unit) at each of fluorescent peaks in the raw water, river water, wastewater and treated water samples at three sampling times is presented in Table 4-4. The fluorescence intensity of humic and fulvic-like substances (the summation of F, G and H peaks in the FEEM) of the raw water supply (RW−1 and RW−2) and river water at downstream ranged from 5.8 to 18.2 QSU and 12.5 to 16.9 QSU, respectively. The fluorescence intensity of humic and fulvic-like substances ranged from 8.8 to 27.7 QSU for wastewater (WW−1 and WW−2),and ranged from 13.8 to 22.8 QSU for treated wastewater (TWW−1 and TWW−2). In general, humic and fulvic-like substances could able to be detected in natural water while tryptophan-like substances were mostly detected in anthropogenic substances from wastewater and treated wastewater (Baker, 2001).

Table 4-4. Fluorescence intensity of water samples of the peaks of Excitation (E_x)/Emission (E_m) wavelength.

Samples			Intensity of peaks (QSU)									
			Tyrosine -like	Tyrosine- and Protein-like	Tryptophan-like				Humic- and Fulvic acid-like			
			A	B	C	D	E	Peak C+D+E	F	G	H	Peak F+G+H
			225/290	245/305	230/345	280/360	230/420		275/410	330/410	260/450	
Raw water	RW–1	1st	1.2	1.6	1.9	3.6	4.4	10.0	5.7	5.4	4.9	16.0
		2nd	1.7	0.9	1.6	2.9	3.8	8.3	5.6	3.0	3.4	12.0
		3rd	1.1	0.4	1.7	2.4	2.8	6.9	3.8	3.1	3.5	10.4
	RW–2	1st	1.2	1.5	1.7	2.9	4.8	9.4	6.5	5.7	6.0	18.2
		2nd	10.5	7.5	6.5	4.5	8.1	19.0	4.3	4.7	4.0	13.1
		3rd	0.9	0.5	1.2	1.5	1.9	4.7	2.1	1.7	2.0	5.8
River water at downstream		1st	1.1	1.5	1.6	3.2	4.4	9.3	5.9	5.7	5.3	16.9
		2nd	1.0	0.4	2.3	3.0	3.4	8.7	4.4	3.9	4.1	12.5
		3rd	2.0	0.3	3.5	5.4	3.7	12.6	5.7	5.1	5.2	15.9
Wastewater	WW–1	1st	2.4	1.4	3.4	4.5	5.6	13.4	6.7	6.9	6.4	20.0
		2nd	1.8	0.5	6.4	8.2	5.8	20.4	8.1	6.8	6.7	21.5
		3rd	1.5	0.4	2.8	3.6	5.6	12.0	3.0	3.0	2.7	8.8
	WW–2	1st	6.7	1.6	5.0	8.0	6.2	19.2	8.5	9.0	7.1	24.6
		2nd	1.9	0.5	20.9	34.2	6.7	61.8	10.9	8.8	8.1	27.7
		3rd	6.4	1.1	7.0	11.3	4.8	23.2	6.8	6.3	4.7	17.8
Treated wastewater	TWW–1	1st	0.9	1.1	2.9	5.1	4.6	12.6	6.6	6.3	5.9	18.8
		2nd	0.3	0.4	2.3	7.6	2.0	12.0	6.1	5.0	5.0	16.1
		3rd	1.9	0.5	2.0	4.3	2.5	8.8	5.3	4.8	4.8	14.8
	TWW–2	1st	1.9	1.2	3.6	5.1	5.6	14.3	7.8	8.2	6.8	22.8
		2nd	1.1	0.3	3.9	6.0	5.6	15.5	7.4	7.5	6.9	21.8
		3rd	1.8	0.5	3.1	4.2	3.3	10.6	4.6	4.9	4.2	13.8

Peak A is tyrosine; Peak B is tyrosine- and protein- like substances; Peak C, D and E are tryptophan-like substances; Peak F, G and H are humic- and fulvic-like substances

The fluorescent of tyrosine-like substance peaks (peaks A or B) were shown in the range of 0.4 and 10.5 QSU for raw water, 0.3 and 2.0 QSU for river water, 0.4 and 6.7 QSU for wastewater, and 0.3 and 1.9 QSU for treated wastewater. The tyrosine-like substances exhibited distinct fluorescent organic matter in the RW−2 of the Singburi WTP from the second sampling. For the FEEM of the studied water samples, tryptophan-like substances were detected at peaks C, D and E with a fluorescence intensity (the summation of F, G and H peaks in the FEEM) ranging from 4.7 to 48.9 QSU for raw water, 8.7 to 12.6 QSU for river water, 9.0 to 61.8 QSU for wastewater, and 8.8 to 15.5 QSU for treated wastewater. The tryptophan-like substances in the wastewater exhibited intensities relatively higher than those in other water samples. Tryptophan and tyrosine can be considered as being an organic nitrogen compound. The high DON in the wastewaters of the WWTPs could therefore be related to the detection of tyrosine and tryptophan-like substances. Some studies have suggested that tryptophan-like compounds are most likely associated with biochemical oxygen demand and contamination from domestic effluents (Knapik et al., 2014). The increase in organic pollution in the wastewater discharge can therefore be related to the more intense fluorescence peaks of these tryptophan-like substances.

4.3.5 Formation potential of C-DBPs

THMs' formation

THMFP, the ratio of THMFP to the WHO guideline, and I–THMFP for raw water, river water, domestic wastewater, and treated wastewater are presented in Figure 4-2. THMFP ranged from 121 to 265 µg/L and 103 to 210 µg/L for the raw water from the BK WTP (RW−1) and SB WTP (RW−2), respectively. For the river water at downstream, the THMFP ranged from 204 to 449 µg/L. The level of THMFP in raw and river water varies with seasonally (Table 4-5). As previously reported by Musikavong et al. (2016), the THMFP of the U-Tapao canal water in Hatyai, Songkhla, Thailand ranged from 165 to 729 µg/L. A THMFP ranging from 150 to 300 µg/L has been detected in the Ohio River basin, USA (Jack et al., 2002). The formation of THM in river waters varied according to geographical location.

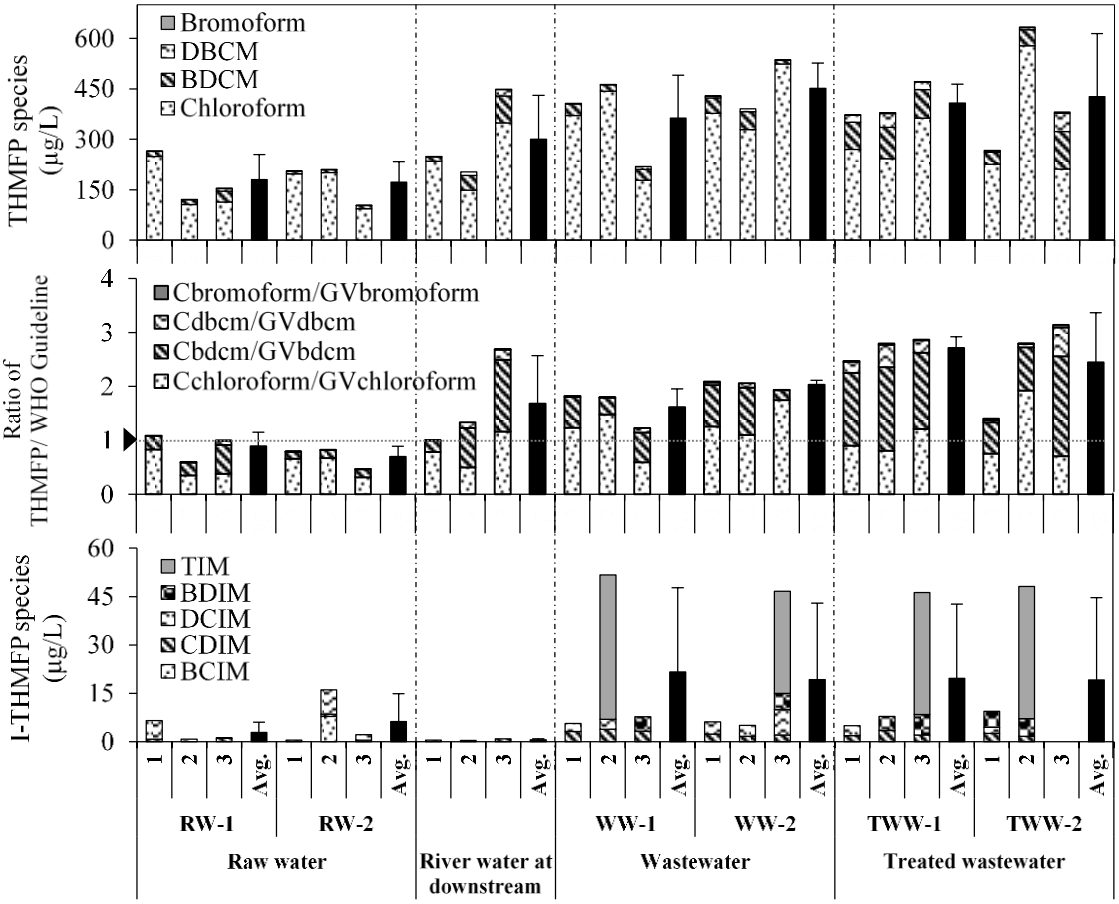


Figure 4-2. THMFP, the ratio of THMFP to the WHO guideline and I–THMFP for raw water, river water, domestic wastewater, and treated wastewater.
(Na Pattalung and Musikavong, 2019)

The THMFP ranged from 220 to 463 µg/L, and from 390 to 536 µg/L were determined for the domestic wastewater of the WW–1 and WW–2, respectively. For the TWW–1 and TWW–2, the THMFP ranged from 373 to 472 µg/L and 267 to 633 µg/L, respectively. The highest THMFP level of 633 µg/L was observed in the TWW–2 at the second sampling, possibly due to the high level of THM precursors in the water. An increase in the soluble humic material, chloride, and bromide in water may cause an increase in THM formation (Adin et al., 1991). The average value of THMFP of treated wastewater was 2.3 to 2.5 times higher than that of raw water. The river water, wastewater, and treated wastewater sources had a high potential to form THMs over the maximum contamination level set by the US EPA of 80 µg/L (US EPA, 2006) and the level in the European Union standard of 100 µg/L (EECD, 1998).

The percent distribution of each THMFP species is tabulated in Table 4-6. Chloroform ($CHCl_3$) was the major THMFP species detected in all water samples. The chloroform

accounted within the range from 87 to 96%, 73 to 95%, 81 to 98%, and 56 to 91% of the total THMFP for the raw water, river water, domestic wastewater, and treated wastewater, respectively. Chloroform was more frequently observed than other THM species in chlorinated water (Tokmak et al., 2004). The obtained result in this current study corresponds well with earlier studies.

Table 4-5. DBPFP of raw water (RW), river water, domestic wastewater (WW), and treated wastewater (TWW) for the three sampling times.

Samples	THMFP (µg/L)				I-THMFP (µg/L)				HANFP (µg/L)				TCNMFP (µg/L)			
	1st	2nd	3rd	Ave.± SD	1st	2nd	3rd	Ave.± SD	1st	2nd	3rd	Ave.± SD	1st	2nd	3rd	Ave.± SD
Raw water																
RW-1	265	121	154	180±75	7	1	1	3±3.2	21	9	9	13±7	3	2	2	2±0.5
RW-2	205	210	103	173±60	1	16	2	6±8.6	18	30	40	29±11	N.D.	6	3	3±2.9
River water	249	204	449	300±130	1	0.4	1	1±0.3	18	10	8	12±5	3	2	1	2±1.2
Wastewater																
WW-1	407	463	220	363±127	6	52	8	22±26	20	18	14	17±3	9	17	4	10±6.6
WW-2	430	390	536	452±75	6	5	47	19±24	14	40	30	28±13	24	23	13	20±6.2
Treated wastewater																
TWW-1	373	379	472	408±56	5	8	46	20±23	17	45	38	33±15	18	36	26	27±8.8
TWW-2	267	633	381	427±187	9	48	N.D.	19±26	25	26	47	33±12	21	27	6	18±10.9

N.D. is not detected (Na Patthalung and Musikavong, 2019)

Table 4-6. Percent distribution of THMFP, I–THMFP, and HANFP species of raw water, river water, domestic wastewater and treated wastewater.

Water sources		4-THMFP, %				5-ITHMFP, %					4-HANFP, %			
		Chloroform	BDCM	DBCM	Bromoform	BCIM	CDIM	DCIM	BDIM	TIM	TCAN	DCAN	BCAN	DBAN
Raw water														
RW-1	1st	94.1	5.7	0.2	N.D.	N.D.	12.3	87.7	N.D.	N.D.	17.5	67.0	15.5	N.D.
(BK WTP)	2nd	87.4	11.5	1.1	N.D.	N.D.	N.D.	100	N.D.	N.D.	18.7	57.1	24.2	N.D.
	3rd	73.9	20.7	5.2	0.1	N.D.	91.7	8.3	N.D.	N.D.	17.6	64.7	N.D.	17.6
	Avg.	85.1	12.7	2.2	0.03	N.D.	34.7	65.3	N.D.	N.D.	17.9	62.9	13.2	5.9
RW-2	1st	96.0	3.9	0.1	N.D.	N.D.	100	N.D.	N.D.	N.D.	11.0	73.5	15.5	N.D.
(SB WTP)	2nd	95.6	4.3	0.1	N.D.	48.4	4.3	47.2	N.D.	N.D.	11.4	76.3	12.4	N.D.
	3rd	90.9	8.7	0.4	N.D.	22.7	N.D.	77.3	N.D.	N.D.	5.2	46.4	36.9	11.5
	Avg.	94.2	5.6	0.2	N.D.	23.7	34.8	41.5	N.D.	N.D.	9.2	65.4	21.6	3.8
River water at downstream														
	1st	94.5	5.2	0.2	N.D.	N.D.	100	N.D.	N.D.	N.D.	11.4	71.0	17.6	N.D.
	2nd	73.2	21.6	5.2	N.D.	N.D.	100	N.D.	N.D.	N.D.	10.6	52.9	26.9	9.6
	3rd	77.8	17.8	4.2	0.1	N.D.	100	N.D.	N.D.	N.D.	26.6	51.9	21.5	N.D.
	Avg.	81.8	14.9	3.2	N.D.	N.D.	100	N.D.	N.D.	N.D.	16.2	58.6	22.0	3.2
Domestic wastewater														
WW-1	1st	91.1	8.4	0.5	N.D.	N.D.	55.4	44.6	N.D.	N.D.	10.0	35.3	32.3	22.4
(AT)	2nd	95.7	4.1	0.2	N.D.	N.D.	7.4	6.0	N.D.	86.7	16.4	75.4	8.2	N.D.
	3rd	81.1	15.0	3.9	N.D.	N.D.	41.6	N.D.	58.4	N.D.	10.3	43.4	29.4	16.9
	Avg.	89.3	9.2	1.5	N.D.	N.D.	34.8	16.9	19.5	28.9	12.2	51.4	23.3	13.1
WW-2	1st	87.7	10.7	1.2	0.4	N.D.	39.3	60.7	N.D.	N.D.	24.3	54.9	20.8	N.D.
(AY)	2nd	84.3	13.6	2.1	N.D.	N.D.	34.0	66.0	N.D.	N.D.	40.7	47.4	11.9	N.D.
	3rd	97.8	2.1	0.1	N.D.	N.D.	4.5	16.7	10.9	67.8	3.0	83.5	13.5	N.D.

Table 4-6. (Cont.) Percent distribution of THMFP, I–THMFP, and HANFP species of raw water, river water, domestic wastewater and treated wastewater.

Water sources		4-THMFP, %				5-ITHMFP, %					4-HANFP, %			
		Chloroform	BDCM	DBCM	Bromoform	BCIM	CDIM	DCIM	BDIM	TIM	TCAN	DCAN	BCAN	DBAN
	Avg.	90.0	8.8	1.1	0.1	N.D.	26.0	47.8	3.6	22.6	22.7	61.9	15.4	N.D.
Treated wastewater														
TWW-1	1st	72.4	21.7	5.6	0.2	N.D.	38.8	61.2	N.D.	N.D.	15.0	38.3	29.3	17.4
(AT)	2nd	63.8	24.5	10.9	0.7	N.D.	43.6	N.D.	56.4	N.D.	10.4	37.2	18.8	33.6
	3rd	76.9	18.0	4.8	0.3	N.D.	4.5	N.D.	13.6	81.8	11.1	62.1	13.9	12.9
	Avg.	71.1	21.4	7.1	0.4	N.D.	29.0	20.4	23.3	27.3	12.1	45.9	20.7	21.3
TWW-2	1st	84.6	13.1	1.6	0.7	N.D.	27.7	19.1	53.2	N.D.	12.0	67.9	15.7	4.4
(AY)	2nd	91.4	7.6	1.1	N.D.	N.D.	3.5	N.D.	11.2	85.2	13.3	74.9	11.8	N.D.
	3rd	55.6	29.1	14.1	1.1	N.D.	N.D.	N.D.	N.D.	N.D.	1.3	51.4	32.5	14.8
	Avg.	77.2	16.6	5.6	0.6	N.D.	10.4	6.4	21.5	28.4	8.9	64.7	20.0	6.4

Remark: BK WTP = Bangkhen Water Treatment Plant, SB WTP = Sing Buri Water Treatment Plant, AT = Ang Thong, AY = Ayutthaya, Avg. = Average, N.D. is not detected

(Na Patthalung and Musikavong, 2019)

Brominated THM species including BDCM, DBCM, and bromoform are considerably more toxic than their chlorinated analogues (Yang and Zhang, 2013). BDCM had a higher proportion in RW−1 from the BK WTP (6–21%) than in RW−2 from the SB WTP (4–9%). The BDCM accounted within the range from 5 to 22%, 2 to 15%, and 8 to 29% of the total THMFP in river water, domestic wastewater, and treated wastewater samples, respectively. The high percent distribution of DBCM was observed only in treated wastewater (1 to 14% of the total THMFP). For other water samples, the DBCM was detected <6% of the total THMFP. Among these four THMFP species, bromoform was not detected (N.D.) or detected only for 1.1%.

Bromoform in the chlorination of bromide-rich water has been found in a high concentration compared with that of DBCM, BDCM, and chloroform (Basu et al., 2011). It was suggested that the yield of THM species in chlorinated water could depend on the type of their precursors such as bromide ions, DOC, and Br/DOC ratio (Watson et al., 2015). The increase in levels of brominated species of THMs in chlorinated water should be seriously considered due to its greater toxicity.

The THMFP/WHO ratio of RW−1 and RW−2 ranged from 0.6 to 1.1 and 0.5 to 0.8, respectively (Figure 4-2). The RW−1 had the potential to form THMs with slightly higher than the standard guideline of ≤ 1 whereas RW−2 had a tendency to form THMs with lower than the standard guideline. In general, THMFP of raw water represents the highest possible THMs' formation without removing the precursors. A high chlorine dosage was used in the experiment. In practice, the water treatment plant can remove some amount of DOM, and a low amount of chlorine was used that can reduce the amount of THMs' formation and THM/WHO ratio.

The values of the THMFP/WHO guidelines for the river water at downstream ranged from 1.0 to 2.7. In treated wastewater from WWTPs, the THMFP/WHO values were detected in a relatively high range from 1.4 to 3.1 compared with that of 1.2 to 2.1 of wastewater samples. When the treated wastewater was discharged to a raw water source, the high ratio of THMFP/WHO in the treated wastewaters can contribute to the influence of organic loading and the formation of THMs. A good management practice of the water treatment plant must be proposed as a key to reduce and control THMs' formation.

I-THMs formation

I–THMs are much more toxic and potentially more carcinogenic than THMs (Cemeli et al., 2006). I–THMs are considered as emerging C–DBPs. From Figure. 4-2, the low levels of I–THMFP (sum of five I–THMFP species) in the RW−1 (raw water of BK WTP) and RW−2 (raw water of SB WTP) were detected in the range from 1 to 7 µg/L and 1 to 16 µg/L, respectively. The variations of I–THMFP in raw water could be affected by the seasonal changes and geographical location of the raw water sources (Table 4-5). The river water at the downstream location formed the lowest value within the range from 0.4 to 1 µg/L. The precursors of I–THMs in raw water and river water reveal the low potential to form I–THMs.

Relatively high levels of I–THMFP ranging from 6 to 52 µg/L for WW−1 and 5 to 47 µg/L for WW−2 were found. For treated wastewater, ranges of I–THMFP from 5 to 46 µg/L for TWW−1 and N.D. to 48 µg/L for TWW−2 were found. A wide range of I–THMFP in wastewater and treated wastewater was determined. This may be due to the variation of I–THMs precursors that originated from the sources of wastewater. The average value of I–THMFP of treated wastewater was 3.2 to 6.7 times higher than that of raw water.

For RW−1, DCIM and CDIM accounted for N.D. to 91.7% and 8.3 to 100%, respectively. BCIM, BDIM, and TIM were not detected (Table 4-6). The percent distribution of BCIM, CDIM, and DCIM of RW−2 ranged from N.D. to 48.4%, N.D. to 100%, and N.D. to 77.3%, respectively. I–THMFP species that contained one bromide compound was detected in RW−2. BDIM and TIM were not detected. Only CDIM was found in river water at the downstream location.

For wastewater and treated wastewater, four I–THMFP species were detected. Percent distribution of CDIM, DCIM, BDIM, and TIM for WW−1 ranged from 7.4 to 55.4%, N.D. to 44.6%, N.D. to 58.4%, and N.D. to 86.7%, respectively. For WW−2, CDIM, DCIM, BDIM, and TIM ranged from 4.5 to 39.3%, 16.7 to 66.0%, N.D. to 10.9%, and N.D. to 67.8%, respectively. For TWW−1, CDIM, DCIM, BDIM, and TIM ranged from 4.5 to 43.6%, N.D. to 61.2%, N.D. to 56.4%, and N.D. to 81.8%, respectively. CDIM, DCIM, BDIM, and TIM for TWW−2 ranged from N.D. to 27.7%, N.D. to 19.1%, N.D. to 53.2% and N.D. to 85.2%, respectively. BCIM was not detected for wastewater and treated wastewater.

The three I–THMFP species (DCIM, CDIM, and BCIM) detected in this study were the most frequently occurring in raw waters of the WTPs, similar to the description of total I–THM levels in drinking water from surveys in other countries (Richardson et al., 2008;

Goslon et al., 2009; Wei et al., 2013a). In Scotland, DCIM and BCIM were detected ranging from N.D. to 3.7 µg/L, with median 0.9 µg/L in chloraminated and chlorinated water from seven drinking WTPs (Goslan et al., 2009). In the USA and Canada, DCIM and BCIM were detected ranging from 0.09 to 7.8 µg/L in chloraminated and chlorinated water from 23 cities in drinking WTPs (Richardson et al., 2008). In China, DCIM of 1.42±0.05 µg/L and TIM ranging from 0.01 to 1.25 µg/L were detected in water after the chloramination process from drinking WTPs (Wei et al., 2013a,b).

In the case of iodoform (or TIM), it was the dominant species of I–THMFP detected at relatively high levels (N.D. to 44.8 µg/L) in the wastewater and treated wastewater samples at WWTPs, while a lower level of iodoform (< 21.66 µg/L) was present in the effluent water after disinfection at drinking WTPs in the findings of other studies (Krasner et al., 2006; Tugulea et al., 2018; Wei et al., 2013b). The greater formation of I–THMs may possibly be because of the different characteristics of organic precursors in water sources. The previous studies have indicated that some waters with high bromide, iodide, and ammonium concentrations were associated with the formation of I–THMs (Tugulea et al., 2018; Ioannou et al., 2016).

4.3.6 Formation potential of N–DBPs

HANs' formation

Four HANFP species, namely, DBAN, BCAN, DCAN, and TCAN were detected in all water samples (Figure 4-3). The range of HANFP from 9 to 21 µg/L in RW−1 of the BK WTP was lower than that of RW−2 of the SB WTP from the upstream location (18−40 µg/L). For the river at the downstream location, the HANFP ranged from 8 to 18 µg/L. During the rainy season, the high HANFP level in RW−1 and river water at the downstream location (the first sampling) was found in compared to during summer and winter. The highest HANFP level in RW−2 (the third sampling) at the upstream location was found during winter. These observations showed the effect of seasonal variations and location of water sources on the formation of HANs in raw water and river water. The HANFP levels of raw water from four WTPs in Korea have been reported in the range of 10.3 to 33.6 µg/L (Kim et al., 2003), HANFP of about 17 µg/L was detected in raw water from the Dez River in Iran (Ahmadiab and Ramavandie, 2014). The range of HANFP values of raw water found in this current work was similar to that of raw water from other studies (Kim et al., 2003; Ahmadiab and Ramavamdic, 2014).

The HANFP level of WW−1 and WW−2 ranged from 14 to 20 µg/L and 14 to 40 µg/L, respectively. HANFP levels ranging from 17 to 45 µg/L for TWW−1 and 25 to 47 µg/L for TWW−2 were determined. The average value of HANFP of treated wastewater was 1.1 to 2.5 times higher than that of raw water. A number of precursors such as carboxylic acid functional groups, amino acids, proteins, polypeptides, and carbohydrates which produce high levels of HANs have been identified (Chu et al., 2012). The presence of untreated HANs' precursors in the discharge of treated wastewater to raw water source may influence HANs' formation in the water supply.

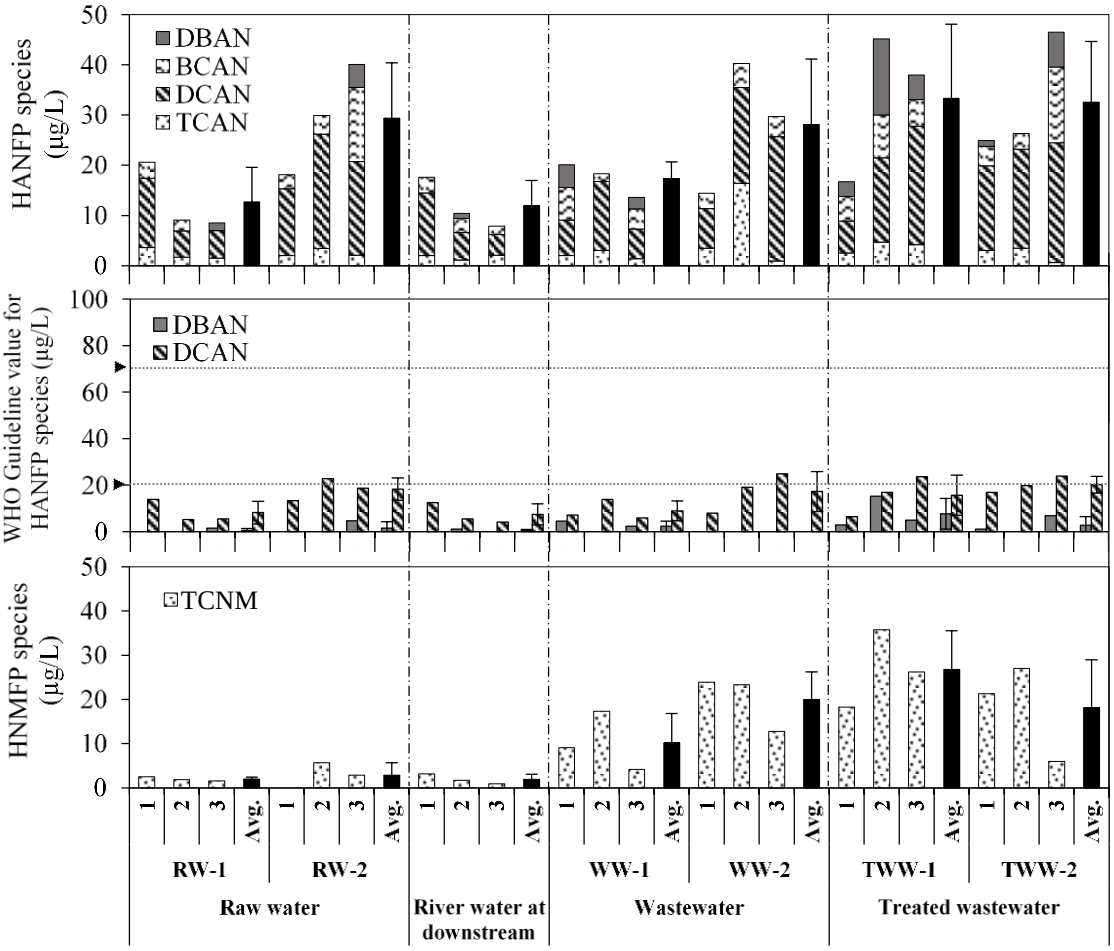


Figure 4-3. HANFP and HNMFP for raw water, river water, domestic wastewater, and treated wastewater. (Na Patthalung and Musikavong, 2019)

The formation of HANFP species is presented in Table 4-6. Among four HANFP species, DCAN concentration was the most abundant in raw waters (46 to 76% of the total HANFP), river waters (52 to 71%), wastewaters (35 to 84%), and treated wastewaters (37 to 75%). BCAN (8 to 33%) and TCAN (1 to 41%) were the other HANFP species found in both

wastewater and treated wastewater samples. The BCAN (N.D. to 37%) and TCAN (5 to 27%) in raw and river waters were detected as a lower portion than those in wastewater and treated wastewater. DBAN (N.D. to 34%) was the dominant HAN species in treated wastewater rather than in other water sources. As reported previously, DCAN, BCAN, and DBAN were the most frequently found species in treated water samples from drinking WTPs in England (Bond et al., 2015). The detected HANs species in this study corresponded with previous work.

The concentration of DBAN and DCAN species should not exceed their guideline values of 70 and 20 μg/L, respectively (WHO, 2008). The total HANFP of river water was lower than the standard guideline (Figure 4-3). The values of the DCAN for the raw water were lower than the guideline value, except for the RW−2 of the SB WTP at the second sampling. The DCAN values were slightly higher in some samples from wastewater and treated wastewater, which could represent the greater potential to form HANs higher than the WHO guideline value.

HNM formation

HNM is considered as an emerging N−DBP. In this work, the trichloronitromethane (TCNM) species was detected at a low concentration from 2 to 3 μg/L for RW−1 (BK WTP) and N.D. to 6 μg/L for RW−2. In the case of river water at the downstream location, TCNM ranged from 1 to 3 μg/L (Figure 4-3). The level of TCNMFP in raw and river water has slightly varied with the changes of season (Table 4-5). TCNM was typically detected at a lower level (ng/L to μg/L) in natural surface waters. For drinking water in the USA WTPs, TCNM ranged from N.D. to 2.0 μg/L in finished water (Krasner et al., 2006). A low concentration of TCNM was reported from N.D. to 7.6 μg/L with a median of 0.5 μg/L in finished water of surveyed plants (Mitch et al., 2009). The TCNM concentrations detected in raw water and river water in this study had similar levels to that of other survey studies (Krasner et al., 2006; Mitch et al., 2009).

For domestic wastewaters, the WW−1 and WW−2 gave high TCNM levels from 4 to 17 μg/L and 13 to 24 μg/L, respectively. The high level of TCNM from 18 to 36 μg/L and 6 to 27 μg/L for TWW−1 and TWW−2 still occurred in the treated wastewaters. The TCNM level obtained in this study was higher than that of the level of TCNM from 0.9 to 1.5 μg/L in a municipal WWTP effluent in the US (Song et al., 2010). The average value of HNMFP of treated wastewater was 6 to 13.5 times higher than that of raw water. The high level of some reactive HNM precursors in the municipal WWTP effluents may cause an increase in the level

of TCNM formation. Previous studies showed that organic nitrogen compounds (e.g., tryptophan and alanine), and algal cells with high organic nitrogen content could be the major sources for TCNM during the chlorination process (Yang et al., 2011; Yang et al., 2012). In general, tryptophan was detected in treated wastewater (Lee and Ahn, 2004) and was the dominant N–DBPs precursor.

4.3.7 The relationship between DBPFP and DOC concentration, DBPFP and bromide, and DBPFP and iodide

The correlation and regression between each DBPFP (4 THMs, 5 I–THMs, 4 HANs and TCNM) and DOM surrogate parameters (DOC, DON, and DOC/DON) for each water source are presented in Table 4-7. According to AWWA (AWWA, 1993), it has been recognized that correlation levels were divided in four categories as a correlation coefficient (R^2) > 0.9 was considered a good correlation, 0.7 < R^2 < 0.9 a moderate correlation, 0.5 < R^2 < 0.7 a fair correlation, and R^2 < 0.5 a poor correlation. In this study, DOC was a good surrogate parameter for DOM to predict THMs and TCNM.

Table 4-7. Linear correlation coefficients (R^2) between DBPFP and DOM surrogate parameters of raw water, domestic wastewater, and treated wastewater.

Water sources	Regression parameter				N	R^2	Sig. level	Correlation level
	Dependent variables (y)	Independent variables (x)	Slope (m)	Intercept (C)				
Raw water								
DOC 2.4-4.8 mg C/L	THMFP	DOC	60.8	-54.6	6	0.8076	0.01	Moderate
DON 0.12-0.44 mg N/L	THMFP	DON	-	-	6	0.0798	Not	Poor
DOC/DON 7-29	THMFP	DOC/DON	-	-	6	0.4309	Not	Poor
	I–THMFP	DOC	-	-	6	0.0627	Not	Poor
	I–THMFP	DON	-	-	6	0.0002	Not	Poor
	I–THMFP	DOC/DON	-	-	6	0.0001	Not	Poor
	HANFP	DOC	-	-	6	0.1172	Not	Poor
	HANFP	DON	-	-	6	0.3616	Not	Poor
	HANFP	DOC/DON	-	-	6	0.0870	Not	Poor
	HNMFP	DOC	-	-	5	0.0528	Not	Poor
	HNMFP	DON	-	-	5	0.0074	Not	Poor
	HNMFP	DOC/DON	-	-	5	0.0017	Not	Poor

Table 4-7 (cont.). Linear correlation coefficients (R^2) between DBPFP and DOM surrogate parameters of raw water, domestic wastewater, and treated wastewater

Water sources	Regression parameter				N	R^2	Sig. level	Correlation level
	Dependent variables (y)	Independent variables (x)	Slope (m)	Intercept (C)				
Wastewater								
DOC 3.0-7.9 mg C/L	THMFP	DOC	48.1	101.4	6	0.6903	0.04	Fair
DON 0.39-2.62 mg N/L	THMFP	DON	-	-	6	0.0160	Not	Poor
DOC/DON 3-19	THMFP	DOC/DON	-	-	6	0.1077	Not	Poor
	I–THMFP	DOC	-	-	6	0.0103	Not	Poor
	I–THMFP	DON	-	-	6	0.0098	Not	Poor
	I–THMFP	DOC/DON	-	-	6	0.0010	Not	Poor
	HANFP	DOC	-	-	6	0.2260	Not	Poor
	HANFP	DON	-	-	6	0.0134	Not	Poor
	HANFP	DOC/DON	-	-	6	0.0176	Not	Poor
	HNMFP	DOC	-	-	6	0.3137	Not	Poor
	HNMFP	DON	-	-	6	0.0317	Not	Poor
	HNMFP	DOC/DON	-	-	6	0.2090	Not	Poor
Treated Wastewater								
DOC 4.8-7.0 mg C/L	THMFP	DOC	-	-	6	0.1707	Not	Poor
DON 0.20-2.58 mg N/L	THMFP	DON	-	-	6	0.0357	Not	Poor
DOC/DON 3-27	THMFP	DOC/DON	-	-	6	0.0002	Not	Poor
	I–THMFP	DOC	-	-	5	0.2605	Not	Poor
	I–THMFP	DON	-	-	5	0.0707	Not	Poor
	I–THMFP	DOC/DON	-	-	5	0.0590	Not	Poor
	HANFP	DOC	-	-	6	0.0448	Not	Poor
	HANFP	DON	-	-	6	0.2293	Not	Poor
	HANFP	DOC/DON	-	-	6	0.3216	Not	Poor
	HNMFP	DOC	10.2	-34.4	6	0.7901	0.01	Moderate
	HNMFP	DON	9.0	13.2	6	0.6051	0.06	Fair
	HNMFP	DOC/DON	-	-	6	0.0204	Not	Poor

Remark: Regression equation is y = mx+C; Regression analysis was not carried out for $R^2 < 0.5$. Hence, slope (m) and intercept (C) for equation were not computed; DBPFP was dependent variable whereas DOC, DON and DOC/DON were independent variables; N = Sample size; Sig. = Significant

(Na Patthalung and Musikavong, 2019)

The positive relationship between THMFP and DOC for raw water and domestic wastewater is shown in Figure 4-4A. A moderate correlation was obtained from the relationship between THMFP and DOC with R^2 of 0.8076 for raw water whereas a fair (R^2 = 0.6903) correlation was obtained from the relationship between THMFP and DOC for wastewater (Table 4-7). There was no consistent pattern between DOC and THMFP concentration for treated wastewater. A moderate correlation was observed for the relationship between TCNMFP and DOC with R^2 of 0.7901 of treated wastewater (Figure 4-4B). In summary, a DOM surrogate parameter like DOC was the most positively correlated parameter with the occurrence of THMFP in the raw water and TCNMFP in the treated wastewater in this study.

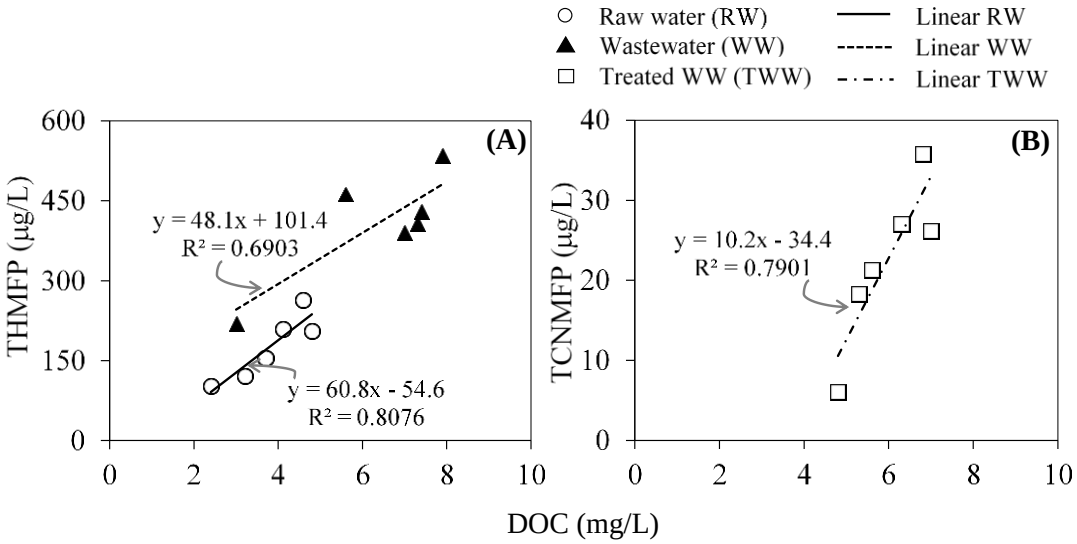


Figure 4-4. Relationship between DOC of raw water, domestic wastewater and treated wastewater samples and THMFP and TCNMFP. (Na Pattalung and Musikavong, 2019)

The correlation and regression between DBPFP species and the Br^- and I^- concentrations for each water source are presented in Table 4-8. For almost all water sources, poor correlations were found between DBPFP species and Br^- and DBPFP species and I^-. In the case of raw water, only a fair correlation was obtained from the relationship between $CHBrCl_2FP$ and Br^- with a R^2 of 0.6200 and a moderate correlation (R^2 = 0.7343) was obtained from the relationship between $CHBr_2ClFP$ and Br^-. This presents the negative relationship between the $CHBrCl_2FP$ and $CHBr_2ClFP$ and the Br^- concentration. A moderate correlation was observed for the relationship between $CHClI_2FP$ species and I^- in raw water with a R^2 equal to 0.8303 (Table 4-8). The $CHClI_2FP$ decreased with an increasing I^- concentration.

In the case of treated wastewater, only a fair correlation was observed between the $CHBrI_2$ species and Br^- with a R^2 of 0.5392. The $CHBrI_2FP$ decreased when increased Br^- concentration. Two HANFP species (CCl_3CN and Cl_2CHCN) were negatively correlated with Br^- with a $R^2 > 0.60$. The total concentration of HANFP decreased when Br^- concentration of treated wastewater increased. This work analyzed 14 DBPs species. Negative relationships may occur for some species, although some positive relationships may form for other species. This could not, however, significantly be determined in this work.

Table 4-8. Linear correlation coefficients (R^2) between DBPFP species and the bromide ion (Br^-) and iodide ion (I^-) of raw water, domestic wastewater, and treated wastewater.

Water sources	Regression parameter				N	R^2	Sig. level	Correlation level
	Dependent variables (y)	Independent variables (x)	Slope (m)	Intercept (C)				
Raw water	**THMFP**							
Br^- 16-51 µg/L	(1) $CHCl_3FP$	Br^-	-	-	5	0.2835	Not	Poor
	(2) $CHBrCl_2FP$	Br^-	-53.3	35.9	5	0.6200	0.11	Fair
	(3) $CHBr_2ClFP$	Br^-	-20.4	9.8	5	0.7343	0.06	Moderate
	(4) $CHBr_3FP$	Br^-	-	-	1	NA	NA	NA
	Total (1)+(2)+(3)	Br^-	-	-	5	0.1608	Not	Poor
	I–THMFP							
	(1) CHBrClIFP	Br^-	-	-	1	NA	NA	NA
	(2) $CHClI_2FP$	Br^-	-	-	4	0.3553	Not	Poor
	(3) $CHCl_2IFP$	Br^-	-	-	4	0.0042	Not	Poor
	(4) $CHBrI_2FP$	Br^-	-	-	0	NA	NA	NA
	(5) CHI_3FP	Br^-	-	-	0	NA	NA	NA
	Total (1)+(2)+(3)	Br^-	-	-	5	0.0156	Not	Poor
	HANFP							
	(1) CCl_3CNFP	Br^-	-	-	5	0.0923	Not	Poor
	(2) $Cl_2CHCNFP$	Br^-	-	-	5	0.0366	Not	Poor
	(3) $C_2HBrClNFP$	Br^-	-	-	4	0.4850	Not	Poor
	(4) C_2HBr_2NFP	Br^-	-	-	1	NA	NA	NA
	Total (1)+(2)+(3)+(4)	Br^-	-	-	5	0.0565	Not	Poor
I^- 3.2-16.9 µg/L	**I–THMFP**							
	(1) CHBrClIFP	I^-	-	-	1	NA	NA	NA
	(2) $CHClI_2FP$	I^-	-0.06	0.9	4	0.8303	0.03	Moderate
	(3) $CHCl_2IFP$	I^-	-	-	4	0.0006	Not	Poor
	(4) $CHBrI_2FP$	I^-	-	-	0	NA	NA	NA
	(5) CHI_3FP	I^-	-	-	0	NA	NA	NA
	Total (1)+(2)+(3)	I^-	-	-	5	0.0014	Not	Poor
Wastewater	**THMFP**							
Br^- 785-7,844 µg/L	(1) $CHCl_3FP$	Br^-	-	-	6	0.0601	Not	Poor
	(2) $CHBrCl_2FP$	Br^-	-	-	6	0.2377	Not	Poor
	(3) $CHBr_2ClFP$	Br^-	-	-	6	0.0083	Not	Poor
	(4) $CHBr_3FP$	Br^-	-	-	1	NA	NA	NA

Table 4-8. (Cont.) Linear correlation coefficients (R^2) between DBPFP species and the bromide ion (Br^-) and iodide ion (I^-) of raw water, domestic wastewater, and treated wastewater

Water sources	Regression parameter				N	R^2	Sig. level	Correlation level
	Dependent variables (y)	Independent variables (x)	Slope (m)	Intercept (C)				
Wastewater	Total (1)+(2)+(3)+(4)	Br^-	-	-	6	0.0374	Not	Poor
	I–THMFP		-	-				
	(1) $CHBrClIFP$	Br^-	-	-	0	NA	NA	NA
	(2) $CHClI_2FP$	Br^-	-	-	6	0.1882	Not	Poor
	(3) $CHCl_2IFP$	Br^-	-	-	5	0.3404	Not	Poor
	(4) $CHBrI_2FP$	Br^-	-	-	2	NA	NA	NA
	(5) CHI_3FP	Br^-	-	-	2	NA	NA	NA
	Total (2)+(3)+(4)+(5)	Br^-	-	-	6	0.0882	Not	Poor
	HANFP							
	(1) CCl_3CNFP	Br^-	-	-	6	0.0950	Not	Poor
	(2) $Cl_2CHCNFP$	Br^-	-	-	6	0.2936	Not	Poor
	(3) $C_2HBrClNFP$	Br^-	-	-	6	0.0028	Not	Poor
	(4) C_2HBr_2NFP	Br^-	-	-	2	NA	NA	NA
	Total (1)+(2)+(3)+(4)	Br^-	-	-	6	0.0354	Not	Poor
I^- 1.2-846 µg/L	**I–THMFP**							
	(1) $CHBrClIFP$	I^-	-	-	0	NA	NA	NA
	(2) $CHClI_2FP$	I^-	-	-	6	0.0673	Not	Poor
	(3) $CHCl_2IFP$	I^-	-	-	5	0.0346	Not	Poor
	(4) $CHBrI_2FP$	I^-	-	-	2	NA	NA	NA
	(5) CHI_3FP	I^-	-	-	2	NA	NA	NA
	Total (2)+(3)+(4)+(5)	I^-	-	-	6	0.0984	Not	Poor
Treated Wastewater	**THMFP**							
Br^- 23-5,050 µg/L	(1) $CHCl_3FP$	Br^-	-	-	4	0.3030	Not	Poor
	(2) $CHBrCl_2FP$	Br^-	-	-	4	0.0052	Not	Poor
	(3) $CHBr_2ClFP$	Br^-	-	-	4	0.0646	Not	Poor
	(4) $CHBr_3FP$	Br^-	-	-	4	0.0007	Not	Poor
	Total (1)+(2)+(3)+(4)	Br^-	-	-	4	0.4005	Not	Poor
	I–THMFP							
	(1) $CHBrClIFP$	Br^-	-	-	0	NA	NA	NA
	(2) $CHClI_2FP$	Br^-	-	-	4	0.0733	Not	Poor
	(3) $CHCl_2IFP$	Br^-	-	-	2	NA	NA	NA
	(4) $CHBrI_2FP$	Br^-	-0.07	5.3	3	0.5392	0.26	Fair
	(5) CHI_3FP	Br^-	-	-	1	NA	NA	NA
	Total (2)+(3)+(4)+(5)	Br^-	-	-	4	0.3868	Not	Poor
	HANFP							
	(1) CCl_3CNFP	Br^-	-0.03	4.1	4	0.6956	0.16	Fair
	(2) $Cl_2CHCNFP$	Br^-	-0.19	19.2	4	0.6562	0.19	Fair
	(3) $C_2HBrClNFP$	Br^-	-	-	4	0.0650	Not	Poor
	(4) C_2HBr_2NFP	Br^-	-	-	3	0.1514	Not	Poor
	Total (1)+(2)+(3)+(4)	Br^-	-0.4	36.2	4	0.5423	0.27	Fair

Table 4-8. (Cont.) Linear correlation coefficients (R^2) between DBPFP species and the bromide ion (Br^-) and iodide ion (I^-) of raw water, domestic wastewater, and treated wastewater

Water sources	Regression parameter				N	R^2	Sig. level	Correlation level
	Dependent variables (y)	Independent variables (x)	Slope (m)	Intercept (C)				
Treated Wastewater	**I–THMFP**							
I^- 0.2-270 µg/L	(1) $CHBrClIFP$	I^-	-	-	0	NA	NA	NA
	(2) $CHClI_2FP$	I^-	-	-	5	0.0381	Not	Poor
	(3) $CHCl_2IFP$	I^-	-	-	2	NA	NA	NA
	(4) $CHBrI_2FP$	I^-	-	-	4	0.1166	Not	Poor
	(5) CHI_3FP	I^-	-	-	2	NA	NA	NA
	Total (2)+(3)+(4)+(5)	I^-	-	-	5	0.1983	Not	Poor

Remark: Regression equation is y = mx+C; Regression analysis was not carried out for $R^2 < 0.5$. Hence, slope (m) and intercept (C) for equation were not computed; DBPFP was dependent variable whereas Br^- and I^- were independent variables; N = Sample size; Sig. = Significant; NA is not available

(Na Patthalung and Musikavong, 2019)

4.3.8 Evaluation of cytotoxicity risk caused by C–DBPs and N–DBPs

The cytotoxicity index is typically expressed as the LC_{50} value all of the individual compounds of a single class of DBPs. The LC_{50} represents the DBP concentration that induced a 50% reduction of cell growth as compared with the cell growth in the concurrent negative controls. The cytotoxicity values of several DBP chemical classes using a Chinese hamster ovary cells assay have been investigated and used to determine the level of toxicity in this study (Richardson et al., 2008; Muellner et al., 2007; Plewa et al., 2004; Plewa et al., 2009). This work used the LC_{50} and lowest cytotoxicity of THMs (Plewa et al., 2009), I–THMs (Richardson et al., 2008), HANs (Muellner et al., 2007), and LC_{50} of TCNM (Plewa et al., 2004) in the analysis.

The results of weight measured concentration and the toxicity-weight basis among C–DBPs and N–DBPs chemical classes (4 THMFP, 5 I–THMFP, 4 HANFP, and 1 HNMFP) in different water sources are shown in Figure 4-5. Based on a mass basis of the DBP concentrations (Figure 4-5A), the THMFP is considered more unsafe than the other DBPs classes because it had much greater cumulative concentration than the others and exceeded the US.EPA maximum contaminant level of 80 µg/L in all the water sources. With considering the average value, weight measured the concentration of C–DBPs and N–DBPs of RW–1 of the BK WTP and RW–2 of the SB WTP from high to low was THMFP > HANFP > I–THMFP >

TCNMFP. For the river waters, wastewaters, and treated wastewaters, the rank order of these DBPs on a mass concentration basis was THMFP > HANFP > TCNMFP > I–THMFP.

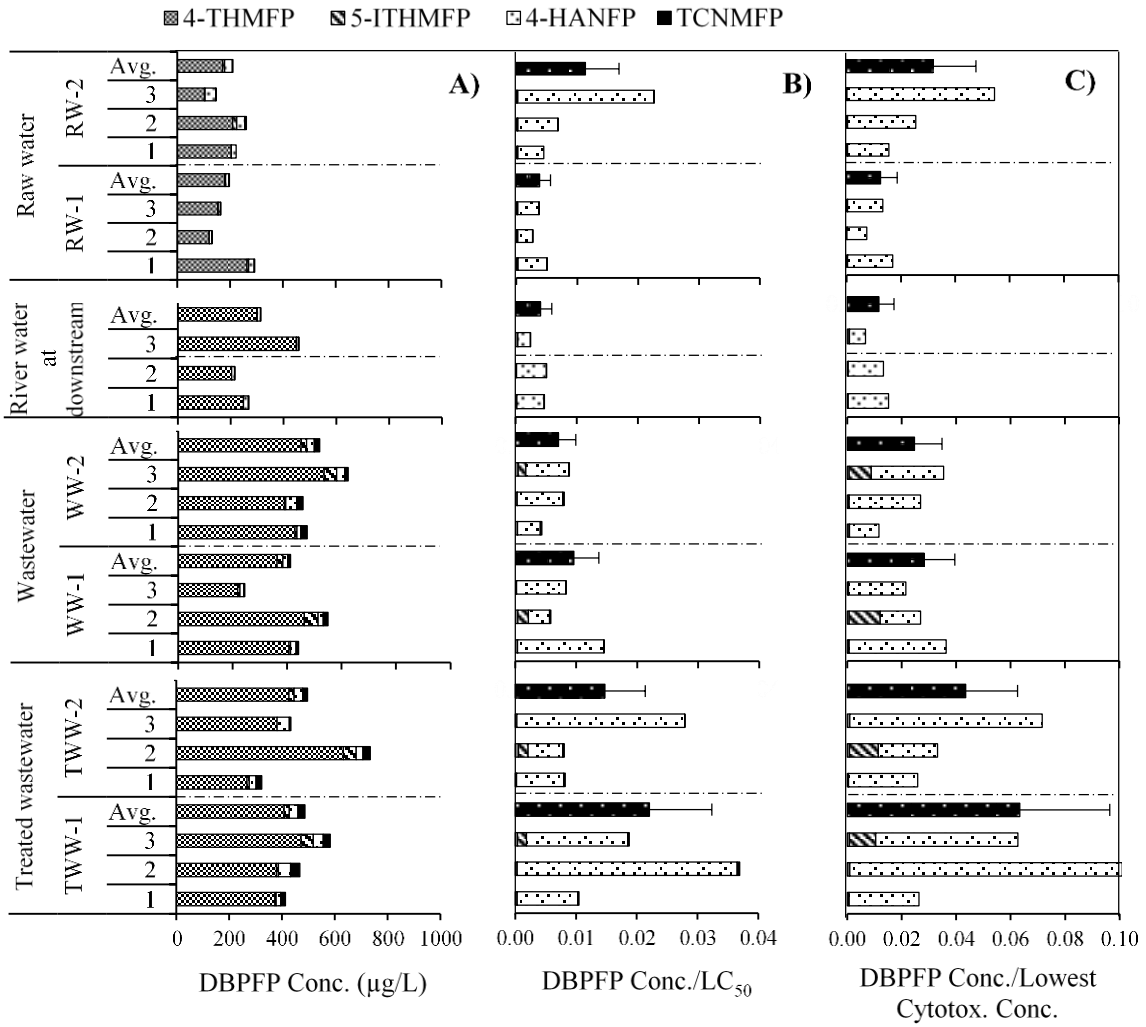


Figure 4-5. Weight measured concentration (A), lethal concentration 50-weighted (B), and lowest cytotoxicity-weighted concentrations (C) of DBPs. (Na Pattalung and Musikavong, 2019)

For the toxic risk, the value of the LC_{50}-weighted concentration of C–DBPs and N–DBPs in water sources is shown in Figure 4-5B. The rank order for toxic risk caused by these DBPs was HANFP > THMFP >TCNMFP > I–THMFP in raw waters and river waters. For wastewater, the rank order for toxic risk was HANFP > THMFP > I–THMFP >TCNMFP. Treated wastewaters contained highly toxic HANFP, followed by I–THMFP, THMFP, and TCNMFP. The average value of the LC_{50}-weighted HANFP concentration of treated wastewater was 1.2 to 5.7 times higher than that of raw water.

Considering the value of the lowest cytotoxicity-weighted concentration of C–DBPs and N–DBPs in water sources (Figure 4-5C), the rank order for toxic risk caused by these DBPs was HANFP > THMFP > I–THMFP in raw waters and river waters. For wastewaters and treated wastewaters, the rank order of these DBPs was HANFP > I–THMFP > THMFP. The average value of the lowest cytotoxicity-weighted HANFP concentration of treated wastewater was 1.2 to 4.8 times higher than that of raw water. Based on the toxicity-weighted basis, the most cytotoxic in all the water sources were HANFP. The HANFP is considered the least safe because it features higher concentrations of the toxicity drivers. A similar level of HANFP concentration was also found in polluted source waters (Bond et al., 2011). Thus, the toxic risk class of HANs cannot be ignored with other DBPs as it may cause adverse effects on human health through water consumption.

Chapter V

Formation of carbonaceous and nitrogenous disinfection by-products of fractionated dissolved organic matter in raw water, wastewater, and treated wastewater

5.1 Introduction

Source and nature of dissolved organic matter (DOM) play a crucial role in the water treatment plant. DOM can react with either chlorine or chloramines during the disinfection process of WTP to form disinfection by-products (DBPs). Different types of water have a distinguished level and characteristic of DOM. According to the obtained results in Chapter IV, the high levels of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), carbonaceous DBPs (C-DBPs) and nitrogenous (N-DBPs) formation potential of domestic wastewater and its treated wastewater were found in compared with that of raw water. The DBP formation potential/Lethal Dose 5O (LC_{50}) and DBP formation potential/lowest cytotoxicity of treated wastewater were higher than that of raw water.

The series of ultrafiltration membrane can be used to separate into the several sizes of molecular weight (MW) size cut-offs: 100, 30, 10, 5 and 1 kDa (Ma et al., 2013; Zhou et al., 2015). DOM can be classified according to its chemical property by using resin fractionation technique. DAX-8 and XAD-4 resin are used to separate DOM into three fractions including hydrophobic organic fraction (HPO), transphilic organic fraction (TPI), and hydrophilic organic fraction (HPI) (Aiken and McKnight, 1992; Leenheer et al., 1981). The DOM size can be determined by using the UF membrane. The DOM size and chemical property of DOM have significantly affected the removal of DBPs precursors, the formation of DBPs, and the control of water treatment plant (WTP).

Trihalomethanes (THMs) are the first group of carbonaceous DBPs (C-DBPs) that detected from the reaction between DOM and chlorine in water (Rook, 1974). The chloride and bromide compounds are considered in the THMs formation. THMs consists of four compounds, including chloroform (trichloromethane, TCM), bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform. When the presence of iodide in raw water from natural or human-made sources has occurred, then, the reaction among DOM, chlorine, bromide, and iodide causes the formation of iodo-trihalomethanes (I-THMs). Six I-THMs have been found in water, including iodoform (triiodomethanes, TIM), bromochloroiodomethane (BCIM), chlorodiiodomethane (CDIM), dibromoiodomethane

(DBIM), dichloroiodomethane (DCIM), and bromidiiodomethane (BDIM) (Richardson et al., 2007; Krasner et al., 2006). I-THMs is considered as the emerging DBPs in the water supply. The cytotoxicity and genotoxicity of I-THMs in mammalian cells assays were higher than that of brominated and chlorinated analogs (Bichsel and von Gunten, 2000; Cancho et al., 2000).

Haloacetronitriles (HANs) are the primary group of N-DBPs detected in the water supply. Four HANs compounds that were frequency found in drinking water composed of trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN). The World Health Organization (WHO) has set guidelines values of 20 and 70 µg/L for DCAN and DBAN, respectively (WHO, 2008). Emerging N-DBPs in drinking water are halonitromethanes (HNMs) compounds. HNMs are composed of chloronitromethane, dichloronitromethane, trichloronitromethane, bromo-chloronitromethane, bromodichloronitromethane, bromonitromethane, dibromonitro-methane, dibromochloronitromethane, and tribromonitromethane. HMNs were detected in low concentration in compared with that of THMs and haloacetic acids (HAAs). HMNs have not been regulated. However, cytotoxicity and genotoxicity caused by HNMs are comparable or even higher when compared with that of THMs and HAAs (Krasner et al., 2006; Richardson et al., 2007).

The level of DOM fractions and the formation potential of C-DBPs and N-DBPs of raw water are the essential information for the operation and control of water treatment plant. The level of DOM fraction provides the knowledge for determining the significant organic fraction in raw water. The formation potential of DBPs illustrates the major C-DBPs and N-DBPs. The water treatment plant can use this information for selecting the suitable chemical, process, or methods for removal of major organic fraction and C-DBPs and N-DBPs precursors from raw water.

The level of DOM fractions by resin fractionation technique and formations of THMs and HAAs of DOM fraction of raw water of the Bangkok's water supply were determined (Panyapinyophol et al., 2005, Kanokkantapong et al., 2006). The level of DOM fractions according to the molecular weight cut off and their formation of C-DBPs and N-DBPs are limited. For other water sources, the level of DOM fractions and the formation of traditional C-DBPs and N-DBPs in several sources of water were determined (Fan et al., 2014; Han et al., 2015). The determination of formation of emerging DBPs of DOM fractions such as I-THMs and HNMs has been limited. The previous research mostly analyzed the formation of DBPs in

tems of mass. The analysis of DBPs formation of DOM fractions in terms of LC_{50} and the lowest cytotoxicity is very important and have limitedly reported.

This work is aimed at investigating the nature of DOM as DBPs precursors in domestic wastewater and treated wastewater, raw water, and river by using two methods, including ultrafiltration and resin fractionation. Ultrafiltration is utilized for separating DOM into different molecular weights (MW) including MW < 1 kDa, 1 kDa < MW < 3 kDa, 3 kDa < MW <10 kDa, and MW > 10 kDa. Resin fractionations were employed to fractionate DOM into HPO, TPI, and HPI. DOM fractions were conducted for their THMs formation potential (THMFP), iodide THMs formation potential (I-THMFP), HANs formation potential (HANFP), and HANs formation potential (HANFP). The DBP formation potential/LC_{50} and DBP formation potential/lowest cytotoxicity of fractionated water were determined.

5.2 Water samples and experimental procedure

The raw water from two water treatment plants (WTP), river water at a downstream location of the Chao Phraya River, and wastewater and treated wastewater from two domestic WWTPs were collected three times from each source waters. Water samples were collected in October 2016, May 2017, and February 2018 as the representative of emerging C-DBPs' and N-DBPs' formation during the rainy season, summer, and winter, respectively. Raw waters from the Chao Phraya River were collected from the pumping station of Bangkhen WTP (BK WTP) at a downstream location (RW−1) and Singburi WTP (SB WTP) at an upstream location (RW−2). Water samples from the river were obtained from the Siriraj sampling site, which is located downstream of the Chao Phraya River after the BK WTP. This sample stands for water with seawater, treated and untreated wastewater contamination. Domestic wastewater before (WW−1) and after treated wastewater (TWW−1) were collected from the WWTP in Ang Thong (AT) province. Besides, domestic wastewater before (WW−2) and treated wastewater (TWW−2) were obtained from the WWTP in Ayutthaya (AY) province. These two WWTPs are located in the upstream location of the Chao Phraya River. The wastewater and treated wastewater represent the sources of contamination from human activities. All samples were stored at a temperature of 4 °C until analysis.

The raw water (RW−1 and RW−2), domestic wastewater (WW−1 and WW−2) and treated wastewater (TWW−1 and TWW−2) were used for fractionating into the molecular weight (MW) sizes of DOM four groups: MW > 10 kDa, 3 kDa < MW <10 kDa, 1 kDa < MW

< 3 kDa, and MW < 1 kDa, using YM10, YM3, and YM1 Da Ultracel regenerated cellulose membrane (Millipore Corp, Bedford, USA) with decreasing molecular weight cut-off (MWCO) of 10, 3 and 1 kDa. The DOM fractionation procedures by a series of ultrafiltration membranes were adapted from Ma et al. (2013). DAX-8 and XAD-4 resins were used to separate DOM into three fractions including, HPO, HPI, and TPI (Leenheer et al., 1981; Aiken et al., 1992). All samples of DOM fractions were conducted for their THMFP, I-THMFP, HANFP, and trichloronitromethane formation potential (TCNMFP). The DBP formation potential/LC_{50} and DBP formation potential/lowest cytotoxicity of fractionated water were determined.

5.3 Results and discussion

5.3.1 Mass distribution of the fractionated DOM

The DOC of DOM fractions with their percent distributions of raw water, wastewater, and treated wastewater are tabulated in Table 5-1. DOM with MW < 1 kDa was the dominant DOM fraction in raw water of the Bangkhen and Singburi WTPs and domestic wastewater and their treated wastewater of the wastewater treatment plants in Ang Thong and Ayutthaya provinces. DOC of DOM with MW < 1 kDa of raw water, wastewater, and treated wastewater ranged from 1.2 to 2.5, 1.0 to 3.3, and 2.5 to 3.3 mg/L, respectively, with the ranges of percent distribution from 36 to 63, 15 to 48, and 49 to 60% by weight of total DOC, respectively.

The DOM with MW > 10 kDa was found as the second dominant DOM. Ranges of DOC of DOM with MW > 10 kDa in raw water, wastewater, and treated wastewater of 0.9 to 1.1, 1.4 to 2.0, and 1.3 to 1.6 mg/L were determined, respectively. The percent distribution by weight of total DOC of that of water ranged from 19 to 27, 24 to 29, and 11 to 25%, respectively. The order of the DOC distribution of raw water, wastewater, and treated wastewater could be express as follows: DOM with MW < 1 kDa, MW > 10 kDa, 3 kDa < MW < 10 kDa, and 1 kDa < MW < 3 kDa, respectively. The order of the DOC distribution of wastewater and treated wastewater was the same as that of raw water. It implied that the wastewater and treated wastewater could be the DOM contamination sources to raw water.

When DOM in water samples was separated by resin fractionation, the HPO was the dominant DOM fractions. DOC of HPO in raw water, wastewater, and treated wastewater ranged from 1.5 to 2.4, 3.1 to 4.9, and 2.2 to 3.5 mg/L, respectively, with the ranges of percent distribution from 22 to 50, 59 to 67, and 39 to 55% by weight of total DOC, respectively. HPI was the second significant DOM fraction. DOC of HPI of raw water, wastewater, and treated

wastewater ranged from 1.3 to 1.4, 1.6 to 1.8, and 1.9 to 2.6 mg/L, respectively, with the ranges of percent distribution from 28 to 38, 23 to 30, and 33 to 43% by weight of total DOC, respectively. The TPI was found as minority DOM group.

Table 5-1. DOC of DOM fractions and their percent distribution.

		DOC of fraction (mg/L)						
Samples		>10 kDa	3–10 kDa	1–3 kDa	<1 kDa	HPO	TPI	HPI
Raw water	BK–1	0.9 (19)	1.2 (27)	0.5 (11)	1.9 (42)	2.4 (22)	1.0 (22)	1.3 (28)
	BK–2	0.9 (27)	0.4 (12)	0.8 (24)	1.2 (36)	1.5 (43)	0.6 (19)	1.3 (38)
	SB–1	1.1 (27)	0.6 (14)	0.6 (15)	1.8 (43)	2.2 (50)	0.7 (17)	1.4 (33)
	SB–2	0.9 (21)	0.3 (7)	0.4 (9)	2.5 (63)	2.0 (50)	0.6 (16)	1.3 (34)
Wastewater	AT–1	1.8 (26)	0.9 (14)	0.9 (13)	3.3 (48)	4.8 (67)	0.8 (10)	1.6 (23)
	AT–2	1.4 (26)	0.8 (15)	0.8 (16)	2.3 (43)	3.1 (59)	0.6 (12)	1.6 (30)
	AY–1	1.6 (24)	1.5 (22)	0.9 (13)	2.7 (41)	4.9 (66)	0.7 (10)	1.8 (25)
	AY–2	2.0 (29)	3.2 (48)	0.5 (7)	1.0 (15)	4.1 (63)	0.6 (9)	1.8 (28)
Treated	AT–1	1.0 (20)	0.6 (12)	0.9 (18)	2.5 (50)	2.2 (46)	0.7 (16)	1.9 (39)
wastewater	AT–2	1.6 (25)	0.9 (14)	0.8 (12)	3.2 (49)	2.4 (39)	1.1 (18)	2.6 (43)
	AY–1	1.2 (11)	1.4 (13)	1.3 (24)	2.8 (52)	2.4 (46)	0.8 (16)	2.0 (38)
	AY–2	1.3 (20)	1.1 (17)	0.7 (11)	3.3 (52)	3.5 (55)	0.7 (12)	2.1 (33)

Remark: ( ) is percent distribution

The conventional water treatment plant uses the coagulation process typically by iron salts for removing turbidity and DOM. The coagulation process effectively removes DOM with high MW and HPO's character. HPO and DOM with MW > 10 kDa were found as the first and second major DOM according to ultrafiltration and resin fractionation technique, respectively, and could be sufficiently removed by coagulation process. When the dominant DOM fraction in water primary contains low MW and HPI's character, the enhanced coagulation or advanced water treatment process such as activated carbon and ion exchange magnetic (MIEX) resin should be considered as the optional for removal of dominant DOM fractions.

5.3.2 DBPFP of DOM fractions

THMFP

The THMFP species/DOC of DOM fractions of raw water, wastewater, and treated wastewater in terms of molecular sizes are presented in Figure 5-1. For the raw water of the Bangkhen WTP, DOM with MW > 10 kDa had the highest THMFP/DOC (133 μg/mg DOC, on average) followed by that of 1 kDa < MW < 3 kDa (112 μg/mg), 3 kDa < MW < 10 kDa (105 μg/mg), and MW < 1 kDa (75 μg/mg), respectively. In the case of raw water of the Singburi WTP, the order of THMFP/DOC were 1 kDa < MW < 3 kDa (87 μg/mg), 3 kDa < MW < 10 kDa (72 μg/mg), MW > 10 kDa (54 μg/mg), and MW < 1 kDa (33 μg/mg), respectively. Chloroform was determined as the THMFP species of all DOM fractions with the highest THMFP, followed by bromodichloromethane, and dibromochloromethane, respectively. The bromoform could not detected.

In the case of domestic wastewater in the Ang Thong province, the order of THMFP/DOC were 3 kDa < MW < 10 kDa (68 μg/mg), 1 kDa < MW < 3 kDa (48 μg/mg), MW > 10 kDa (33 μg/mg), and MW < 1 kDa (22 μg/mg), respectively. For the wastewater in Ayutthaya province, DOM with 1 kDa < MW < 3 kDa had the highest THMFP/DOC (45 μg/mg) followed by that of MW > 10 kDa (31 μg/mg), 3 kDa < MW < 10 kDa (26 μg/mg), and MW < 1 kDa (23 μg/mg), respectively.

For domestic treated wastewater in the Ang Thong province, DOM with 1 kDa < MW < 3 kDa had the highest THMFP/DOC (72 μg/mg) followed by that of 3 kDa < MW < 10 kDa (68 μg/mg), MW > 10 kDa (56 μg/mg), and MW < 1 kDa (44 μg/mg), respectively. In the case of domestic wastewater in the Ayutthaya province, the order of THMFP/DOC were 1 kDa < MW < 3 kDa (53 μg/mg), MW > 10 kDa (43 μg/mg), 3 kDa < MW < 10 kDa (32 μg/mg), and MW < 1 kDa (12 μg/mg), respectively.

Chloroform was determined as the highest THMFP species of DOM fractions of domestic wastewater and their treated wastewater, followed by bromodichloromethane, and dibromochloromethane, respectively. This has corresponded well with the THMFP species of raw water. The bromoform detected only DOM fraction with MW < 1 kDa of wastewater from Ayutthaya province and treated wastewater from the Ang Thong province. This indicated that the bromoform could be formed in wastewater and treated wastewater rather than raw water.

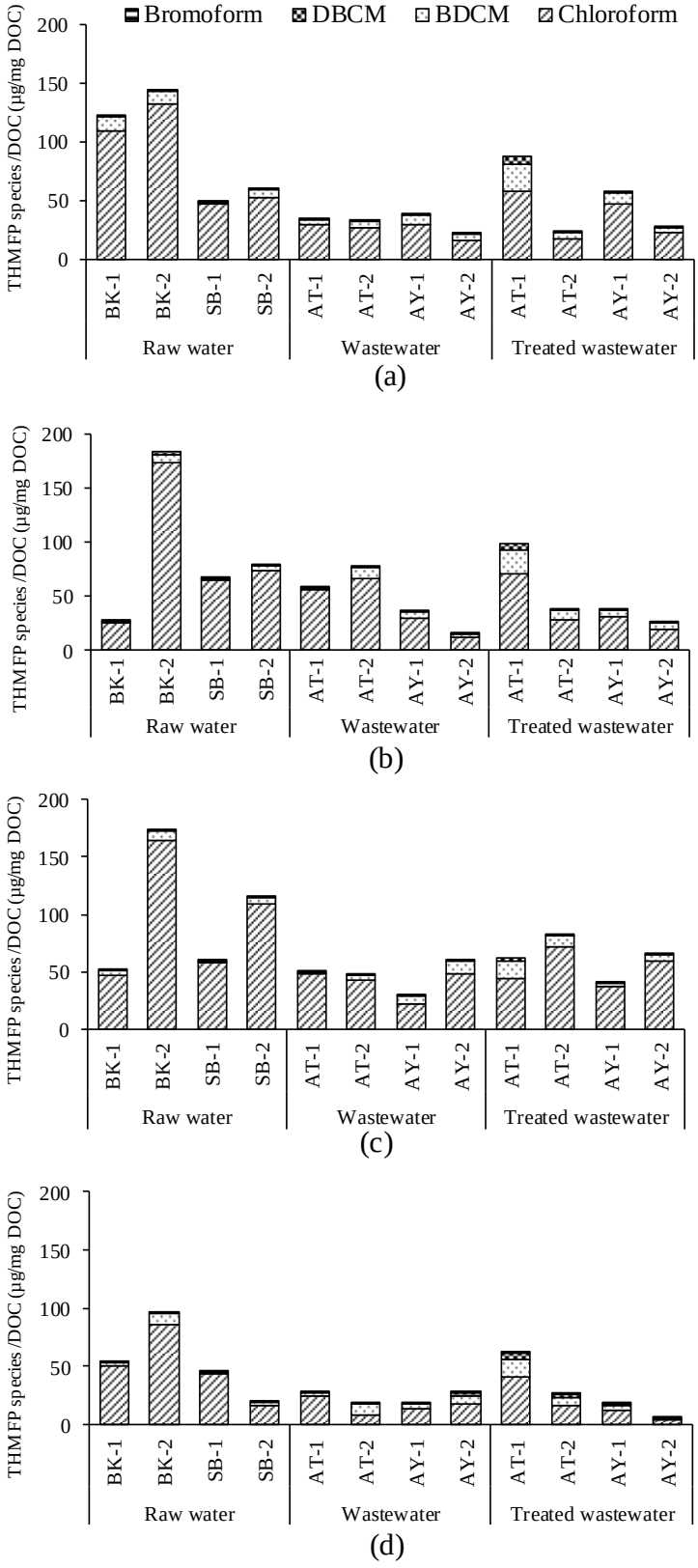


Figure 5-1. THMFP Species/DOC of DOM fractions in raw water, wastewater, and treated wastewater classified by ultrafiltration: (a) MW > 10 kDa; (b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa

The lowest THMFP/DOC for all water samples was determined for DOM with MW < 1 kDa, the dominant DOM fraction. This implied that the dominant DOM compose of less vigorous organic for the formation of THMFP. The THMFPs of DOM fractions of raw water was higher than that of wastewater and treated wastewater.

The THMFP species/DOC of DOM fractions of raw water, wastewater, and treated wastewater by resin fractionation are showed in Figure 5-2. For the raw water of the Bangkhen WTP, TPI had the highest THMFP/DOC (35 μg/mg DOC, on average) followed by that of HPO (31 μg/mg) and HPI (25 μg/mg), respectively. In the case of raw water of the Singburi WTP, the order of THMFP/DOC were HPO (45 μg/mg), TPI (42 μg/mg), and HPI (36 μg/mg), respectively. The THMFP/DOCs of HPO, TPI, and HPI was slightly different. Chloroform was determined as the major THMFP species of DOM fractions followed by bromodichloromethane. Dibromochloromethane was deleted in HPI of the Bangkhen WTP and TPI of the Singburi plant, whereas bromoform was determined in HPI of the Bangkhen WTP.

In the case of domestic wastewater in the Ang Thong province, the order of THMFP/DOC were TPI (72 μg/mg), HPO (13 μg/mg), and HPI (8 μg/mg), respectively. For the wastewater in Ayutthaya province, TPI had the highest THMFP/DOC (55 μg/mg) followed by that of HPO (29 μg/mg), and HPI (3 μg/mg), respectively. For treated wastewater in the Ang Thong province, TPI had the highest THMFP/DOC (159 μg/mg) followed by that of HPO (91 μg/mg), and HPI (47 μg/mg), respectively. In the case of domestic wastewater in the Ayutthaya province, the order of THMFP/DOC were TPI (90 μg/mg), HPO (83 μg/mg), and HPI (45 μg/mg), respectively. TPI in wastewater and treated wastewater had the active DOM for reacting with chlorine to form THMs. The DOM fractions of treated wastewater had a high activity to form THMs in compared with that of wastewater.

Chloroform was determined as the highest THMFP species of DOM fractions of domestic wastewater and their treated wastewater, followed by bromodichloromethane, and dibromochloromethane. This has corresponded well with the THMFP species of DOM fractions of raw water. The bromoform detected only from HPI from wastewater of Ang Thong and treated wastewater from Ang Thong and Ayutthaya provinces. This indicated that the bromoform could be formed in HPI.

The highest THMFP/DOC of DOM fractions of all water samples was determined for TPI, followed by HPO, the dominant DOM fraction, and HPI. In term of DOC distribution,

TPI had the lowest value of DOC, however, TPI had the highest value of THMFP/DOC. DOM in TPI might contain the active character for the formation of THMFP.

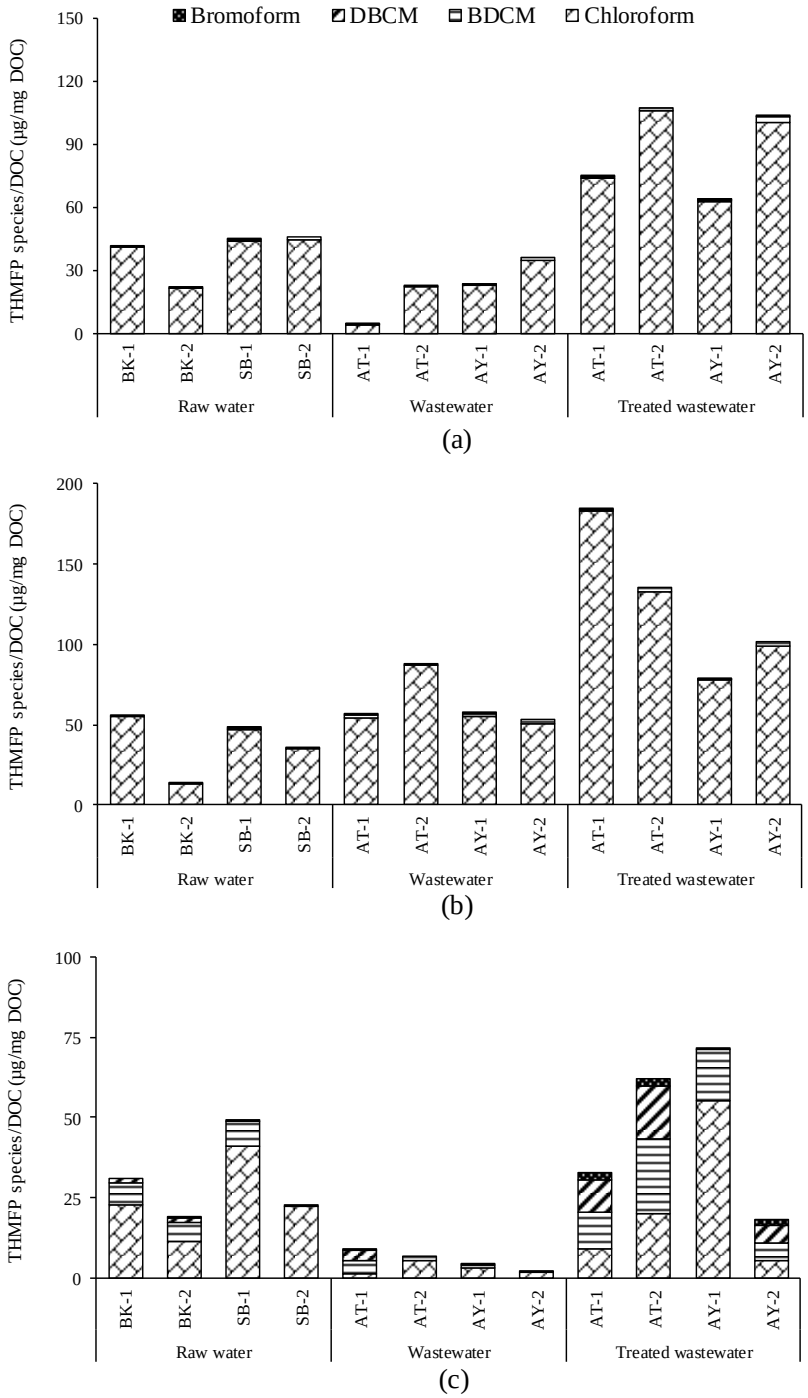


Figure 5-2. THMFP-Species/DOC of DOM fractions in raw water, wastewater, and treated classified by resin fractionation: (a) HPO; (b) TPI; (c) HPI

I-THMFP

The I-THMFP species/DOC of DOM fractions of raw water, wastewater, and treated wastewater in terms of molecular sizes are presented in Figure 5-3. For the raw water of the Bangkhen WTP, DOM with 1 kDa < MW < 3 kDa had the highest I-THMFP/DOC (17.3 μg/mg DOC, on average) followed by that of 3 kDa < MW < 10 kDa (2.4 μg/mg), MW > 10 kDa (1.0 μg/mg), and MW < 1 kDa (0.5 μg/mg), respectively. In the case of raw water of the Singburi WTP, the order of I-THMFP/DOC were 3 kDa < MW < 10 kDa (5.3 μg/mg), 1 kDa < MW < 3 kDa (3.0 μg/mg), MW < 1 kDa (1.9 μg/mg), and MW > 10 kDa (0.7 μg/mg), respectively. CDIM, DCIM, and BDIM were the I-THMFP species that detected in all DOM fractions. TIM detected in 1 kDa < MW < 3 kDa and MW < 1 kDa of the Bangkhen WTP and 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa of the Singburi WTP. The BCIM could not detected.

In the case of domestic wastewater in the Ang Thong province, the order of I-THMFP/DOC were MW < 1 kDa (4.6 μg/mg), 1 kDa < MW < 3 kDa (0.8 μg/mg), 3 kDa < MW < 10 kDa (0.3 μg/mg), and MW > 10 kDa (0.2 μg/mg), respectively. For the wastewater in Ayutthaya province, DOM with 1 kDa < MW < 3 kDa had the highest I-THMFP/DOC (1.7 μg/mg) followed by that of MW < 1 kDa (0.9 μg/mg), 3 kDa < MW < 10 kDa (0.4 μg/mg), and MW > 10 kDa (0.2 μg/mg), respectively.

For treated wastewater in the Ang Thong province, DOM with MW < 1 kDa had the highest I-THMFP/DOC (1.9 μg/mg) followed by that of 1 kDa < MW < 3 kDa (1.8 μg/mg), 3 kDa < MW < 10 kDa (0.6 μg/mg), and MW > 10 kDa (0.5 μg/mg), respectively. In the case of treated wastewater in the Ayutthaya province, the order of I-THMFP/DOC were 1 kDa < MW < 3 kDa (4.9 μg/mg), MW < 1 kDa (1.6 μg/mg), 3 kDa < MW < 10 kDa (0.3 μg/mg), and MW > 10 kDa (0.2 μg/mg), respectively. CDIM, DCIM, and BDIM were the I-THMFP species that detected in all DOM fractions of wastewater and treated wastewater. This was similar to that of raw water. TIM mostly detected in DOM of treated wastewater with MW < 1 kDa and 1 kDa < MW < 3 kDa.

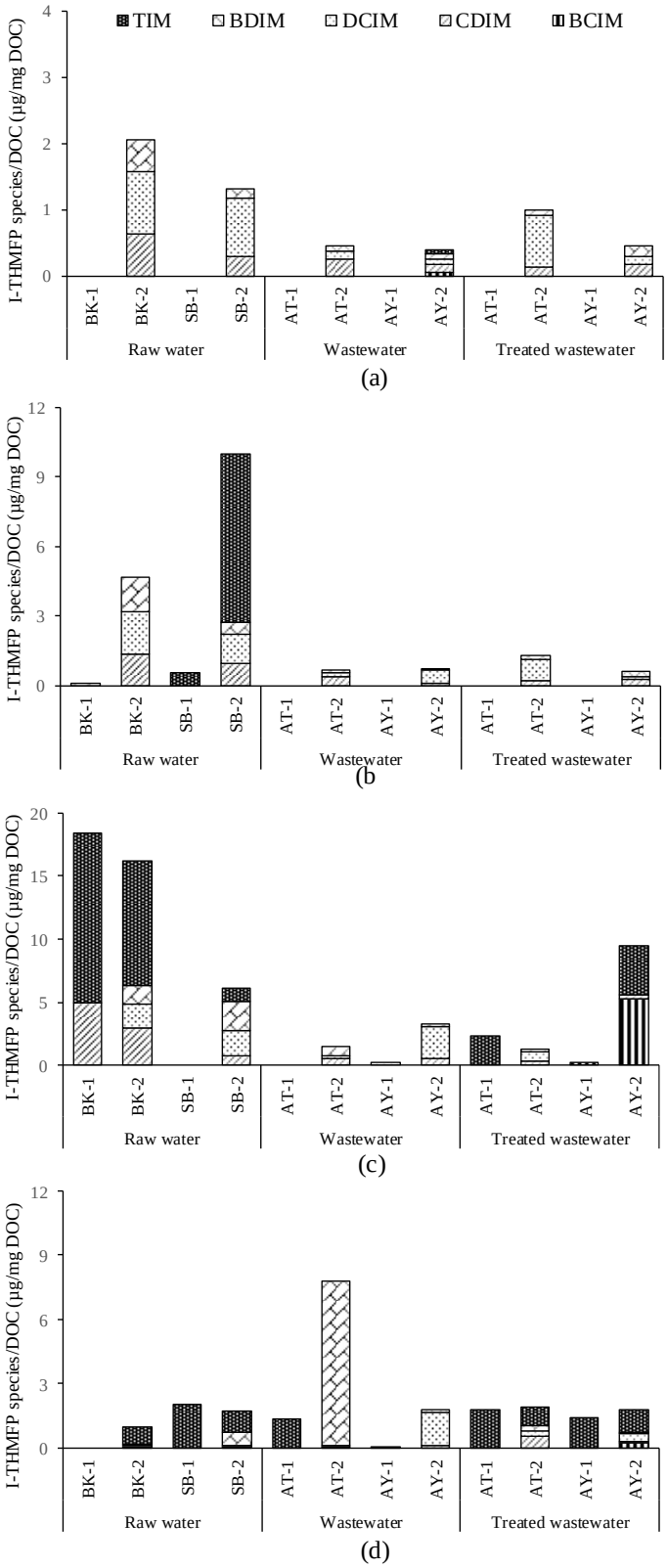


Figure 5-3. I-THMFP-Species/DOC of DOM fractions in raw water, wastewater, and treated wastewater classified by ultrafiltration: (a) MW > 10 kDa; (b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa

The I-THMFP species/DOC of DOM fractions of raw water, wastewater, and treated wastewater by resin fractionation are shown in Figure 5-4. For the raw water of the Bangkhen WTP, the I-THMFP was not detected for all fractions. In the case of raw water of the Singburi WTP, the order of I-THMFP/DOC was TPI (7.9 μg/mg), HPI (3.9 μg/mg), and HPO (2.4 μg/mg), respectively. The I-THMFP/DOCs of HPO, TPI, and HPI was slightly different.

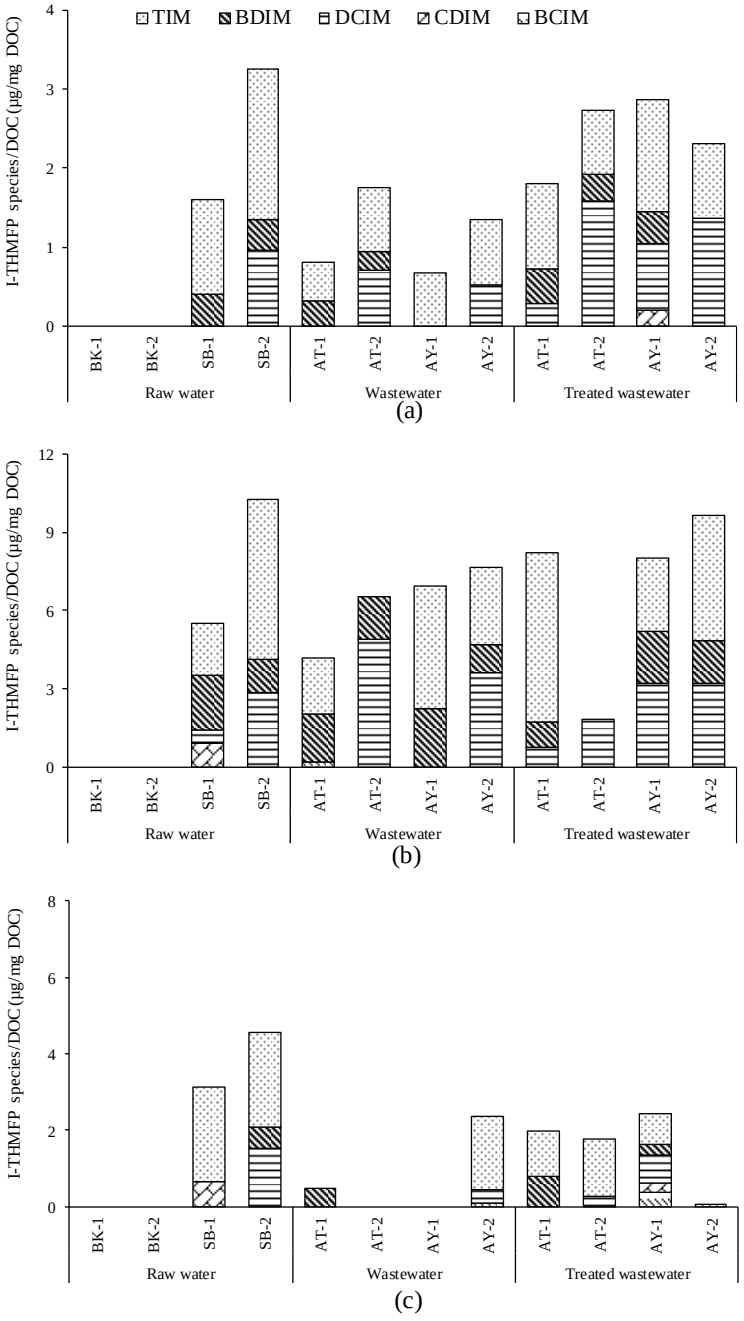


Figure 5-4. I-THMFP-Species/DOC of DOM fractions in raw water, wastewater, and treated wastewater classified by resin fractionation: (a) HPO; (b) TPI, (c) HPI

In the case of domestic wastewater in the Ang thong province, the order of I-THMFP/DOC was TPI (5.3 μg/mg), HPO (1.3 μg/mg), and HPI (0.2 μg/mg), respectively. For the domestic wastewater in the Ayuttaya province, the order of I-THMFP/DOC was TPI (7.3 μg/mg), HPO and HPI were similar (1-1.2 μg/mg), respectively. In the case of treated wastewater in the Ang thong province, the order of I-THMFP/DOC was TPI (5.0 μg/mg), HPO (2.3 μg/mg), and HPI (1.2 μg/mg), respectively. For treated wastewater in the Ayuttaya province, TPI had the highest I-THMFP/DOC (8.8 μg/mg) followed by that of HPO (2.6 μg/mg), and HPI (1.9 μg/mg), respectively. TPI in wastewater and treated wastewater had the active DOM for reacting with Iodine to form I-THMs. The DOM fractions of wastewater and treated wastewater were a similar activity to form I-THMs. TIM was determined as the significant I-THMFP species in all DOM fractions.

HANFP

The HANFP species/DOC of DOM fractions of raw water, wastewater, and treated wastewater in terms of molecular sizes are presented in Figure 5-5. For the raw water of the Bangkhen WTP, DOM with MW > 10 kDa had the highest HANFP/DOC (6.5 μg/mg DOC, on average) followed by that of 1 kDa < MW < 3 kDa (3.8 μg/mg), 1 kDa < MW < 10 kDa (1.3 μg/mg), and MW < 1 kDa (2.3 μg/mg), respectively. In the case of raw water of the Singburi WTP, the order of HANFP/DOC were 3 kDa < MW < 10 kDa (4.4 μg/mg), 1 kDa < MW < 3 kDa (4.0 μg/mg), MW < 1 kDa (3.5 μg/mg), and MW > 10 kDa (2.3 μg/mg), respectively. TCAN, DCAN, and BCAN were the HANFP species that detected in all DOM fractions. TCAN and similar to DCAN mostly formed with MW > 10 kDa, while DBAN was determine highest in DOM fraction with 1 kDa < MW < 3 kDa of the Bangkhen WTP. The formation of DCAN were detected in DOM with all fraction with MW < 1 kDa, 3 kDa < MW < 10 kDa, and 1 kDa < MW < 3 kDa and MW > 10 kDa of the Singburi WTP. The DBAN was slightly detected.

In the case of domestic wastewater in the Ang Thong province, the order of HANFP /DOC were 1 kDa <MW < 3 kDa (15.3 μg/mg), 3 kDa < MW 10 kDa (11.3 μg/mg), MW < 10 kDa (4.3 μg/mg), and MW < 1 kDa (3.9 μg/mg), respectively. For the wastewater in Ayutthaya province, DOM with 1 kDa < MW < 3 kDa had the highest HANFP/DOC (27.7 μg/mg) followed by that of MW < 1 kDa (12.9 μg/mg), MW > 10 kDa (4.7 μg/mg), and 3 kDa < MW < 10 kDa (0.9 μg/mg), respectively

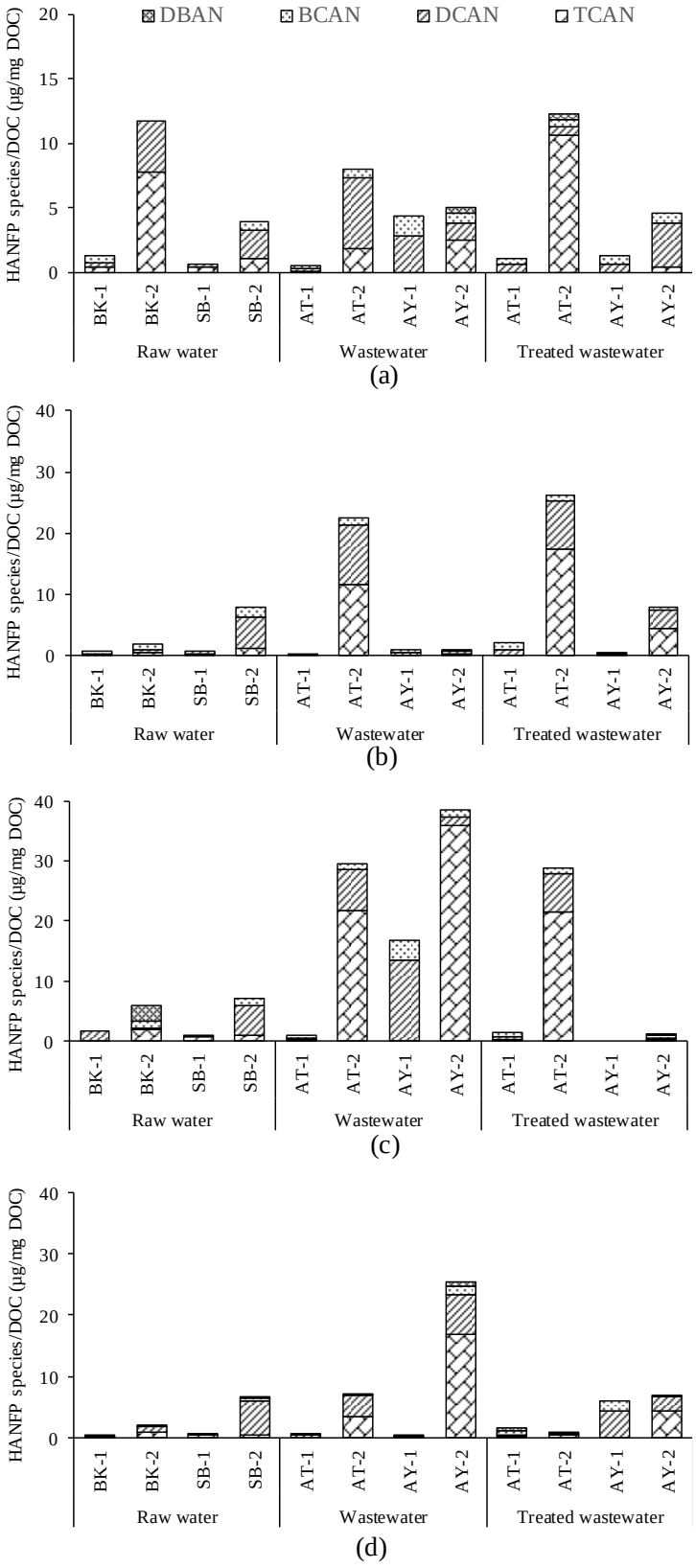


Figure 5-5. HANFP-Species/DOC of each organic size fraction in raw water supply, wastewater and treated wastewater (a) MW > 10 kDa; (b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa

For treated wastewater in the Ang Thong province, DOM with 1 kDa < MW < 3 kDa had the highest I-THMFP/DOC (15.1 μg/mg) followed by that of 3 kDa < MW < 10 kDa (14.2 μg/mg), MW > 10 kDa (6.7 μg/mg), and MW < 1 kDa (1.2 μg/mg), respectively. In the case of treated wastewater in the Ayutthaya province, the order of HANFP/DOC were MW < 1 kDa (6.5 μg/mg), 3 kDa < MW < 10 kDa (4.3 μg/mg), MW > 10 kDa (2.9 μg/mg), and 1 kDa < MW < 3 kDa (0.6 μg/mg), respectively. TCAN, DCAN, and BCAN were the HANFP species that detected in all DOM fractions of wastewater and treated wastewater. This was similar to raw water. TCAN mostly detected in DOM of treated wastewater of Ang thong province with MW > 10 kDa, 3 kDa < MW < 10 kDa, and 1 kDa < MW < 3 kDa,

The HANFP species/DOC of DOM fractions of raw water, wastewater, and treated wastewater by resin fractionation are shown in Figure 5-6. For the raw water of the Bangkhen WTP, TPI had the highest HANFP/DOC (1.2 μg/mg DOC, on average) followed by that of HPI (0.5 μg/mg) and HPO (0.2 μg/mg), respectively. In the case of raw water of the Singburi WTP, the order of HANFP/DOC were HPI (3.3 μg/mg), TPI (3.0 μg/mg), and HPO (1.5 μg/mg), respectively. The HANFP/DOCs of HPO, TPI, and HPI was slightly different. DCAN was determined as the major THMFP species of DOM fractions followed by TCAN and BCAN which were slightly different. TCAN was detected in all fraction of raw water of Singburi WTP but could not found in Bangkhen WTP, whereas DBAN was detected in TPI of the Bangkhen WTP.

In the case of domestic wastewater in the Ang Thong province, the order of HANFP/DOC were TPI (9.3 μg/mg), HPI (3.8 μg/mg), and HPO (0.7 μg/mg), respectively. For the wastewater in Ayutthaya province, TPI had the highest HANFP/DOC (6.1 μg/mg) followed by that of HPI (1.5 μg/mg), and HPO (0.8 μg/mg), respectively. For treated wastewater in the Ang Thong province, TPI had the highest HANFP/DOC (17.7 μg/mg) followed by that of TPI (3.3 μg/mg), and HPO (1.6 μg/mg), respectively. In the case of domestic wastewater in the Ayutthaya province, the order of HANFP/DOC were HPI (4.4 μg/mg), HPO (3.2 μg/mg), and TPI (3.3 μg/mg), respectively. TPI in wastewater and HPI in treated wastewater have the active DOM for reacting with chlorine to form HANs.

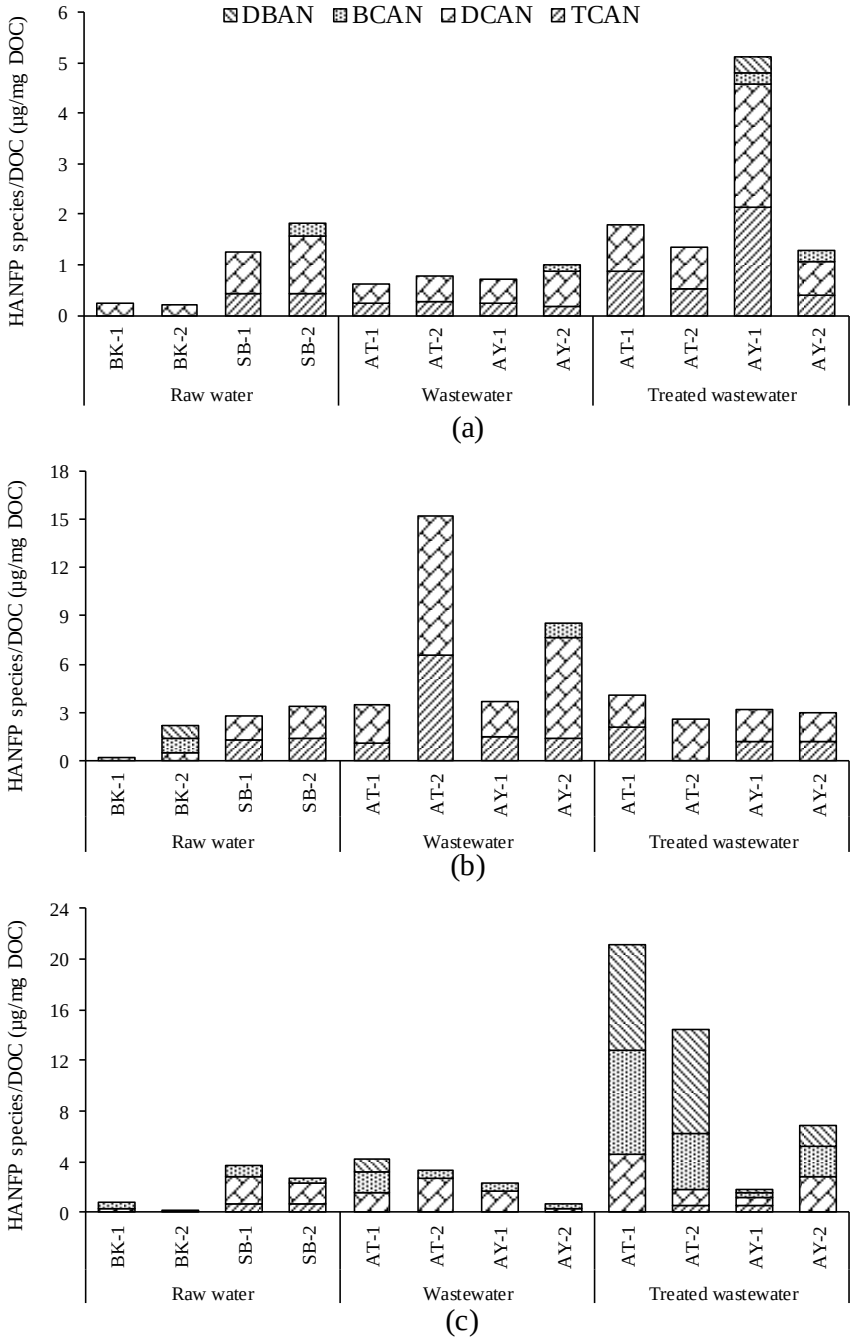


Figure 5-6. HANFP-Species/DOC of each organic resin fraction in raw water supply, wastewater and treated wastewater (a) HPO; (b) TPI, (c) HPI

HNMFP

The HNMFP/DOC of DOM fractions of raw water, wastewater, and treated wastewater in terms of molecular sizes are presented in Figure 5-7. For the raw water of the Bangkhen WTP, DOM with 1 kDa < MW < 3 kDa had the highest I-THMFP/DOC (5.4 μg/mg DOC, on average) followed by that of 3 kDa < MW < 10 kDa (2.7 μg/mg), MW > 10 kDa (2.1 μg/mg), and MW < 1 kDa (0.4 μg/mg), respectively. In the case of raw water of the Singburi WTP, the order of HNMFP/DOC were 3 kDa < MW < 10 kDa (1.8 μg/mg), 1 kDa < MW < 3 kDa (1.6 μg/mg), MW > 10 kDa (1.0 μg/mg), and MW < 1 kDa (0.4 μg/mg), respectively. The TCNM was detected in all DOM fractions.

In the case of domestic wastewater in the Ang Thong province, the order of HNMFP/DOC were 1 kDa < MW < 1 kDa (3.4 μg/mg), MW < 1 kDa (2.7 μg/mg), MW > 10 kDa (2.3 μg/mg), and 3 kDa < MW < 10 kDa (1.3 μg/mg), respectively. For the wastewater in Ayutthaya province, DOM with 1 kDa < MW < 3 kDa had the highest HNMFP/DOC (2.1 μg/mg) followed by that of MW > 10 kDa (1.0 μg/mg), MW < 1 kDa (0.5 μg/mg), and 3 kDa < MW < 10 kDa (0.4 μg/mg), respectively.

For treated wastewater in the Ang Thong province, DOM with 3 kDa < MW < 10 kDa had the highest HNMFP/DOC (14.8 μg/mg) followed by that of 1 kDa < MW < 3 kDa (11.7 μg/mg), MW > 10 kDa (10.7 μg/mg), and MW < 1 kDa (5.7 μg/mg), respectively. In the case of treated wastewater in the Ayutthaya province, the order of HNMFP/DOC were 1 kDa < MW < 3 kDa (9.7 μg/mg), 3 kDa < MW < 10 kDa (2.8 μg/mg) and DOM with MW > 10 kDa MW < 1 kDa could not different (2.2 μg/mg), respectively. TCNM was the HNMFP species that detected in all DOM fractions of wastewater and treated wastewater. This was similar of raw water.

The HNMFP species/DOC of DOM fractions of raw water, wastewater, and treated wastewater by resin fractionation are showed in Figure 5-8. For the raw water of the Bangkhen WTP could not detect the formation of HNMFP/DOC in TPI, HPO, and HPI. In the case of raw water of the Singburi WTP, the order of HNMFP/DOC were HPO (0.9 μg/mg), HPI (0.8 μg/mg), and HPO (0.7 μg/mg), respectively. The HNMFP/DOCs of HPO, TPI, and HPI was slightly different. In the case of domestic wastewater in the Ang Thong province, the order of HNMFP/DOC were TPI (7.5 μg/mg), HPO (1.6 μg/mg), and HPI (1.4 μg/mg), respectively. For the wastewater in Ayutthaya province, HPO and TPI had the high HANFP/DOC (19.7 and 19.6 μg/mg) followed HPI (4.7 μg/mg), respectively.

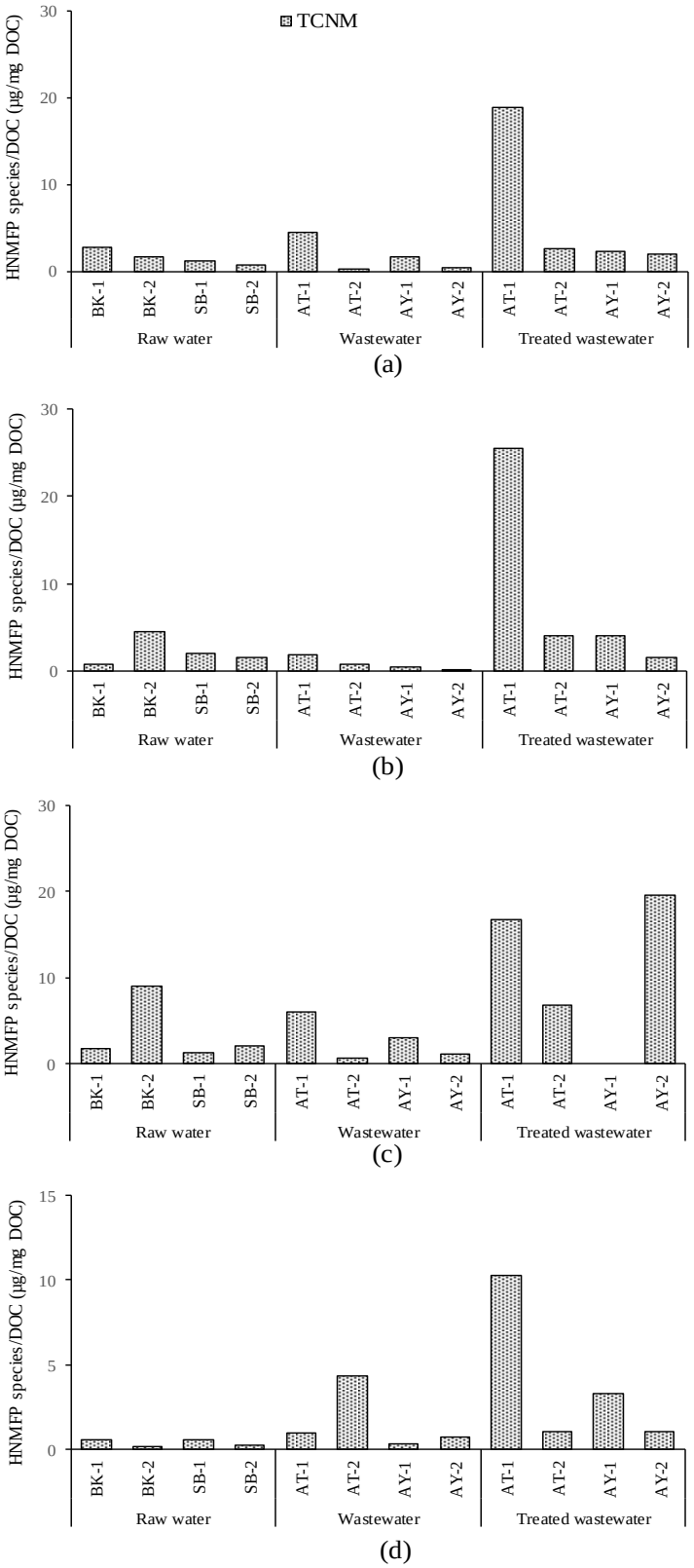


Figure 5-7 HNMFP-Species/DOC of each organic size fraction in raw water supply, wastewater and treated wastewater (a) MW > 10 kDa; (b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa

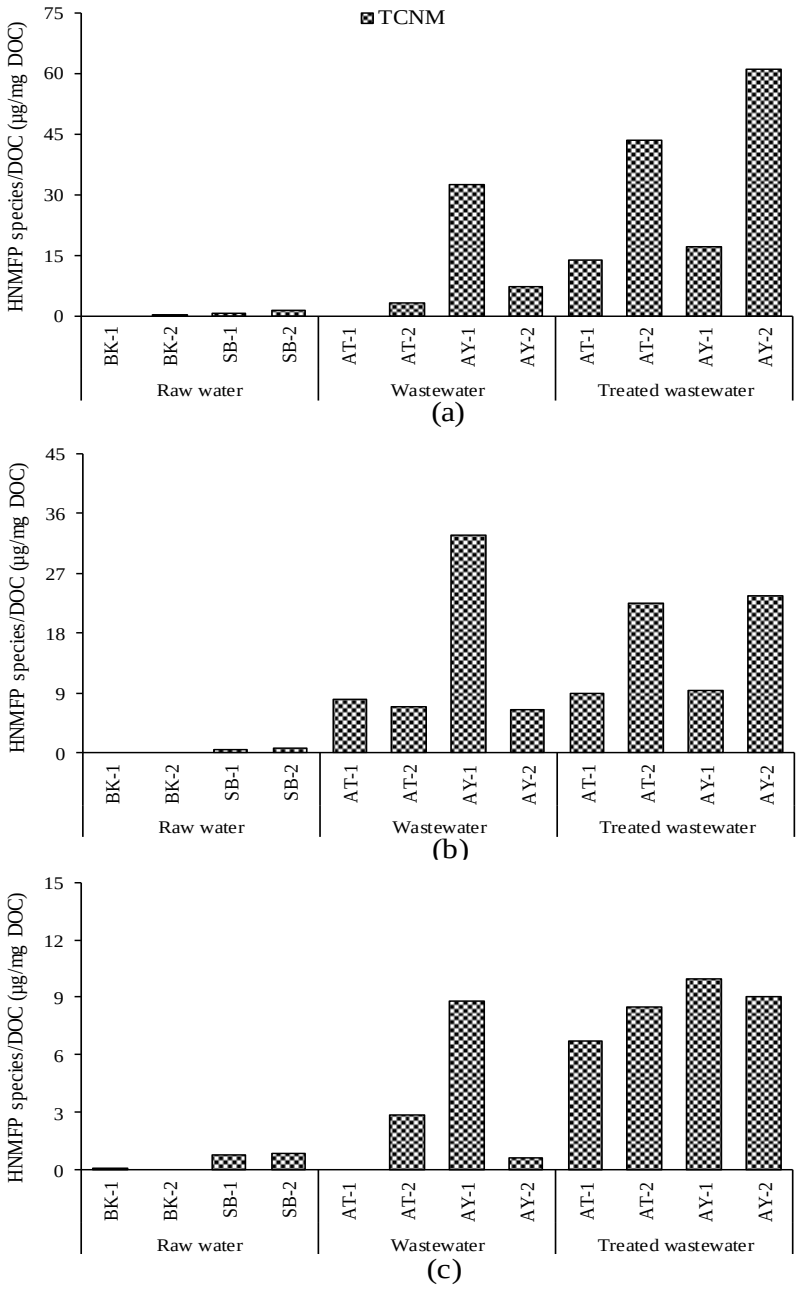


Figure 5-8 HNMFP-Species/DOC of each organic resin fraction in raw water supply, wastewater and treated wastewater (a) HPO; (b) TPI, (c) HPI

For treated wastewater in the Ang Thong province, HPO had the highest HNMFP/DOC (28.7 μg/mg) followed by that of TPI (15.7μg/mg), and HPI (7.6 μg/mg), respectively. In the case of domestic wastewater in the Ayutthaya province, the order of HNMFP/DOC were HPO (39 μg/mg), TPI (16.5 μg/mg), and HPI (9.5 μg/mg), respectively. HPO in wastewater and treated wastewater had the active DOM for reacting with nitromethane to form HNMs. The DOM fractions of treated wastewater had a high activity to form HHMs in compared with that of wastewater.

5.3.3 Toxicity of size fractionation

Size fractionation

Lethal concentration fifty (LC50)

The DBPs species/LC50 of DOM fractions of raw water, wastewater, and treated wastewater in terms of molecular sizes are presented in Figure 5-9. For the raw water of the Bangkhen WTP, DOM with 1 kDa < MW < 3 kDa had the highest DBPs/LC50 (2.45×10^{-3}, on average) followed by that of MW < 1 kDa (7.14×10^{-4}), MW > 10 kDa (4.58×10^{-4}), and 3 kDa < MW < 10 kDa (3.72×10^{-4}), respectively. In the case of raw water of the Singburi WTP, the order of DBPs/LC50 were MW < 1 kDa (2.01×10^{-3}), MW > 10 kDa (4.61×10^{-4}), 3 kDa < MW < 10 kDa (3.90×10^{-4}), and 1 kDa < MW < 3 kDa (3.73×10^{-4}), respectively. HANs were determined as the DBPs species of all DOM fractions with the highest LC50.

In the case of domestic wastewater in the Ang Thong province, the order of DBPs/LC50 were MW < 1 kDa (1.59×10^{-3}, on average), 1 kDa < MW < 3 kDa (1.36×10^{-3}, on average), MW > 10 kDa (1.29×10^{-3}, on average), and 3 kDa < MW < 10 kDa (1.25×10^{-3}, on average), respectively. For the wastewater in Ayutthaya province, DOM with MW > 10 kDa had the highest DBPs/LC50 (3.06×10^{-3}, on average) followed by that of 1 kDa < MW < 3 kDa (2.71×10^{-3}, on average), MW < 1 kDa (2.42×10^{-3}, on average), and 3 kDa < MW < 10 kDa (8.26×10^{-4}, on average), respectively.

For domestic treated wastewater in the Ang Thong province, DOM with MW < 1 kDa had the highest DBPs/LC50 (2.55×10^{-3}, on average) followed by that of MW > 10 kDa (1.74×10^{-3}, on average), 3 kDa < MW < 10 kDa (1.67×10^{-3}, on average), and 1 kDa < MW < 3 kDa (1.53×10^{-3}, on average), respectively. In the case of domestic wastewater in the Ayutthaya province, the order of DBPs/LC50 were MW < 1 kDa (4.43×10^{-3}, on average), MW > 10 kDa (1.14×10^{-3}, on average), 1 kDa < MW < 3 kDa (4.34×10^{-4}, on average), and 3 kDa < MW < 10 kDa (9.31×10^{-4}, on average), respectively.

HANs were determined as the highest LC50 of all DOM fractions of domestic wastewater and their treated wastewater. This has corresponded well with the LC50 of raw water. The highest DBPs/LC50 for mostly water samples was determined for DOM with MW < 1 kDa, the dominant DOM fraction. This implied that the dominant DOM compose of the high toxicity of DBPs when considering of LC50.

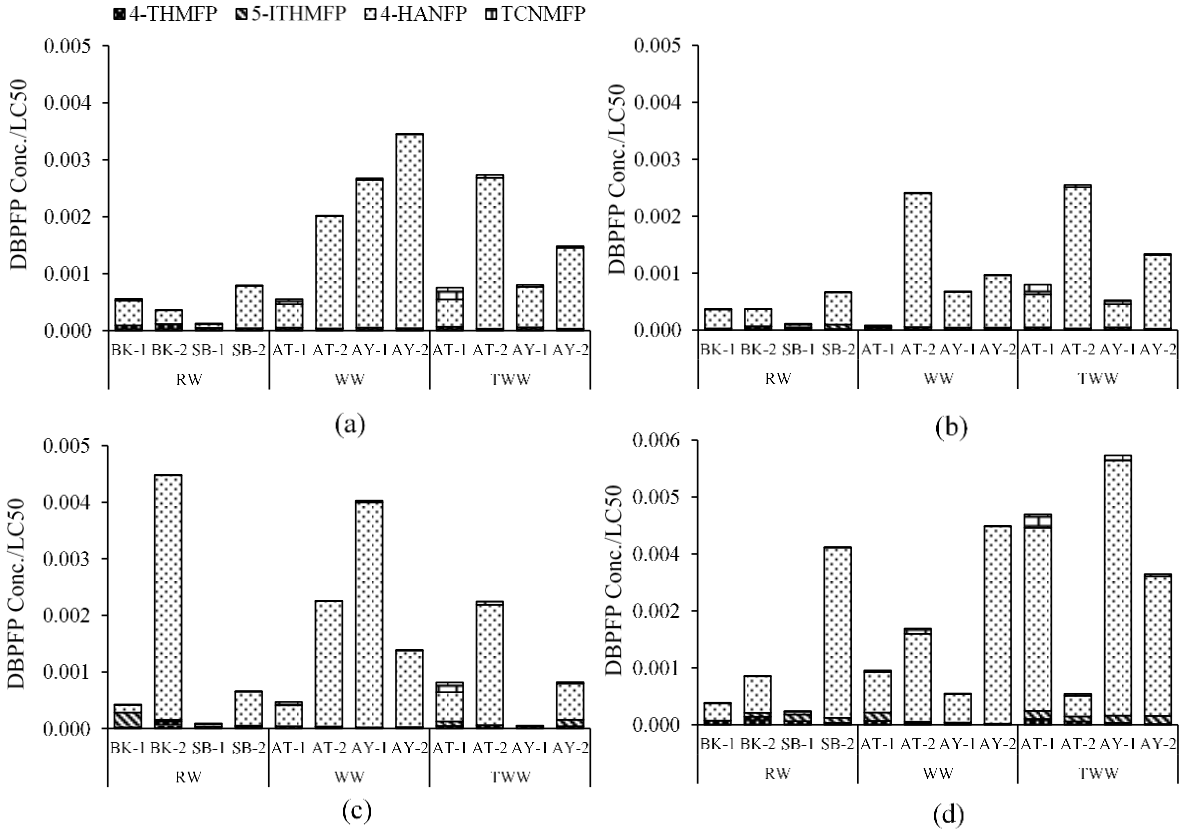


Figure 5-9 DBPs/LC50 of DOM fractions in raw water, wastewater, and treated wastewater classified by ultrafiltration: (a) MW > 10 kDa; (b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa

Lowest cytotoxicity concentration (Lowest Cytotox. Conc.)

The DBPs species/Lowest Cytotox. Conc. of DOM fractions of raw water, wastewater, and treated wastewater in terms of molecular sizes are presented in Figure 5-10. For the raw water of the Bangkhen WTP, DOM with 1 kDa < MW < 3 kDa had the highest DBPs/ Lowest Cytotox. Conc. (2.45×10^{-3}, on average) followed by that of MW < 1 kDa (7.14×10^{-4}), MW > 10 kDa (4.58×10^{-4}), and 3 kDa < MW < 10 kDa (3.72×10^{-4}), respectively. In the case of raw water of the Singburi WTP, the order of DBPs/Lowest Cytotox. Conc. were MW < 1 kDa

(8.94×10^{-3}), MW > 10 kDa (1.49×10^{-3}), 3 kDa < MW < 10 kDa (1.35×10^{-3}), and 1 kDa < MW < 3 kDa (1.25×10^{-3}), respectively. HANs were detected in all DOM fractions of both raw waters with highest cytotoxicity concentration.

In the case of domestic wastewater in the Ang Thong province, the order of DBPs/Lowest Cytotox. Conc. were MW < 1 kDa (6.59×10^{-3}, on average), 1 kDa < MW < 3 kDa (5.68×10^{-3}, on average), 3 kDa < MW < 10 kDa (5.38×10^{-3}, on average), and MW > 10 kDa (4.75×10^{-3}, on average), respectively. For the wastewater in Ayutthaya province, DOM with 1 kDa < MW < 3 kDa had the highest DBPs/Lowest Cytotox. Conc. (9.77×10^{-3}, on average) followed by that of MW < 1 kDa (8.49×10^{-3}, on average), MW > 10 kDa (8.20×10^{-3}, on average), and 3 kDa < MW < 10 kDa (1.86×10^{-3}, on average), respectively.

For domestic treated wastewater in the Ang Thong province, DOM with MW < 1 kDa had the highest DBPs/Lowest Cytotox. Conc. (6.51×10^{-3}, on average) followed by that of 3 kDa < MW < 10 kDa (6.45×10^{-3}, on average), 1 kDa < MW < 3 kDa (5.91×10^{-3}, on average), and MW > 10 kDa (5.45×10^{-3}, on average), respectively. In the case of domestic wastewater in the Ayutthaya province, the order of DBPs/ Lowest Cytotox. Conc. were MW < 1 kDa (1.58×10^{-2}, on average), MW > 10 kDa (3.36×10^{-3}, on average), 3 kDa < MW < 10 kDa (3.01×10^{-3}, on average), and 1 kDa < MW < 3 kDa (1.17×10^{-3}, on average), respectively.

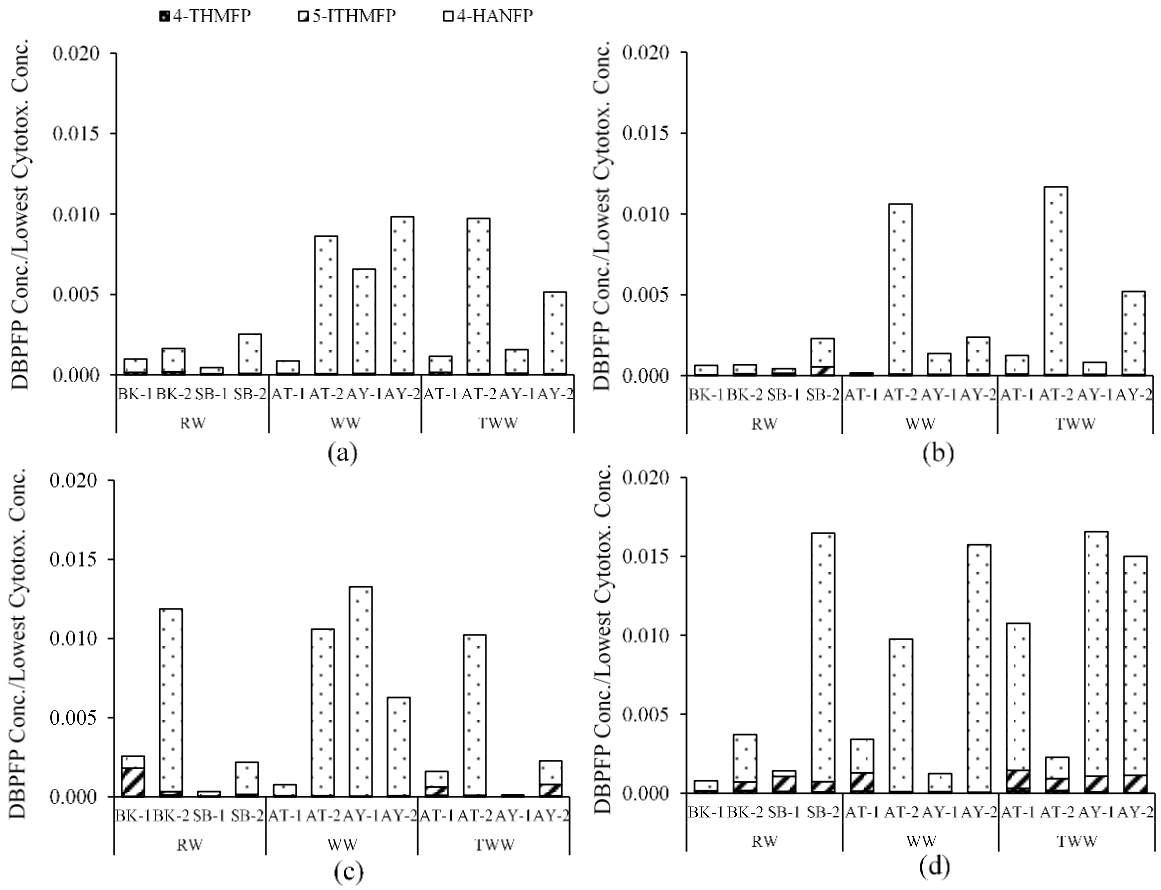


Figure 5-10 DBPs/Lowest Cytotox. Conc. of DOM fractions in raw water, wastewater, and treated wastewater classified by ultrafiltration: (a) MW > 10 kDa; (b) 3 kDa < MW < 10 kDa; (c) 3 kDa < MW < 1 kDa; (d) MW < 1 kDa

HANs were determined as the significant DBPs species of DOM fractions followed by THMs, and I-THMs, respectively. The highest DBPs/Lowest Cytotox. Conc. for mostly water samples were determined for DOM with MW < 1 kDa, the dominant DOM fraction. This implied that the dominant DOM compose of the high toxicity of DBPs when considering of lowest cytotoxicity concentration. This has corresponded well with considering of LC50.

Resin fraction

Lethal concentration fifty (LC50)

The DBPs/LC50 of DOM fractions of raw water, wastewater, and treated wastewater by resin fractionation are shown in Figure 5-11. For the raw water of the Bangkhen WTP, TPI had the highest DBPs/LC50 (1.09×10^{-3}, on average) followed by that of HPI (3.41×10^{-4}) and HPO (1.57×10^{-4}), respectively. In the case of raw water of the Singburi WTP, the order of

DBPs/LC50 were HPI (1.36×10^{-3}), HPO (8.37×10^{-4}), and TPI (3.78×10^{-4}), respectively. HANs were determined as the major DBPs/LC50 of DOM fractions followed by I-THMs, THMs, and TCNM, respectively.

In the case of domestic wastewater in the Ang Thong province, the order of DBPs/LC50 were HPI (3.42×10^{-3}), TPI (1.13×10^{-3}), and HPO (5.93×10^{-4}), respectively. For the wastewater in Ayutthaya province, HPO had the highest DBPs/LC50 (1.53×10^{-3}) followed by that of TPI (1.41×10^{-3}), and HPI (1.12×10^{-3}), respectively. For treated wastewater in the Ang Thong province, HPI had the highest DBPs/LC50 (3.80×10^{-2}) followed by that of HPO (1.42×10^{-3}), and TPI (9.04×10^{-4}), respectively. In the case of domestic wastewater in the Ayutthaya province, the order of DBPs/LC50 were HPI (6.53×10^{-3}), HPO (3.17×10^{-3}), and TPI (9.08×10^{-4}), respectively.

The highest DBPs/LC50 of wastewater and treated wastewater were HANs followed by TCNM. The highest DBPs/LC50 of DOM fractions of mostly water samples was determined for HPI. DBPs/LC50 of HPO and TPI were comparable.

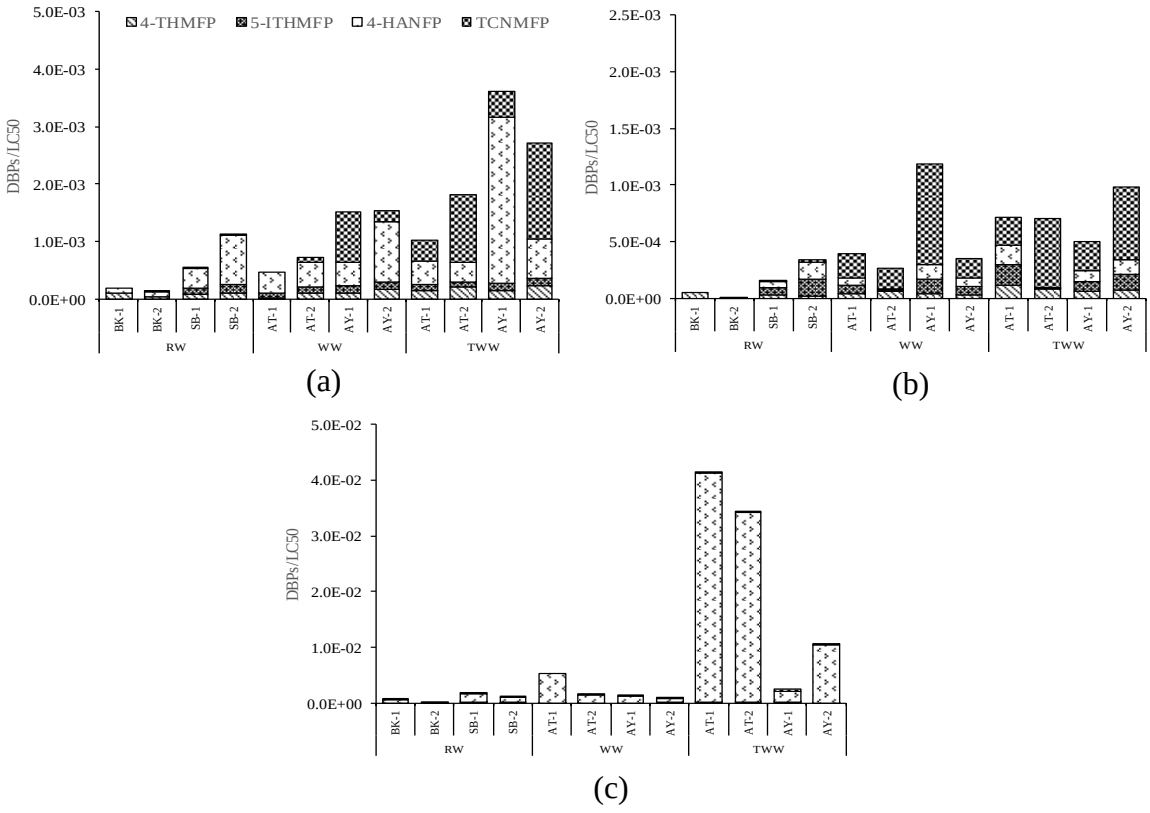


Figure 5-11 DBPs/LC50 of DOM fractions in raw water, wastewater, and treated wastewater classified by resin: (a) HPO; (b) TPI; (c) HPI

Lowest cytotoxicity concentration (Lowest Cytotox. Conc.)

The DBPs/Lowest Cytotox. Conc. of DOM fractions of raw water, wastewater, and treated wastewater by resin fractionation are presented in Figure 5-12. For the raw water of the Bangkhen WTP, TPI had the highest DBPs/Lowest Cytotox. Conc. (2.61×10^{-3}, on average) followed by that of HPI (6.51×10^{-4}) and HPO (6.07×10^{-4}), respectively. In the case of raw water of the Singburi WTP, the order of DBPs/Lowest Cytotox. Conc. were HPI (4.49×10^{-3}), HPO (3.49×10^{-3}), and TPI (2.08×10^{-3}), respectively. HANs were identified as the significant DBPs/Lowest Cytotox. Conc. of DOM fractions followed by I-THMs, and THMs, respectively.

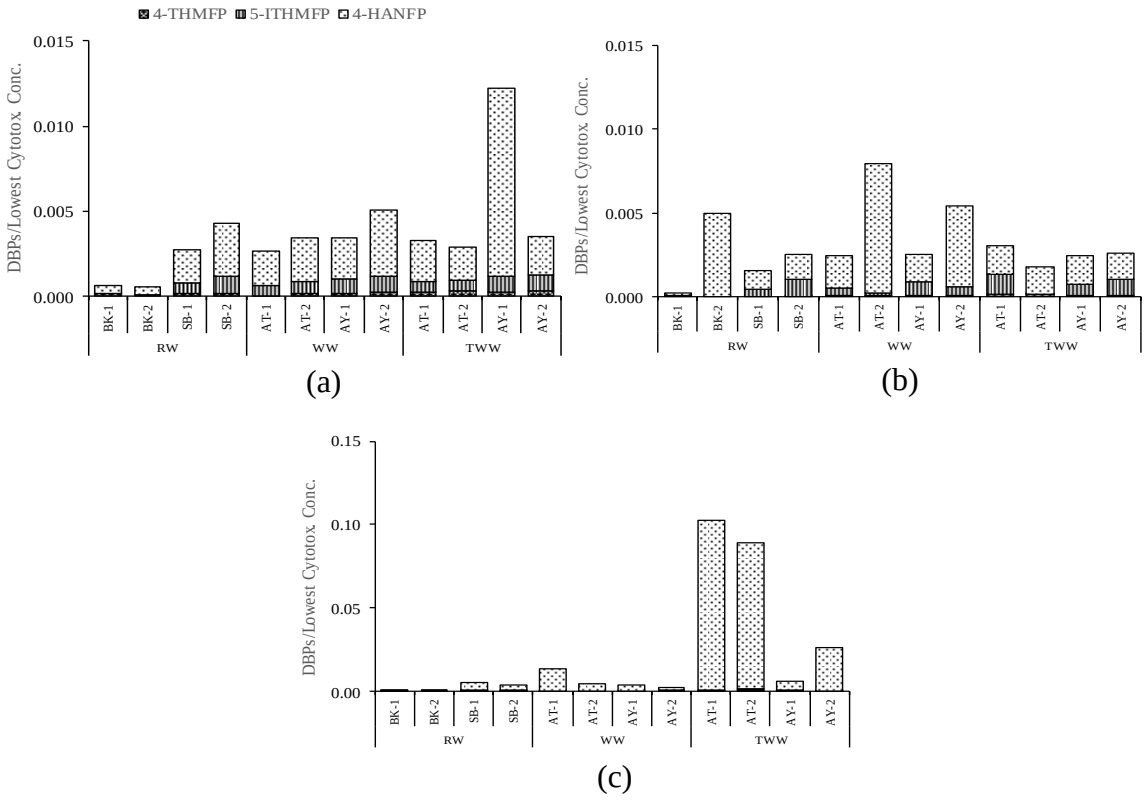


Figure 5-12 DBPs/Lowest Cytotox. Conc. of DOM fractions in raw water, wastewater, and treated wastewater classified by resin: (a) HPO; (b) TPI; (c) HPI

In the case of domestic wastewater in the Ang Thong province, the order of DBPs/Lowest Cytotox. Conc. were HPI (9.07×10^{-3}), TPI (5.23×10^{-3}), and HPO (3.06×10^{-3}), respectively. For the wastewater in Ayutthaya province, HPO had the highest DBPs/Lowest Cytotox. Conc. (4.24×10^{-3}) followed by that of TPI (3.98×10^{-3}), and HPI (2.88×10^{-3}), respectively. For treated wastewater in the Ang Thong province, HPI had the highest DBPs/Lowest Cytotox. Conc. (9.59×10^{-2}) followed by that of HPO (3.06×10^{-3}), and TPI

(2.41×10^{-3}), respectively. In the case of domestic wastewater in the Ayutthaya province, the order of DBPs/Lowest Cytotox. Conc. were HPI (1.61×10^{-2}), HPO (7.85×10^{-3}), and TPI (2.54×10^{-3}), respectively. HANs were classified as the significant DBPs/Lowest Cytotox. Conc. of DOM fractions followed by I-THMs, and THMs, respectively. This has corresponded well with the DBPs/Lowest Cytotox. Conc. of raw water.

The highest DBPs/Lowest Cytotox. Conc. of DOM fractions of mostly water samples was determined for HPI. The highest DBPs/Lowest Cytotox. Conc. of HPO and TPI had a comparable. This was similar to that of raw water.

Chapter VI

Reduction of precursors of emerging disinfection by-products by enhanced coagulation with powder activated carbon and magnetic ion-exchange

6.1 Introduction

Water treatment plants must remove undesirable constituents in raw water to produce a safe and suitable water supply for water consumers. The functional objectives of the conventional water treatment plant are to remove constituents in terms of turbidity and hardness and to disinfect pathogenic organisms. Besides, water treatment plants emphasize the removal of dissolved organic matter (DOM) prior to the chlorine or chloramine disinfection process. This is because DOM can react with chlorine or chloramine to form disinfection by-product (DBPs) such as trihalomethanes (Rook et al., 1974). Many DBPs are possible carcinogenic substances (Plewa et al., 2010; Richardson et al., 2007; US EPA, 1999a).

Dissolved organic carbon (DOC), ultraviolet absorbance at wavelength 254 nm (UV-254), specific ultraviolet absorption (SUVA), and dissolved organic nitrogen (DON) have been used to determine quantities of DOM in raw water. DOC substantially affects the formation of DBPs, especially trihalomethanes (THMs) as representative of carbonaceous DBPs (C-DBPs) in finished water supply by reacting with hypochlorous acid and monochloramine (Richardson et al., 2007; Krasner et al., 2012). DON is usually detected in the low content in raw water. DON could be transformed into nitrogenous DBPs (N-DBPs) in the water treatment process (Shah and Mitch, 2012). The reaction between DON and chlorine can produce N-DBPs such as haloacetonitriles (HANs), nitrosamines, and halonitromethanes (HNMs) (Nawrocki, 2007; Schreiber et al., 2006).

HNMs were detected in the low concentration in compared with that of traditional DBPs such as THMs and haloacetic acids (HAAs). Even though, HMNs have not been regulated. Cytotoxicity and genotoxicity caused by HNMs are comparable or even higher when compared with that of THMs and HAAs. Chlorination of waters in the presence of bromide (Br^-) and iodide (I^-) ions results in the formation of brominated and or iodinated DBPs (Br-DBPs and I-DBPs) group namely iodo-trihalomethanes (I-THMs). The brominated and iodated DBPs are more toxic than their chlorinated analogs (Plewa et al., 2004; Richardson et al., 2007). HNMs and I-THMs are considered as emerging DBPs. Many traditional and emerging DBPs are formed in water supply through the reaction of chemical disinfectants with organic and

inorganic substances in the source water. The organic and inorganic DBP precursors must be primarily removed before water disinfection process to minimize DBPs.

To reduce the DBPs formation, the reduction of DOC by enhanced coagulation and enhanced softening was proposed by the United State Environmental Protection Agency (USEPA) (USEPA, 1999b). However, coagulation had a limitation on the removal of DON (Hu et al., 2016). The conventional water treatment process uses coagulation, flocculation, sedimentation, and filtration for removal of contaminants from raw water. Poly aluminum chloride (PACl) and alum have been used as the primary coagulant in several water treatment plants in Thailand. The main target of the water treatment plant was the removal of turbidity and suspended solids. The complex problems of raw water contamination such as DOM and other emerging contaminant lead to utilization of advanced water treatment together with the conventional water treatment process.

The conventional treatment processes, including coagulation, sedimentation, and filtration are not efficient in the removal of DOM as precursors for DBPs formation (Chen et al., 2011; Teixeira et al., 2011; Mesdaghinia et al., 2006). Powder activated carbon (PAC) is an alternative used for water treatment after the coagulation process. The applying of anion exchange treatment has been suggested for DOM removal from natural water (Leenheer et al., 1995; Mergen et al., 2008). A magnetic ion exchange (MIEX) resin was used as an adsorbent for the effective removal of DOM and other inorganic anions (Humbert et al., 2005; Kitis et al., 2007). To produce the water supply with a low level of DBPs, the investigation of the optimal condition of coagulation and enhanced coagulation by PAC, MIEX, and other chemicals for the removal of DBP precursors and their DBPs are crucial in the water treatment process.

In order to further understand the role and chemistry of DOM in surface water, it is often necessary to fractionate DOM. The characterization of the specific DOM fraction and the removal of DOM fraction responsible for the chlorine demand are essential to enhance the drinking water quality and it will help source management and process selection for the drinking water supply.

DOM is an important precursor to DBPs and composes of a complex mixture of many chemical fractions. The bulk parameters such as UV-254, DOC, DON, and SUVA could not directly represent the organic groups or organic compounds that act as a precursor of DBPs. To provide a better understanding of the chemistry of DOM, fractionation techniques have been employed for DOM characterization. The resin fractionation using DAX-8 and XAD-4 resin has been used to separate DOM into three fractions namely hydrophobic organic fraction

(HPO), transphilic organic fraction (TPI), and hydrophilic organic fraction (HPI) (Aiken, 1985; Krasner, 1999; Leenheer and Croue, 2003). Ultrafiltration (UF), a separation process using membranes, has been used to classify molecular size fractions of DOM into molecular weight (MW) > 10 kDa, 3 < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa (Cai, 1999; Kitis et al., 2002). To identify the organic group, an analysis using three-dimensional fluorescence spectroscopy obtained by a simultaneous collection of fluorescence data over a wide range of different excitation and emission wavelengths (fluorescent excitation-emission matrices, FEEM) has been applied to characterize fluorescent DOM. DOM in natural and wastewaters primary contains fluorescent organic matter, including humic and fulvic acid-like, tyrosine-like, and tryptophan-like substances (Hudson et al., 2007; Suksaroj et al., 2009).

Pyrolysis-gas chromatography/mass spectrometer (Py-GC/MS) has been used to determine the molecular composition and chemical calluses of DOM. Py-GC/MS is one of the advanced techniques that provide the information on pyrolysis fragments of chemical classes of DOM useful and uses to assess the putative origins of DOM. Major pyrolysis fragments including carbohydrates, phenols and lignin monomers, lignin dimers, lipids, alkylaromatics, aromatic nitrogen compounds, sterols, peptides, suberin, and loosely bound fatty acids have been classified in environmental water samples (Schulten and Gleixner, 1999). The study on the putative origin of DOM classification in raw water and raw water mixed with treated wastewater on the formation of I-THMs, HANs, and HMNs is limited recently. It is essential to characterize the specific DOM and to improve the efficiency of DOM removal. This information can support the enhancing of the water supply quality and is adventurous to help the water treatment plant for managing the source water and selecting the treatment process.

The Bangkhen (BK) water treatment plant (WTP) is the largest water supply plant in Thailand. Raw water is taken from Chao Phraya River to produce water supply of about 3.7 million m^3/day. The water supply is distributed to millions of people in Bangkok and nearby provinces. The water in Chao Phraya river flows through the heart of the community, agricultural, and industrial areas from upstream location to the intake location. Then, raw water of BK WTP flows into the water transmission canal of about 20 km through the BK WTP. This canal is designed to protect the discharging of contaminants such as road runoff, wastewater, and treated wastewater. Even though, the raw water has the protection from the contaminant by the canal, it is inevitably contaminated by the suspended solids, pathogen, DOM, and other contaminants from the upstream discharging. The putative origins of DOM and the formation of THMs, I-THMs, HANs, and HNMs of raw water, and wastewater and treated wastewater that were the potentially discharged to the Chao Phraya River is limited.

This work aimed at conducting the coagulation experiments by alum, PAC, and MIEX resin for reducing turbidity, DOC, DON, and formation potentials (FPs) of THMs, I-THMs, HANs, and HNMs of raw water from the BK WTP and treated wastewater from the domestic wastewater treatment plant (WWTP). Levels of DOM fractions, DBPFPs of the water samples, and its removal by the optimum dose of coagulants by conventional and enhanced coagulation were determined. The DOM in the water samples and coagulated waters was fractioned by resin fractionation and ultrafiltration techniques to determine the nature of DOM. Pyrolysis GC/MS was employed to assess the putative origins of organic matter for studying the DBPFPs.

6.2 Experimental procedure

The alum was used as the coagulant in the experiment. The enhanced coagulation experiment was conducted by using PAC and MIEX. The water samples for coagulation and enhanced coagulation consisted of raw water of the Bangkhen WTP in rainy season (RW−1), summer season (RW−2), and winter season (RW−3), the RW−1 mixed with treated wastewater from Ayutthaya (AY) province (TWW−2, AY) at a mixing ratio of 50:50 (volume by volume, v/v). In addition, 100% of treated wastewater from Angthong (AT) (TWW−1, AT) and Ayutthaya province (TWW−1, AY) was chosen for the coagulation treatment. This was assumed that treated wastewater, as indirect potable water reuse, must be discharged to the natural waterways and the water from this source is used as raw water for the water treatment plant.

Water samples were measured for their turbidity, DOC, UV-254, SUVA, DON, FEEM, chemical classes, THMs, HANs, HNMs, I-THMs, THMFP, HANFP, I-THMFP, and HNMFP. Each water sample was conducted in 1 L jars using the conventional procedure. The water samples were coagulated by using five alum dosages of ~ 5 – 120 mg/L under controlled pH of 7. The water samples were rapidly mixed at 100 rpm for one min, followed by a slow mixing at 30 rpm for 30 min, and settling for one h. The supernatant was collected and measured for their turbidity. The optimal dosage for turbidity removal was determined. Then the supernatants were filtered through 0.7 μm GF/F filter and measured for their DOC and DON. The optimal dosage of DOC and DON removal was determined. The enhanced coagulations by PAC and MIEX were performed using alum dosage at optimal DOC and DON reductions on the variation dosage of PAC and MIEX between 10-120 mg/L and 0.5-5 mL/L respectively.

The coagulated water under the optimal turbidity reduction (CW−1), the coagulated water under the optimal DOC and DON reductions (CW−2), and the coagulated water under optimal condition of enhanced PAC or MIEX coagulation (CW−3), were analyzed for their DOC, DON, FEEM, chemical classes, THMFP, HANFP, I-THMFP, and HNMFP. The CW−1, CW−2, and CW−3 were fractionated using resin and UF fractionation techniques. The HPO, TPI, HPI, and DOM of four groups: MW < 1 kDa, 1 kDa < MW < 3 kDa, 3 kDa < MW <10 kDa, and MW > 10 kDa were measured for their DOC, FEEM, THMFP, HANFP, I-THMFP, and HNMFP.

6.3 Results and discussion

6.3.1 Water sample characteristic

The characteristics of raw water (RW) from the BK WTP, treated wastewater (TWW) from the wastewater treatment plant in Angthong and Ayutthaya province, and raw water mixed with treated wastewater (RW+TWW) are presented in Table 6-1. The turbidity of the treated wastewaters from the AT and AY WWTPs from the first sampling (TWW−1, AT and TWW−1, AY) were lower than 5 NTU. In the case of high turbidity raw water, the conventional coagulation process may be proposed as the appropriate process to reduce the content of DOM in water (US EPA, 1999).

The relatively high DOC of from 5.1 to 5.6 mg/L was detected in the treated wastewater and raw water mixed with treated wastewater (RW+TWW). The raw water from BK WTP had DOC between 3.2 and 4.6 mg C/L (Table 6-1). The UV-254 values were in the range of 0.12 and 0.14 cm^{-1} for the BK raw waters, 0.12 and 0.10 cm^{-1} for the AT and AY treated wastewaters and 0.10 cm^{-1} for the RW+TWW. The raw water from BK WTP was more contaminated by aromatic DOM than those of treated wastewater and RW+TWW waters. When the SUVA of water exceeded 2 L/mg·m, the coagulation can be used to remove the DOM (US EPA., 1999). The SUVA detected was > 3 L/mg·m for the raw water of the BK WTP and 2.3 L/(mg·m) for the treated wastewater of the AT WTP. The coagulation can be employed for raw water from the BK WTP and the treated wastewater from Angthong province.

Table 6-1. Characteristics of raw water (RW), treated wastewater (TWW), and raw water mixed treated wastewater (RW+TWW) (50% v/v)

	Turbidity (NTU)	DOC (mg C/L)	UV-254 (cm^{-1})	SUVA (L/mg·m)	DON (mg N/L)	DOC/DON
RW BK at 1st sampling	34	4.6	0.14	3.0	0.16	29
RW BK at 2nd sampling	54	3.2	0.13	4.1	0.44	7
RW BK at 3rd sampling	11	3.7	0.12	3.2	0.25	15
TWW AT at 1st sampling	7	5.3	0.12	2.3	0.20	27
TWW AY at 1st sampling	5	5.6	0.10	1.8	1.22	5
RW BK (1st) + TWW AY (1st)	10	5.1	0.10	1.9	1.07	5

The DON levels were 0.16, 0.44, and 0.25 mg N/L in the BK raw waters from the first, second, and third sampling, respectively. The rather high level of DON of 1.22 mg N/L was detected in treated wastewater from the AY WTP, respectively. DON levels from 0.19 and 2.6 mg N/L have been reported for waters in other countries (Knight et al., 2012; Lee et al., 2006; Xu et al., 2011). DON level of raw water from the BK WTP was slightly low when compared with that of literature values.

The ratio DOC/DON is another indicator associated with N-DBP formation. A low DOC/DON ratio probably yields high N-DBP formation (Muellner et al., 2007). When the DOC/DON ratio exceeds 20, there is a low tendency to form chlorinated N-DBPs (Dotson et al., 2009). DOC/DON ratios of raw waters at the BK WTP from the first, second, and third sampling were 29, 7, and 15, respectively. The TWW AY-1 and RW+TWW had very low DOC/DON ratios of 5. The DOC/DON of raw water reported from other countries ranges from 11 to 20 (Lee et al., 2006; Xu et al., 2011). DOC/DON of raw water from Southeast Queensland, Australia, ranged from 6 to 13 (Knight et al., 2012). DOC/DON ratio of raw water from the U-Tapao canal at upstream, midstream, and downstream locations were 50, 4, and 13, respectively (Na-Phatthalung et al., 2016). The DOC/DON was determined in the low level in the BK WTP raw water. This is because it had a relatively high concentration of DON, which likely increases N-DBP formation during water treatment. Concerning the DOC/DON ratio in this study, treated wastewater and the mixing water (RW+TWW) had a higher probability of forming N-DBPs.

6.3.2. Reduction of turbidity by alum coagulation

The coagulation experiment was conducted to remove turbidity because an alum is an efficient coagulant in waterworks. The alum dosage from 5 to 100 mg/L at a controlled pH of 7.0 was added to the RW BK-1, RW BK-2, and RW BK-3, TWW AT-1, TWW AY-1, and RW+TWW. The turbidity values of the mentioned samples were 34.2, 53.5, 11.0, 4.0, 4.0, and 4.0 NTU, respectively. The WHO regulation has a maximum drinking water standard for turbidity at 4 NTU. The alum dosage of 20 mg/L for the RW BK was considered as the optimum dosage for removing the turbidity with the percent turbidity reduction of 92-95 % (Figure. 6-1).

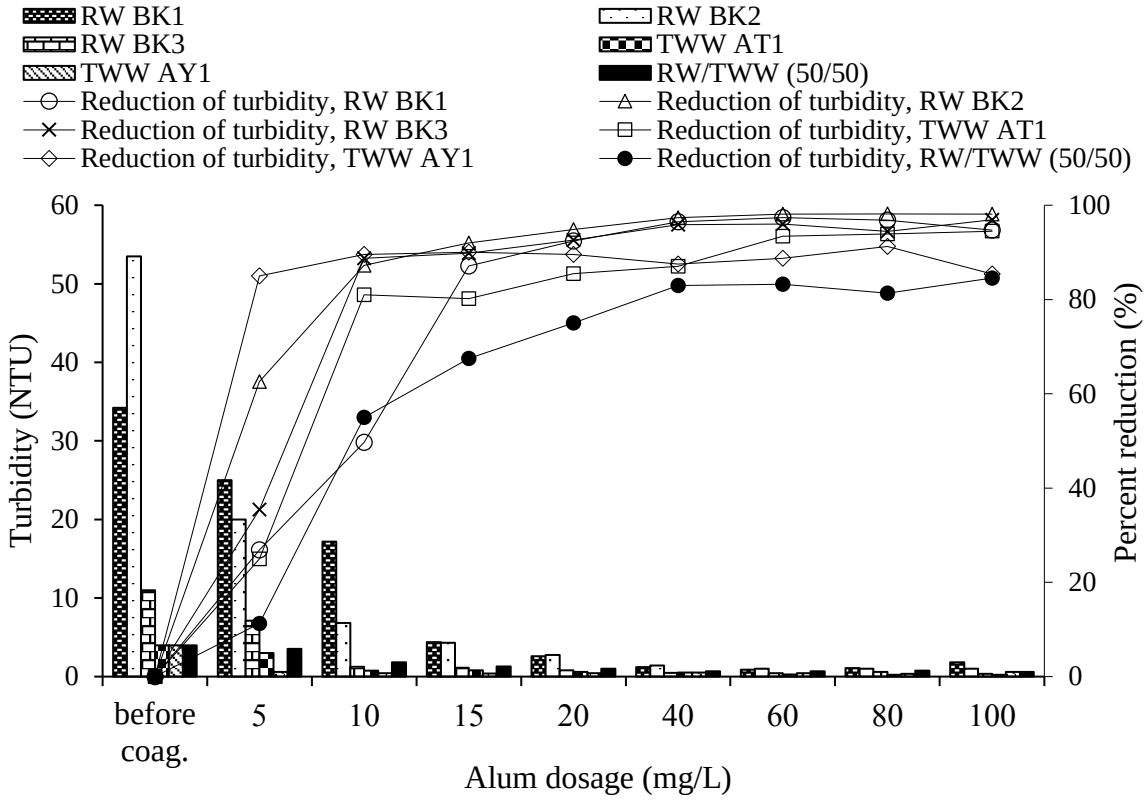


Figure 6-1. Turbidity of the raw water (RW) of BK WTP, treated wastewaters (TWW) of AT, and AY, and the RW mixed with TWW (50% v/v) in the alum coagulation experiment.

The alum dosage of 10 mg/L for the TWW AT-1 could promptly remove turbidity in the supernatant by 81% (Figure 6-1). The maximum turbidity removal in the supernatant for the TWW AT-1 was 94% at the alum dosage of up to 80 mg/L. The turbidity of the TWW AY-1 was reduced from the value of about 4.0 to 0.6 NTU (85% reduction). An increase in dosage above 5 mg/L resulted in a slight increase in turbidity removal. For the RW+TWW, the

turbidity was reduced from 4.0 to 3.6 NTU (11% reduction), at alum dosage of 5 mg/L. The WHO standard for drinking water regulates the turbidity below 4.0 NTU. The optimal dosages for turbidity removal by alum coagulation were 10, 5, and 5 mg/L for the TWW AT-1, TWW AY-1, and RW+TWW, respectively.

6.3.3. Reduction of DOC and DON by alum coagulation, and enhanced alum coagulation with PAC and MIEX

The reductions of DOC and DON are the leading indicators to select the optimal condition for enhanced coagulation experiments. DOC represents the organic matter in raw water and is humic type (Hepplewhite et al., 2004). The result of alum coagulation of raw water from the BK WTP at the first sampling (RW BK-1) on the DOC removal is depicted in Figure 6-2. The DOC of the RW BK-1 was gradually decreased from 4.5 to 3.0 mg/L when alum dosage was increased from 10 to 100 mg/L. An alum dosage of 80 mg/L could be considered as the optimum point for the DOC reduction of the RW BK-1. The DOC was reduced by 37 % to the value of 2.9 mg/L. An increase in alum dosage up to 100 mg/L resulted in non-increasing DOC reduction in compared with a dosage of 80 mg/L.

Besides, the DOC reduction, this study also interested in DON reduction. DON is an important parameter that implies the formation of N-DBPs (e.g. nitrosamines, HANs, HNMs, and others) in the chlorination of water treatment. In Figure 6-2A, DON of the RW BK-1 was gradually decreased from 0.19 to 0.14 mg-N/L when alum dosage was increased from 10 to 100 mg/L. The raw water of the RW BK-1 had the optimal coagulation condition at a dosage of 80 mg/L of alum at pH 7. It could reduce DON to 19 %. The removal of DOC and DON are essential. The coagulation by alum could reduce some portions of DOC and DON from raw water. To increase the percent DOC and DON reduction for the conventional water treatment process, the enhanced coagulation was considered for the removal of DOC and DON.

The baseline condition of alum coagulation for raw waters of the RW BK-1 was at controlled at pH 7 and dosage of 80 mg/L. DOC and DON reductions by enhanced coagulation by PAC and MIEX of the RW BK-1 are presented in Figure 6-2B, 6-2C. A reduction of DOC represents the reduction of both aromatic and aliphatic DOM in water. The alum dosage of 80 mg/L with the PAC dosage of 40 mg/L could reduce DOC from 4.6 to 2.7 mg/L, a reduction of 42 % (Figure 6-2B). An increase in the PAC dosage above 40 mg/L resulted in a slight decrease in DOC. An alum dosage of 80 mg/L combined with MIEX dosage of 4 mL/L provided the best reduction (approximately 68 %) of DOC (Figure 6-2C). DON in the RW BK-1 raw water was reduced from 0.16 mg-N/L to 0.11 mg-N/L when using alum at 80 mg/L with

PAC at 40 mg/L (Figure 6-2B). This provided the highest result of a reduction by alum with PAC of 31 %. Increasing the PAC dosage above 40 mg/L resulted in the indifferent DON levels. The best DON reduction of the RW BK-1 was considered at an alum dosage of 80 mg/L combined with MIEX at 4 mL/L under a controlled pH of 7, a reduction 69 % (Figure 6-2C).

The alum coagulation of raw water from the BK WTP at the second sampling (RW BK-2) on the DOC removal is depicted in Figure 6-3. The DOC of the RW BK-2 was gradually decreased from 2.5 mg/L to 1.8 mg/L when alum dosage was increased from 10 to 100 mg/L. A dosage of 80 mg/L alum can be considered as an excellent point for DOC reduction in the RW BK-2. The DOC was reduced by 41% to the value of 1.8 mg/L. An increase in dosage of 100 mg/L was not increased in the DOC removal. In Figure 6-3A, DON of the RW BK-2 was gradually decreased from 0.21 to 0.15 mg-N/L when alum dosage was increased from 10 to 100 mg/L. The raw water of the RW BK-2 had the optimal coagulation condition at a dosage of 80 mg/L of alum at pH 7. It could reduce DON to 65 %.

The baseline conditions of alum coagulation for raw waters of the RW BK-2 were at controlled at pH 7 and dosage of 80 mg/L. DOC and DON reductions by enhanced coagulation with PAC and MIEX of the RW BK-2 are presented in Figure 6-3B, 6-3C. Alum at 80 mg/L combined with PAC 80 mg/L could reduce DOC from 3.1 to 0.9 mg/L, a reduction of 71 % (Figure 6-3B). Increasing PAC up to 100 mg/L was not increased the DOC reduction. By using alum and MIEX, the alum 80 mg/L with MIEX 2 mL/L was the optimal condition for DOC reduction (approximately 50 %) in the RW BK-2 (Figure 6-2C). DON was decreased from 0.44 mg-N/L to 0.17 mg-N/L when using alum dosage of 80 mg/L combined with a PAC dosage of 80 mg/L (Figure 6-3B). This provided the highest result of a reduction of 60 %. Increasing the PAC dosage up to 100 mg/L resulted in the indifferent in DON levels. The best DON reduction of the RW BK-2 was considered at an alum dosage of 80 mg/L combined with a MIEX dosage of 2 mL/L under a controlled pH of 7, a reduction 65 % (Figure 6-3C).

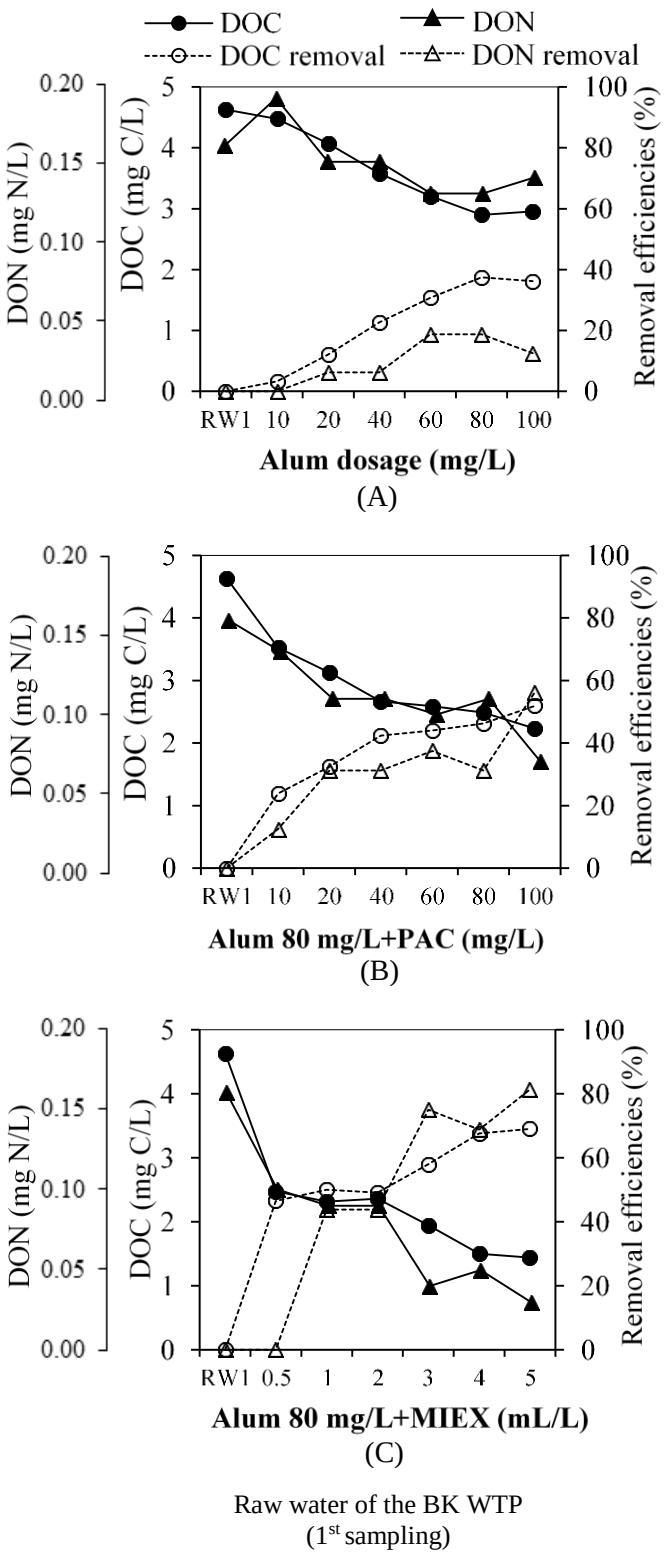


Figure 6-2. Residual of DOC and DON and the percentage of DOC and DON reduction by the alum coagulation (A), the enhanced alum coagulation (80 mg/L alum) with PAC (B), and MIEX (C) for raw water of the BK WTP at the first sampling.

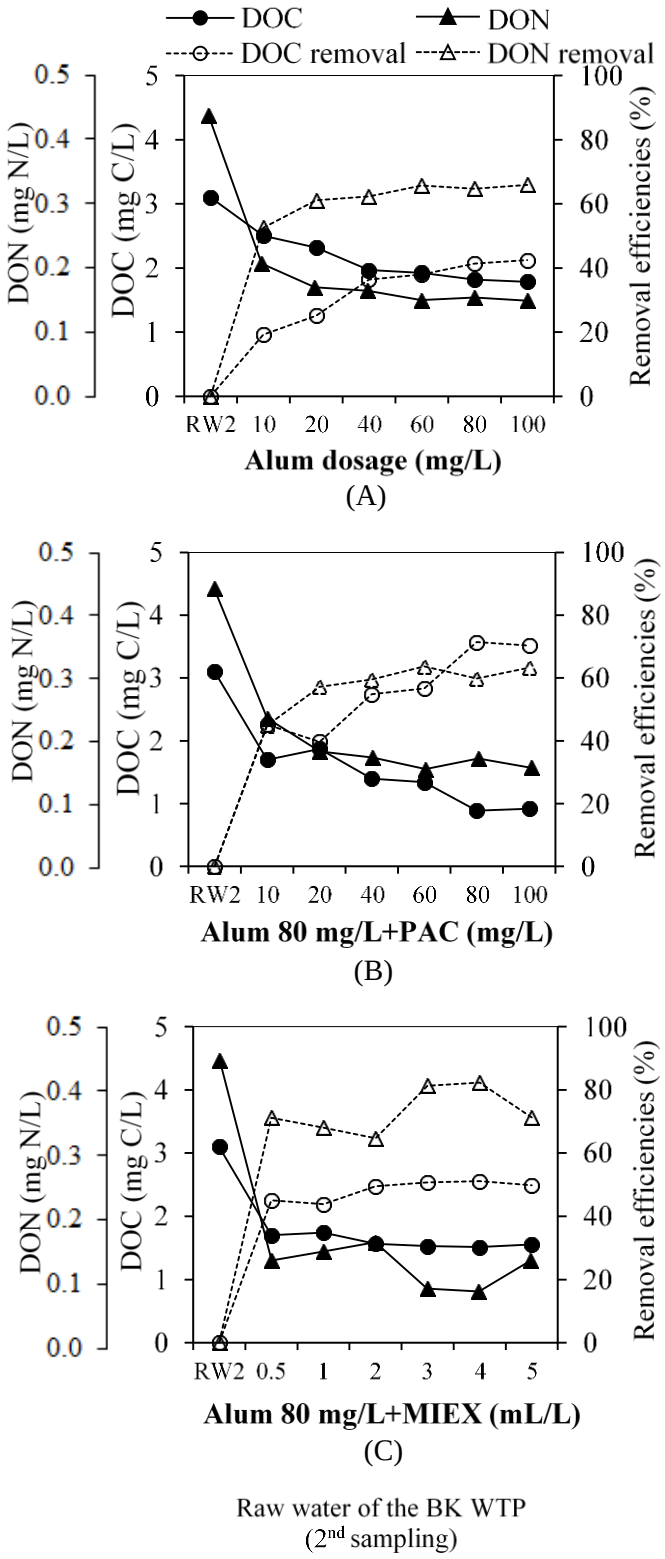


Figure 6-3. Residual of DOC and DON and the percentage of DOC and DON reduction by the alum coagulation (A), the enhanced alum coagulation (80 mg/L alum) with PAC (B), and MIEX (C) for raw water of the BK WTP at the second sampling.

Alum coagulation of raw water from the BK WTP at the third sampling (RW BK-3) on the DOC removal is depicted in Figure 6-4. The DOC of the RW BK-3 was gradually decreased from 3.7 mg/L to 3.4 mg/L when alum dosage was increased from 10 to 100 mg/L. A dosage of 80 mg/L alum can be considered as an optimum point for DOC reduction in the RW BK-3. The DOC was reduced by 10% to the value of 3.3 mg/L. An increase in dosage of 100 mg/L was slightly increased in DOC. In Figure 6-4A, DON of the RW BK-3 was gradually decreased from 0.25 to 0.02 mg-N/L when alum dosage was increased from 10 to 100 mg/L. The RW BK-3 had the optimal coagulation condition at a dosage of 80 mg/L of alum at pH 7. It could reduce DON to 96 %.

The baseline condition of alum coagulation for the RW BK-3 was at controlled at pH 7 and dose level 80 mg/L. DOC and DON reductions by enhanced coagulation by PAC and MIEX of the RW BK-3 is presented in Figure 6-4B, 6-4C. The alum at 80 mg/L with PAC at 80 mg/L could reduce DOC from 3.7 to 3.1 mg/L, a reduction of 17% (Figure 6-4B). An increase in the PAC dosage up to 100 mg/L could not improve DOC reduction. When alum and MIEX were used, the alum 80 mg/L with MIEX 4 mL/L was the optimal condition for DON reduction (approximately 36%) in RW BK-3 (Figure 6-4C). DON was decreased from 0.25 mg-N/L to 0.02 mg-N/L when using an alum dosage of 80 mg/L combined with a PAC dosage of 80 mg/L (Figure 6-4B). This provided the highest result of a DOC reduction of 94%. Increasing the PAC dosage up to 100 mg/L resulted in a slight increase in DON removal. The best DON reduction of the RW BK-3 was considered at an alum dosage of 80 mg/L combined with a MIEX dosage of 4 mL/L under a controlled pH of 7, a 97% reduction (Figure 6-4C).

Alum coagulation of raw water from the AT at the first sampling (TWW AT-1) and from the AY at the first sampling (TWW AY-1) on the DOC removal is depicted in Figure 6-5. The DOC of the TWW AT-1 was gradually decreased from 5.2 to 4.2 mg/L when alum dosage was increased from 10 to 200 mg/L. A dosage of 100 mg/L alum can be considered as an optimum point for the DOC reduction in the TWW AT-1. The DOC was reduced by 21% to the value of 4.2 mg/L. An increase in the alum dosage above 100 mg/L resulted in the indifferent in DOC levels. In Figure 6-5A, DON of the TWW AT-1 was gradually decreased from 0.21 to 0.17 mg-N/L when alum dosage was increased from 10 to 200 mg/L. The TWW AT-1 water had the optimal coagulation condition at a dosage of 100 mg/L of alum at pH 7. It could reduce DON to 10 %.

The baseline condition of alum coagulation for TWW AT-1 was at controlled at pH 7 and dosage of 100 mg/L. DOC and DON reductions by enhanced coagulation by PAC and MIEX of the TWW AT-1 are presented in Figure 6-5B, 6-5C. The alum at 100 mg/L with PAC

at 100 mg/L could reduce DOC from 5.3 to 2.9 mg/L, a reduction of 45% (Figure 6-5B). An increase in the PAC dosage up to 100 mg/L did not improve DOC reduction. When alum and MIEX were used, the alum 100 mg/L with MIEX 6 mL/L was optimal for DOC reduction (approximately 44%) in TWW AT-1 (Figure 6-5C). DON was decreased from 0.20 to 0.14 mg-N/L when using an alum dosage of 100 mg/L combined with a PAC dosage of 100 mg/L (Figure 6-5B). This provided the best result of a reduction of 31% by alum with PAC. Increasing the PAC dosage up to 150 mg/L resulted in a slight increase in DON removal. The DON reduction of the TWW AT-1 was considered at an alum dosage of 100 mg/L combined with a MIEX dosage of 6 mL/L under a controlled pH of 7, a 28% reduction (Figure 6-5C).

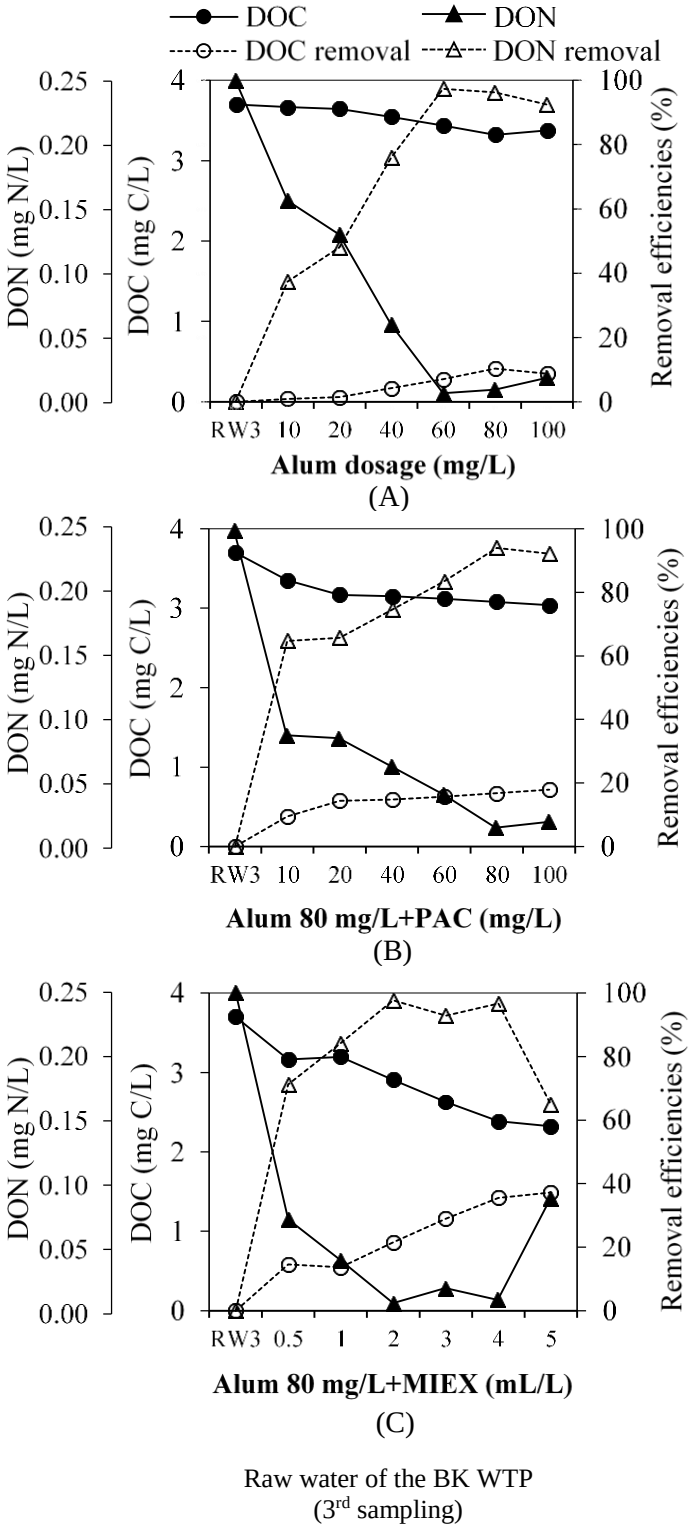


Figure 6-4. Residual of DOC and DON and the percentage of DOC and DON reduction by the alum coagulation (A), the enhanced alum coagulation (80 mg/L alum) with PAC (B), and MIEX (C) for raw water of the BK WTP at the third sampling.

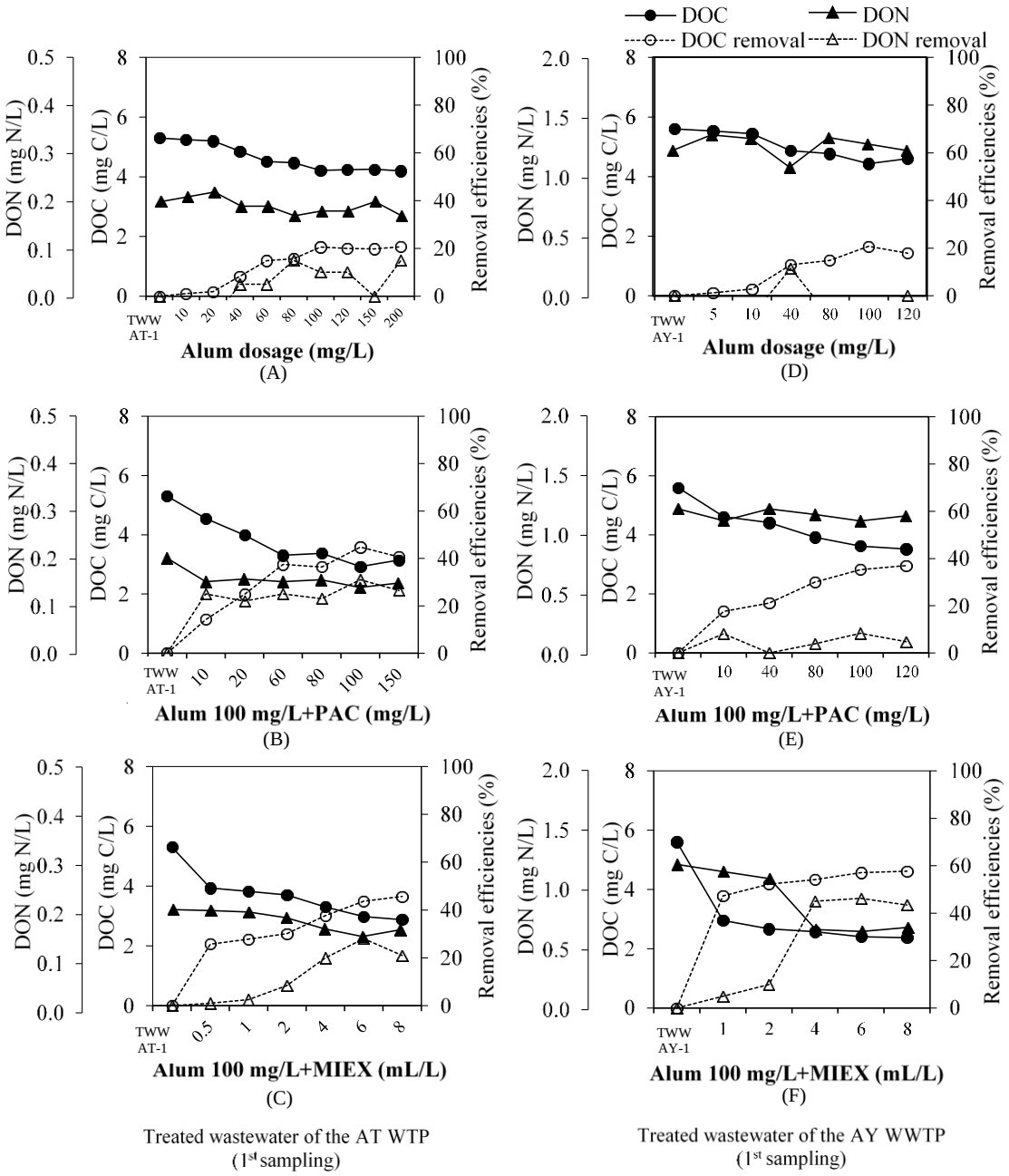


Figure 6-5. Residual of DOC and DON and the percentage of DOC and DON reduction by the alum coagulation, the enhanced alum coagulation with PAC, and MIEX for treated wastewater (TWW) of the AT from the first sampling (A, B, C) and the AY from the first sampling (D, E, F).

Alum coagulation of treated wastewater from AY at the first sampling (TWW AY-1) and from the AY at the first sampling (TWW AY-1) on the DOC removal is depicted in Figure 6-5. The DOC of the TWW AY-1 was gradually decreased from 5.5 to 4.6 mg/L when alum dosage was increased from 5 to 120 mg/L. A dosage of 100 mg/L alum can be considered as

an optimum point for DOC reduction in the TWW AY-1. The DOC was reduced by 21% to the value of 4.4 mg/L. An increase in the alum dosage up to 120 mg/L resulted in a slight decrease in DOC removal. In Figure 6-5D, DON of the TWW AY-1 was gradually decreased from 1.35 to 1.08 mg-N/L when alum dosage was increased from 5 to 40 mg/L. The addition of alum dosage from 80 to 120 mg/L was not increased DON removal. The reduction in DON by alum coagulation varies from not adequate to 11%. Considering the removal of both DOC and DON by alum coagulation, the TWW AY-1 water had the optimal coagulation condition at a dosage of 100 mg/L of alum at pH 7.

The baseline condition of alum coagulation for treated wastewaters of the TWW AY-1 was at controlled at pH 7 and dose level 100 mg/L. DOC and DON reductions by enhanced coagulation with PAC and MIEX of the TWW AY-1 are presented in Figure 6-5E, 6-5F. The alum at 100 mg/L with PAC at 100 mg/L could reduce DOC from 5.6 to 3.6 mg/L, a reduction of 35% (Figure 6-5E). An increase in the PAC dosage up to 100 mg/L resulted in a slight increase in DOC removal. When alum and MIEX were used, the alum 100 mg/L with MIEX 6 mL/L was the optimal condition for DOC reduction (approximately 57%) in TWW AY-1 (Figure 6-5F). DON was decreased from 1.22 to 1.12 mg-N/L when using an alum dosage of 100 mg/L combined with a PAC dosage of 100 mg/L (Figure 6-5E). This provided the highest result of a reduction of 8% with alum and PAC. Increasing the PAC dosage up to 120 mg/L resulted in indifferent in DON level. The best DON reduction of the TWW AY-1 was obtained at an alum dosage of 100 mg/L combined with a MIEX dosage of 6 mL/L under a controlled pH of 7, a 46% reduction (Figure 6-5F).

For the RW+TWW, the alum coagulation on the DOC removal is shown in Figure 6-6. The DOC of the RW+TWW was gradually decreased from 5.0 to 3.8 mg/L when alum dosage was increased from 10 to 120 mg/L. A dosage of 100 mg/L alum can be considered as an optimum point for DOC reduction in the RW+TWW. The DOC was reduced by 24% to the value of 3.9 mg/L. An increase in the alum dosage of up to 120 mg/L resulted in the indifferent in DOC level. In Figure 6-6A, the DON of the RW+TWW was gradually decreased from 0.41 to 0.27 mg-N/L when alum dosage was increased from 10 to 120 mg/L. The RW+TWW had the optimal coagulation condition at a dosage of 100 mg/L of alum at pH 7. It could reduce DON to 76 %.

The baseline condition of alum coagulation for RW+TWW water was at the controlled at pH 7 and dose level 100 mg/L. DOC and DON reductions by enhanced coagulation by PAC and MIEX of the RW+TWW are presented in Figure 6-6B, 6-6C. The alum at 100 mg/L with PAC at 80 mg/L could reduce DOC from 5.1 to 3.0 mg/L, a reduction of 42% (Figure 6-6B).

An increase in the PAC dosage above 80 mg/L resulted in a slight increase in DOC reduction. By using alum and MIEX, the alum 100 mg/L with MIEX 4 mL/L was optimal for DOC reduction (approximately 71%) in RW+TWW (Figure 6-6C). DON was decreased from 1.07 to 0.43 mg-N/L when using an alum dosage of 100 mg/L combined with a PAC dosage of 80 mg/L (Figure 6-6B). This provided the highest result of a reduction of 60% by alum and PAC. Increasing the PAC dosage of up to 80 mg/L resulted in the indifferent DOC level. The reduction for DON removing of the RW+TW water was considered at an alum dosage of 100 mg/L combined with a MIEX dosage of 4 mL/L under a controlled pH of 7, a 32% reduction (Figure 6-6C).

A previous study has reported that the use of only the aluminum sulfate or PACl may unsuccessful on DON reduction in raw water with an average DON of 0.27 mg/L (Lee et al., 2006). The addition of cationic polymer was found in a slight increase in DON removal by 15 to 20% over the PACl alone (Lee et al., 2006). The enhanced coagulation using alum and microfiltration could remove by approximately 69% from the initial DON of between 1.1 and 1.2 mg N/L in wastewater effluents (Arnaldos and Pagilla, 2010). The reduction of DON by coagulation with alum alone in this work was comparable to the result of DON reduction from the previous works.

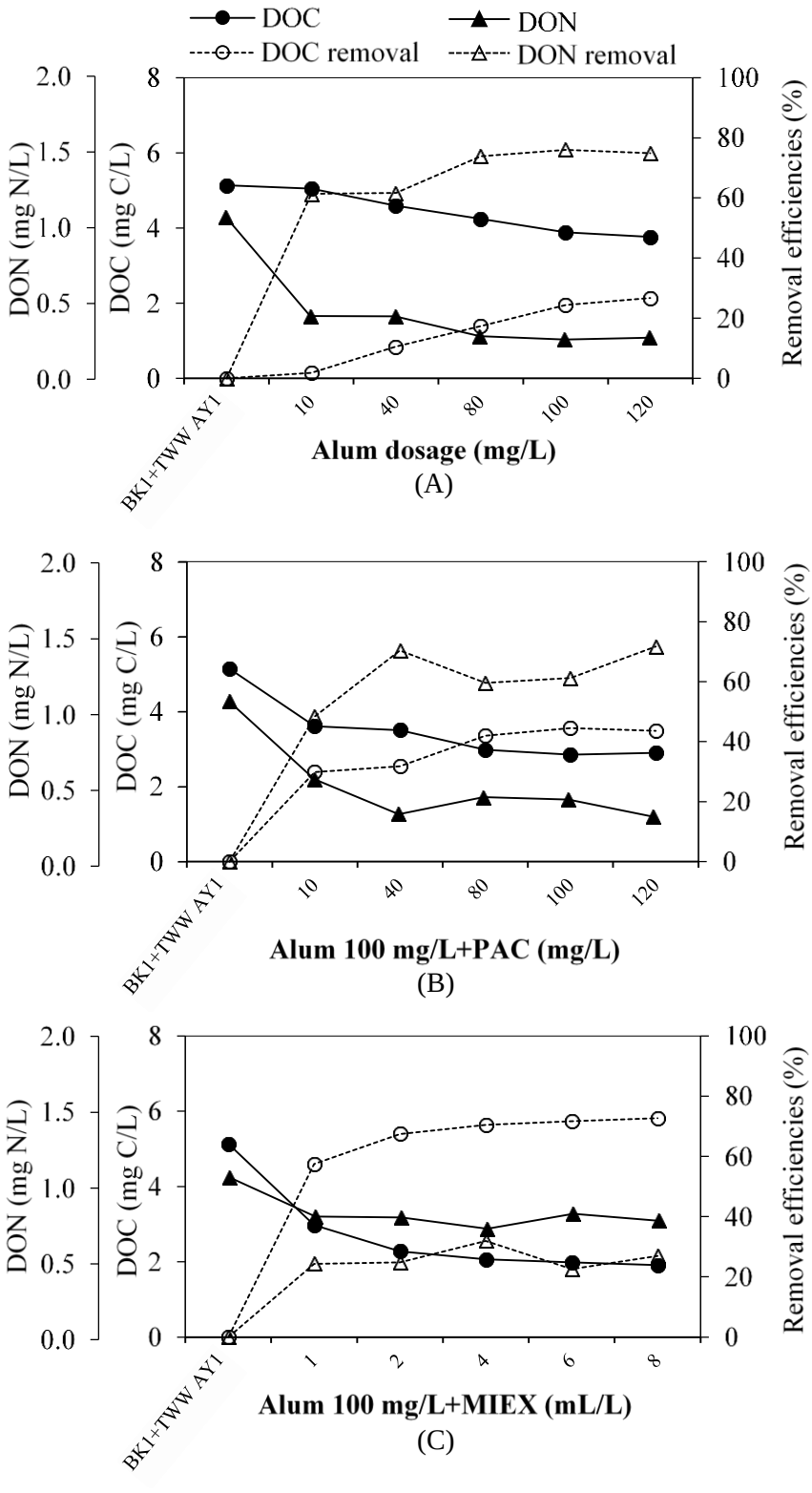


Figure 6-6. Residual of DOC and DON and the percentage of DOC and DON reduction by the alum coagulation (A), the enhanced alum coagulation (100 mg/L alum) with PAC (B), and MIEX (C) for treated wastewater (TWW) of the AY WTP from the first sampling mixed with raw water of the BK WTP (50% v/v).

6.3.4. DBPFP species and their reduction at optimal coagulation; alum coagulation, enhanced alum coagulation by PAC, and enhanced coagulation by MIEX

a) Reduction of THMFP

The THMFP species and the ratio of THMFP to the WHO guideline for the RW BK-1 and its coagulated water by alum, enhanced coagulation with PAC, and enhanced coagulation with MIEX are shown in Figure 6-7 and Table 6-2. Chloroform of coagulated water ranged from 87.9 to 93.3% of total THMFP. Dichlorobromoform (BDCM) and dibromochloroform (DBCM) were also found in coagulated water. The percentages of these species of coagulated water were 6.2 – 11.1% and 0.4 – 1.1%, respectively. This observation has corresponded well with that of RW BK-1. Chloroform was the dominant THMFP species in the RW BK-1 and its treated water while BDCM and DBCM were found in the minority.

Total THMFP of 257, 258, 240 and 132 μg/L were detected in treated water of the BK RW-1 by alum 20 mg/L, alum 80 mg/L, alum 80 mg/L with PAC 40 mg/L, and alum 80 mg/L with MIEX 4 mL/L respectively. The best coagulation condition for total THMFP reduction from the RW BK-1 was at the alum dosage of 80 mg/L with MIEX 4 mL/L at pH 7.0. Under such condition, total THMFP could be reduced to 132 μg/L, a reduction of 50%. The total THMFP concentrations found in treated water by alum 80 mg/L with PAC 40 mg/L, alum 80 mg/L, and alum 20 mg/L were 240 (a reduction of 10%), 258 (3%), and 257 μg/L (3%), respectively. The THMFP/WHO ratio of the BK-1 raw water and treated waters by alum 20 mg/L, alum 80 mg/L, alum 80 mg/L with PAC 40 mg/L, and alum 80 mg/L with MIEX 4 mL/L were 1.1, 1.1, 1.1, 1.0 and 0.6 respectively. The BK-1 treated water by alum enhanced with MIEX tended to form THMs with lower than the standard guideline of ≤ 1 (Figure 6-7).

For the BK-2 raw water and its treated water. The chloroform was the major THMFP species detected in treated water in ranging from 80.0 to 87.5% of total THMFP. BDCM and DBCM were found in treated water. The percentage of BDCM in raw and coagulated water was 15.4-20.0%. The DBCM was not detected in all treated waters of RW BK-2. Total THMFP was 122 μg/L for the BK-2 raw water. The reduction efficiency of THMFP by alum 20 mg/L, alum 80 mg/L, alum 80 mg/L with PAC 80 mg/L, and alum 80 mg/L with MIEX 2 mL/L were 12, 18, 23, and 27%, respectively. The enhanced coagulation by MIEX was the best coagulation condition for total THMFP reduction in the RW BK-2. The THMFP/WHO ratio of the raw water of RW BK-2 and all the coagulated waters by alum coagulation and enhanced coagulation tended to form THMs with lower than the standard guideline of ≤ 1 (Figure 6-7).

In the case of the BK-3 raw water and its treated water, the chloroform was the dominant THMFP species detected in treated water in ranging from 60.7 to 76.2% of total THMFP. BDCM, DBCM, bromoform were found in treated water. The percentages of these species in raw and coagulated water were 16.3-26.3%, 5.7-12.8%, and 0.1-0.2%, respectively. Total THMFP was 154 μg/L for the BK-3 raw water. The removal efficiency of THMFP by alum 20 mg/L, alum 80 mg/L, alum 80 mg/L with PAC 80 mg/L, and alum 80 mg/L with MIEX 4 mL/L were 6, 10, 33, and 57%, respectively. The enhanced coagulation with MIEX provided the best coagulation condition for total THMFP reduction in the BK-3 raw water. The THMFP/WHO ratio of the RW BK-3 and all treated waters by alum coagulation and enhanced coagulation had tended to form THMs with lower than the standard guideline of ≤ 1 (Figure 6-7).

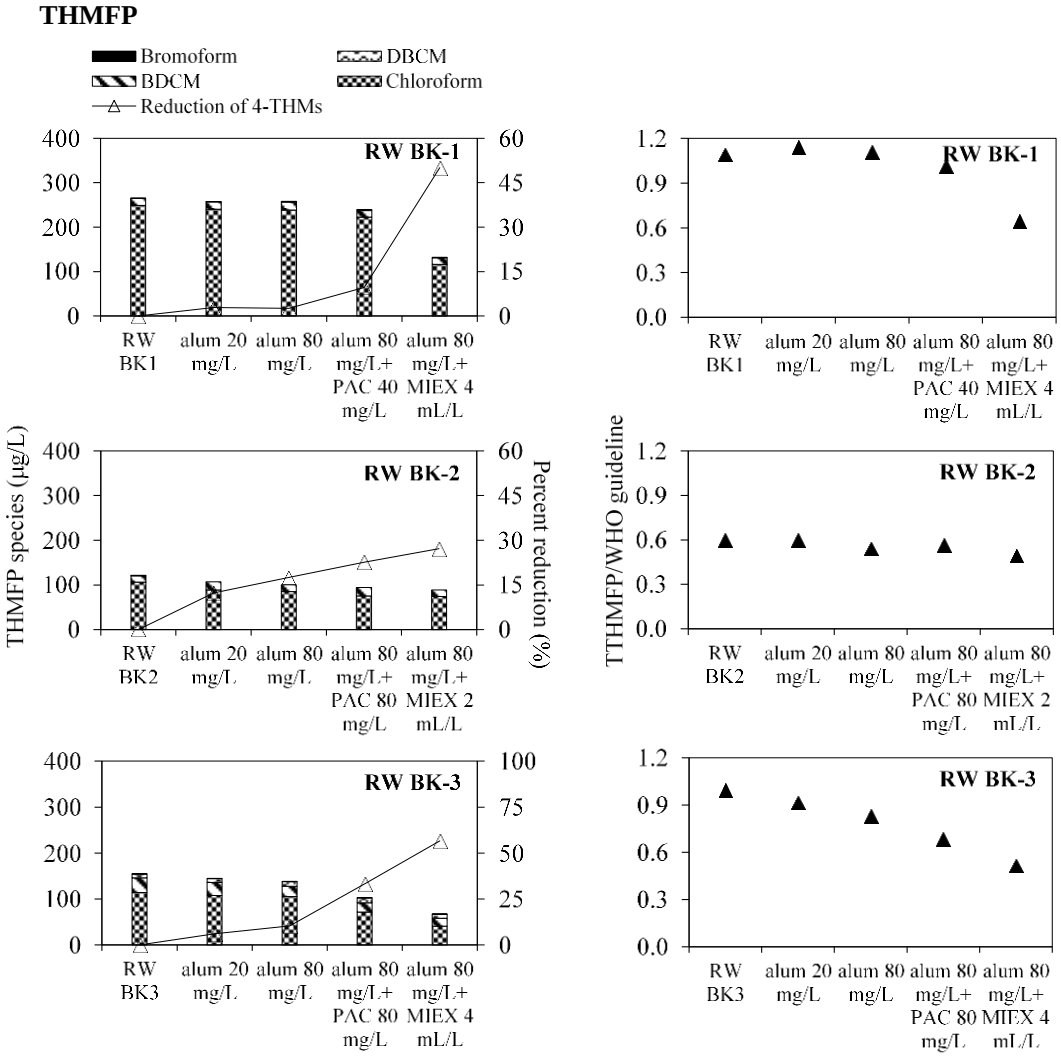


Figure 6-7. THMFP species, and the ratio of THMFP to the WHO guideline for raw water of the BK WTP and their treated waters.

For treated wastewater, the THMFP species and the ratio of THMFP to the WHO guideline for the TWW AT-1 water and its treated water by alum, enhanced coagulation by PAC or MIEX are shown in Figure 6-8. The chloroform formation potential of 36.2-43.9% of total THMFP was detected in treated water, followed by BDCM of 32.9-40.0%, and DBCM of 12.6-21.6%, respectively. Bromoform formation potential was detected at a level of less than about 8%. Total THMFP of as high as 268 μg/ L was detected in the TWW AT-1. The reductions of THMFP of 40, 41, 93, and 91% by the coagulation with alum 10 mg/L, alum 100 mg/L, alum 100 mg/L with PAC 100 mg/L, and alum 100 mg/L with MIEX 6 mL/L were obtained. The enhanced coagulation with PAC showed the best coagulation condition for total THMFP reduction of the TWW AT-1. Treated waters of the TWW AT-1 by alum alone had high ratios of the THMFP/WHO Guideline values than for those of treated waters by enhanced coagulation with PAC or MIEX (Figure 6-8)

Table 6-2. Concentrations and percent distributions of THMFP, I-THMFP, HANFP and HNMFP species in raw water, treated wastewater, and raw water mixed with treated wastewater, and their treated water at the optimal dosages of alum, alum with PAC, and alum with MIEX coagulation.

Samples	4-THMFP (μg/L)					5-Iodo-THMFP (μg/L)						4-HANFP (μg/L)					TCNMFP (μg/L)
	Chloroform	BDCM	DBCM	Bromoform	Total	BCIM	CDIM	DCIM	BDIM	TIM	Total	TCAN	DCAN	BCAN	DBAN	Total	
Raw water																	
RW BK-1	249 (94.0)	15 (5.8)	1 (0.2)	ND	265	ND	0.8 (12)	5.7 (88)	ND	ND	6.5	3.6 (17)	13.8 (67)	3.2 (15)	ND	20.6	2.5
· alum 20 mg/L	240 (93.3)	16 (6.3)	1 (0.4)	ND	257	ND	ND	4.6 (100)	ND	ND	4.6	2.7 (20)	4.7 (36)	3.0 (23)	2.8 (21)	13.3	2.5
· alum 80 mg/L	238 (92.3)	18 (6.8)	2 (0.9)	ND	258	ND	ND	2.9 (100)	ND	ND	2.9	0.6 (5)	6.7 (55)	4.0 (33)	0.9 (7)	12.0	2.5
· alum 80 mg/L +PAC 40 mg/L	222 (92.8)	15 (6.2)	3 (1.1)	ND	240	1.6(100)	ND	ND	ND	ND	1.6	2.2 (16)	5.1 (50)	3.3 (24)	1.0 (10)	11.6	2.3
· alum 80 mg/L +MIEX 4 mL/L	116 (87.9)	15 (11.1)	1 (0.9)	ND	132	ND	ND	1.1 (100)	ND	ND	1.1	2.1 (40)	2.0 (37)	1.3 (24)	ND	5.4	2.1
RW BK-2	106 (87.5)	14 (11.4)	1 (1.1)	ND	122	ND	ND	0.8 (100)	ND	ND	0.8	1.7 (19)	5.2 (57)	2.2 (24)	ND	9.1	1.92
· alum 20 mg/L	89 (83.1)	18 (16.9)	ND	ND	107	ND	ND	0.8 (100)	ND	ND	0.8	1.1 (13)	4.5 (54)	2.7 (33)	ND	8.3	1.84
· alum 80 mg/L	85 (84.6)	15 (15.4)	ND	ND	101	ND	ND	0.8 (100)	ND	ND	0.8	1.4 (17)	3.8 (46)	3.1 (37)	ND	8.3	1.81
· alum 80 mg/L +PAC 80 mg/L	76 (80.0)	19 (20.0)	ND	ND	94	ND	ND	0.9 (100)	ND	ND	0.9	0.9 (11)	3.6 (47)	3.2 (41)	ND	7.7	1.63
· alum 80 mg/L +MIEX 2 mL/L	74 (83.3)	15 (16.7)	ND	ND	89	ND	ND	0.8 (100)	ND	ND	0.8	0.8 (12)	3.0 (44)	3.0 (44)	ND	6.8	1.53
RW BK-3	114 (73.9)	32 (20.7)	8 (5.2)	0.2 (0.1)	154	ND	1.1 (92)	0.1 (8)	ND	ND	1.2	1.5 (18)	5.5 (65)	ND	1.5 (18)	8.5	1.6
· alum 20 mg/L	108 (74.5)	28 (19.7)	8 (5.7)	0.3 (0.2)	145	ND	ND	ND	ND	ND	ND	0.9 (33)	1.8 (67)	ND	ND	2.7	ND
· alum 80 mg/L	105 (76.2)	23 (16.3)	10 (7.4)	0.2 (0.1)	138	ND	ND	ND	ND	ND	ND	0.9 (35)	1.7 (65)	ND	ND	2.6	ND
· alum 80 mg/L +PAC 80 mg/L	71 (69.6)	20 (19.8)	11 (10.4)	0.2 (0.2)	103	ND	ND	ND	ND	ND	ND	0.8 (41)	1.2 (59)	ND	ND	2.1	ND
· alum 80 mg/L +MIEX 4 mL/L	41 (60.7)	18 (26.3)	9 (12.8)	0.1 (0.2)	67	ND	ND	ND	ND	ND	ND	0.3 (24)	1.0 (76)	ND	ND	1.3	ND

( ) is Percent distribution of THMFP, I-THMFP, and HANFP species (%)

ND is not detected

Table 6-2. (Cont.) Concentration and percent distribution of THMFP, iodo-THMFP, HANFP and HNMFP species in raw water, treated wastewater, and raw water mixed with treated wastewater and their coagulated water at the optimal dosages of alum, PAC, and MIEX coagulation.

Sample	4-THMFP (μg/L)					5-Iodo-THMFP (μg/L)						4-HANFP (μg/L)					TCNMFP (μg/L)
	Chloroform	BDCM	DBCM	Bromoform	Total	BCIM	CDIM	DCIM	BDIM	TIM	Total	TCAN	DCAN	BCAN	DBAN	Total	
Treated wastewater																	
TWW AT-1	200 (74.5)	51 (19.2)	16 (6.0)	0.7 (0.3)	268	ND	1.9 (39)	3.0 (61)	ND	ND	4.9	2.5 (15)	6.4 (38)	4.9 (29)	2.9 (18)	16.7	18.3
· alum 10 mg/L	71 (43.9)	55 (34.4)	31 (19.3)	4.0 (2.5)	160	ND	ND	ND	ND	ND	ND	ND	7.6 (50)	4.4 (29)	3.2 (21)	15.2	ND
· alum 100 mg/L	70 (43.9)	53 (32.9)	33 (20.5)	4.2 (2.7)	159	ND	ND	ND	ND	ND	ND	ND	6.2 (42)	5.1 (34)	3.7 (25)	14.9	ND
· alum 100 mg/L +PAC 100 mg/L	8 (39.8)	8 (40.0)	2 (12.6)	1.5 (7.6)	20	ND	ND	ND	ND	ND	1.8	ND	2.7 (26)	4.1 (40)	3.5 (34)	10.3	ND
· alum 100 mg/L +MIEX 6 mL/L	9 (36.2)	9 (36.5)	5 (21.6)	1.4 (5.6)	24	ND	ND	ND	ND	ND	1.9	ND	5.8 (40)	5.2 (36)	3.4 (24)	14.4	ND
TWW AY-1	226 (84.6)	35 (13.1)	4.3 (1.6)	1.9 (0.7)	267	ND	2.6 (28)	1.8 (19)	5 (53)	ND	9.4	3 (12)	16.9 (68)	3.9 (16)	1.1 (4)	24.9	21.3
· alum 5 mg/L	9 (73.4)	3 (26.6)	ND	ND	12	ND	ND	ND	ND	ND	ND	0.8 (47)	0.9 (53)	ND	ND	1.6	ND
· alum 100 mg/L	8 (71.8)	3 (28.2)	ND	ND	11	ND	ND	ND	ND	ND	ND	0.9 (46)	1.0 (54)	ND	ND	1.9	ND
· alum 100 mg/L +PAC 100 mg/L	11 (77.5)	3 (22.5)	ND	ND	14	ND	ND	ND	ND	ND	ND	0.6 (50)	0.6 (50)	ND	ND	1.3	ND
· alum 100 mg/L +MIEX 6 mL/L	2 (41.1)	3 (58.9)	ND	ND	5	ND	ND	ND	ND	ND	ND	0.5 (66)	0.3 (34)	ND	ND	0.8	ND
Mixed raw water																	
RW+TWW	189 (79.0)	41 (17.2)	9 (3.9)	ND	239	ND	0.6 (19)	0.5 (16)	2 (65)	ND	3.1	ND	32.4 (67)	13.7 (28)	2.0 (4)	48.1	21.3
· alum 5 mg/L	18 (92.3)	1.2 (6.3)	0.3 (1.5)	ND	20	ND	ND	ND	ND	ND	ND	ND	0.7 (100)	ND	ND	0.7	ND
· alum 100 mg/L	13 (91.5)	1.0 (6.9)	0.2 (1.6)	ND	14	ND	ND	ND	ND	ND	ND	ND	0.8 (100)	ND	ND	0.8	ND
· alum 100 mg/L +PAC 80 mg/L	13 (89.1)	1.3 (8.9)	0.3 (1.8)	ND	14	ND	ND	ND	ND	ND	ND	ND	0.7 (100)	ND	ND	0.7	ND
· alum 100 mg/L +MIEX 4 mL/L	3.7 (94.0)	0.2 (5.5)	ND	0.1 (0.5)	4	ND	ND	ND	ND	ND	ND	ND	0.4 (100)	ND	ND	0.4	ND

( ) is Percent distribution of THMFP, I-THMFP, and HANFP species (%)

ND is not detected

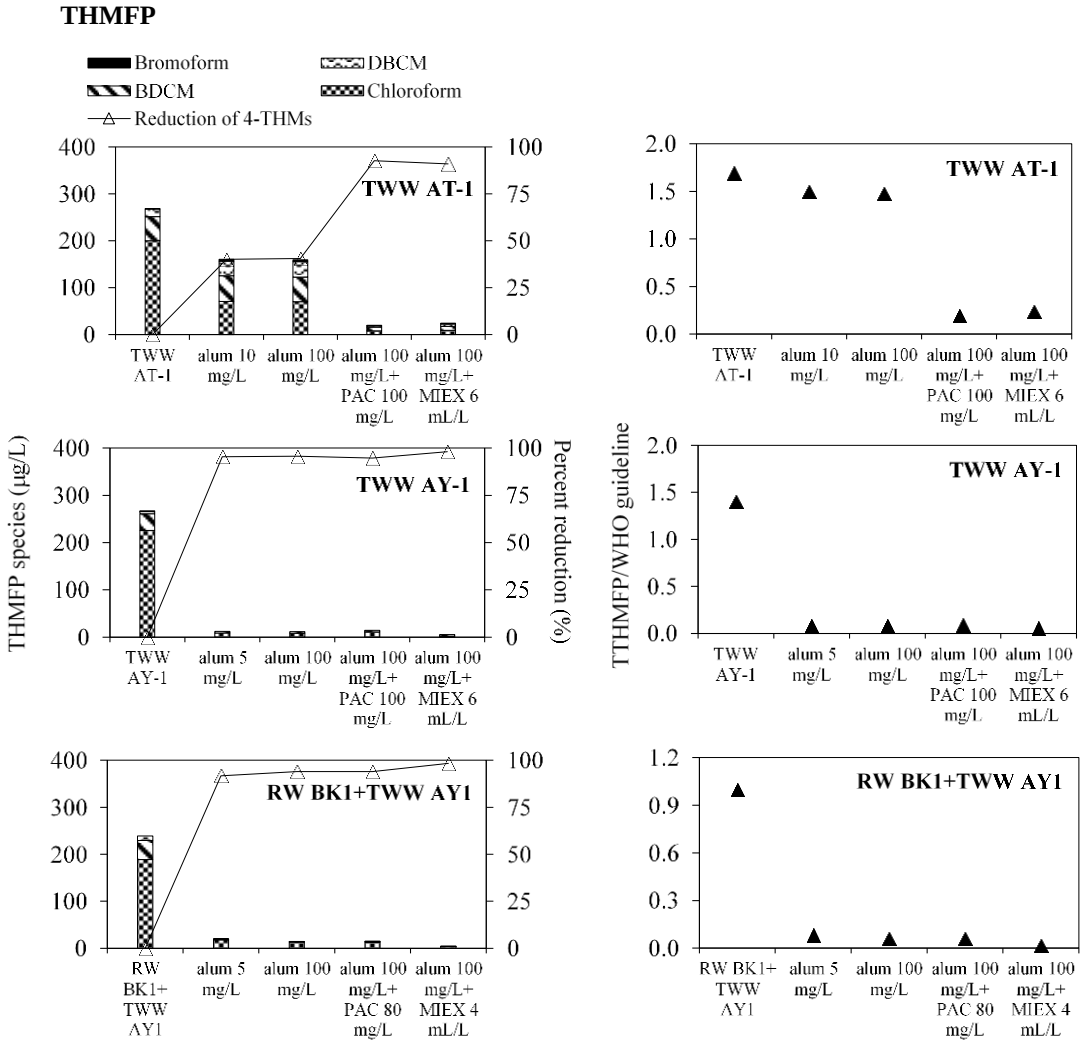


Figure 6-8. THMFP species, and the ratio of THMFP to the WHO guideline for treated wastewater from AT and the AY from the first sampling (TWW AT-1 and TWW AY-1), and raw water of the BK WTP mixed with treated wastewater of the AY (RW BK1+TWW AY1) at 50% v/v and their treated waters.

In the case of treated water of TWW-AY-1, chloroform was the dominant THMs species in the TWW AY-1 and made up about 84.6% of the total THMFP; while the percentages of BDCM, DBCM, and bromoform were 13.1, 1.6 and 0.7%, respectively. Total THMFP of as high as 267 μg/L was detected in the TWW AY-1 water. The reductions of THMFP of 95, 96, 95, and 98% by the coagulation with alum 5 mg/L, alum 100 mg/L, alum 100 mg/L with PAC 100 mg/L, and alum 100 mg/L with MIEX 6 mL/L were obtained, respectively. The alum coagulation and enhanced coagulation with PAC or MIEX were very useful for the removal of THMFP in the TWW AT-1 by 95 to 98%. The treated waters by alum

coagulation and enhanced coagulation by PAC or MIEX had the ratio of THMFP/ WHO guideline values of about 0.1 (Figure 6-8).

Concerning the THMFP species for the RW+TWW in Figure 6-8 and Table 6-2, under optimal conditions for alum coagulation and enhanced coagulation by PAC or MIEX, chloroform was the dominant THMs species in treated water in ranging from 89.1 to 94.0% of total THMFP. BDCM, DBCM, and bromoform were found in the raw and treated water. The percentages of these species in the treated water were ranging from 5.5 to 8.9%, not detected (ND) to 1.8%, and ND to 0.5%, respectively.

Total THMFP of as high as 239 μg/ L was detected in the RW+TWW. The reductions of THMFP of 92, 94, 94, and 98% by coagulation with alum 5 mg/L, alum 100 mg/L, alum 100 mg/L with PAC 80 mg/L, and alum 100 mg/L with MIEX 4 mL/L were determined. The enhanced coagulation with MIEX demonstrated the best coagulation condition for total THMFP reduction from the RW+TWW. The treated waters by alum coagulation and enhanced coagulation by PAC or MIEX had the ratio of THMFP/ WHO guideline values of about 0.1 (Figure 6-8) that below the maximum acceptable level recommended by the WHO.

b) Reduction of I-THMFP

I-THMs are potentially toxic and had greater carcinogenic character than THMs (Cemeli et al., 2006). The I-THMFP species for the BK-1 raw water and its treated water by alum coagulation, and enhanced coagulation with PAC or MIEX based on the optimum conditions are presented in Figure 6-9 and Table 6-2. Total I-THMFP of 6.5 μg/L was detected in the BK-1 raw water. Total I-THMFP were detected in treated raw water by alum 20 mg/L, alum 80 mg/L, alum 100 mg/L with PAC 40 mg/L, and alum 100 mg/L with MIEX 4 mL/L at 4.6, 2.9, 1.6, and 1.1 μg/L, respectively.The reduction of total I-THMFP by alum alone and the enhanced alum coagulation by PAC or MIEX ranged from 29 to 83%. The alum coagulation at 20 mg/L slightly reduced the DCIM of I-THMFP species. The enhanced coagulation by MIEX 4 mL/L was found to be effective for reducing total I-THMFP in the BK-1 raw water.

In the case of BK-2 raw water and its treated water, only DCIM was detected in the BK-2 raw water. Total I-THMFP of the BK-2 raw water was 0.8 μg/ L. Under optimal conditions, for the BK-2 raw water, the alum dosages at 20 and 80 mg/L, and the enhanced alum coagulation by PAC 80 mg/L or MIEX 2 mL/L did not show any reduction of DCIM formation potential. CDIM and DCIM in the BK-3 raw water made up 92% of total I-THMFP and 8%, respectively. Total I-THMFP in the BK-3 raw water was 1.2 μg/ L. Concerning

coagulation by alum, and enhanced coagulation with PAC or MIEX under the optimum conditions, the I-THMFP did not detect in treated water from all experiments.

For treated wastewater, DCIM and CDIM were the dominant I-THMFP species in the TWW AT-1, which accounted for 61.0% of total I-THMFP and 39%, respectively (Figure 6-9). BCIM, BDIM, and TIM were not found in the TWW AT-1 and its treated water. Total I-THMFP in the TWW AT-1 water was 4.9 μg/L. I-THMFP in treated water of the TWW AT-1 by alum coagulation, and alum coagulation with PAC or MIEX was not detected. The reduction of I-THMFP species by optimal coagulation or enhanced coagulation for the TWW AY-1 presents in Figure 6-9. BDIM, CDIM, and DCIM in the TWW AY-1 made up 53% of total I-THMFP, 28% and 19%, respectively. Total I-THMFP in the TWW AY-1 water was 9.4 μg/L. In all cases, I-THMFP could not detect in treated water.

In the case of RW+TWW, BDIM, CDIM, and DCIM in the RW+TWW water made up 65% of total I-THMFP, 19%, and 16%, respectively. Total I-THMFP in the RW+TWW water was 3.1 μg/L. In all cases, I-THMFP could not detect in treated water.

Iodo-THMFP

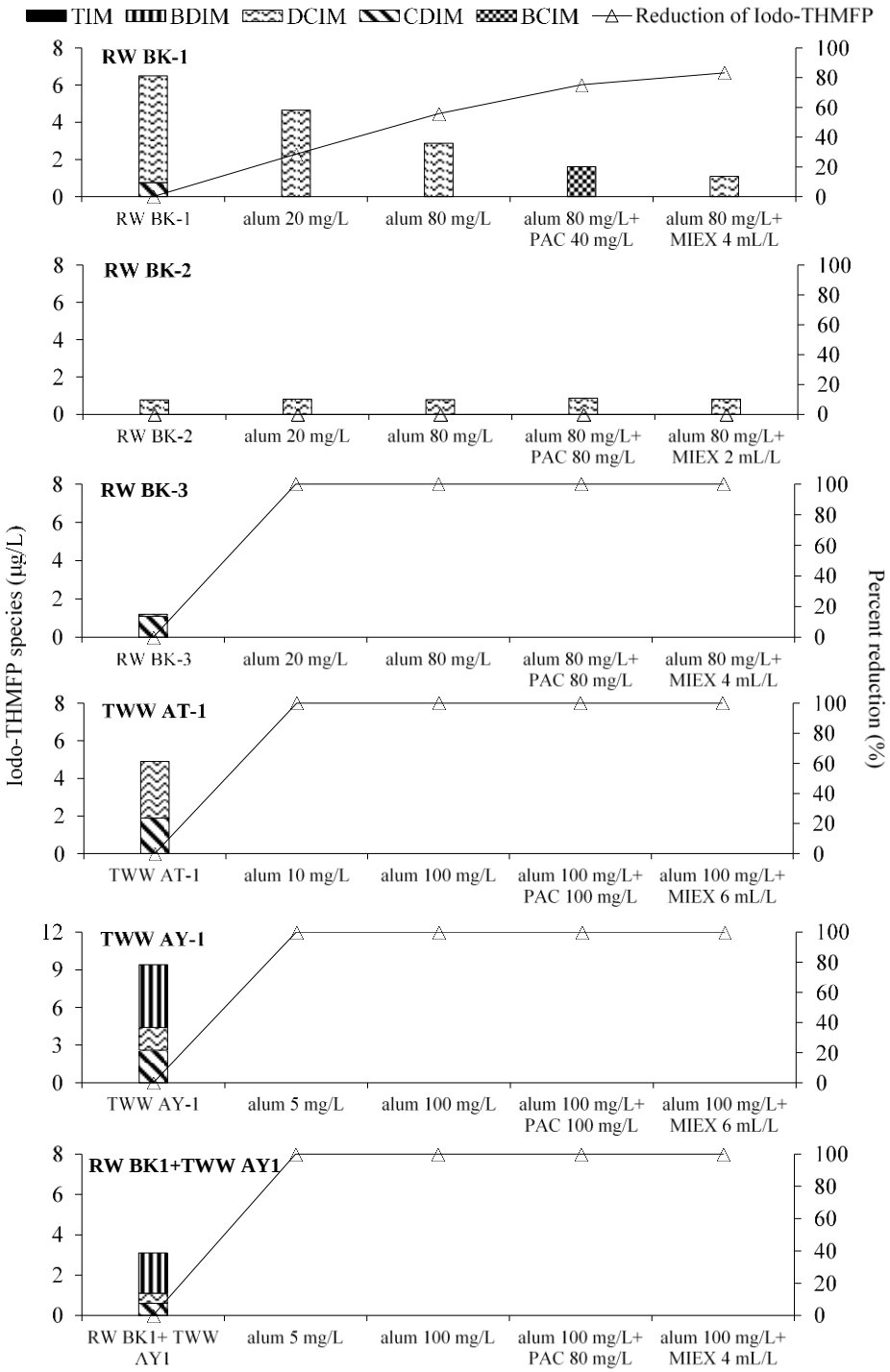


Figure 6-9. I-THMFP of raw water, treated wastewater, raw water mixed with treated wastewater and their treated waters.

c) Reduction of HANFP

As shown in Figure 6-10, HANFP species, namely, DCAN, TCAN, and BCAN were detected in the raw water of BK-1. The mentioned species accounted for 67% of total HANFP, 17%, and 15%, respectively (Table 6-2). Total HANFP in the BK-1 raw water was 20.6 μg/L. The alum coagulation at a dosage of 20 and 80 mg/L at pH 7.0 could reduce total HANFP by 36 and 42%, respectively. Concerning the enhanced alum coagulation by PAC 40 mg/L or MIEX 4 mL/L, the reduction efficiencies of total HANFP by 44 and 74% were obtained, respectively. The enhanced alum coagulation by MIEX is more useful than alum coagulation alone, and alum coagulation with PAC in reducing HANFP.

For the raw water of BK-2 and it treated water, DCAN of about 57% of total HANFP made up the major HANFP of the BK-2 raw water. BCAN and TCAN were found in the BK-2 raw water and treated water. DBAN was not detected in the raw water of BK-2. Total HANFP of the BK-2 raw water was 9.1 μg/L. The reduction efficiency of HANFP by alum 20 mg/L and alum 80 mg/L was about 9%, while HANFP was reduced by 16 and 25% when using enhanced alum coagulation with PAC and MIEX, respectively. In the case of BK-3 raw water and coagulated water, DCAN, TCAN, and DBAN were the three HANFP species detected in the BK-3 raw water, by 65% of total HANFP, 18%, and 18%, respectively. Total HANFP was 8.5 μg/L for the BK-3 raw water. The reduction efficiency of HANFP by alum 20 mg/L, alum 80 mg/L, alum 80 mg/L with PAC 80 mg/L, and alum 80 mg/L with MIEX 4 mL/L were 68, 70, 76, and 84%, respectively. The enhanced alum coagulation by PAC or MIEX of the BK-3 raw water was more effective than alum alone in reducing HANFP.

In the case of TWW AT-1 and its treated water, the DCAN formation potential of 38% of total HANFP was detected in the TWW AT-1, followed by BCAN of 29%, TCAN of 15% and DBAN of 18%, respectively. Total HANFP of 16.7 μg/L was detected in the TWW AT-1 water. The reductions of HANFP of 9, 11, 38, and 14% by the coagulation with alum 10 mg/L, alum 100 mg/L, alum 100 mg/L with PAC 100 mg/L, and alum 100 mg/L with MIEX 6 mL/L were determined. The reduction efficiencies of HANFP by enhanced alum coagulation with PAC or MIEX were higher than that of the coagulation by alum alone.

For the TWW AY-1, DCAN, BCAN, TCAN, and DBAN in the TWW AY-1 made up 68% of total HANFP, 16%, 12%, and 4%, respectively. Total HANFP of the TWW AY-1 was 24.9 μg/L. The HANFP reduction by 94% for alum coagulation at 5 mg/L, 92% for alum coagulation at 100 mg/L, 95% for enhanced alum coagulation with PAC 100 mg/L, and 97% for enhanced alum coagulation with MIEX 6 mL/L.

Concerning RW+TWW and its treated water, DCAN, BCAN, and DBAN in the RW+TWW made up 67% of HANFP, 28%, and 4%, respectively. Total HANFP in the RW+TWW was as high as 48.1 μg/L. Using alum alone, and the combination of alum and PAC or MIEX under the optimal coagulant dosages provided efficiency satisfactorily for HANFP reduction between 98 and 99%.

d) Reduction of HNMFP

As shown in Figure 6-11, TCNMFP species was detected at a low concentration of 2.5, 2.1, and 1.6 μg/L for the BK-1, BK-2, and BK-3 raw water, respectively. For the BK-1 raw water, alum coagulation at 20 mg/L and 80 mg/L could not reduce the TCNMFP. The enhanced coagulation based on the optimum conditions was more useful than alum alone in reducing TCNMFP. A reduction of 8% TCNMFP by alum with PAC, and a reduction of 17% TCNMFP by alum with MIEX were obtained from the BK-1 raw water. For the BK-2 raw water, the reduction efficiencies of TCNMFP by alum 20 mg/L, alum 80 mg/L, enhanced alum coagulation with PAC 80 mg/L, and alum with MIEX 2 mL/L were 3, 5, 14 and 19%, respectively. Enhanced coagulation by MIEX of both the BK-1 and BK-2 raw water was more effective than alum alone, and alum with PAC in reducing TCNMFP. For the BK-3 raw water, TCNMFP was not detected from treated water by alum coagulation and enhanced coagulation by PAC or MIEX.

In this work, the TCNM species was detected at 18.3, 21.3, and 21.3 μg/L for TWW AT-1, TWW AY-1, and RW+TWW water, respectively. Based on the optimum conditions, TCNMFP was not detected from treated water by alum coagulation and enhanced coagulation by PAC or MIEX.

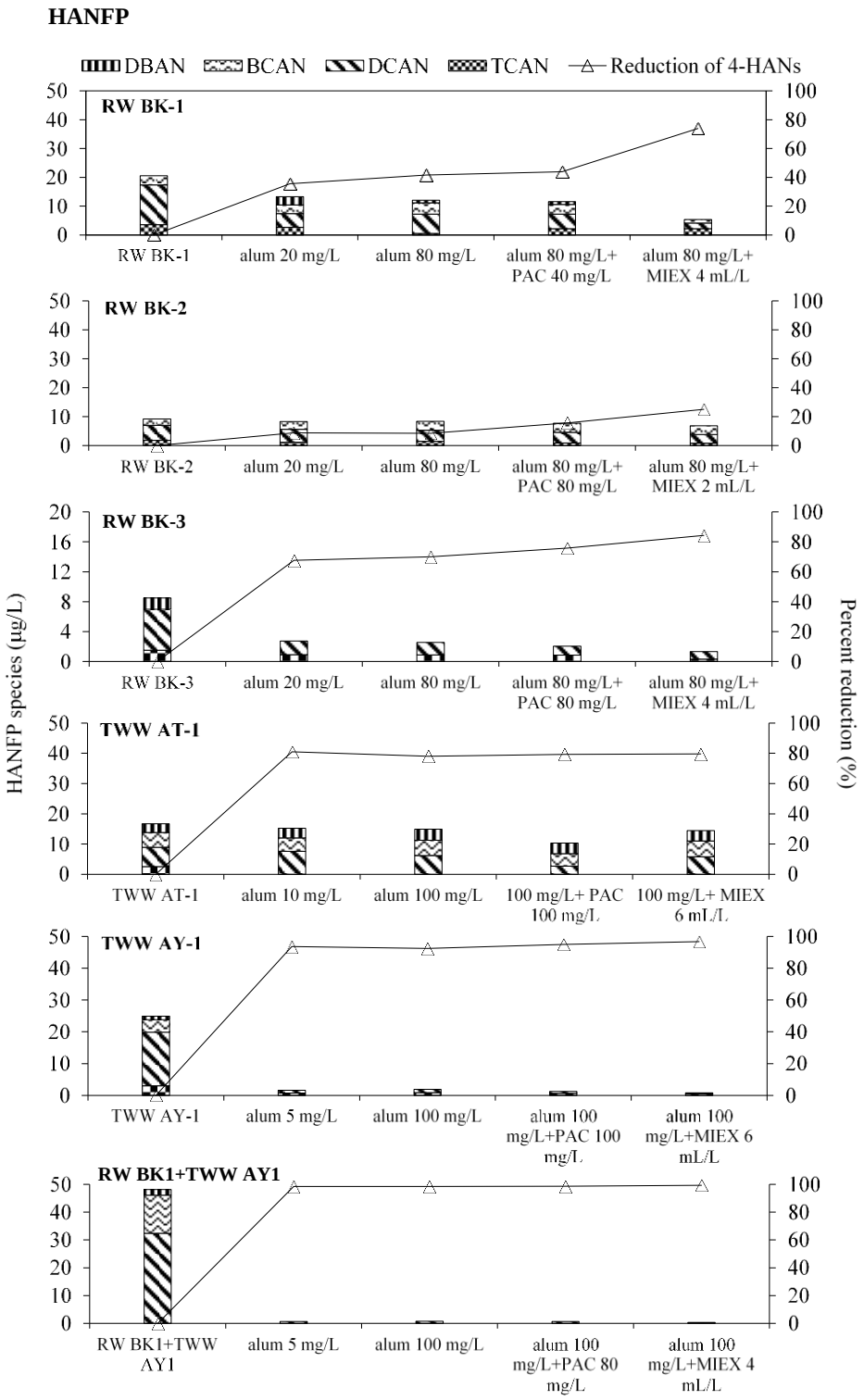


Figure 6-10. HANFP for raw water, treated wastewater, raw water mixed with treated wastewater and their treated waters.

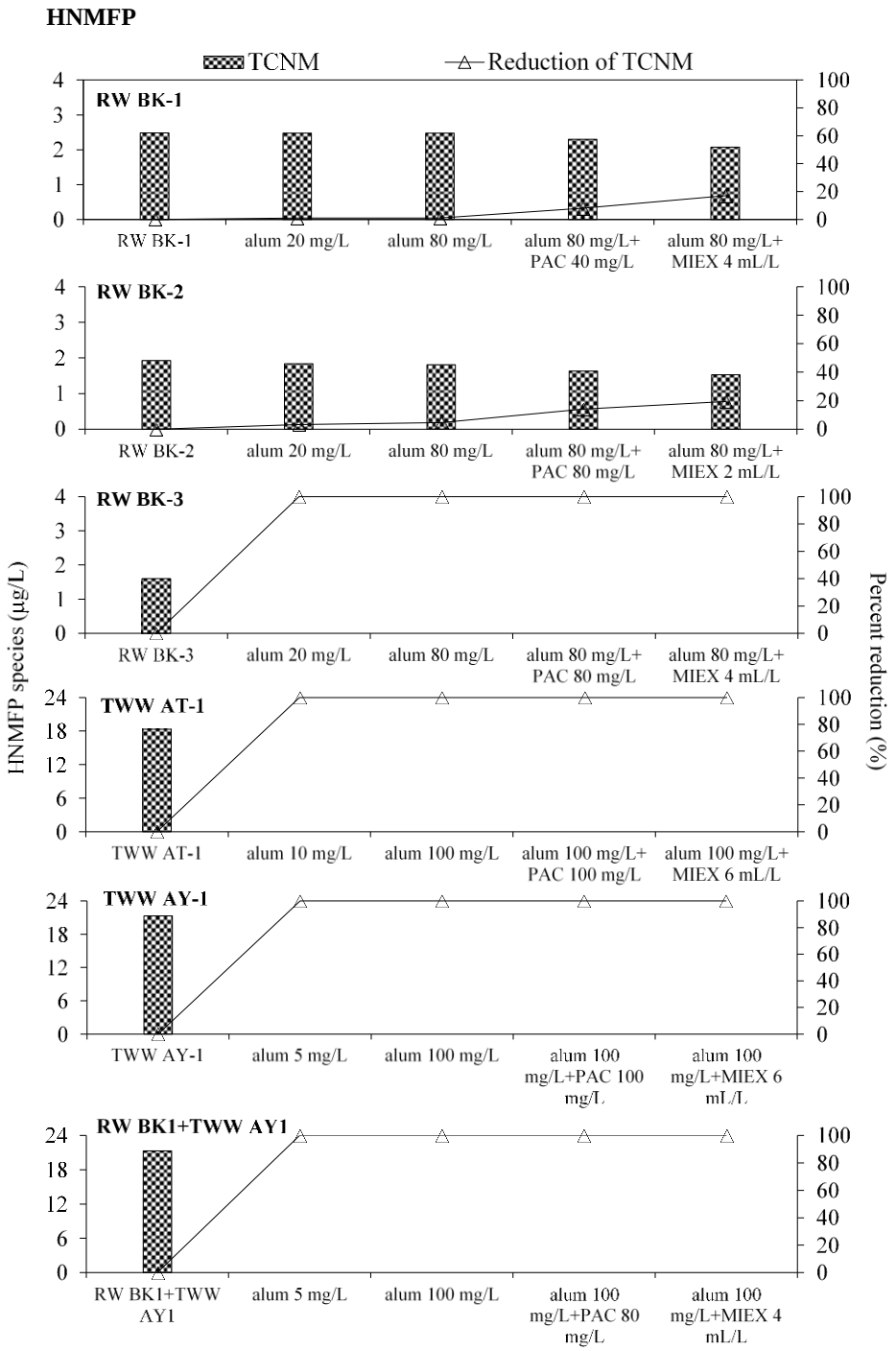


Figure 6-11. TCNMFP for raw water, treated wastewater, raw water mixed with treated wastewater and their treated waters.

6.3.5 DOM fractions and their reductions

a) Reduction of DOC of each MW size fraction

Table 6-3 shows the DOC of various MW size fraction of treated water. In the BK-1 raw water, coagulation using alum of 20 mg/L provided the most reduction of the DOM fraction with 3 kDa < MW < 10 kDa by 67%. The DOM fraction with 1 kDa < MW < 3 kDa could not be removed. Enhanced coagulation using alum of 80 mg/L had the highest removal of DOM fraction with MW > 10 kDa with percent reduction of 49%. The other DOM fractions were removed within the range from 11 to 42%. Enhanced alum coagulation with PAC resulted in the highest reduction with MW >10 kDa by 67%. The other DOM fractions were removed within the range from 16 to 42%. When enhanced alum coagulation with MIEX was used, the percent reductions of 67, 67, 40, and 74% was found in DOM fractions with MW >10 kDa, 3kDa < MW < 10 kDa, 1 kDa < MW <3 kDa, and MW < 1 kDa, respectively.

Table 6-3. DOC of DOM fractions and their percent distribution by ultrafiltration in raw water, treated wastewater and their treated water.

Samples	DOC of fraction (mg/L)			
	>10 kDa	3–10 kDa	1–3 kDa	< 1 kDa
Raw water				
RW BK-1	0.9 (20)	1.2 (27)	0.5 (11)	1.9 (42)
· alum 20 mg/L	0.7 (20, 22)	0.4 (12, 67)	0.5 (14, -)	1.8 (54, 0.7)
· alum 80 mg/L	0.5 (15, 49)	0.7 (21, 42)	0.3 (10, 40)	1.7 (54, 11)
· alum 80 mg/L +PAC 40 mg/L	0.3 (9, 67)	0.7 (24, 42)	0.3 (11, 40)	1.6 (56, 16)
· alum 80 mg/L +MIEX 4 mL/L	0.3 (22, 67)	0.4 (24, 67)	0.3 (21, 40)	0.5 (33, 74)
RW BK-2	0.9 (27)	0.4 (12)	0.8 (24)	1.2 (36)
· alum 20 mg/L	0.7 (32, 22)	0.4 (18, -)	0.8 (36, -)	0.3 (14, 75)
· alum 80 mg/L	0.6 (34, 34)	0.4 (23, 0)	0.3 (20, 56)	0.4 (23, 67)
· alum 80 mg/L +PAC 80 mg/L	0.2 (23, 74)	0.2 (24, 39)	0.2 (19, 75)	0.4 (34, 71)
· alum 80 mg/L +MIEX 2 mL/L	0.5 (31, 47)	0.3 (19, 27)	0.4 (25, 51)	0.4 (26, 67)
Treated wastewater				
TWW AT-1	1.0 (20)	0.6 (12)	0.9 (18)	2.5 (50)
· alum 10 mg/L	1.0 (21, -)	0.6 (13, -)	0.8 (17, 11)	2.4 (50, 4)
· alum 100 mg/L	0.6 (15, 40)	0.6 (15, -)	0.9 (22, -)	2.0 (49, 20)
· alum 100 mg/L +PAC 100 mg/L	0.6 (19, 40)	0.5 (16, 17)	0.4 (13, 56)	1.6 (52, 36)

Remark: (x, y) x is percent distribution, y is percent reduction

Table 6-3. DOC of DOM fractions and their percent distribution by ultrafiltration in raw water, treated wastewater and their treated water (Cont.).

Samples	DOC of fraction (mg/L)			
	>10 kDa	3–10 kDa	1–3 kDa	< 1 kDa
Treated wastewater				
· alum 100 mg/L +MIEX 6 mL/L	0.5 (16, 50)	0.5 (16, 17)	0.4 (13, 56)	1.7 (55, 32)
TWW AY-1	1.2 (18)	1.4 (21)	1.3 (19)	2.8 (42)
· alum 10 mg/L	1.2 (23, -)	0.7 (13, 50)	1.1 (21, 15)	2.3 (43, 18)
· alum 100 mg/L	1.1 (24, 9.4)	0.9 (20, 35)	0.9 (21, 30)	1.5 (35, 45)
· alum 100 mg/L +PAC 100 mg/L	1.1 (27, 9.9)	0.8 (21, 40)	0.9 (23, 29)	1.1 (28, 60)
· alum 100 mg/L +MIEX 6 mL/L	0.6 (19, 53)	0.7 (24, 50)	0.5 (16, 64)	1.2 (41, 56)
Mixed raw water				
RW + TWW	1.3 (23)	1.0 (18)	1.2 (22)	2.1 (37)
· alum 5 mg/L	0.6 (17, 54)	0.6 (17, 40)	0.7 (20, 42)	1.7 (46, 19)
· alum 100 mg/L	0.9 (22, 31)	0.8 (20, 17)	0.8 (20, 33)	1.6 (38, 24)
· alum 100 mg/L +PAC 80 mg/L	0.6 (19, 54)	0.6 (19, 40)	0.8 (25, 33)	1.3 (38, 38)
· alum 100 mg/L + MIEX 6 mL/L	0.5 (20, 62)	0.5 (18, 56)	0.5 (18, 64)	1.1 (44, 48)

Remark: (x, y) x is percent distribution, y is percent reduction

For the BK-2 raw water, coagulation with alum 20 mg/L and alum 80 mg/L resulted in the highest reduction of DOM fraction with MW < 1 kDa by 75 and 67% respectively. The DOM fraction 3 kDa < MW < 10 kDa and 1 kDa < MW < 3 kDa could not be reduced when using alum of 20 mg/L. When enhanced coagulation with alum 80 mg/L was used, the DOM fraction with 1 kDa < MW < 3 kDa was removed by 56% while the DOM fraction with 3 kDa < MW < 10 kDa could not be removed. When using alum combined with a PAC, the DOM fraction with 1 kDa < MW < 3 kDa, MW > 10 kDa, and MW <1 kDa were reduced by 74, 75, and 71%, respectively. While the DOM fraction with 3 kDa < MW < 10 kDa was removed by 39%. Enhanced alum coagulation with MIEX resulted in the highest reduction of DOM fraction of MW < 1 kDa by 67%. While this condition could remove the DOM fraction of MW > 10 kDa, 3 kDa < MW < 10 kDa, and 1 kDa < MW < 3 kDa by 47, 27, and 51%, respectively.

In the AT-1 treated water, coagulation with alum 10 mg/L could slightly reduce DOM fraction with 1 kDa < MW < 3 kDa and MW < 1 kDa while DOM fraction of MW >10 kDa and 3 kDa < MW < 10 kDa could not be reduced. Enhanced coagulation with alum 100 mg/L

could remove 40 and 20% of DOM fraction with MW > 10 kDa and MW < 1 kDa, respectively. While DOM fraction of 3 kDa < MW < 10 kDa and 1 kDa < MW < 3 kDa could not be reduced by alum 80 mg/L. Enhanced alum coagulation with PAC, and alum with MIEX provided the best reduction of DOM fraction of MW 1 kDa < MW < 3 kDa with the same percent reduction of 56%.

In the AY-1 treated water, coagulation with alum 10 mg/L could remove about 50% of DOM fraction with 3 kDa < MW < 10 kDa and could slightly reduce DOM fraction with 1 kDa < MW <3 kDa, and MW < 1 kDa while DOM fraction with MW >10 kDa could not be reduced. Enhanced coagulation with alum 100 mg/L could remove 35, 30, and 45% of DOM fraction with 3 kDa < MW < 10 kDa, 1 < kDa < MW <3 kDa, and MW < 1 kDa, respectively. This condition could slightly reduce DOM fraction of MW >10 kDa. Enhanced alum coagulation with PAC causes the highest DOM fraction with MW < 1 kDa reduction (60%) when compared with the other DOM fraction. Enhanced alum coagulation with MIEX efficiently removes all MW fractions. The percent removal of DOM fraction of more than 50% when using this condition. The highest removal efficiency of 64%, in this case, was observed in DOM fraction with 1 kDa < MW < 3 kDa.

In RW+TWW water, coagulation with alum 5 mg/L could reduce DOM fraction with MW > 10 kDa by 52%. The other DOM fractions were removed less than 50% under this condition. Enhanced coagulation with alum 100 mg/L could remove DOM fraction of MW > 10 kDa and 1 kDa < MW <3 kDa by 31 and 33%, respectively. The DOM fractions with 3 kDa < MW <10 kDa and MW < 1 kDa were removed less than 30% by this condition. Enhanced alum coagulation with PAC efficiently removed DOM fraction of MW > 10 kDa by 54% and could remove other MW fractions within the range from 33 to 40%. When enhanced alum coagulation with MIEX was used for treatment, the percent reduction of 62, 56, 64, and 48% was found in DOM fraction of MW >10 kDa, 3 kDa < MW <10 kDa, 1 kDa < MW <3 kDa, and MW < 1 kDa, respectively.

In summary, the enhanced coagulation with MIEX provided the best coagulation condition for all DOM fractions in all samples. Mainly, this condition mostly exhibits a higher removal the DOM fraction with 1 kDa < MW < 3 kDa and MW < 1 kDa.

b) Reduction of DOC of each organic resin fraction

Table 6-4 shows the DOC of HPO, HPI, and TPI fractions in treated waters of BK-1 and BK-2, and treated wastewater of AT-1. The DOC concentration in the water sample is the sensitive factor for organic characterizing by resin fractionation. The resin fractionation technique has a limitation in the case of water that has low DOC value. In this work, the DOC of HPO, HPI, and TPI were not available when the DOC in water was lower than 2 mg/L.

In the BK-1 raw water, the enhanced alum coagulation at dosage 20 mg/L could remove DOC of HPO, TPI, and HPI by 4.2, 21, and 38% respectively. Coagulation with alum 80 mg/L and alum coagulation with PAC could remove DOC of HPO by 41 and 62%, respectively, while the DOC of HPI could not be removed and the DOC of TPI was not detected.

Table 6-4. DOC of DOM fractions and their percent distribution by resin fractionation in raw water, treated wastewater and their treated water

Samples	DOC of fraction (mg/L)		
	HPO	TPI	HPI
Raw water			
RW BK-1	2.4 (51)	1.0 (22)	1.3 (28)
· alum 20 mg/L	2.3 (59,4.2)	0.8 (21,21)	0.8 (21,38)
· alum 80 mg/L	1.4 (52,41)	ND	1.3 (48,0)
· alum 80 mg/L +PAC 40 mg/L	0.9 (41,62)	ND	1.3 (59,0)
· alum 80 mg/L +MIEX 4 mL/L	NA	NA	NA
RW BK-2	1.5 (43)	0.7 (20)	1.3 (37)
· alum 20 mg/L	1.4 (54,4.9)	0.7 (28,0)	0.5 (19,62)
· alum 80 mg/L	0.9 (47,40)	ND	1.0 (53,23)
· alum 80 mg/L +PAC 80 mg/L	NA	NA	NA
· alum 80 mg/L +MIEX 2 mL/L	NA	NA	NA
Treated wastewater			
TWW AT-1	2.2 (46)	0.7 (16)	1.9 (39)
· alum 100 mg/L +PAC 100 mg/L	1.4 (48,36)	0.7 (24,0)	0.8 (28,56)

Remark: (x, y) x is percent distribution, y is percent reduction

NA is not available; ND is not detected

In the BK-2 raw water, the enhanced alum coagulation at dosage 20 mg/L could remove DOC of HPO and HPI by 4.9 and 62% respectively. This condition could not remove the DOC of TPI. When using alum coagulation at dosage 80 mg/L, the reduction of DOC of HPO and HPI of 40 and 23% were obtained, respectively. Under this condition, the DOC of TPI was not detected.

For the AT-1 treated water, the DOM fraction was conducted only enhanced coagulation at the optimal condition of DOC removal. Enhanced alum coagulation with PAC could remove the DOC of HPO and HPI by 36 and 56%, respectively. Under this condition, the DOC of TPI was not available.

6.3.6 DBPFPs of DOM fractions and their reduction

a) DBPFP/DOC of each organic fraction by ultrafiltration

In order to investigate the reactivity of the DBPFP of each molecular weight (MW) size fractions, all the THMFP, iodo-THMFP, HANFP and HNMFP data was normalized by DOC content of each MW size fraction to obtain specific DBPFP yield.

THMFP/DOC reduction

Figure 6-12 shows the THMFP/DOC of various MW size fractions of coagulated water of the BK-1 and BK-2 raw waters, the AT-1 and AY-1 treated wastewaters, and the raw water mixed with treated wastewater.

For the BK-1 raw water, after the coagulation by alum alone or alum with PAC, DOM fraction with MW 1-3 kDa had the highest specific THMFP followed by MW > 10 kDa, MW 3-10 kDa, and MW > 1 kDa, respectively. Coagulation by alum with MIEX 4 mL/L can effectively reduce the specific THMFP in DOM fractions with MW > 10 kDa, 3 kDa < MW < 10 kDa, and 1 kDa < MW < 3 kDa higher than those in coagulated water by alum alone and alum with PAC. Enhanced alum coagulation with PAC gave the highest reduction in the specific THMFP of the fraction with < 1 kDa. In the BK-2 raw water, coagulation by alum alone could reduce the specific THMFP of DOM in all MW fractions lower than those in coagulated water by alum with PAC or MIEX. Enhanced alum coagulation with PAC resulted in the reduction of specific THMFP of all MW fractions, except for the MW > 10 kDa, higher than those in treated water by alum with MIEX.

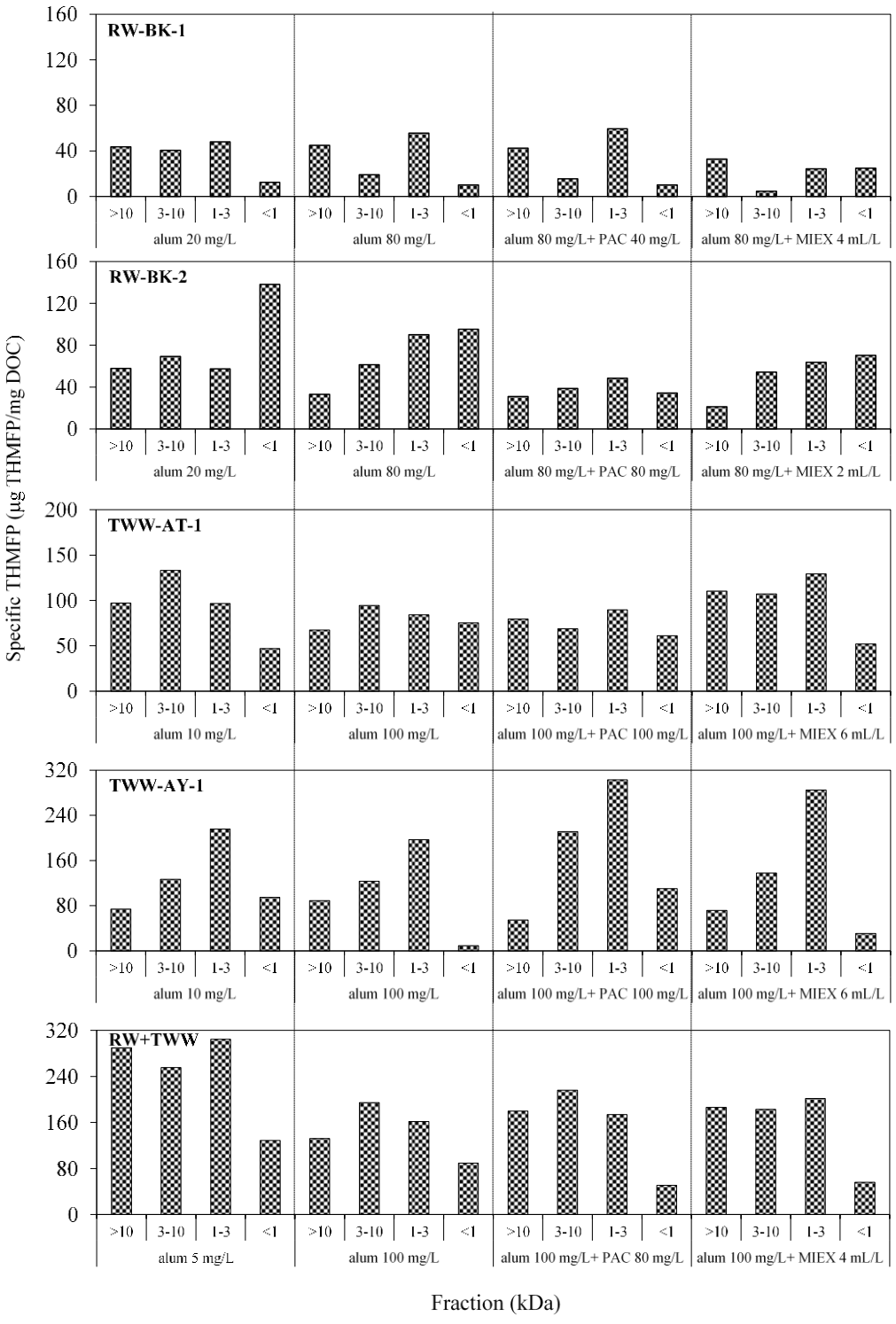


Figure 6-12. THMFP/DOC of each organic size fraction for raw water, treated wastewater, raw water mixed with treated wastewater and their treated waters by alum, alum with PAC, and alum with MIEX.

For the AT-1 treated wastewater, after the coagulation by alum alone, DOM fraction with MW 3 kDa < MW <10 kDa had the highest specific THMFP. In the coagulated water by

alum with PAC or MIEX, the highest specific THMFP occurred in the fraction with MW 1 kDa < MW < 3 kDa. In AY-1 treated wastewater, after coagulation by alum alone, and alum with PAC or MIEX, DOM fraction with MW 1 kDa < MW < 3 kDa had the highest specific THMFP. Coagulation by alum at 100 mg/L could reduce the specific THMFP of DOM fraction with MW < 1 kDa higher than those in coagulated water by alum with PAC or MIEX, and alum at 10 mg/L. In RW+TWW water, relatively high specific THMFP values (129 to 304 μg/mg DOC) of all MW fraction in the coagulated water at alum 5 mg/L were observed. Enhanced alum coagulation with PAC resulted in the reduction of specific THMFP of DOM fraction with MW < 1 kDa, higher than those in coagulated water by alum with MIEX, alum at 100 mg/L, and alum at 5 mg/L, respectively.

Iodo-THMFP/DOC reduction

The iodo-THMFP/DOC of various MW size fractions in the BK-1 coagulated water is presented in Figure 6-13. By enhanced alum coagulation with MIEX 4 mL/L, DOM fraction with MW >10 kDa gave the highest specific iodo-THMFP of 16 μg/mg DOC, indicating the fraction with > 10 kDa was highly reactive in the reaction with chlorine to form iodo-THMs. DOM fraction with MW > 10 kDa gave the highest specific iodo-THMFP concentration in treated water of the BK-2 by alum with MIEX 2 mL/L than those in treated water by alum alone or alum with PAC.

For AT-1 treated wastewater after alum coagulation with PAC 100 mg/L, DOM fraction with MW > 10 kDa was observed to be the most active organic fraction to form iodo-THMs during chlorination. In AY-1 treated wastewater after alum coagulation and enhanced alum with PAC or MIEX, the highest specific iodo-THMFP occurred in DOM fraction of MW < 1 kDa. Specific iodo-THMFP concentrations of the fractions with < 1 kDa were 94, 82, 80, and 47 μg/mg DOC in the treated water by alum with PAC, alum with MIEX, alum 100 mg/L, and alum 10 mg/L, respectively.

Similar to the treated water of the AY-1, DOM fraction with MW < 1 kDa fraction in treated water of the RW+TWW by alum alone and enhanced alum coagulation with PAC or MIEX gave the highest specific iodo-THMFP. The specific iodo-THMFP concentrations were 37, 24, 11, and 2 μg/mg DOC in the treated water by alum with PAC, alum 100 mg/L, alum with MIEX, and alum 10 mg/L, respectively.

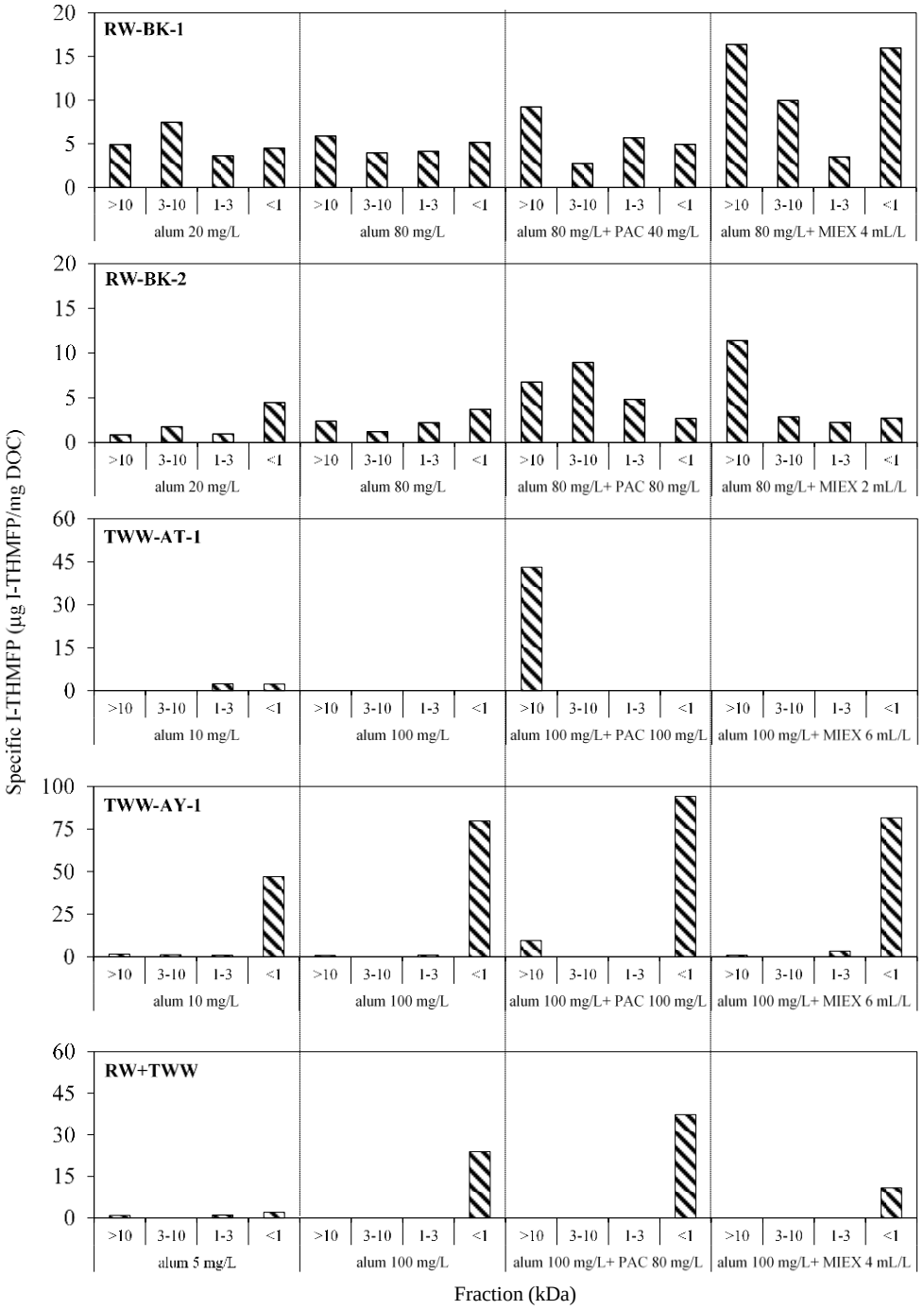


Figure 6-13. I-THMFP/DOC of each organic size fraction for raw water, treated wastewater, raw water mixed with treated wastewater and their treated waters by alum, alum with PAC, and alum with MIEX.

HANFP/DOC reduction

The HANFP/DOC of various MW size fractions in coagulated water is shown in Figure 6-14. DOM fraction with MW > 10 kDa and 1-3 kDa gave relatively high specific HANFP concentration in treated water of the BK-1 by alum alone, and alum with PAC. Enhanced alum coagulation with MIEX can effectively reduce the specific HANFP in DOM fraction with MW > 10 kDa, 3 kDa < MW < 10 kDa, and 1 kDa < MW < 3 kDa higher than those in treated water of the BK-1 by alum alone and alum with PAC. By enhanced alum coagulation with MIEX, DOM fraction with MW < 1 kDa gave the specific HANFP higher than other fractions, indicating the most active organic fraction to form HANs during chlorination. For BK-2 raw water, DOM fraction with MW < 1 kDa gave the highest specific HANFP concentration after coagulation by alum alone and alum with PAC or MIEX. The specific HANFP concentrations of the fractions with MW < 1 kDa were 44, 54, 46, and 36 μg/mg DOC in the treated water by alum with PAC, alum 20 mg/L, alum with MIEX, and alum 80 mg/L, respectively.

For AT-1 treated wastewater after coagulation with alum alone, DOM fraction with MW 1 kDa < MW < 3 kDa was observed to be the most active organic fraction to form HANs higher than those in coagulated water by enhanced coagulation with PAC or MIEX. By alum coagulation with MIEX 6 mL/L, DOM fraction with MW > 10 kDa gave the highest specific HANFP concentration in coagulated water of the AT-1, indicating the most active organic fraction to form HANs during chlorination. In AY-1 treated wastewater after coagulation with alum 10 mg/L, DOM fraction with MW < 1 kDa gave the specific HANFP of 3.9 μg/mg DOC higher than those in coagulated water by alum at 100 mg/L and enhanced alum coagulation by PAC or MIEX.

In RW+TWW water after alum coagulation with MIEX, DOM of all MW fractions gave the specific HANFP in ranging from 1.2 to 1.5 μg/mg DOC relatively higher than those in the treated water by alum alone, and alum with PAC. DOM fractions with MW 3 kDa < MW < 10 kDa and MW < 1 kDa in the treated water by alum with MIEX could form the high value of HANs during chlorination.

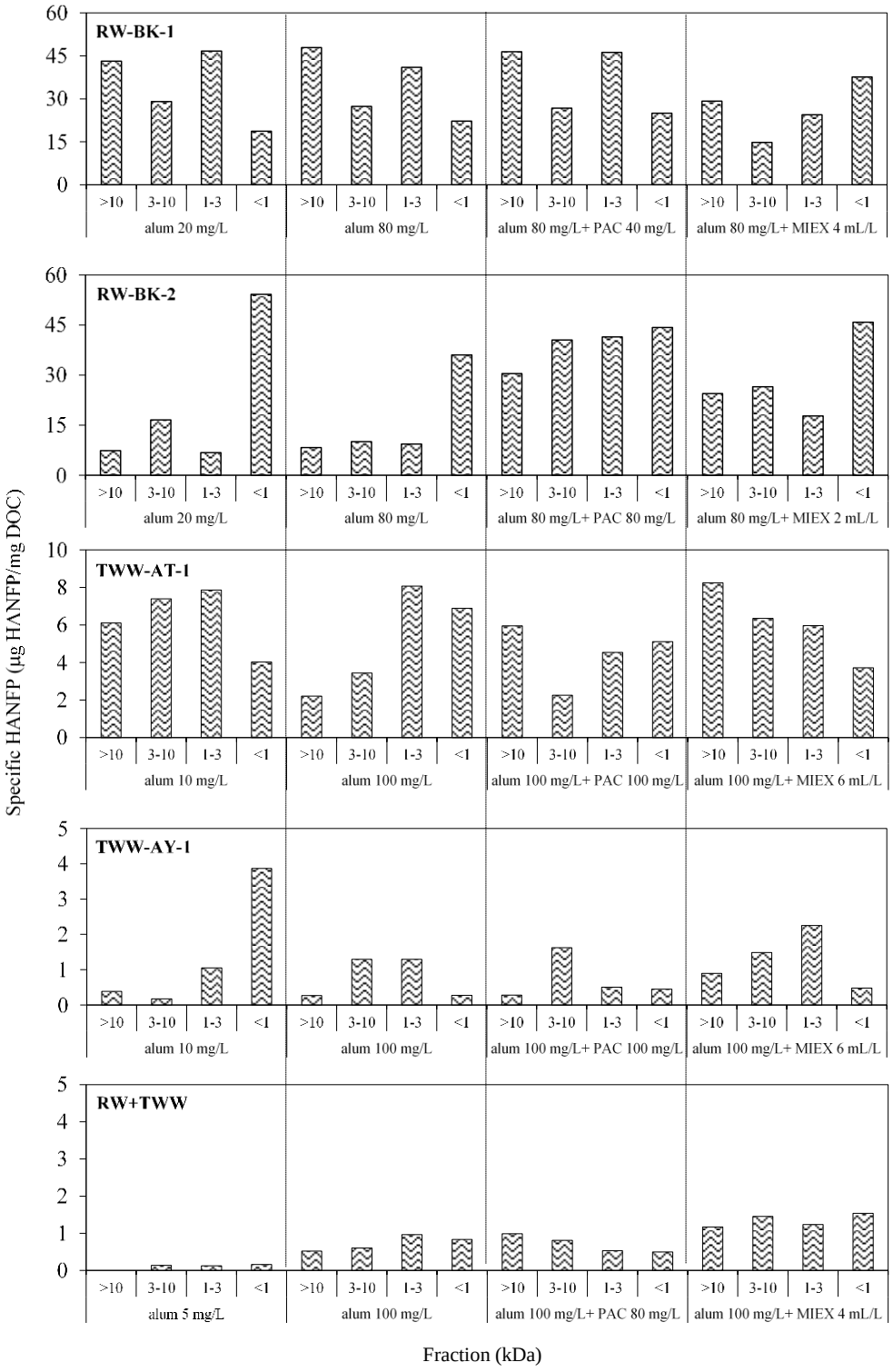


Figure 6-14. HANFP/DOC of each organic size fraction for raw water, treated wastewater, raw water mixed with treated wastewater and their coagulated waters by alum, alum with PAC, and alum with MIEX.

HNMFP/DOC reduction

The TCNMFP/DOC of various MW size fractions in treated water of the BK-1 and BK-2 raw waters and the AY-1 treated wastewater is shown in Figure. 6-15. DOM fraction with MW > 10 kDa gave the highest specific TCNMFP concentration in the BK-1 water after coagulation by alum alone and alum with PAC. By enhanced alum coagulation with MIEX, DOM fraction with MW >10 kDa, 3 kDa <MW < 10 kDa, and 1 kDa < MW <3 kDa gave the specific TCNMFP lower than those in treated water by using alum alone, and alum with PAC. DOM fraction with MW < 1 kDa in the treated water by alum with MIEX was observed to be the most active fraction to form HANs during chlorination.

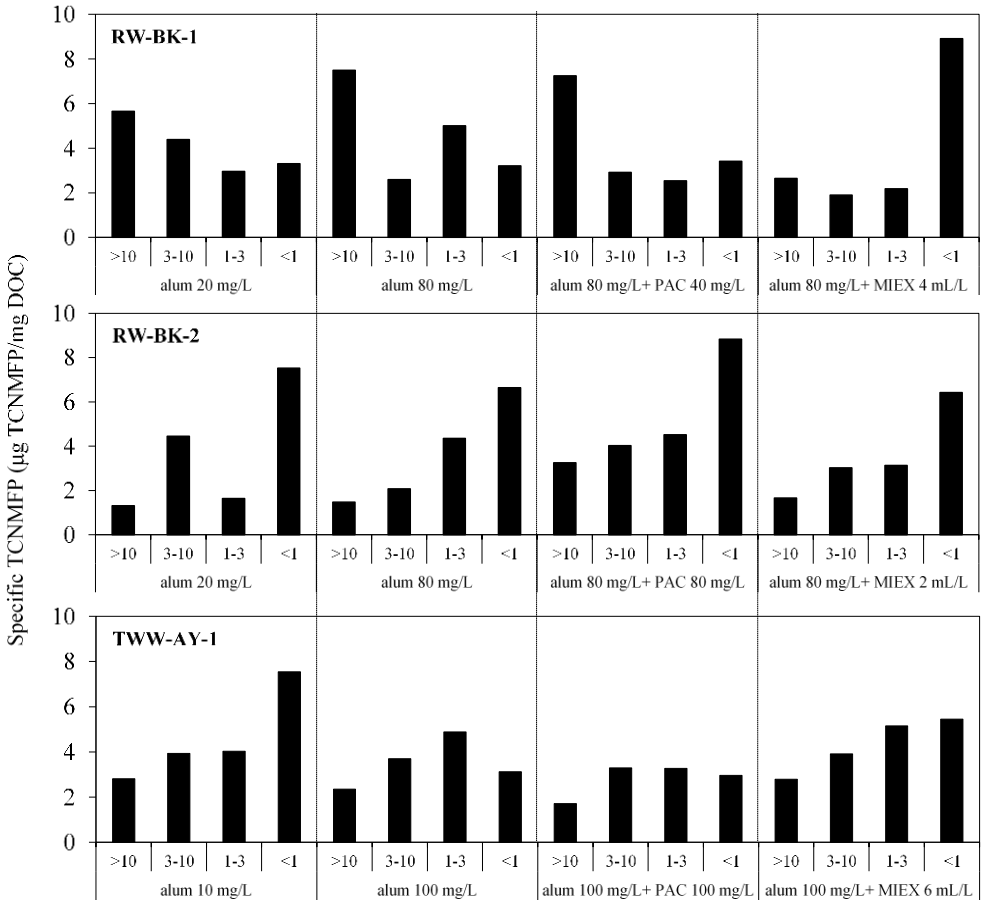


Figure 6-15. HNMFP/DOC of each organic size fraction for raw water and treated wastewater, and their coagulated waters by alum, alum with PAC, and alum with MIEX

For BK-2 raw water, DOM fraction with MW < 1 kDa in coagulated water by enhanced alum coagulation with PAC had the highest specific TCNMFP of 9 μg/mg DOC, followed by the fraction in treated water by alum at 20 mg/L, alum at 80 mg/L, and alum with MIEX. The coagulation by alum with MIEX could reduce the specific TCNMFP of DOM fractions with 3

kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa compared to those in the BK-2 water after coagulation by alum alone, and alum with PAC.

In AY-1 treated wastewater, DOM fraction with MW < 1 kDa after coagulation with alum 10 mg/L was observed to be the most active organic fraction to form TCNM. By alum coagulation with PAC, the specific TCNMFP concentrations of all MW fractions were lower than those in the coagulated water by alum alone, and by alum with MIEX.

b) DBPFP/DOC of each organic fraction by resin fraction

In order to investigate the reactivity of the DBPFP of each HPO, HPI and TPI fractions, all the THMFP, iodo-THMFP, HANFP, and TCNMFP data was normalized by DOC content of each organic fraction to obtain specific DBPFP yield. Figure 6-16 shows the specific DBPP of HPO, HPI and TPI fractions in treated water of BK-1 and BK-2, and treated wastewater of AT-1. The specific DBPPs of HPI, HPI, and TPI fractions by optimum alum coagulation for the BK raw waters, and optimum condition using enhanced coagulation for the AT-1 treated wastewater were considered in the work.

It was found that TPI gave the highest specific THMFP in the treated waters of BK-1, BK-2 and AT-1. This indicating that the TPI fraction was highly reactive in the reaction with chlorine to form THMs. Specific THMFP of the three organic fractions, from high to low, were TPI, HPO, and HPI, respectively. In the treated water of BK-1 and BK-2 by alum alone, the HPI fraction was the most active organic fraction to form iodo-THMs and HANs during chlorination. Moreover, the HPI fraction was the most reactive in the reaction with chlorine to form TCNM of HNM species in the coagulated water of TWW AT-1 by alum with PAC.

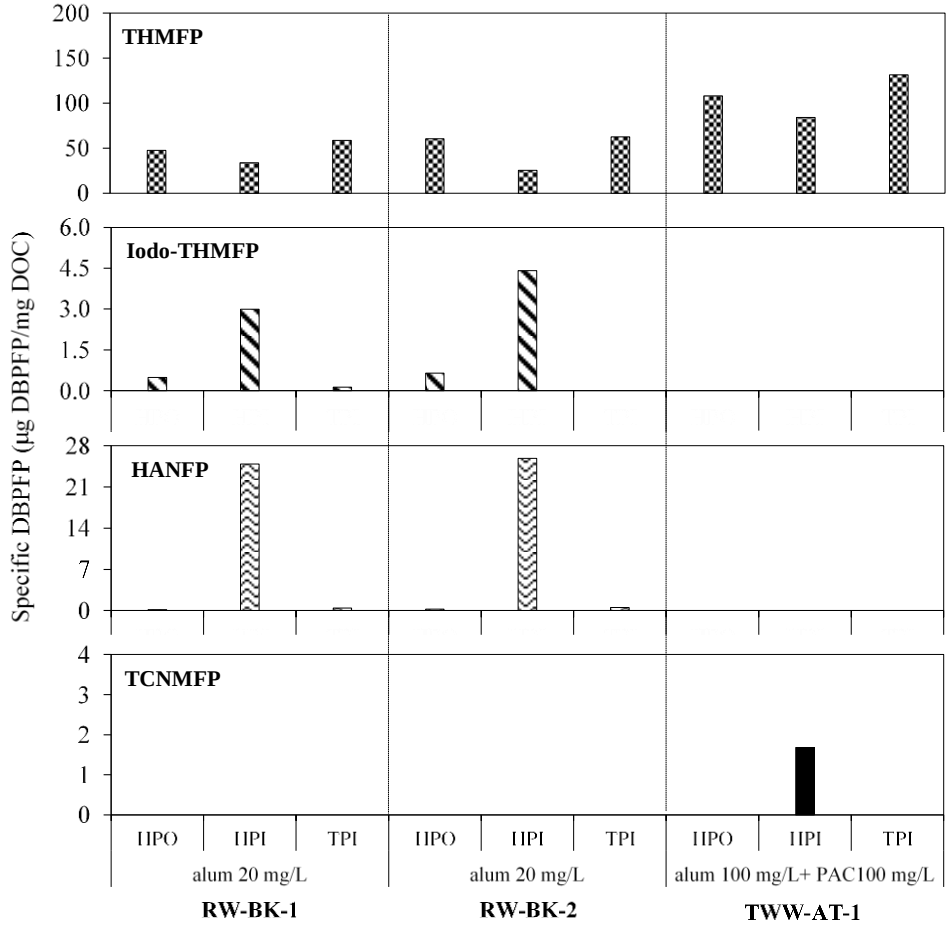


Figure 6-16. DBPFP/DOC of HPO, HPI and TPI for raw water and treated wastewater, and their coagulated waters by alum, and alum with PAC.

6.3.7. FEEM analysis of DOM fractions at optimal coagulation

a) FEEM of DOM fractions by resin fractionation

The fluorescent intensities at each fluorescent peak of tyrosine-like, tyrosine- and protein-like, tryptophan-like, and humic- and fulvic acid-like of each MW size fractions of raw water, treated wastewater, raw water mixed with treated wastewater after the coagulation are illustrated in Figure. 6-17.

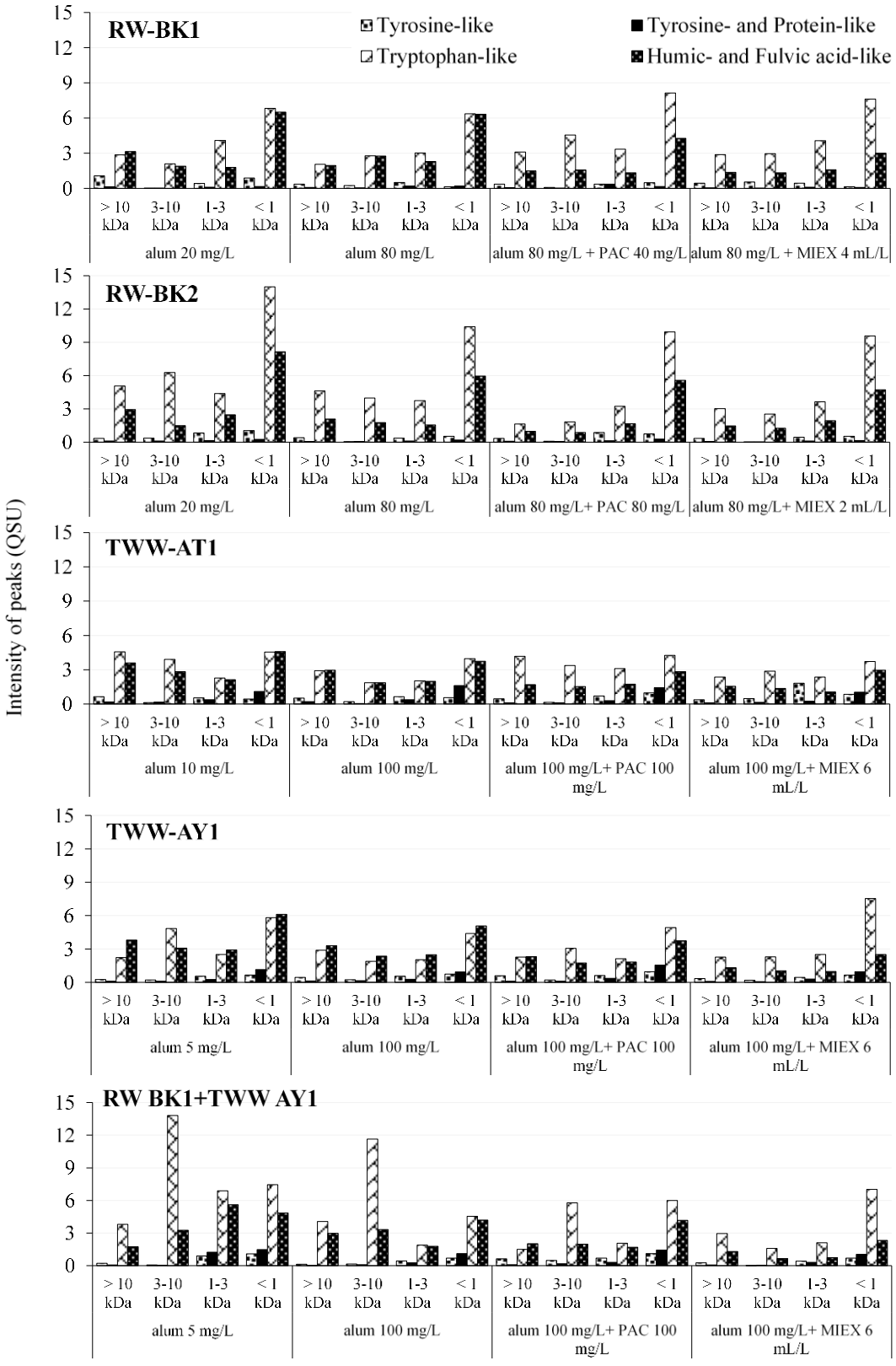


Figure 6-17. Fluorescence intensity of DOM size fractions for raw water, treated wastewater, raw water mixed with treated wastewater after coagulation by alum, alum with PAC, and alum with MIEX.

The fluorescent substances found in treated water of the BK-1 and BK-2 in all size fractions were tyrosine-like, tyrosine- and protein-like, tryptophan-like, and humic- and fulvic acid-like. The highest fluorescence intensities of tryptophan- like and humic- and fulvic acid-like substances in DOM fraction were MW < 1 kDa were determined. Enhanced coagulation for the raw waters of BK-1 and BK-2 could reduce humic- and fulvic acid-like substances of the fraction of MW < 1 kDa when compared with coagulation by alum alone. Based on the FEEM results of the BK-1 and BK-2 waters, the tryptophan-like substance of the fraction of MW < 1 kDa in the treated water was the most difficult to remove.

For the AT-1 treated wastewater, fluorescence intensities of tryptophan-like and humic- and fulvic acid-like substances in all MW size fractions were relatively high when coagulation with alum alone and enhanced alum coagulation with PAC were conducted. Enhanced alum coagulation with MIEX and coagulation with alum 100 mg/L could better reduce tryptophan-like substances of the fractions with MW > 10, 3 kDa < MW <10 kDa, and 1 kDa < MW < 3 kDa than those in the treated water after coagulation by alum at 10 mg/L and alum with PAC 100 mg/L.

For the AY-1 treated wastewater**,** enhanced alum coagulation with MIEX was highly effective in reducing the fluorescence intensities of humic- and fulvic acid-like substances of all MW size fractions in comparison to the coagulation by alum alone or alum with PAC. However, enhanced alum coagulation with MIEX could slightly reduce the fluorescence intensity of tryptophan-like substances of the fractions with MW < 1 kDa.

For the RW+TWW water, fluorescence intensities of tryptophan- like substances in all MW size fractions were detected in the high level when coagulation with only alum at 5 mg/L was conducted. Enhanced alum coagulation with MIEX could better reduce tryptophan-like substances of the fractions with MW > 10, 3 kDa < MW < 10 kDa, and 1 kDa < MW < 3 kDa than those in the treated water after coagulation by alum alone and alum with PAC 100 mg/L.

b) Reduction of HPO, HPI and TPI fractions

The fluorescent intensities at each of the fluorescent peak of tyrosine-like, tyrosine- and protein-like, tryptophan-like, and humic- and fulvic acid-like of each HPO, HPI, and TPI fractions in the FEEMs of raw water and treated wastewater after the coagulation are illustrated in Figure. 6-18. The fluorescent intensities of HPO, HPI, and TPI fractions at optimal

coagulation for the BK raw waters and enhanced coagulation for the treated wastewater of AT-1 were considered in work.

As can be seen from Figure. 6-18, tryptophan-like substances in HPO in treated water of the BK-1, BK-2, and AT-1 exhibited the highest in fluorescent intensity followed by TPI and HPI fractions. Humic- and fulvic acid-like substances of HPO were the dominant compound in the treated water of BK-1 and BK-2, while humic- and fulvic acid -like substances of HPI were the dominant compound in the treated water of AT-1. Tyrosine-like substances in HPO was detected in the high fluorescent intensity level in treated waters of BK-1, BK-2, and AT-1. The results showed that both HPO and HPI were the significant DBPFP precursors in the treated water; thus the coagulation technique must be mainly focused on the HPO and HPI removal.

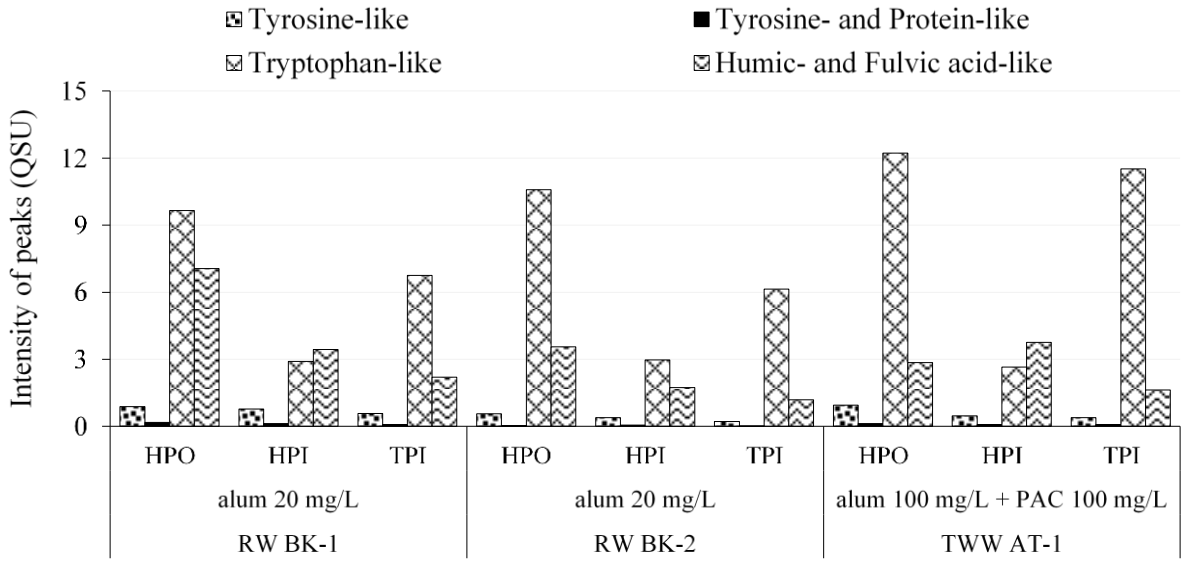


Figure. 6-18. Fluorescence intensity of DOM resin fractions for raw water and treated wastewater, and their coagulated waters by alum, and alum with PAC.

6.3.8. Chemical classes in coagulated water

The treated waters at the optimal conditions were selected for investigation on the reduction of chemical classes. For the RW BK-1, aliphatic hydrocarbon in the RW BK-1 could be reduced by alum at 20 and 80 mg/L (Case 1 and Case 2) by about 58% (Table 6-5). The 48 and 44% reduction in aliphatic hydrocarbon were obtained with 80 mg/L alum combined with 40 mg/L PAC (Case 3), and 80 mg/L alum followed by 4 mL/L MIEX (Case 4), respectively. This indicated that coagulation with alum alone was more effective in reducing aliphatic hydrocarbon than enhanced alum coagulation with PAC or MIEX. The coagulation with alum

alone (Case 1 and 2) and alum at 80 mg/L combined with PAC or MIEX (Case 3 and 4) reduced 18-24% of aromatic hydrocarbon. The enhanced alum coagulation with MIEX provided the best reduction of aromatic hydrocarbon. An alum at 80 mg/L (Case 2) provided the best reduction in organic nitrogen from the RW BK-1 by 75%, followed by enhanced alum coagulation with 4 mL/L MIEX (Case 4). Aldehydes in the RW BK-1 could be reduced up to 100% when using alum at 80 mg/L (Case 2) and enhanced alum coagulation with MIEX (Case 4). Ketone in the RW BK-1 could be reduced by 100, 70, 70, and 60% when using alum at 80 mg/L, alum at 20 mg/L, alum with MIEX, and alum with PAC, respectively. The enhanced alum coagulation with 4 mL/L MIEX (Case 4) had the capability in removal of alcohol class in the RW BK-1 by 20%. Furan of 100 % could be reduced by coagulation with alum alone or enhanced alum coagulation with PAC or MIEX for the RW BK-1. In almost all cases, coagulation could not reduce phenol, ester, ether, and carboxylic acid classes.

Table 6-5 Summary of the prominent major fragments of each chemical class in the raw water of BK-1 and their reduction

		Percent distributions of the chemical classes of DOM in the RW BK-1			
Chemical class	RW BK-1	Coagulation		nhanced coagulation wit PAC	Enhanced coagulation with MIEX
		(1) alum 20 mg/L	(2) alum 80 mg/L	(3) alum 80 mg/L + PAC 40 mg/L	(4) alum 80 mg/L + MIEX 4 mL/L
AL	44.7	18.7 (58)	18.9 (58)	23.4 (48)	25.3 (44)
AR	5.2	4.1 (18)	3.9 (22)	4.0 (20)	3.8 (24)
PN	11.1	13.7 (-)	11.2 (0)	14.7 (-)	11.1 (-)
ON	7.6	2.6 (68)	2.0 (75)	7.0 (13)	2.4 (70)
AH	0.4	0.7 (-)	0 (100)	1.0 (-)	0 (100)
KT	1.2	0.3 (70)	0 (100)	0.4 (60)	0.3 (70)
Alc	8.3	8.9 (-)	11.4 (-)	10.8 (-)	6.4 (20)
ES	0	0 (-)	0 (-)	0 (-)	1.5 (-)
ET	7.7	18.7 (-)	42.5 (-)	29.4 (-)	36.6 (-)
CA	0	0 (-)	0 (-)	0 (-)	4.2 (-)
FR	1.6	0 (100)	0 (100)	0 (100)	0 (100)
OT	1.0	0.9 (10)	0 (100)	1.6 (-)	4.4 (-)
Unknown	11.3	31.4 (-)	10.0 (8)	7.7 (30)	4.0 (64)

AL = aliphatic, AR = aromatic hydrocarbon, PN = phenol, ON = organic nitrogen, AH =aldehydes, KT = ketones, Alc = alcohol, ES = ester, ET = ether, CA = carboxylic acid, FR = furan, and OT = others, ( ) is the percent reduction (%)

For the RW BK-2 water, in Table 6-6, the reductions of the aliphatic hydrocarbon were 25 and 22% in the case of coagulation enhanced by PAC and MIEX, respectively higher than those in the case of coagulation with alum alone (Case 1 and Case 2). Aromatic hydrocarbon class decreased to 25 and 18% when using alum at 20 mg/ L, and alum at 80 mg/L combined with MIEX at 2 mL/L. Enhanced coagulation by MIEX at 2 mL/L provide the phenol reduction by 44%. Alum at 20 mg/L coagulation (Case 1), and alum at 80 mg/L coagulation with PAC at 80 mg/L (Case 3) reduced the organic nitrogen from the raw water of RW BK-2 by 17% and 11%, respectively. Furan of 100 % could reduce by coagulation or enhanced coagulation for the RW BK-2. In all cases, ketone was completely reduced, except for the coagulation enhanced by MIEX (case 4). The alum coagulation at 2 mL/L MIEX (Case 4) had capability in the removal of alcohol class by 23%. Aldehyde and ether classes were not reduced by coagulation or enhanced coagulation for the RW BK-2.

Table 6-6 Summary of the prominent major fragments of each chemical class and their reduction in the raw water of BK-2

	Percent distributions of the chemical classes of DOM in the RW BK-2				
Chemical class	Raw water (RW BK-2)	Coagulation		Enhanced coagulation with PAC	Enhanced coagulation with MIEX
		(1) alum 20 mg/L	(2) alum 80 mg/L	(3) alum 80 mg/L + PAC 80 mg/L	(4) alum 80 mg/L + MIEX 2 mL/L
AL	24.2	21.2 (13)	20.6 (15)	18.1 (25)	18.9 (22)
AR	3.9	2.9 (25)	7.6 (-)	4.8 (-)	3.2 (18)
PN	10.8	11.1 (0)	12.0 (-)	10.9 (-)	6.0 (44)
ON	6.1	4.5 (17)	7.0 (-)	5.4 (11)	6.1 (0)
FR	0.3	0 (100)	0 (100)	0 (100)	0 (100)
AH	0	0	0.6 (-)	1.0 (-)	0
KT	0.5	0 (100)	0 (100)	0 (100)	0.6 (-)
Alc	9.0	9.7 (-)	8.4 (7)	10.6 (-)	6.9 (23)
ES	0	0	0	0	0
ET	12.8	44.3 (-)	24.1 (-)	43.9 (-)	48.8 (-)
OT	1.7	1.5 (25)	1.7 (0)	2.2 (-)	2.0 (-)
Unknown	30.6	4.8 (85)	18.1 (41)	3.0 (90)	7.5 (75)

AL = aliphatic, AR = aromatic hydrocarbon, PN = phenol, ON = organic nitrogen, FR = furan, AH =aldehydes, KT = ketones, Alc = alcohol, ES = ester, ET = ether, and OT = others, ( ) is the percent reduction (%)

For the RW+TWW water, in Table 6-7, alum coagulation enhanced by MIEX at 4 mL/L reduced aliphatic hydrocarbon by 21%. In all cases, the aromatic hydrocarbon class of the RW+TWW water was almost reduced by the coagulation with alum at 5 mg/L and the alum enhanced with PAC. Organic nitrogen class was reduced after coagulation by alum at 5 mg/L. The coagulation by alum alone or enhanced alum coagulation by PAC had the capability in removal of aldehyde, ketone, ester, and furan classes. In all cases, the carboxylic acid class was completely reduced, except for the alum coagulation enhanced by PAC (case 3). Phenol and alcohol classes were not reduced by coagulation or enhanced coagulation for the RW+TWW water.

Table 6-7 Summary of the prominent major fragments of each chemical class and their reduction in the raw water mixed with treated wastewater (RW+TWW)

	Percent distributions of the chemical classes of DOM in the RW+TWW				
Chemical class	RW+TWW	Coagulation		Enhanced coagulation with PAC	Enhanced coagulation with MIEX
		(1) alum 5 mg/L	(2) alum 100 mg/L	(3) alum 100mg/L + PAC 80 mg/L	(4) alum 100 mg/L + MIEX 4 mL/L
AL	17.3	30.1 (-)	29.7 (-)	18.9 (-)	13.6 (21)
AR	8.4	1.4 (83)	4.0 (52)	1.4 (83)	2.7 (68)
PN	0	3.0 (-)	4.4 (-)	4.5 (-)	0
ON	9.1	7.1 (22)	10.0 (-)	12.2 (-)	9.6 (-)
AH	2.7	0 (100)	0 (100)	1.8 (33)	4.5 (-)
KT	1.8	3.7 (-)	0.2 (89)	0.3 (83)	3.1 (-)
Alc	3.6	14.0 (-)	24.4 (-)	10.1 (-)	10.1 (-)
ES	2.4	1.7 (29)	2.7 (-)	0 (100)	3.0 (-)
ET	3.3	8.9 (-)	2.8 (15)	7.3 (-)	30.7 (-)
CA	0.4	0 (100)	0 (100)	2.3 (-)	0 (100)
FR	0.8	0.6 (25)	0 (100)	0.3 (63)	7.1 (-)
OT	6.4	9.6 (-)	6.3 (2)	9.0 (-)	7.6 (-)
Unknown	44	19.7 (55)	15.5 (65)	32.0 (27)	7.9 (82)

AL = aliphatic, AR = aromatic hydrocarbon, PN = phenol, ON = organic nitrogen, AH =aldehydes, KT = ketones, Alc = alcohol, ES = ester, ET = ether, CA = carboxylic acid, FR = furan, and OT = others, ( ) is the percent reduction (%)

With regard to the chemical class reduction in the TWW AT-1 water (Table 6-8), coagulation with alum at 10 mg/L, alum at 100 mg/L, and alum combined with PAC at 100 mg/L or MIEX at 6 mL/L could not reduce the aliphatic hydrocarbon class. Aromatic hydrocarbon class decreased to 10% when using alum combined with PAC at 100 mg/L. Coagulation at alum 100 mg/L could reduce organic nitrogen class of 77%. Enhanced alum coagulation with PAC, alum combined with MIEX, and alum alone at 100 mg/L provided the ether class reduction by 64, 45, and 44%, respectively. Ketone class was completely reduced by the enhanced alum coagulation with MIEX. Alcohol class of the TWW AT-1 was not reduced by both alum coagulation and enhanced coagulation.

Table 6-8 Summary of the prominent major fragments of each chemical class and their reduction in the treated wastewater of AT-1

	Percent distributions of the chemical classes of DOM in the TWW AT-1				
Chemical class	TWW AT-1	Coagulation		Enhanced coagulation with PAC	Enhanced coagulation with MIEX
		(1) alum 10 mg/L	(2) alum 100 mg/L	(3) alum 100 mg/L + PAC 100 mg/L	(4) alum 100 mg/L + MIEX 6 mL/L
AL	15.3	22.6 (-)	18.9 (-)	20.4 (-)	36.7 (-)
AR	2.1	22.2 (-)	2.2 (-)	1.9 (10)	2.1 (0)
PN	0	0	1.2 (-)	2.7 (-)	0.7 (-)
ON	5.3	4.9 (8)	1.2 (77)	10.6 (-)	6.6 (-)
AH	0	4.0 (-)	0	0	3.0 (-)
ES	0	0	0	0.4 (1)	3.5 (-)
ET	52.1	0	29.2 (44)	18.6 (64)	28.7 (45)
KT	0.4	2.6 (-)	1.8 (-)	4.6 (-)	0 (100)
Alc	4.4	23.5 (-)	17.1 (-)	25.0 (-)	10.8 (-)
FR	0	0.5 (-)	0.7 (-)	0.9 (-)	0
CA	0	0	0.4 (-)	0	0
OT	1.8	11.9 (-)	4.5 (-)	14.0 (-)	3.7 (-)
Unknown	18.9	7.8 (58)	23.0 (-)	0.9 (95)	4.1 (78)

AL = aliphatic, AR = aromatic hydrocarbon, PN = phenol, ON = organic nitrogen, AH =aldehydes, ES = ester, ET = ether, KT = ketones, Alc = alcohol, FR = furan, CA = carboxylic acid, and OT = others, ( ) is the percent reduction (%)

For the TWW AY-1 water (Table 6-9), only 6% of aliphatic and aromatic hydrocarbon was reduced when using alum at 100 mg/L combined with PAC at 100 mg/L. Coagulation by alum at 5 mg/L, alum at 100 mg/L, alum with PAC, and alum with MIEX provided the organic nitrogen reduction by 53, 67, 69 and 52%, respectively. Only 1% of ether class was reduced when using alum at 5 mg/L. In all cases, phenol, aldehyde, ketone, ester, alcohol and furan classes were not reduced by coagulation or enhanced coagulation for the TWW AY-1.

Table 6-9 Summary of the prominent major fragments of each chemical class and their reduction in the treated wastewater of AY-1

	Percent distributions of the chemical classes of DOM in the TWW AY-1				
Chemical class	TWW AY-1	Coagulation		Enhanced coagulation with PAC	Enhanced coagulation with MIEX
		(1) alum 5 mg/L	(2) alum 100 mg/L	(3) alum 100 mg/L + PAC 100 mg/L	(4) alum 100 mg/L + MIEX 6 mL/L
AL	14.2	28.7 (-)	24.0 (-)	25.3 (6)	28.4 (-)
AR	1.8	3.6 (-)	2.4 (-)	1.7 (6)	2.4 (-)
PN	0	5.6 (-)	6.9 (-)	4.5 (-)	0 (-)
ON	18.2	8.5 (53)	6.0 (67)	5.6 (69)	8.8 (52)
AH	0	0	0	0	6.1 (-)
KT	0	1.6 (-)	2.7 (-)	1.3 (-)	0.4 (-)
ET	22.8	21.8 (1)	9.9 (-)	11.3 (-)	0
ES	0	1.3 (-)	1.1 (-)	0	0
Alc	5.6	13.4 (-)	22.5 (-)	17.9 (-)	11.5 (-)
FR	0	0.5 (-)	0	0.4 (-)	0.7 (-)
OT	0.6	8.9 (-)	3.6 (-)	2.4 (-)	30.5 (-)
Unknown	36.7	6.1 (83)	20.8 (43)	29.6 (19)	11.4 (69)

AL = aliphatic, AR = aromatic hydrocarbon, PN = phenol, ON = organic nitrogen, AH =aldehydes, KT = ketones, ET = ether, ES = ester, Alc = alcohol, FR = furan, and OT = others, ( ) x is the percent reduction (%)

Chapter VII

Kinetics of DBPs formation from dissolved organic matter fractions and inorganic ions in the raw water

7.1 Introduction

Halogenated compounds formed in chlorinated water as a result of the reaction between chlorine and organic and inorganic precursors. Due to its low cost, stability and effectiveness, chlorine is the most commonly used as a disinfectant in the water treatment plant in Thailand. A primary concern for using chlorine as a disinfectant is the formation of disinfection by-products (DBPs) by the reaction between dissolved organic matter (NOM) with inorganic species and chlorine. Many DBPs have been detected in the chlorination of the water treatment plant. These include trihalomethanes (THMs), haloacetic acids (HAA), haloacetonitriles (HANs), and halonitromethanes (HNMs).

THMs are one of the carbonaceous DBPs (C-DBPs), which are the most frequently detected in chlorinated water (Rook, 1974; Richardson, 2011). Nitrogenous DBPs (N-DBPs) including HANs and HNMs are in general, present in the water supply at a much lower level than THMs (Bond et al., 2011; Liew et al., 2016). The presence of bromide ion (Br^-) and/or iodide ion (I^-) in water were important factors on the formation and speciation of bromo- and iodo-organic DBPs such as iodinated THMs (I-THMs) and THMs (Jones et al., 2012; Liu et al., 2011). The I-THMs, HANs, and HNMs are reported to be more toxic than THMs (Muellner et al., 2007; Richardson et al., 2007, 2008; Woo et al., 2002).

The formation of DBPs is a function of several variables such as type and amount of DOM, pH and temperature of water, water characteristics, contact time between chlorine and DOM, and the presence of inorganic compounds such as bromide, iodide, and ammonia (Najm et al. 1994; Krasner, 2009; Liang and Singer, 2003; Ye et al., 2011). A mathematical predictive model, therefore, is essential and should be examined on the DBP formation in order to control DBP formation in water for human health and to assure an appropriate treatment aimed at DBPs or their precursors' removal.

This present study is selected raw water of the Bangkhen water treatment plant (RW–1 and RW–2, BK) and treated domestic wastewaters from Ang thong province (TWW–1, AT) and Ayuthaya province (TWW–1, AY) as the water sample. The influences of dissolved organic carbon (DOC), dissolved organic nitrogen (DON), DOC/DON, iodide and bromide

containing the water samples on the THMs, I-THMs, HANs, and HNMs formation during chlorination were determined. The effect of retention time on the formation of the mentioned DBPs of the raw water and treated water was also examined. Besides, the kinetics of DOM in terms of the molecular weight (MW) size fractions and the resin fractions of hydrophobic (HPO), transphilic (TPI) and hydrophilic (HPI), with chlorine on the DBPs formation were investigated. The obtained results could be helpful for researchers and water treatment plant operator to understand the DBPs formation and to prioritize the management of the high reactive disinfection by-product formation potential (DBPFP) for control the DBP formation.

7.2 Experimental procedure

In this experiment, the effect of iodide and bromide concentrations, DOC, and DON of reaction on the formation of C-DBPs and N-DBPs was conducted. The variation parameters were iodide, bromide, DOC, DON, DOC/DON, and reaction times. The raw water samples (RW−1 and RW−2, BK), treated wastewater (TWW−1, AT and TWW−1, AY) were used for this experiment. For the formation of C-DBPFP and N-DPBFP analysis, treated wastewater (TWW−1, AY) was used to mix raw water of the WTP (RW−1, BK) to obtain water samples that have DOC (~3.2 to 5.6 mg/L), DON (~0.20 to 1.22 mg N/L), and DOC/DON (~5 to 29). The iodide and bromide were added into the raw water of the WTP (RW−1, BK) to obtain water samples that have iodide (~0.5 to 5 µg/L) and bromide (~0.1 to 10 mg/L). All water samples of each experiment were measured for their trihalomethane formation potential (THMFP), haloacetonitrile formation potential (HANFP), iodo-THMFP (I-THMFP), and halonitromethane formation potential (HNMFP). For the kinetic of precursors on the formation of carbonaceous-DPBFP and nitrogenous-DPBFP analysis, the treated water (coagulation at alum 20 mg/L under controlled pH of 7 followed by sedimentation and filtered by GF/F filter) from Bangkhen WTP was fractionated. The treated water, HPO, TPI, HPI, and DOM with MW < 1 kDa, 1 kDa < MW < 3 kDa, 3 kDa < MW < 10 kDa, and MW > 10 kDa were carried out the DBPFP test at the reaction times 3 to 72 h.

7.3 Results and discussion

7.3.1 Water sample characteristic

Raw water (RW), treated wastewater (TWW), and the RW mixed with TWW (50% v/v) were selected as water samples in this Chapter. Their water quality is summarized in Table 7-1. It must be noted that the values of DOC, DON, DOC/DON, and the formation potential of

THMs, I-THMs, HANs and TCNM concentration for the raw water and treated wastewater used for this experiment were obtained from the result in previous Chapter 4. The discussion of the DBPFP of each water samples also described in Chapter 4. DOC is a general parameter for measuring an amount of organic matter dissolved in natural water. DON is an essential precursor of N-DBPs in the water supply. Low level of DOC/DON ratio has a high density of organic nitrogen. For the RW+TWW water, the values of DOC, DON, and DOC/DON ratio were 5.1 mg C/L, 1.07 mg N/L, and 5, respectively. The result suggests that when raw water contaminated with treated wastewater, high contamination with DOM was determined.

Table 7-1 Characteristics of the water samples tested.

Samples	DOC	DON	DOC/DON	DBPFP (μg/L)			
	(mg C/L)	(mg N/L)		THMFP	I-THMFP	HANFP	TCNMFP
RW BK-1*	4.6	0.16	29	265	6.5	21	3
RW BK-2*	3.2	0.44	7	121	0.8	9	2
TW AT-1*	5.3	0.20	27	373	4.9	17	18
TW AY-1*	5.6	1.22	5	267	9.4	25	21
RW BK1+TW AY1	5.1	1.07	5	263	ND.	7	ND.

ND. is not detected
Remark**:** *Data for the raw water and treated wastewater obtained from Chapter 4.

7.3.2 Effect of iodide (I^-) and bromide (Br^-) content on the DBP formation potential (DBPFP)

The I^- and Br^- ions in water can be oxidized by chlorine to bromine and chlorine, leading to react with DOM to form brominated and iodinated DBPs subsequently. In this section, I^- in the range from 0.5 to 5 μg/L and Br^- in the range from 0.1 to 10 mg/L were added in raw water of the BK-1 to evaluate the effect on the THMFP, I-THMFP, HANFP, and TCNMFP. Various I^- and Br^-concentrations were prepared by diluting with distilled water free of iodide and bromide ions. The raw water samples were spiked with the I^- and Br^- solution.

(a) Influence of iodide content

Figure 7-1 shows the effect of iodide in raw water of the BK-1 on THMFP; chlorination experiments were performed in the presence of various concentrations of iodide added. The total THMFP decreased from 126 μg/L for 0.5 μg/L iodide concentration to 70 μg/L THMFP for 1 μg/L iodide concentration. As the iodide content increased from 1 to 5 μg/L, the total

THMFP concentration increased to 211 μg/L. The formation potential of chloroform and bromodichloromethane (BDCM) decreased initially but then their formation increased. The chloroform and BDCM species tends to increase with increasing I^- concentrations from 1 to 5 μg/L.

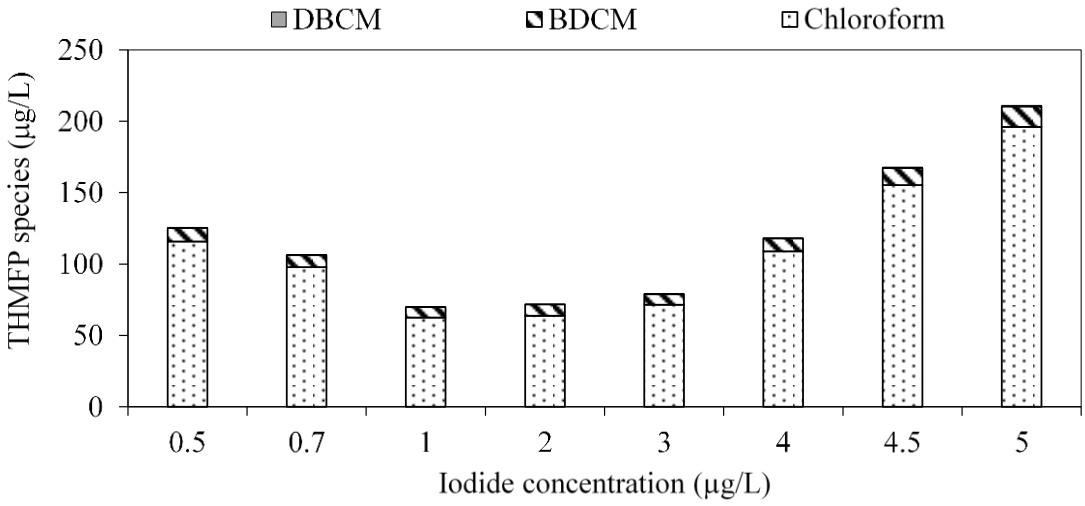


Figure 7-**1** The influence of iodide ion on the formation potential of THMs of raw water. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

As can be seen from Figure 7-2, increase in iodide dosage from 0.5 to 0.7 μg/L could lead to slightly increase in the total HANFP from 5.2 to 5.8 μg/L. When the iodide concentration increased from 0.7 to 2 μg/L, the HANFP slightly decreased. However, the maximum HANFP of 10 μg/L was taken place in iodide dose of 5 μg/L. Dichloroacetonitrile formation potential (DCANFP) decreased initially but then increased when the I^- level was increased from 2 to 5 μg/L. Trichloroacetronitrile (TCAN) did not form at the initial I^- concentration of 0.5 μg/L. The range of TCAN formation potential (TCANFP) from 0.4 to 0.9 μg/L was detected in the presence of I^- in ranging from 0.7 to 4.5 μg/L. In this study, the I-THMs and trichloronitromethane (TCNM) did not form when the iodide dosages increase from 0.5 to 5 μg/L.

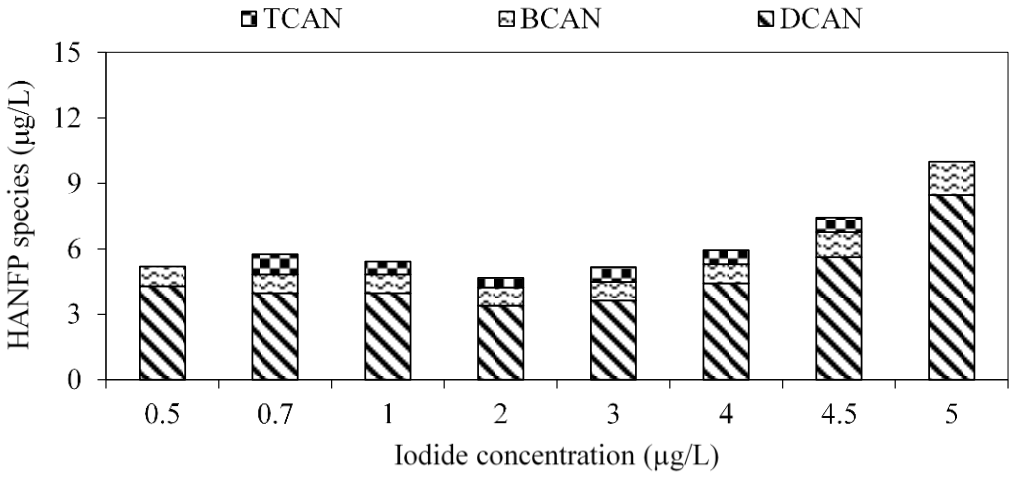


Figure 7-2 The influence of iodide ion on the formation potential of HANs of raw water. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

(b) Influence of bromide content

In this section, the effect of Br^- content (100–10,000 µg/L) of raw water on the THMFP was evaluated. The total THMFP increased by increasing Br^- concentration from 100 to 1,000 µg/L, while further increase in the Br^- level did not lead to an increase in the total THMFP (Figure 7-3). The formation of bromoform species tends to increase with increasing Br^- concentrations from 100 to 1,000 µg/ L, whereas chloroform decreased. Dibromochloromethane (DBCM) and BDCM increased initially, but then they decreased. DBDM and BDCM maximum concentration occurred at Br^-concentration of 500 and 200 µg/L, respectively.

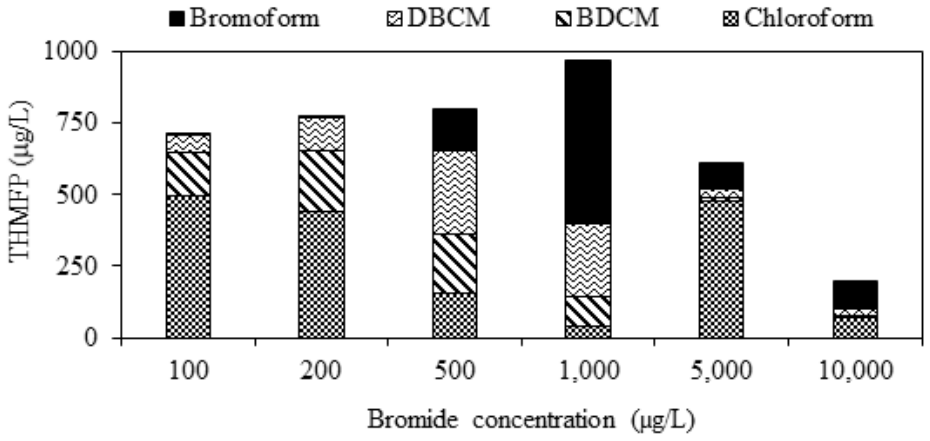


Figure 7-**3** The influence of bromide ion on the formation potential of THMs of raw water. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

The formation potential of total I-THMs decreased by increasing Br^- concentration from 100 to 10,000 mg/L (Figure 7-4). The maximum I-THMFP of 15,341 μg/L was taken place in Br^- concentration of 100 μg/L. Triiodomethane formation potential (TIMFP) and dichloroiodomethane formation potential (DCIMFP) species decreased by increasing the Br^- concentration. The level of bromidiiodomethane formation potential (BDIMFP) was formed only in the highest Br^- concentration of 10,000 μg/L.

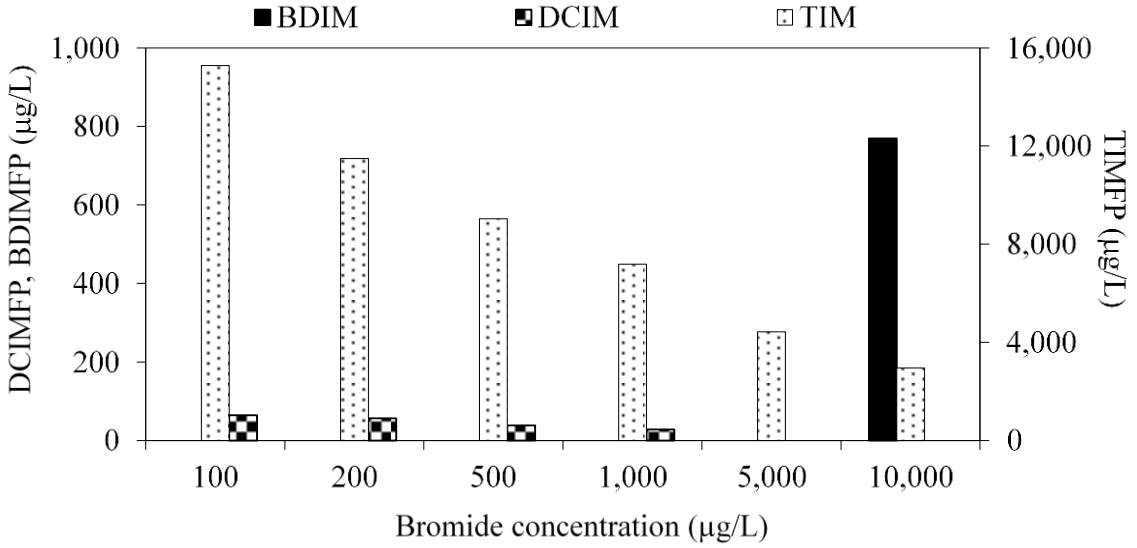


Figure 7-**4** The influence of bromide ion on the formation potential of I-THMs of raw water. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

The influence of Br^- concentration on the HANFP shows in Figure 7-5. Increasing Br^- concentrations from 200 to 1,000 μg/L resulted in decreased total HANFP concentrations. While further increase in the Br^- level leads to an increase in the total HANFP. Dibromoacetonitrile (DBAN) did not form at the initial Br^- concentration of 100 μg/L. The DBAN formation potential (DBANFP) species exhibited high levels in the Br^- concentration at 5,000 and 10,000 μg/L. BCAN increased initially but then decreased and its maximum concentration occurred at Br^- concentration of 200 μg/L. DCANFP was measured at low concentration when the Br^- level was increased from 100 to 500 μg/L. The range for bromide dosage (0.1–10 mg/L) in this study was not formed TCNM during chlorination of the raw water.

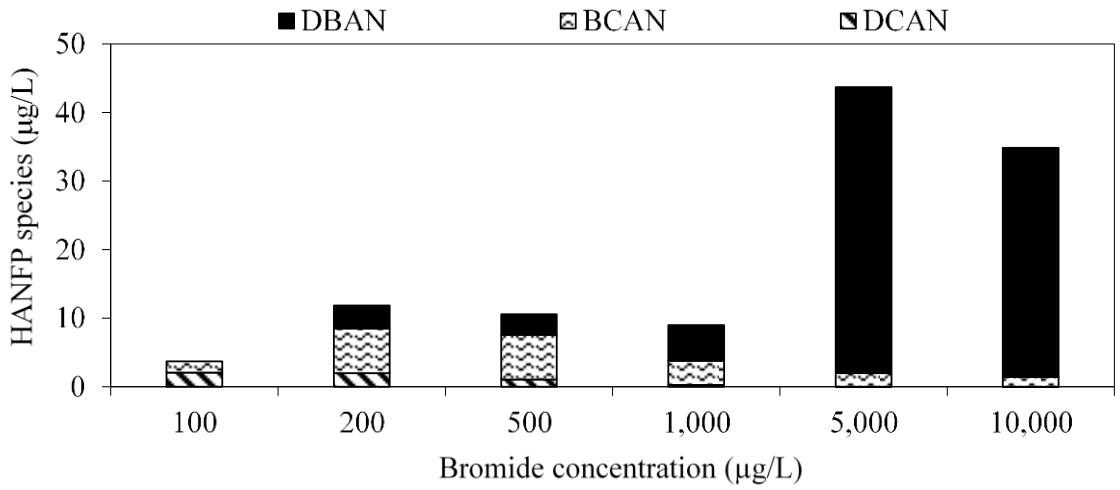


Figure 7-**5** The influence of bromide ion on the formation potential of HANs of raw water. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

7.3.3 Kinetics of THMs, I-THMs, HANs, and HNMs formation in raw water and coagulated water

The formation potential of THMs, I-THMs, and HANs of raw water and treated water of the BK-1 was reported in terms yields of each THMs, I-THMs, and HANs species, calculated by normalizing their concentrations with initial DOC concentration. The yield of each DBPs species after chlorination expressed in µg DBPFP/mg C. In this study, the TCNM mostly did not form. Therefore, the kinetics of TCNM could not be determined. In this work, the kinetic rates of the yield of each DBPFP species were fitted well with zero- and first-order models. The formation or degradation rates were calculated using the following equations:

For zero-order reaction,

$$[DBPs_{yield}] = kt + [DBPs_{yield}]_0 \qquad (1)$$

Where k is the rate constant (µg-DBPFP L^{-1} h^{-1}) of the yield of each DBPs ($DBPs_{yield}$, µg DBPFP/mg C) at the chlorination time (t, hour); $[DBPs_{yield}]_0$ is the yield of each DBPs of water sample before chlorination

For first-order reaction,

$$\frac{d[DBPs_{yield}]}{dt} = k[DBPs_{yield}] \qquad (2)$$

$$\ln [DBPs_{yield}] = kt + \ln [DBPs_{yield}]_0 \qquad (3)$$

Where *k* is the rate constant (h^{-1}) of the yield of each DBPs ($DBPs_{yield}$, µg DBPFP/mg C) at the chlorination time (t, hour); $[DBPs_{yield}]_0$ is the yield of each DBPs of water sample before chlorination

Figure 7-6 presents the yields of each THMFP species (chloroform, BDCM, and DBCM) formed after chlorination of the raw water and treated waters. In terms of specific chloroform and BDCM in the raw water, the highest yield of 129 and 12.1 µg/mg C, respectively was observed at 3 h of the reaction time, while the highest yield of DBCM was 1.36 µg/mg C at 6 h. For the treated water, the chloroform and BDCM were gradually formed in the first 24 h of the reaction time, then decrease a slow rate. The highest yields of chloroform and BDCM in the coagulated water were 154 and 19.4 µg/mg C at 24 h. For DBCM, the highest yield was 1.9 µg/mg C at 12 h.

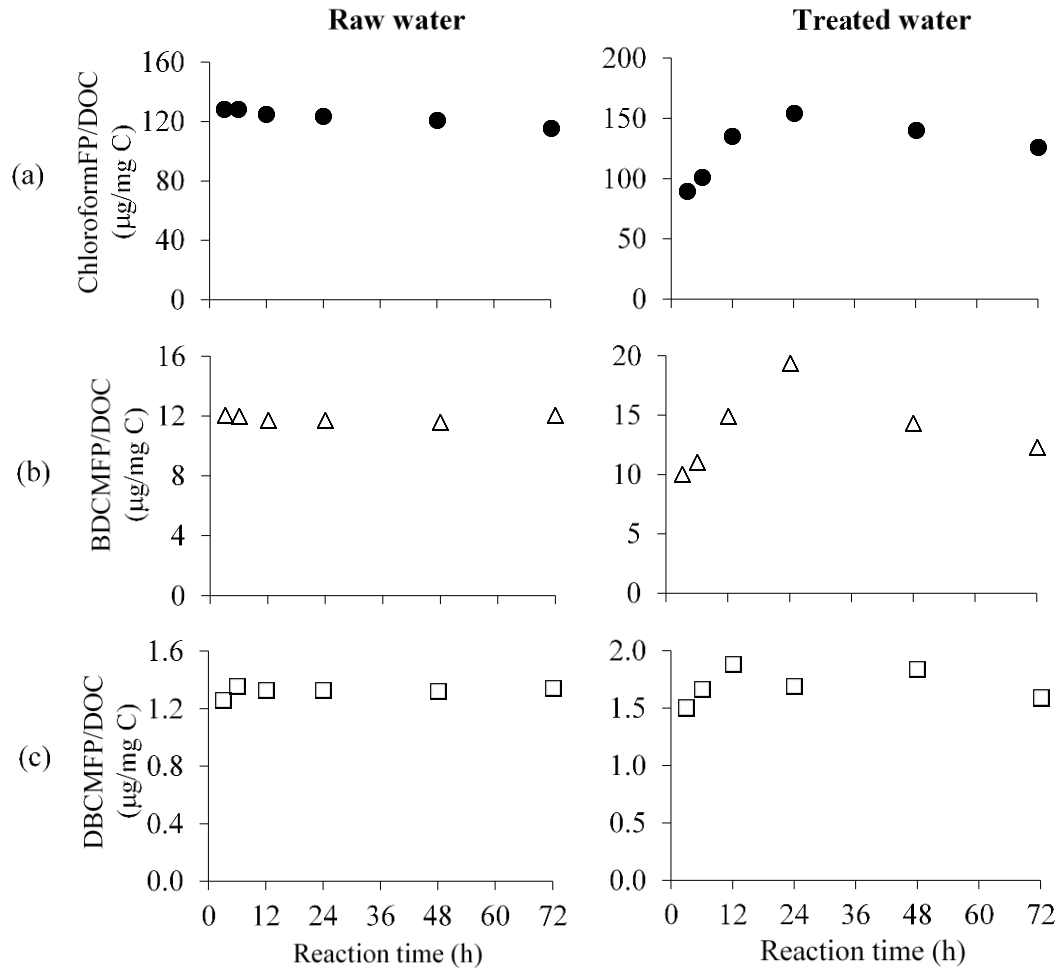


Figure 7-6 The effect of retention time on the formation potential of (a) chloroform, (b) BDCM, and (c) DBCM species of THMFP of raw and treated water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

The kinetic rates of THMFP species in raw water and treated water of the BK-1 are presented in Table 7-2. For the raw water, the R-square (R^2) values for the zero- and first-order kinetic rates were in the range of 0.77 to 1.00. The first-order specific degradation rates of THMFP species, ranked in order, were chloroform > BDCM. For DBCM, the slow degradation rate at 0.01 μg L^{-1} h^{-1} for the zero-order reaction was observed in the reaction time between 6 and 12 h, then stable degradation. The THMFP formation from 3 to 72 hour in raw water seems to be constant or slightly decreased.

From Figure 7-6, the kinetic rate of chloroform, BDCM, and DBCM yield in the treated water can be divided into a two-stage pattern: a formation rate and then a degradation rate. The formation and degradation kinetics of chloroform, BDCM, and DBCM were estimated using a zero- and first-order kinetics for the first and second stage patterns, respectively. The R^2 values in the first and second stages of water were in the range of 0.91 to 0.99 and 0.77 to 0.99, respectively (Table 7-2). In the first stage, the zero-order specific formation rates of THMFP species for the treated water, ranked in order, were chloroform > BDCM > DBCM (Table 7-2). The kinetic rates of THMFP species in the second stage, ranked in order, were BDCM > chloroform > DBCM.

Figure 7-7 presents the yields of DCIM and TIM of I-THMFP species formed after chlorination of the raw and coagulated waters. The DCIM yields in the BK raw water increased from 1.04 to 1.70 μg/mg C in 24 h of reaction time and then gradually decrease to 1.33 μg/mg C in 72 h. In terms of specific TIM, the rapid formation in the BK raw water was observed in the first 12 h of the reaction time. The TIM gave the highest yield of 3.73 μg/mg C at 12 h. For the treated water, the DCIM and TIM were gradually formed in the first 12 h of the reaction time, then decrease a slow rate. The highest yields of DCIM and TIM in the treated water were 2.73 and 3.77 μg/mg C at 12 h.

Table 7-2 Specific formation and degradation rates of THMFP, I-THMFP, and HANFP after 72 h of incubation in raw and coagulated water of the BK-1.

DBPFP	Incubation period (h)	Zero-order specific rate (μg DBPFP species L^{-1} h^{-1})	Fist-order specific rate (h^{-1})	R^2	Range of DBPFP (μg/mg C)
Raw water					
THMFP					
Chloroform	3-72	-	-1.40×10^{-3}	0.9651	116-129
BDCM	3-48	-	-0.80×10^{-3}	0.7741	11.6-12.1
DBCM	6-48	-	-	0.4495	1.32-1.36
I-THMFP					
DCIM	3-12	0.11	-	0.8765	1.04-1.70
	12-72	-	-3.80×10^{-3}	0.8264	1.33-1.70
TIM	3-12	-	2.25×10^{-2}	0.9589	3.02-3.73
HANFP					
TCAN	3-12	0.03	-	0.8871	0.35-0.65
	12-72	-	-1.10×10^{-2}	0.7158	0.28-0.65
DCAN	6-72	-	-1.77×10^{-2}	0.8372	1.09-4.13
BCAN	6-24	-	-2.78×10^{-2}	0.6472	0.25-0.44
Coagulated water					
THMFP					
Chloroform	3-24	3.10	-	0.9174	90-154
	24-72	-	-4.20×10^{-3}	0.9996	126-154
BDCM	3-24	0.45	-	0.9865	10.0 -19.4
	24-72	-	-9.40×10^{-3}	0.9641	12.3-19.4
DBCM	3-12	0.04	-	0.9906	1.51-1.89
	12-72	-	-2.40×10^{-3}	0.7763	1.59-1.89
I-THMFP					
DCIM	3-12	0.12	-	0.9812	1.67-2.73
	12-72	-	-5.10×10^{-3}	0.8588	1.93-2.73
TIM	3-12	0.16	-	0.6789	2.16-3.77
	12-72	-	-5.40×10^{-3}	0.6787	2.56-3.77
HANFP					
TCAN	3-12	0.01	-	0.8273	0.36-0.40
	12-72	-	-9.50×10^{-3}	0.9897	0.23-0.40
DCAN	6-72	-	-5.51×10^{-2}	0.9894	0.04-1.48
BCAN	6-24	-	-1.26×10^{-1}	1.0000	ND-0.31

ND is not detected

The kinetic rate of DCIM and TIM yield in the raw and treated waters can be divided into a two-stage pattern: a formation rate and then a degradation rate (Figure. 7-8). The formation and degradation kinetics of DCIM in the raw water and treated waters were estimated using a zero- and first-order kinetics with the $R^2 > 0.67$ for the first and second stage patterns. For TIM, the kinetic formation rates in 3-12 h of the reaction time were best fitted to a first-

order reaction with the $R^2 > 0.95$ of the raw water and a zero-order reaction with the $R^2 > 0.67$ for the treated water (Table 7-2). The zero-order specific formation rate of DCIM species in the first stage was higher in the treated water than that in the raw water (Table 7-2). The result was similar to the kinetic degradation rates of the DCIM in the second stage pattern. In the treated water, the zero-order specific formation rates of I-THMFP species in 3-12 h, ranked in order, were TIM > DCIM.

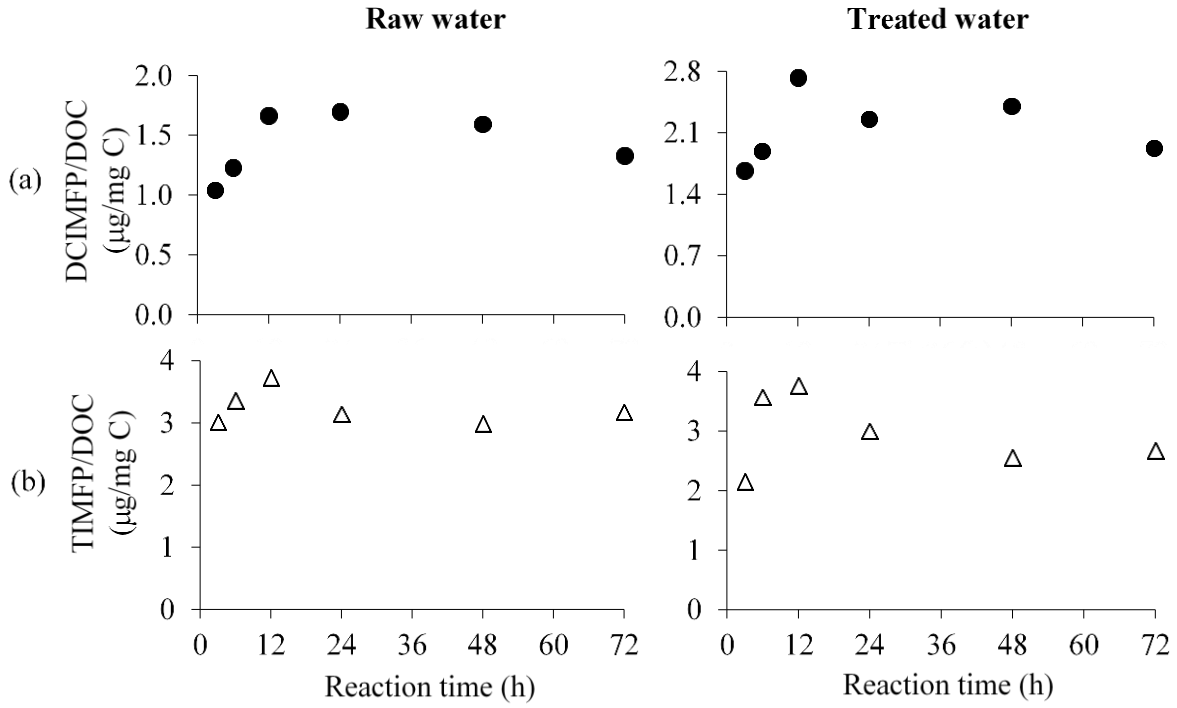


Figure 7-7 The effect of retention time on the formation potential of (a) DCIM and (b) TIM species of I-THMFP of raw water and treated water of the BK WTP from the first sampling (RW BK-1). (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

The yields of each HANFP species (TCAN, DCAN, and BCAN) formed after chlorination of the raw and coagulated waters are shown in Figure 7-8. In terms of specific TCAN, DCAN and BCAN, the formations in the raw water and coagulated waters were observed in the first 12, 6 and 6 h of the reaction time, respectively. The TCAN in the raw water gave the highest yield of 0.65 µg/mg C at 12 h while the highest yield of DCAN and BCAN were 4.13 and 0.43 µg/mg C at 6 hr, respectively. For the treated water, the highest yield of TCAN of 0.40 µg/mg C, DCAN of 1.48 µg/mg C, and BCAN of 0.31 µg/mg C were detected at 12, 6 and 6 h of the reaction time, respectively.

From Figure 7-8, the kinetic rate of TCAN, DCAN, and BCAN yield in the raw water and coagulated waters can be divided into a two-stage pattern: a formation rate and then a degradation rate. The formation and degradation kinetics of TCAN, DCAN, and BCAN were estimated using a zero- and first-order kinetics for the first and second stage patterns, respectively. The R^2 values of > 0.82 and ranging from 0.64 to 1.00 were obtained using the zero- and first-order models, respectively (Table 7-2). At the initial stage for 3-12 h, the zero-order specific formation rate of TCANFP species was higher for the raw water than of the treated water. For both of the raw water and treated water, the first-order specific degradation rates of HANFP species in the second stage, ranked in order, were BCAN > DCAN > TCAN (Table 7-2).

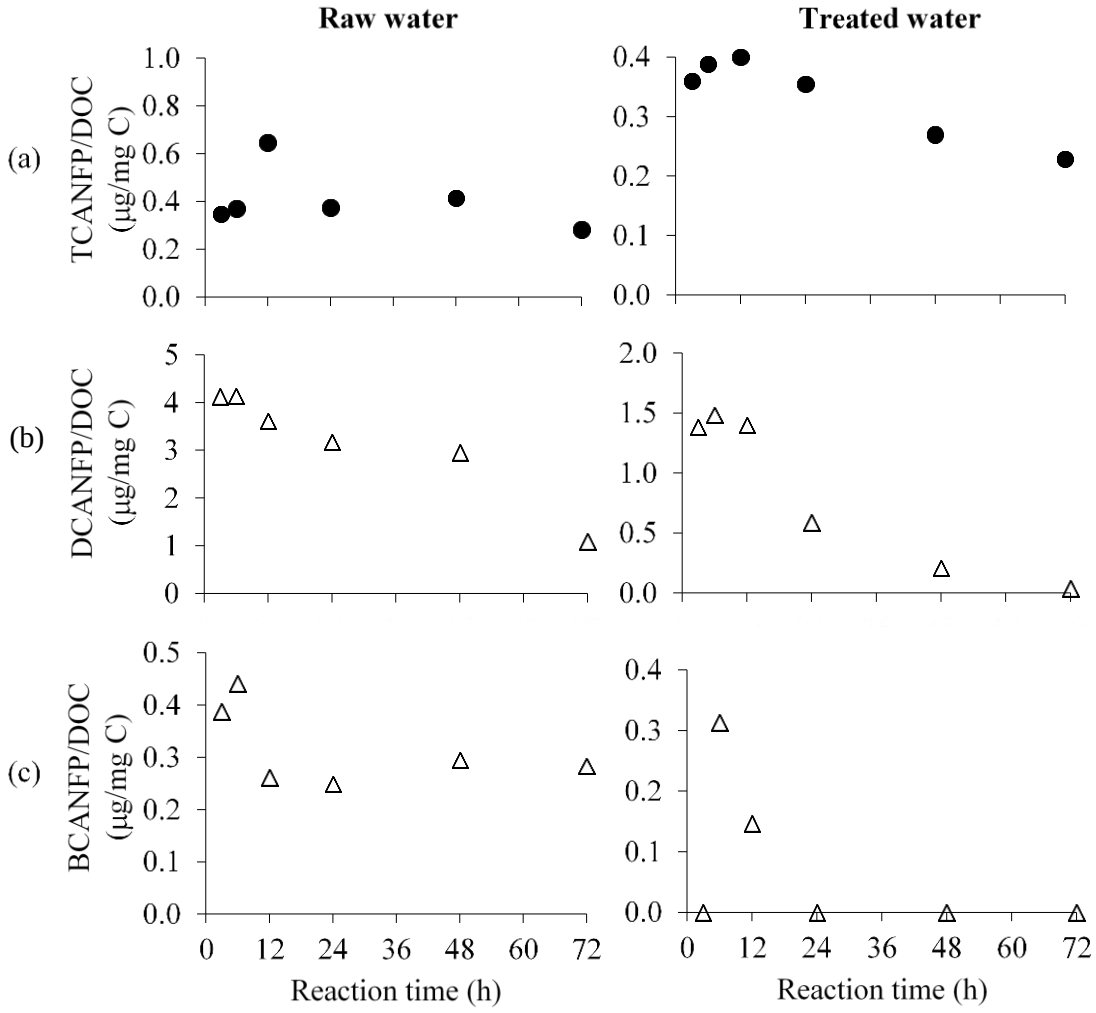


Figure 7-8 The effect of retention time on the formation potential of (a) TCAN, (b) DCAN, and (c) BCAN species of HANFP of raw water and treated water of the BK WTP from the first sampling (RW BK-1). (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

From the results, the rank order for the formation rate of THMFP yield in the first stage for the treated water was chloroform > BDCM > DBCM. The rank order for the formation rate of I-THMFP yield in the first stage for the treated water was TIM > DCIM. The rank order for degradation rate of HANFP yield in the second stage for both the raw water and treated water was BCAN > DCAN > TCAN.

7.3.4 Kinetics of DOM size fraction on the formation potential of THMs, I-THMs and HANs in raw water

From Figure 7-9, the formation kinetics of chloroform, BDCM, and DBCM of each DOM size fractions were estimated using a zero-kinetic model. The R^2 values of the formation kinetics of THMFP of raw water in each DOM size fractions were in the range of 0.70 to 0.98 (Table 7-3). For DOM fraction with MW > 10 kDa, the zero-order specific formation rate of chloroform was higher than that of BDCM in 72 h of incubation (Table 7-3). For DBCM, the specific formation rate of DOM with MW > 10 kDa was slightly low at 0.007 $\mu g\ L^{-1}\ h^{-1}$ from 3 to 48 h. After 48 h of reaction time, the DBCM shows a gradual decrease (Figure. 7-10). Under 48 hours of retention time, the formation kinetic rates of THMFP yield of DOM with MW ranges of 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa ranked in order were chloroform > BDCM > DBCM (Table 7-3).

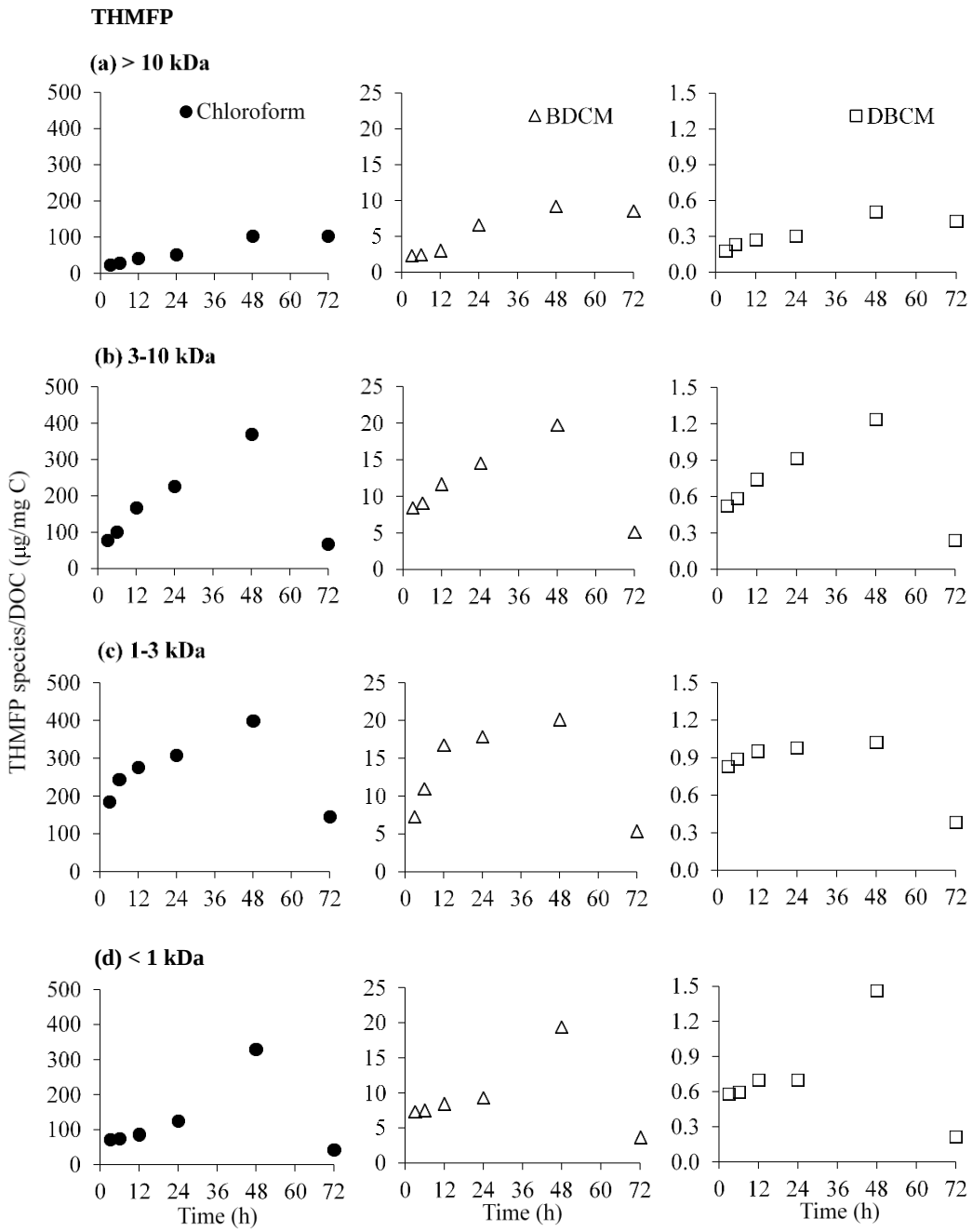


Figure 7-9 The effect of DOM size fraction and retention time on the formation potential of (a) chloroform, (b) BDCM, and (c) DBCM species of THMFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

Table 7-3 Specific formation and degradation rates of THMFP, I-THMFP, and HANFP under 72 h of incubation in each DOM size fractions of the BK-1 raw water.

DBPFP	Fractions	Incubation period (h)	Zero-order specific rate (μg DBPFP species L^{-1} h^{-1})	Fist-order specific rate (h^{-1})	R^2	Range of DBPFP (μg/mg C)
THMFP						
Chloroform	> 10 kDa	3-72	1.26	-	0.9231	24-104
	3-10 kDa	3-48	6.38	-	0.9872	78-371
	1-3 kDa	3-48	4.22	-	0.9339	185-400
	<1 kDa	3-48	5.80	-	0.9314	71-331
BDCM	> 10 kDa	3-72	0.10	-	0.8217	2.30-9.23
	3-10 kDa	3-48	0.25	-	0.9862	8.40-19.7
	1-3 kDa	3-48	0.24	-	0.7055	7.32-20.2
	<1 kDa	3-48	0.26	-	0.9101	7.37-19.4
DBCM	> 10 kDa	3-48	0.007	-	0.9711	0.18-0.51
	3-10 kDa	3-48	0.015	-	0.9855	0.53-1.24
	1-3 kDa	3-48	0.004	-	0.7883	0.83-1.02
	<1 kDa	3-48	0.019	-	0.8914	0.58-1.46
I-THMFP						
BCIM	<1 kDa	3-72	-0.01	-	0.8963	0.30-1.05
HANFP						
TCAN	> 10 kDa	3-48	0.01	-	0.9748	0.39-0.87
	3-10 kDa	3-12	0.06	-	0.8212	0.77-1.34
		12-72	-	-1.65×10^{-2}	0.9312	0.45-1.34
	1-3 kDa	3-12	0.17	-	0.9999	1.90-3.48
		12-72	-	-1.62×10^{-2}	0.9829	1.39-3.48
	<1 kDa	3-24	0.03	-	0.8989	0.33-1.04
		24-72	-	-2.75×10^{-2}	0.9598	0.28-1.04
DCAN	> 10 kDa	3-72	-	-2.48×10^{-2}	0.9102	0.17-0.95
	3-10 kDa	3-72	-	-3.24×10^{-2}	0.7100	0.12-2.31
	1-3 kDa	3-72	-	-3.31×10^{-2}	0.7605	0.21-4.82
	<1 kDa	3-72	-0.04	-	0.7099	0.30-4.38
BCAN	<1 kDa	3-24	-0.02	-	0.9317	ND-0.48

ND is not detected

From Figure 7-10, the degradation kinetic of BCIM of DOM with MW < 1 kDa was estimated using a zero-order kinetic with the R^2 value of 0.89 (Table 7-3). Under 72 h of reaction time, the zero-order specific formation rate of BCIM was slightly low at 0.01 μg L^{-1} h^{-1}.

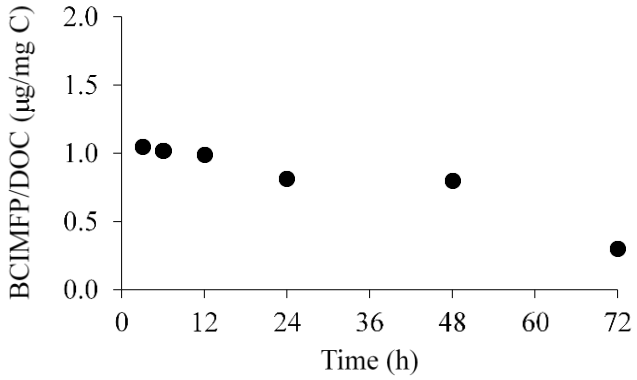


Figure 7-10 The effect of DOM size fraction of < 1 kDa and retention time on the formation potential of BCIM species of I-THMFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

From Figure 7-11, the kinetic formation rates of TCAN yield of DOM with MW fraction of > 10 kDa in 3-48 h of the incubation time of the raw water was estimated using a zero-order kinetic with the R^2 value of > 0.82 (Table 7-3). For DOM with 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa, the kinetic rates of TCAN can be divided into a two-stage pattern: a formation rate and then a degradation rate. The formation and degradation kinetics of TCAN were estimated using zero- and first-order kinetics for the first and second stage patterns, respectively. The R^2 values in the first and second stages were > 0.82 (Table 7-3). In the first stage, the zero-order specific formation rate of TCAN species of DOM with 1 kDa < MW < 3 kDa of 0.17 µg L^{-1} h^{-1} was higher that of DOM with 3 kDa < MW < 10 kDa and MW < 1 kDa, respectively (Table 7-3). In the second stage, the TCAN shows a gradual decrease (Figure 7-11) with the specific degradation rate of 2.75 x 10^{-2} µg L^{-1} h^{-1} for DOM with MW < 1 kDa, 1.65 x 10^{-2} for DOM with 3 kDa < MW < 10 kDa, and 1.62 x 10^{-2} for DOM with 1 kDa < MW <3 kDa.

For DCAN yield of DOM with MW > 10 kDa, 3 kDa < MW < 10 kDa, and 1 kDa < MW <3 kDa, the kinetic degrdation rates in 3-72 h was estimated using a first-order kinetic with the R^2 value of > 0.71 (Table 7-3). After 3 h of the incubation time, the first-order specific degradation rate of DCAN species for DOM with 1 kDa < MW < 3 kDa was higher than that of DOM with 3 kDa <MW < 10 kDa and MW > 10 kDa, respectively (Table 7-3).

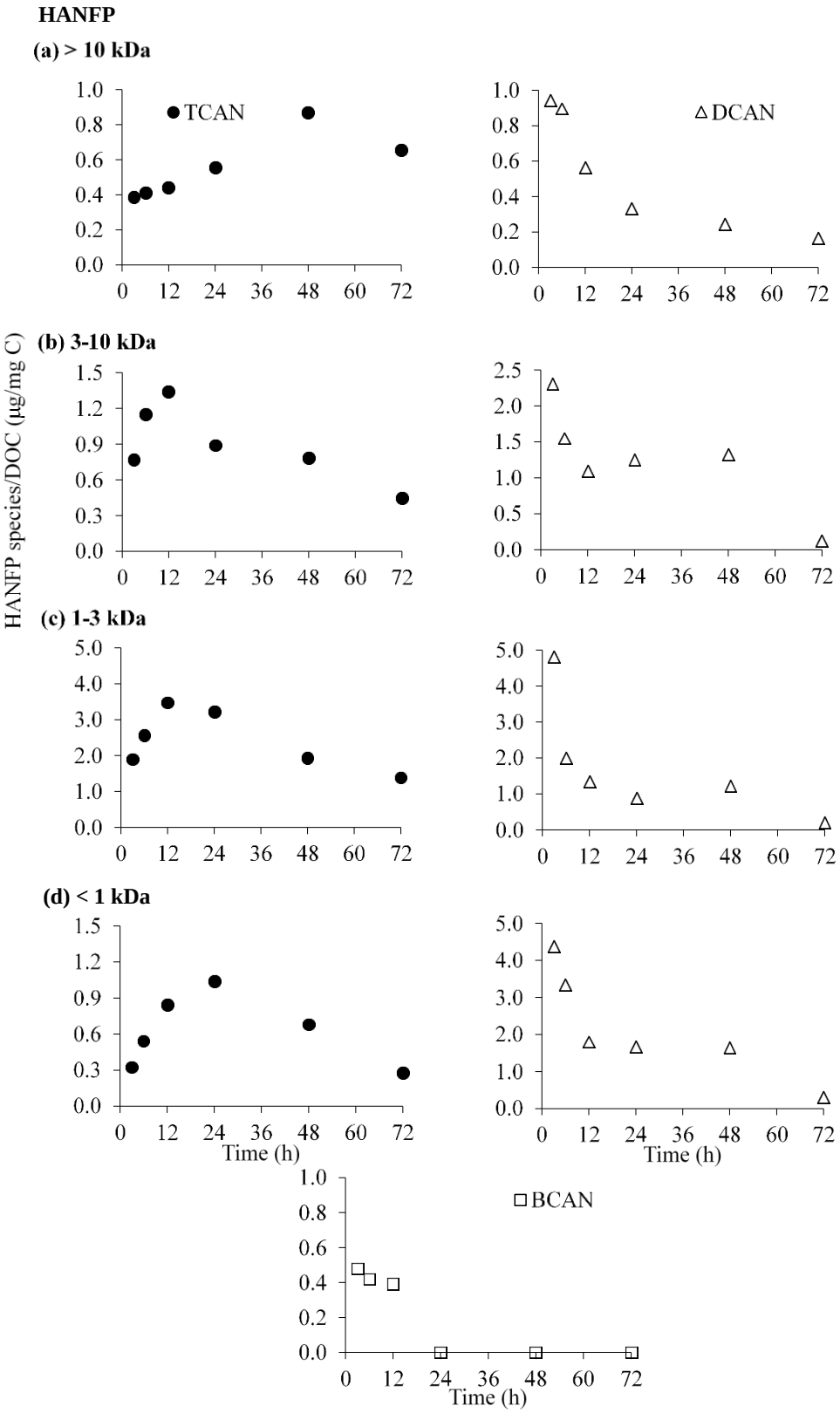


Figure 7-11 The effect of DOM size fraction and retention time on the formation potential of TCAN, DCAN, and BCAN species of HANFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

For DOM with MW < 1 kDa of DCAN and BCAN, the kinetic degradation rates were estimated using a zero-order kinetic with the R^2 value of > 0.70 (Table 7-3). After 3 h of the reaction time, the zero-order specific degradation rates of HANFP species of DOM with MW < 1 kDa, ranked in order, were DCAN > BCAN (Table 7-3).

7.3.5 Kinetic of HPO, TPI, and HPI on the formation of THMs, I-THMs and HANs in raw water

The kinetic rate of chloroform, BDCM, and DBCM yield of HPO in the raw water can be divided into a two-stage pattern: a formation rate and then a degradation rate (Figure 7-12a). The formation kinetics of chloroform and BDCM of HPO in the first stage were estimated using a zero-order kinetic with the R^2 value in the range of > 0.85 (Table 7-4). For BDCM yield of HPO, the kinetic degradation rate in the second stage (24-72 h) were best fitted with a first-order kinetic with the R^2 value of 0.99. In the first stage, the zero-order specific formation rates of chloroform of HPO was higher than that of BDCM (Table 7-4). After 24 h of reaction time, the degradation of chloroform and DBCM of HPO was relative stable, whereas that of BDCM shows a gradual decrease (Figure 7-12a).

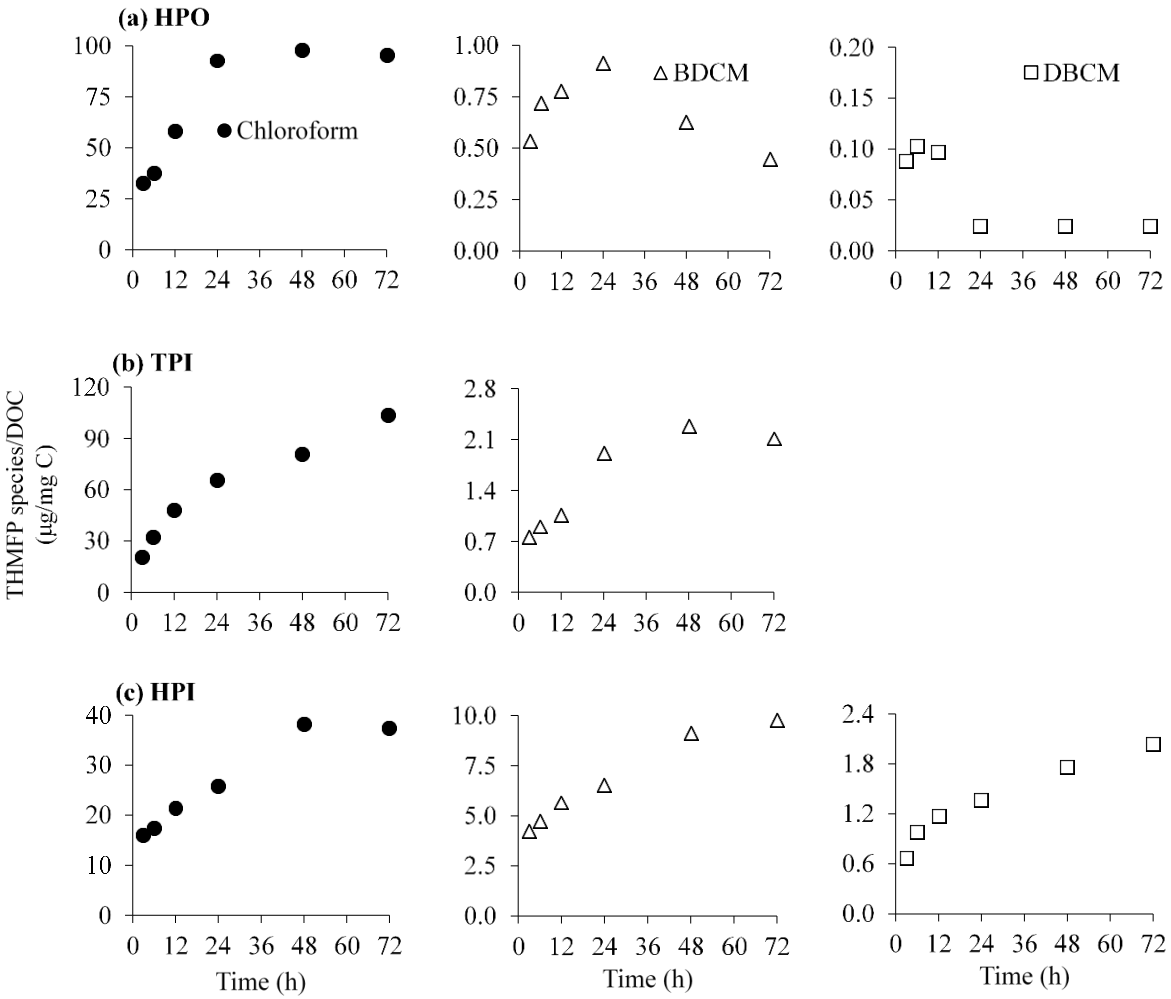


Figure 7-12 The effect of DOM resin fraction and retention time on the formation potential of (a) chloroform, (b) BDCM, and (c) DBCM species of THMFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

The kinetic formation rate of chloroform and BDCM yield of TPI in the raw water was estimated using a zero-order kinetic with the R^2 values of > 0.75 under the 72 h of retention time tests (Table 7-4). The zero-order specific formation rates of THMFP species of TPI, ranked in order, were chloroform > BDCM (Table 7-4). The formation kinetics of chloroform, BDCM, and DBCM yield of HPI in the raw water were estimated using a first-order kinetic with the R^2 values in the range of 0.82 to 0.92 under the 72 h of retention time tests (Table 7-4). The first-order specific formation rates of THMFP species of HPI, ranked in order, were DBCM > chloroform > BDCM (Table 7-4).

Table 7-4 Specific formation and degradation rates of THMFP, I-THMFP, and HANFP under 72 h of incubation in HPO, TPI and HPI fractions of the BK-1 raw water.

DBPFP	Fractions	Incubation period (h)	Zero-order specific rate (μg DBPFP species L^{-1} h^{-1})	Fist-order specific rate (h^{-1})	R^2	Range of DBPFP (μg/mg C)
THMFP						
Chloroform	HPO	3-24	2.94	-	0.9961	32.6-92.7
		24-72	-	-	-	92.7-98.0
	TPI	3-72	1.25	-	0.8893	20.8-103
	HPI	3-72	-	1.28×10^{-2}	0.8770	16.1-37.3
BDCM	HPO	3-24	0.02	-	0.8513	0.53-0.91
		24-72	-	-1.49×10^{-2}	0.9991	0.45-0.91
	TPI	3-72	0.021	-	0.7538	0.76-2.29
	HPI	3-72	-	1.19×10^{-2}	0.9200	4.26-9.78
DBCM	HPO	6-24	-0.01	-	0.9333	0.02-0.10
		24-72	-	-	-	0.02
	HPI	3-72	-	1.35×10^{-2}	0.8206	0.67-2.04
I-THMFP						
DCIM	HPO	3-24	-	2.55×10^{-2}	0.7769	ND-0.85
		24-72	-	-	-	0.85-0.88
	TPI	3-24	-	1.95×10^{-2}	0.9452	1.60-2.41
		24-72	-	-	-	2.13-2.46
TIM	HPO	3-6	2.01	-	1.0000	ND-6.05
		6-72	-0.03	-	0.8013	3.97-6.05
	TPI	3-6	4.5	-	1.0000	ND-13.6
		6-72	-	-5.00×10^{-3}	0.8187	9.52-13.6
	HPI	3-72	-1.01 x 10-2	-	0.9360	7.79-16.6
HANFP						
TCAN	HPI	3-24	0.03	-	0.9039	0.41-1.08
		24-72	-	-1.55×10^{-2}	0.9238	0.51-1.08
DCAN	HPI	6-72	0.08	-	0.9639	9.86-15.55
BCAN	HPI	6-72	0.01	-	0.8093	1.62-1.94

ND is not detected

From Figure 7-13, the kinetic rate of DCIM and TIM yield of HPO in the raw water can be divided into a two-stage pattern: a formation rate and then a degradation rate. The formation kinetics of DCIM and TIM of HPO were estimated using a first- and zero-order kinetic, respectively, with the R^2 value of > 0.77 (Table 7-4). In the second stage (6-72 h), the kinetic degradation rate of TIM was best fitted with a zero-order kinetic with the R^2 value of 0.80. For TPI fraction, the kinetic rate of DCIM and TIM yield in the raw water can be divided into a two-stage pattern. In the first stage, the formation kinetics of DCIM and TIM of TPI were estimated using a first- and zero-order kinetic, respectively, with the R^2 value of > 0.94

(Table 7-4). In the second stage, the kinetic degradation rate of TIM of TPI was best fitted with a first-order kinetic with the R^2 value of 0.81. For HPI fraction, the degradation kinetic of TIM yield in the raw water was estimated using a first-order kinetic with the R^2 value of 0.93 under the 72 h of retention time tests (Table 7-4). The result showed that the first-order specific formation rate of DCIM of HPO was higher than that of DCIM of TPI during the reaction time between 3 to 24 h (Table 7-4). Furthermore, the zero-order specific formation rates of TIM of TPI was higher than that of TIM of HPO during the reaction time between 3 to 6 h (Table 7-4).

The kinetic rate of TCAN yield of HPI in the raw water can be divided into a two-stage pattern: a formation rate and then a degradation rate (Figure 7-14). The formation and degradation kinetics of TCAN were estimated using a zero- and first-order kinetic, respectively, with the R^2 value of > 0.90 (Table 7-4). For both DCAN and BCAN of HPI, the kinetic formation rates were estimated using a zero-order kinetic with the R^2 values of > 0.80 (Table 7-4). In the first stage, TCAN of HPI was increased gradually in the 24 h of the reaction time with the specific formation rates of 0.03 μg L^{-1} h^{-1}. DCAN and BCAN of HPI were increased rapidly in the first six hour. After 6 h of the reaction time, the DCAN and BCAN of HPI were slowly increased. The zero-order specific formation rate of DCAN of HPI was higher than that of BCAN in the reaction time from 6 to 72 h (Table 7-4).

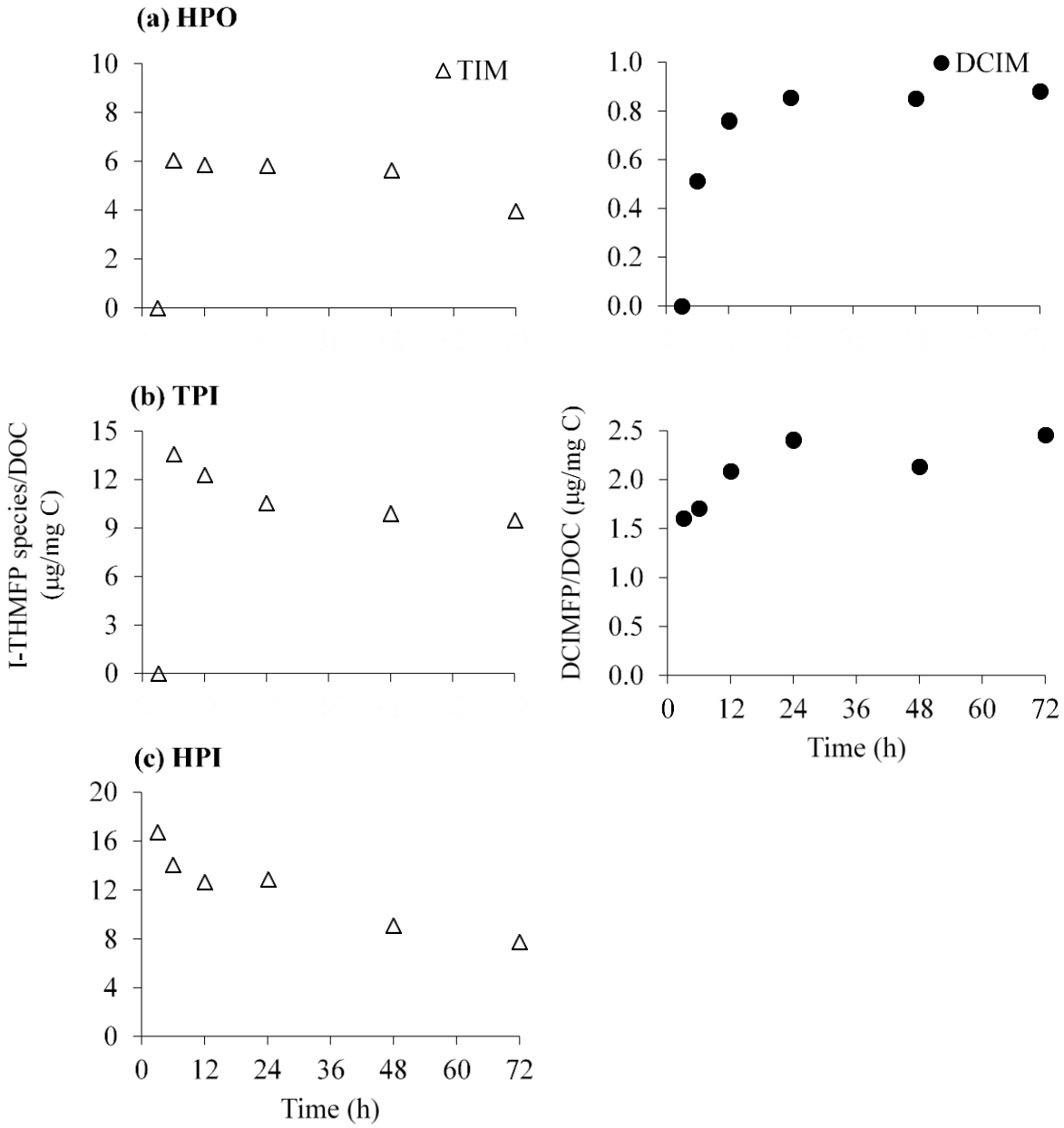


Figure 7-13 The effect of DOM resin fraction and retention time on the formation potential of TIM and DCIM species of I-THMFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, Cl_2 free Cl_2 residual = 3-5 mg/L)

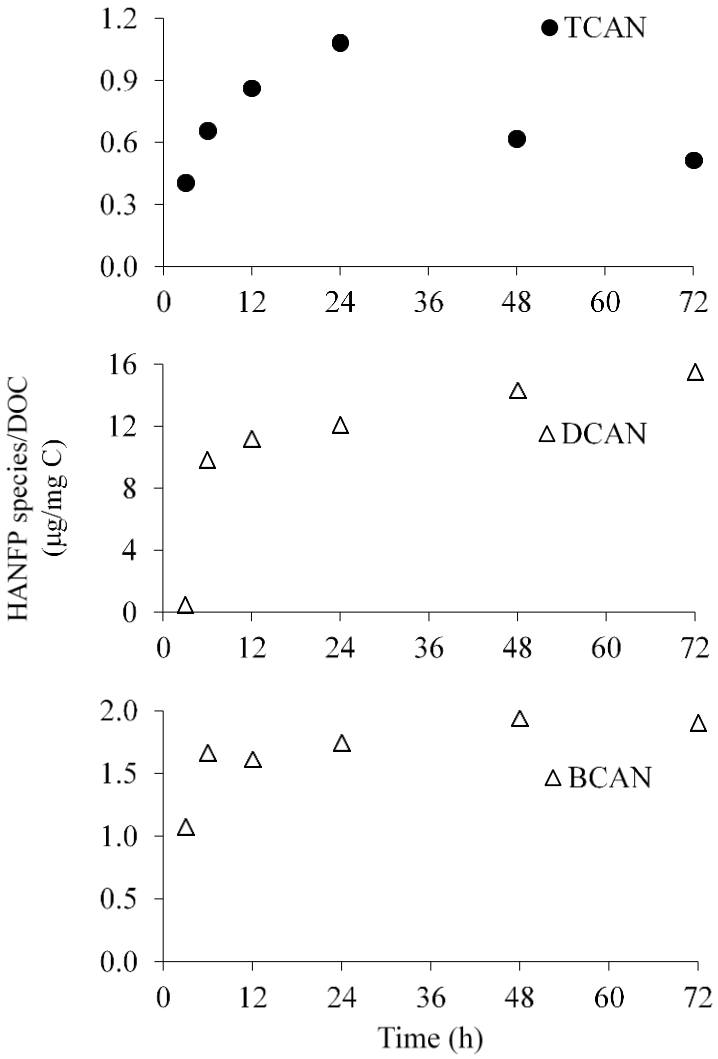


Figure. 7-14 The effect of HPI fraction and retention time on the formation potential of TCAN, DCAN, and BCAN species of HANFP of raw water of the BK WTP from the first sampling. (Reaction conditions; pH = 7, temperature = 25 °C, free Cl_2 residual = 3-5 mg/L)

Chapter VIII

Conclusions

The conclusions are based on the obtained experimental results of four parts.

The first part: Carbonaceous and nitrogenous disinfection-products' formation potential in raw water, wastewater, and treated wastewater

The formation potential of trihalomethanes (THMs), iodo-trihalomethanes (I-THMs), haloacetronitrile (HANs), and halonitromethanes (HNM) and their individual species were determined in the raw water, river water, and domestic wastewater and final treated wastewater from two provinces. The levels of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in the wastewater and treated wastewater were slightly higher than those in the raw and river water. The river water, wastewater, and treated wastewater have potential to form THMs which exceed the trihalomethane formation potential (THMFP)/ WHO guideline value of ≤ 1. The average value of THMFP of treated wastewater was about two times higher than that of raw water. Relatively high levels of iodo trihalomethane formation potential (I-THMFP) were found in wastewater and treated wastewater. The average value of I-THMFP of treated wastewater was three to seven times higher than that of raw water. Iodoform was the dominant species of I-THMFP detected at high level in the wastewater and treated wastewater, while bromochloroiodomethane (BCIM), chlorodiiodomethane (CDIM), and di-chloroiodomethane (DCIM) were identified in most of the samples in the raw water. Haloacetronitriles formation potential (HANFP) was detected in all water sources. The average value of HANFP of treated wastewater was one to three times higher than that of raw water. dichloroacetonitrile (DCAN) was the most abundant species for HANFP in all the water sources. For HNM species, the trichloronitromethane (TCNM) mainly remain in the treated wastewater samples at a relatively high level. The average value of TCNM formation potential (TCNMFP) of treated wastewater was six to thirteen times higher than that of raw water. The discharge of treated wastewater to raw water must be prevented and controlled. In linear regression analysis, only moderate associations were obtained for the correlations between DOC and THMFP in the raw water samples and TCNMFP in the treated wastewater samples. THMs were the most prevalent class of disinfection by-products (DBPs) and their formation potential was above the US EPA maximum contaminant level of 80 µg/ L. However, the

haloacetronitriles (HANs) and I-THMs were considered the least safe because they feature higher concentrations of the toxicity drivers. Considering the weight measured concentration of carbonaceous-DBPs (C-DBPs) and nitrogenous-DBPs (N-DBPs), THMFP was found as the highest DBPs. The highest LC50-weighted and lowest cytotoxicity-weighted concentrations of C-DBPs and NDBPs were determined for HANFP.

The second part: **Formation of carbonaceous and nitrogenous disinfection by-products of fractionated dissolved organic matter in raw water, wastewater, and treated wastewater**

Dissolved organic matter (DOM) with molecular weight (MW) < 1 kDa was the dominant DOM fraction in all water samples. The DOM with MW > 10 kDa was found as the second dominant DOM. The order of the DOC distribution of raw water, wastewater, and treated wastewater could be express as follows: DOM with MW < 1 kDa, MW > 10 kDa, 3 kDa < MW < 10 kDa, and 1 kDa < MW < 3 kDa, respectively. The order of the DOC distribution of wastewater and treated wastewater was the same as that of raw water. The wastewater and treated wastewater could be the DOM contamination sources to raw water.

The hydrophobic organic fraction (HPO) was the dominant DOM fractions. Hydrophilic organic fraction (HPI) was the second significant DOM fraction. The transphilic organic fraction (TPI) was found as minority DOM group. The coagulation process effectively removes DOM with high MW and HPO's character. HPO and DOM with MW > 10 kDa were found as the significant DOM and could be sufficiently removed by coagulation process. When the dominant DOM fraction in water primary contains low MW and HPI's character, the enhanced coagulation or advanced water treatment process such as powder activated carbon (PAC) and ion exchange magnetic (MIEX) resin should be considered as the optional for removal of dominant DOM fractions.

DOM with 1 kDa < MW < 3 kDa has a high THMFP/DOC. DOM with 3 kDa < MW < 10 kDa and MW > 10 kDa have a moderate THMFP/DOC. DOM with MW < 1 kDa had a low value of THMFP/DOC. Chloroform, bromodichloromethane (BDCM), and dibromochloromethane (DBCM) were the THMFP species that detected in all DOM fractions. In the case of resin fractionation, the highest THMFP/DOC of DOM fractions of all water samples was determined for TPI, followed by HPO, the dominant DOM fraction. HPI has a less active in THMs formation. In term of DOC distribution, chloroform was the main THMFP species. TPI had the lowest value of DOC; however, TPI had the highest value of THMFP/DOC. DOM in TPI might contain the active character for the THMs formation.

In the case of raw water, DOM with 1 kDa < MW < 3 kDa and 3 kDa < MW < 10 kDa has a high I-THMFP/DOC. DOM with MW > 10 kDa and MW < 1 kDa had a low value of I-THMFP/DOC. For wastewater and treated wastewater, DOM with MW < 1 kDa and 1 kDa < MW < 3 kDa were the active fraction on I-THMs formation. DOM with MW > 10 kDa and 3 kDa < MW < 10 kDa have a less active on I-THMs formation. CDIM, DCIM, and BDIM were the I-THMFP species that mostly detected in all DOM fractions. In the case of resin fractionation, the highest I-THMFP/DOC of DOM fractions of all water samples was determined for TPI, followed by HPO, the dominant DOM fraction. HPI has a less active in I-THMs formation. DOM in TPI might contain the active character for the I-THMs formation. DCIM, BDIM, and TIM were I-THMFP species detected.

DOM with 1 kDa < MW < 3 kDa and 3 kDa < MW < 10 kDa have an active character on the HANs formation, whereas DOM with MW < 10 kDa and MW > have a less active nature on the HANs formation. The detected HANs species in almost all fractions were trichloroacetonitrile (TCAN), DCAN, and bromochloroacetonitrile (BCAN). In the case of resin fractionation, the high HANFP/DOC of DOM fractions of all water samples was determined for TPI and HPI, followed by HPO. TCAN and DCAN were the main species. DOM in TPI and HPI might contain the active character for the HANs formation.

The active DOM fraction on HNM formation was DOM with 1 kDa < MW < 3 kDa. DOM with 3 kDa < MW < 10 kDa of raw water and treated wastewater have an active character on the HANs formation, whereas DOM with MW < 1 kDa has a less active nature on the HANs formation. In the case of resin fractionation, the high HNMFP/DOC of DOM fractions of all water samples was determined for HPO and TPI, followed by HPI. TCNM was the detected HNMFP species.

DOM with MW < 1 kDa has the high DBPs species/LC50 followed by the DOM with MW > 10 kDa. The DOM with 1 kDa < MW < 3 kDa has a moderate value of DBPs species/LC50. The DOM with 3 kDa < MW < 10 kDa has a low value of DBPs species/LC50. In the case of resin fractionation, the value of DBPs species/LC50 of HPI was higher than that of HPO and TPI. HANs were determined as the DBPs species of all DOM fractions with the highest LC50.

The significant DOM with MW < 1 kDa has the high DBPs/Lowest Cytotox. Conc followed by the DOM with 1 kDa < MW < 3 kDa. The DOM with 3 kDa < MW < 10 kDa and MW > 10 kDa have a moderate or low value of DBPs/Lowest Cytotox. Conc. In the case of resin fractionation, the value of DBPs/Lowest Cytotox. Conc of HPI was higher than that of

HPO and TPI. HANs were determined as the DBPs species of all DOM fractions with the highest of the lowest Cytotoxicity concentration.

The third part: **Reduction of precursors of emerging disinfection by-products by enhanced coagulation with powder activated carbon and magnetic ion-exchange**

The alum dosage of 20 mg/L was the optimum dosage for removing the turbidity for the Bangkhen (BK) raw water (RW). The optimal condition for DOC and DON removal from BK raw water was determined at alum dosage at 80 mg/L under controlled pH 7. Under this condition, it could reduce DOC and DON by 29 and 60%, on average. The enhanced alum coagulation by PAC of RW-1, RW-2, and RW-3 of 80 and 40, 80 and 80, and 80 and 80 (alum and PAC in mg/L), respectively, effectively removed DOC and DON by 43 and 62% (on average), respectively. The optimal dosage for DOC and DON removal for RW-1, RW-2, and RW-3 by alum with MIEX were 80 and 4, 80 and 2, and 80 and 4 (alum in mg/L and MIEX in mL/L), respectively. Under such condition, it could reduce DOC and DON by 51 and 77% (on average), respectively.

In the case of treated wastewater (TWW) Ang thong (AT-1), TWW Ayutthaya (AY-1) and RW mixed with TWW (AY-1), the optimal dosage for removing DOC and DON was alum at 100 mg/L, and these could reduce DOC and DON by 21 and 10%, and 24 and 76%, respectively. The enhanced alum coagulation by PAC of TWW (AT-1), TWW (AY-2) and RW mixed with TWW (AY-1) of 100 and 100, 100 and 100, and 100 and 80 (alum and PAC in mg/L), respectively. This condition effectively removed DOC and DON of treated wastewater and raw water mixed with treated wastewater by 40 and 20% (on average) and 42 and 60% respectively. The optimal dosage for DOC and DON removal for TWW (AT-1), TWW (AY-2) and RW mixed with TWW (AY-1) by alum with MIEX were 100 and 6, 100 and 6, and 100 and 4 (alum in mg/L) and MIEX in mL/L), respectively. Under such condition, it could reduce DOC and DON of treated wastewater and raw water mixed with treated wastewater by 50 and 37% (on average) and 71 and 32%, respectively.

Under optimal condition for the BK raw water, alum coagulation, alum coagulation with PAC, and alum coagulation with MIEX reduced THMFP and HANFP by 9 and 39%, 22 and 45%, and 45 and 61%, respectively. The reduction of I-THMFP and HNMFP varied according to the sampling period. For treated wastewater and raw water mixed with treated wastewater, optimal dosing of alum coagulation, alum coagulation with PAC, and alum

coagulation with MIEX provide the successful reduction of THMFP. The I-THMFP, HANFP, and HNMFP mostly did not detect or detected at low level after treatment.

For raw water, at optimal condition, alum coagulation could reduce fractions of MW > 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa by 41, 21, 48, and 39%, respectively. Optimal dosing of alum with PAC and alum with MIEX could reduce DOM with MW > 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa by 71, 41, 58, and 44% and 57, 47, 46, and 71%, respectively. In the case of treated wastewater and raw water mixed with treated wastewater, alum coagulation could reduce fractions of MW > 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa by 27, 17, 21, and 30%, respectively. Alum coagulation with PAC and alum coagulation with MIEX could reduce fractions of MW > 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa by 35, 32, 39, and 45% and 55, 41, 61, and 45%, respectively. In all cases, fractions of 1 kDa < MW < 3 kDa and MW < 1 kDa in all samples were mostly reduced by the enhanced coagulation with MIEX.

Considering the DOM fraction by resin fractionation of the raw water, the alum coagulation removed DOC of the HPO and HPI fractions by 41 and 12% (on average), respectively. The DOC of TPI was not available. In the case of alum coagulation enhanced with PAC or MIEX, the results of the DOM fraction did not conduct. For treated wastewater, the alum coagulation with PAC removed the DOC of HPI fraction (56%) slightly better than the HPO (36%) fraction. TPI could not be removed.

Aliphatic hydrocarbon, phenolic, ether, alcohol, and organic nitrogen classes in raw water accounted for 34, 11, 10, 9, and 7% (on average), respectively. Other classes were determined in minority. Alum coagulation, alum coagulation with PAC, and alum coagulation with MIEX could reduce aliphatic hydrocarbon and organic nitrogen by 36 and 40%, 37 and 12%, and 33 and 35%, respectively. Only alum coagulation with MIEX could reduce phenol and alcohol by 22 and 21% (on average), respectively. Ether could not reduce by the coagulation and enhanced coagulation.

In the case of treated wastewater, ether, aliphatic hydrocarbon, and organic nitrogen were the major chemical classes and accounted for 37, 15, and 12% (on average), respectively. The other classes were determined as a minority. Alum coagulation, alum coagulation with PAC, and alum coagulation with MIEX could reduce ether and organic nitrogen by 22 and 72%, 32 and 34%, and 22 and 26%, respectively. Alum coagulation with PAC could slightly reduce aliphatic hydrocarbon by only 6%. For raw water mixed with treated wastewater, aliphatic hydrocarbon, organic nitrogen, aromatic hydrocarbon, and other compounds

accounted for 17, 9, 8, and 6%, respectively. Alum coagulation, alum coagulation with PAC, and alum coagulation with MIEX could reduce aromatic hydrocarbon by 52, 83, and 68 %, respectively. Only coagulation with MIEX could reduce aliphatic hydrocarbon by 21%.

The fourth part: **Kinetics of DBPs formation from dissolved organic matter fractions and inorganic ions in the raw water**

The formation potential of chloroform and BDCM decreased initially (I^- concentration 0.5 and 0.7 μg/L), then the chloroform and BDCM species tend to increase with increasing I^- from 1 to 5 μg/L. Increase in iodide from 0.5 to 0.7 μg/L slightly increased in the total HANFP. When the iodide concentration increased from 0.7 to 2 μg/L, the HANFP slightly decreased. The maximum HANFP of 10 μg/L was taken place in iodide dose of 5 μg/L. The I-THMs and TCNM did not form when the iodide dosage from 0.5 to 5 μg/L.

The total THMFP increased by increasing Br^- from 0.1 to 1 mg/L, while further increase in the Br^- level to 10 mg/L did not increase in the total THMFP. The formation of bromoform tends to increase with increasing Br^- from 0.1 to 1 mg/L, whereas chloroform decreased. DBCM and BDCM increased initially, but then they decreased. The formation potential of total I-THMs decreased by increasing Br^- from 0.1 to 10 mg/L. TIM formation potential and DCIM formation potential decreased by increasing the Br^-. The level of BDIM formation potential was formed only in the highest Br^- of 10 mg/L. Increasing Br^- from 0.2 to 10 mg/L resulted in decreased total HANFP. While further increase in the Br^- level leads to an increase in the total HANFP. DBAN did not form at the initial Br^- of 0.1 mg/L. The DBAN formation potential exhibited high levels in the Br^- at 5 and 10 mg/L. BCAN increased initially but then decreased, and its maximum concentration occurred at Br^- of 0.2 mg/L. DCAN formation potential was measured at low concentration when the Br^- level was increased from 0.1 to 0.5 mg/L. TCNM did not form when the Br- increase from 0.1 to 10 mg/L.

The kinetic rates of THMFP of raw water explained by zero-order and first-order reaction. THMFP formation from 3 to 72 h seems to be constant or slightly decreased. A two-stage pattern including a formation (the zero-order kinetic) and degradation (the first-order kinetic) rate was determined for THMFP of treated water, I-THMFP of raw water and its treated water, and HANFP of raw water and treated wastewater.

The zero-order kinetics of THM formation of DOM fraction with MW > 10 kDa, 3 kDa < MW < 10 kDa, 1 kDa < MW < 3 kDa, and MW < 1 kDa were assessed. The zero-order kinetic of BCIM degradation was determined for DOM with MW < 1 kDa. In the case of HANs, a zero-order kinetic of HANs formation followed first-order kinetic of HANs degradation were determined. THMs formation of HPI and TPI expressed by a first-order kinetic and zero-order kinetic, respectively. The kinetic of THMs of HPO based on species. Chloroform and BDCM and DBCM have a formation (zero-order kinetic) followed by degradation (first-order kinetic), respectively. I-THMs of HPO and TPI had a formation pattern (a zero- and first-order kinetic). I-THMs of HPI has a degradation pattern (zero-order kinetic). HAN formation of HPI could be expressed by a zero-order kinetic.

Reference

Adin, A.; Katzhendler, J.; Alkaslassy, D.; Rav-Acha, C. Trihalomethanes formation in chlorinated drinking water: a kinetic model. Water Res. **1991**, *25*, 797-805.

Ahmadiab, M.; Ramavandic, B. The formation potential of haloacetonitriles in the Dez River water, Iran. Environ. Technol. **2014**, *35*, 2347-2355.

Aiken, G.R. Isolation and concentration techniques for aquatic humic substances. In: Aiken, G.R., McKinght, D.M., Wershaw, R.L.; MacCarthy, P. (eds) Humic Substances in Soil, Sediment, and Water, Wiley, New York **1985**.

Aiken, G.R.; Cotsaris, E. Soil and hydrology: their effect on NOM. J. Am. Water Works Assoc. **1995**, *87*, 36-45.

Amy, G.L., Collins M.R., Kuo C.J., King P.H. Comparing gel permeation chromatography and ultrafiltration for the molecular weight characterization of aquatic organic matter. J. Am. Water Works Assn. **1987,** *79*(1): 43-49.

APHA, AWWA, & WPCF. Standard Method for the Examination of Water and Wastewater. *19th edn, Washington, DC,* **1995,** *44*, 5376-5384.

Arnaldos, M.; Pagilla, K. Effluent dissolved organic nitrogen and dissolved phosphorus removal by enhanced coagulation and microfiltration. Water Res. **2010**, *44*, 5306-5315.

AWWA. Characterization of natural organic matter and its relationship to treatability, First Ed.; AWWARF and AWWA, USA, **1993**.

Aydin, E., Yaman, F. B., Genceli, E. A., Topuz, E., Erdim, E., Gurel, M., Pehlivanoglu Mantas, M.. Occurrence of THM and NDMA precursors in a watershed: Effect of seasons andanthroropogenic pollution. *J. Hazardous materials,* **2012**, *221-222*, 86-91.26

Baker, A. Fluorescence excitation-emission matrix characterization of some sewage-impacted rivers. Environ. Sci. Technol. **2001**, *35*(5), 948-953.

Basu, M.; Gupta, S.K.; Singh, G.; Mukhopadhyay, U. Multi-route risk assessment from trihalomethanes in drinking water supplies. Environ. Monit. Assess. **2011**, *178*, 121-134.

Bichsel, Y.; von Gunten, U. Formation of iodo-trihalomethanes during disinfection and oxidation of iodide-containing waters. Environ. Sci. Technol. **2000**, *34*, 2784-2791.

Bond, T.; Huang, J.; Templeton, M.R.; Graham, N. Occurrence and control of nitrogenous disinfection by-products in drinking water—a review. Water Res. **2011**, *45*, 4341-4354.

Bond, T.; Templeton, M.R.; Kamal, N.H.M.; Graham, N.; Kanda, R. Nitrogenous disinfection byproducts in English drinking water supply systems: Occurrence, bromine substitution and correlation analysis. Water Res. **2015**, *85*, 85-94.

Bougeard, C.M.M.; Goslan, E.H.; Jefferson, B.; Parsons, S.A. Comparison of the disinfection by-product formation potential of treated waters exposed to chlorine and monochloramine. Water Res. **2010**, *44*, 729-740.

Butterworth, B.E. Science-based risk assessments for drinking water disinfection by- products. Environ. Res. **2005**, *98*, 276-278.

Cai Y. Size distribution measurements of dissolved organic carbon in natural waters using ultrafiltration technique. Water Res. **1999**, *33*(13), 3056-3060.

Cancho, B., Ventura, F., Galceran, M., Diaz, A., Ricart S., Determination, Synthesis and survey of iodinated trihalomethanes in water treatment processes, Water Res. **2000,** *34*, 3380–3390.

Cemeli, E.; Wagner, E.D.; Anderson, D.; Richardson, S.D.; Plewa, M.J. Modulation of the cytotoxicity and genotoxicity of the drinking water disinfection byproduct iodoacetic acid by suppressors of oxidative stress. Environ. Sci. Technol. **2006**, *40*, 1878-1883.

Chandramouleeswaran, S.; Vijaylakshmi, B.; Kartihkeyan, S.; Rao, T.P.; Iyer, C.S.P. Ion-chromatographic determination of iodide in sea water with UV detection. Mikrochim. Acta. **1998**, *128*, 75-77.

Chang, H.; Wang, G. Fractionation of nitrogen-enriched dissolved organic matter in water. Sep. Purif. Technol. **2013**, *117*, 89-97.

Chen, B.; Westerhoff, P. Predicting disinfection by-product formation potential in water. Water Res. **2010**, *44*, 3755-3762. Chen, C.; Zhang, X.; Zhu, L.; He, W.; Han, H. Changes in different organic matter fractions during conventional treatment and advanced treatment. J Environ Sci. **2011**, *23*(4), 582-586.

Chen, W.; Westerhoff, P.; Leenheer, J.A. Fluorescent excitation emission matrix regional integration to quantify spectra for dissolved organic matter. Environ. Sci. Technol. **2003**, *37*(24), 5701-5710.

Chen, W. H., Young, T. M. NDMA formation during chlorination and chloramination of aqueous diuron solutions. Environ. Sci. Technol., **2008**, *42*(4), 072-107.

Chu, W.; Gao, N.; Krasner, S.W.; Templeton, M.R.; Yin, D. Formation of halogenated C-, N-DBPs from chlor(am)ination and UV irradiation of tyrosine in drinking water. Environ. Pollut. **2012**, *161*, 8-14.

Chu, W.; Gao, N.; Yin, D.; Krasner, S.W. Formation and speciation of nine haloacetamides, an emerging class of nitrogenous DBPs, during chlorination or chloramination. J. Hazard. Mater. **2013**, *260*, 806-812.

Choi, J. H., Valentile, R. L. 2002. Formation of N-nitrosodimethylamine (NDMA) from reaction of monochloroamine: a new disinfection by product. Water Res. **2002**, *36 (4)*, 817-824.

Coble, P.G. Characterization of marine and terrestrial DOM in seawater using excitation emission matrix spectroscopy. Mar. Chem. **1996**, *51*, 325-346.

Dotson, A.; Westerhoff, P.; Chen, B.; Lee, W. Organic nitrogen occurrence and characterization. In *Disinfection by-products in drinking water: occurrence, formation, health effects, and control;* Karanfil, T.; Krasner, S.W.; Westerhoff, P.; Xie, Y., Eds.; American Chemical Society, Washington, DC, **2008**, pp. 274-288.

Dotson, A.; Westerhoff, P.; Krasner, S.W. Nitrogen enriched dissolved organic matter (DOM) isolates and their affinity to form emerging disinfection by-products. Water Sci. Technol. **2009**, *60*, 135-143.

EECD. Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption. Official Journal of the European Community. **1998**, *L330*(32), 32-54.

European Economic Community Directive. Amended proposal for a Council Directive concerning the quality of water intended for human consumption-common position. Proc. Council of the European Union, Directive 80/778EEC, Com (97)228 final 95/0010 SYN, Brussels, 1997.

Fan, Z.; Zhang, H.; Xu, X.; Liu, B.; Zhang, D.; Yu, X. Dissolved organic nitrogen (DON) in full scale two-stage O_3-BAC with nitrate as sole inorganic nitrogen source. Int. J. Environ. Res. **2012,** *6*, 985-994.

Gangolli, S.D., van den Brandt, P.A., Feron, V.J., Janzowsky, C., Koeman, J.H. Speijers, G.J., Spiegelhalder, B., Walker, R., Wisnok, J.S.. Nitrate, nitrite and Nnitrosocompounds. European Journal of Pharmacology: Environ. Toxicol. Pharmaco. **1994**, *292*(1), 1-38.

Gong, T.; Zhang, X. Detection, identification and formation of new iodinated disinfection byproducts in chlorinated saline wastewater effluents. Water Res. **2015**, *68*, 77-86.

Goslan, E.H.; Krasner, S.W.; Bower, M.; Rocks, S.A.; Holmes, P.; Levy, L.S.; Parsons, S.A. A comparison of disinfection by-products found in chlorinated and chloraminated drinking waters in Scotland. Water Res. **2009**, *43*, 4698-4706.

Guo j., Liu H. Liu J., Wang L.,. Ultrafiltration performance of EfOM and NOM under different MWCO membranes: Comparison with fluorescence spectroscopy and gel filtration chromatography**.** Desalination. **2014**, 344, 129-136.

Han, Q.; Yan, H.; Zhang, F.; Xue, N.; Wang, Y.; Chu, Y.; Gao, B. Trihalomethanes (THMs) precursor fractions removal by coagulation and adsorption for bio-treated municipal

wastewater: Molecular weight, hydrophobicity/hydrophily and fluorescence. J. Hazard. Mater. **2015**, *297*, 119-126.

Hansen, A.M.; Kraus, T.E.C.; Pellerin, B.A.; Fleck, J.A.; Downing, B.D.; Bergamaschi B.A. Optical properties of dissolved organic matter (DOM): Effects of biological and photolytic degradation. Limnol. Ocean ogr. **2016**, *61*, 1015-1032.

Hepplewhite, C.; Newcombe, G.; Knappe, D.R.U. NOM and MIB, who wins inthe competition for activated carbon adsorption sites? J. Water Sci. Technol. **2004**, *49*(9), 257-265.

Hong, H.C.; Huang, F.Q.; Wang, F.Y.; Ding, L.X.; Lin, H.J.; Liang, Y. Properties of sediment NOM collected from a drinking water reservoir in south China, and its association with THMs and HAAs formation. J. Hydrol. **2013**, *476*, 274-279.

Huo, S.; Xi, B.; Yu, H.; Qin, Y.; Zan, F.; Zhang, J. Characteristics and transformations of dissolved organic nitrogen in municipal biological nitrogen removal wastewater treatment plants. Environ. Res. Lett. **2013**, *8*, 044005 (9pp).

Hu, H.Y., Ye, D., Wu, Q.Y., Xin, Z., Xin, T., Zhuo, C. Differences in dissolved organic matter between reclaimed water source and drinking water source. Sci. Total Environ. **2016**, *551-552*, 133-142

Hu J, Song H, Karanfil T. Comparative analysis of halonitromethane and trihalomethane formation and speciation in drinking water: the effects of disinfectants, pH, bromide, and nitrite. Environ. Sci. Technol, **2010** ;44:794–9.

Hudson, N.; Baker, A.; Reynolds, D. Fluorescence analysis of dissolved organic matter in natural waste and polluted waters—A review. River. Res. Applic. **2007**, *23*, 631-649.

Humbert, H.; Gallard, H.; Suty, H.; Croúe. J.P. Performance of selected anion exchange resins for the treatment of a high DOC content surface water. Water Res. **2005**, *39*(9), 1699-1708

Ioannou, P.; Charisiadis, P.; Andra, S.S.; Makris, K.C. Occurrence and variability of iodinated trihalomethanes concentrations within two drinking-water distribution networks. Sci. Total Environ. **2016**, *543*, 505-513.

Ito, K.; Ichihara, T.; Zhuo, H.; Kumamoto, K.; Timerbaev, A.R.; Hirokawa, T. Determination of trace iodide in seawater by capillary electrophoresis following transient isotachophoretic preconcentration: Comparison with ion chromatography. Anal Chim Acta. **2003**, *497*, 67-74.

Jack, J.; Sellers, T.; Bukaveckas, P.A. Algal production and trihalomethane formation potential: an experimental assessment and inter-river comparison. Can. J. Fish. Aquat. Sci. **2002**, *59*, 1482-1491.

Jia, A.; Wu, C.; Duan, Y. Precursors and factors affecting formation of haloacetonitriles and chloropicrin during chlor(am)ination of nitrogenous organic compounds in drinking water. J. Hazard. Mater. **2016**, *308*, 411-418.

Jia Hu., Hocheol S., Halonitromethane formation potentials in drinking waters. Water Res. **2009**., *44*, 105- 114.

Jones, D.; Saglam, A.; Song, H.; Karanfil, T. The impact of bromide/iodide concentration and ratio on iodinated trihalomethane formation and speciation. Water Res. **2012**, *46*(1), 11-20.

Kanokkantapong, V.; Marhaba, T.F.; Wattanachira, S.; Panyapinyophol, B.; Pavasant, P. Interaction between organic species in the formation of haloacetic acids following disinfection. J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng. **2006**, *41*, 1233-1248.

Karanfil, T.; Hu, J.; Jones, D.B.; Addison, J.W.; Song, H. Formation of halonitromethanes and iodo-trihalomethanes in drinking water. Water Research Foundation, Denver, CO, USA, **2011**.

Kasuga, I., Nakajima, F., Furumai, H. Analysis of dissolved organic matter and bacterial community in degradation of algal bloom by EEMs and PCR-DGGE. J. JSWE. **2003**, *26* (3): 171- 174.

Kim, J.; Chung, Y.; Shin, D.; Kim, M.; Lee, Y.; Lim, Y.; Lee, D. Chlorination by-products in surface water treatment process. Desalination **2003**, *151*, 1-9.

Kitis, M.; Harman, B.I.; Yigit, N.O.; Beyhan, M.; Nguyen, H.; Adams, B. The removal of natural organic matter from selected Turkish source waters using magnetic ion exchange resin (MIEX®). Reactive & Functional Polymers **2007**, *67*(12), 1495-1504.

Kitis, M.; Karanfil, T.; Wigton, A.; Kilduff, J. E. Probing reactivity of dissolved organic matter for disinfection by-product formation using XAD-8 resin adsorption and ultrafiltration fractionation. Water Res. **2002**, *36*, 3834-3848.

Knapik, H.G.; Fernandes, C.V.; de Azevedo, J.C., do Amaral Porto, M.F. Applicability of fluorescence and absorbance spectroscopy to estimate organic pollution in rivers. Environ. Eng. Sci. **2014**, *31*(12), 653-663.

Knight, N.; Watson, K.; Farre, M.J.; Shaw, G. N-nitrosodimethylamine and trihalomethane formation and minimisation in Southeast Queensland drinking water. Environ. Monit. Assess. **2012**, *184*(7), 4207-4222.

Krasner, S.W. **1999** Chemistry of disinfection by-product formation. In: Singer, P.C. (ed.) Formation and Control of Disinfection Association, Denver, CO, pp. 27-52.

Krasner, S.W.; Weinberg, H.S.; Richardson, S.D.; Pastor, S.J.; Chinn, R.; Sclimenti, M.J.; Onstad, G.D.; Thruston, A.D. Occurrence of a new generation of disinfection byproducts. Environ. Sci. Technol. **2006**, *40*, 7175-7185.

Krasner, S.W.; Westerhoff, P.; Chen, B.; Rittmann, B.E.; Nam, S.N.; Amy, G. Impact of wastewater treatment processes on organic carbon, organic nitrogen, and DBP precursors in effluent organic matter. Environ. Sci. Technol. **2009**, *43*, 2911-2918.

Kumsuvan J., Wongrueng A. Musikavong C.. Removal of N-nitrosodimethylamine precursors in Bangkok source water by alum and polyaluminium chloride. The proceeding of Annual Conference on Engineering and Information Technology, March, **2014**, Tokyo, Japan

LDD. Land Development Department (LDD), Ministry of Agriculture and Cooperatives. **2017**. Available at http://www.ldd.go.th/www/lek_web/web.jsp?id=18907 (accessed Jan 2019).

Lee, C., Yoon, J., Von Gunten, U.. Oxidative degradation of Nnitrosodimethylamine by conventional and the advanced oxidation process ozone/hydrogen peroxide, Water Res. **2007**, *41*, 581-590.

Lee N, Amy G, Croue J, Buisson H. Identification and understanding of fouling in low-pressure membrane (MF/UF) filtration by natural organic matter (NOM). Water Res. **2004**, *38* (20):4511–4523.

Lee, S.; Ahn, K.H. Monitoring of COD as an organic indicator in waste water and treated effluent by fluorescence excitation-emission (FEEM) matrix characterization. Water Sci. Technol. **2004**, *50*, 57-63.

Lee, W.; Westerhoff, P. Dissolved organic nitrogen removal during water treatment by aluminium sulfate and cationic polymer coagulation. Water Res. **2006**, *40*, 3767-3774.

Lee, W.; Westerhoff, P.; Croue, J.P. Dissolved organic nitrogen as a precursor for chloroform, dichloroacetonitrile, *N*-nitrosodimethylamine, and trichloronitromethane. Environ. Sci. Technol. **2007**, *41*, 5485-5490.

Lee, W.; Westerhoff, P.; Esparza-Soto, M. Occurrence and removal of dissolved organic nitrogen in US water treatment plants. J. Am. Water Works Assoc. **2006**, *98*, 102-110.

Leenheer, L.A. Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural water and wastewater. Environ. Sci. Tech. **1981**, *15*, 578-587.

Leenheer, J.A.; Wershaw, R.L.; Reddy, M.M. **1995**. Strong-acid, carboxyl group structures in fulvic-acid from the Suwannee River, Georgia. Environ. Sci. Technol. *29* (2), 393-398.

Leenheer, J.A.; Croue, J.P. Characterizing aquatic dissolved organic matter. Environ. Sci. Technol. **2003**, *37*(1), 18a-26a.

Liang, L., Singer, P.C. Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. Environ. Sci. Tech. **2003**, *37*(13), 2920-2928.

Liew, D.; Linge, K.L.; Joll, C.A. Formation of nitrogenous disinfection by-products in 10 chlorinated and chloraminated drinking water supply systems. Environ Monit Assess. **2016**, *188*(9), 518.

Liu, S.; Zhu, Z.; Qiu, Y.; Zhao, J. Effect of ferric and bromide ions on the formation and speciation of disinfection byproducts during chlorination. J Environ Sci (China). **2011**, *23*(5), 765-772

Liu, X.; Chen, Q.; Zhu, L. Improving biodegradation potential of domestic wastewater by manipulating the size distribution of organic matter. J. Environ. *Sci.* **2016**, *47*, 174-182.

Ma, D.; Gao, B.; Sun, S.; Wang, Y.; Yue, Q.; Li, Q. Effects of dissolved organic matter size fractions on trihalomethanes formation in MBR effluents during chlorine disinfection. Bioresour. Technol. **2013**, *136*, 535-541.

Ma, Q., Xi, H-W., Wang, C., Bai, H., Xi, G-C., Su, N., Xu, L-Y., Wang, J-B. Determinatio of ten volatile nitrosamines in cosmetics by gas chromatography tandem mass spectrometry. Chinese J Anal Chem. **2011**, *39*(8), 1201-1207.

Maizel, A.C.; Remucal, C.K. The effect of advanced secondary municipal wastewater treatment on the molecular composition of dissolved organic matter. Water Res. **2017**, *122*, 42-52.

Matilainen A, Vepsalainen M, Sillanppa M. Natural organic matter removal by coagulation during water treatment: A review. Adv Colloid Interface Sci. **2010**, *159*, 189-97.

Matilainen A, Sillanppa, M. Removal of natural organic matter from drinking water by advanced oxidation processes. Chemosphere. **2010**, 80, 351–65.

Matilainen A, Gjessing ET, Lahtinen T, Hed L, Bhatnagar A, Sillanp ¨ a ¨ a M. An overview of the methods used in the characterization of natural organic matter in relation to drinking water treatment plant. Chemosphere. **2011**, *83*, 1431–42.

Mergen, M.R.D.; Jefferson, B.; Parsons, S.A.; Jarvis, P. **2008**. Magnetic ion-exchange resin treatment: Impact of water type and resin use. Water Res. *42*, 1977-1988.

Mesdaghinia, A.; Rafiee, M.; Vaezi, F.; Mahvi, A.; Torabian, A.; Ghasri, A. Control of isinfection by products formation potential by enhanced coagulation. Int. J. Environ. Sci. Technol. **2006**, *2*(4), 335-342.

Mitch W A, Sharp J O, Trussell R R, Valentine R L, Alvarez-Cohen L, Sedlak D L,. N-nitrosodimethylamine (NDMA) as a drinking water contaminant: A review. Environ Eng Sci, **2003** *20*(5): 389–404.

Mitch, W. A., Sedlak, D. L. Characterization and fate of NDMA precursors in municipal wastewater treatment plants. Environ. Sci. Technol. **2004**, *38*, 1445–1454.

Mitch, W.A.; Krasner, S.W.; Westerhoff, P.; Dotson, A. Occurrence and formation of nitrogenous disinfection by-products. Water Research Foundation, Denver, CO, USA, **2009**.

Muellner, M.G.; Wagner, E.D.; McCalla, K.; Richardson, S.D.; Woo, Y.T.; Plewa, M.J. Haloacetonitriles vs. regulated haloacetic acids: are nitrogen-containing DBPs more toxic? Environ. Sci. Technol. **2007**, *41*, 645-651.

Munch, D.J.; Hautman, D.P. Method 551.1, Determination of chlorinated disinfection byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water by liquid/liquid extraction and gas chromatography with electron capture detection. USEPA, Cincinnati, OH, **1995**.

Musikavong C. **2007**. Characterization of fractionated dissolved organic matter in industrial estate wastewater by sprectrofluorometry and pyrolysis GC/MS . Ph.D Dissertation. Inter Department Program in Environmental Management, Chlolalongkorn Uiversity.

Musikavong, C., Wattanachira, S. Identification of dissolved organic matter in raw water supply from reservoirs and canals as precursors to trihalomethanes formation. J Environ Sci Health A Tox Hazard Subst Environ Eng. **2013**, *48*(7)), 760-771.

Musikavong, C.; Srimuang, K.; Suksaroj, T.T.; Suksaroj, C. Formation of trihalomethanes of dissolved organic matter fractions in reservoir and canal waters. J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng. **2016**, *51*, 782-791.

Najm, I., Patania, N.L., Jacangelo, J.G. ; Krasner, S.W. Evaluating surrogates for disinfection by-products. J. Am. Water Works Ass. **1994**, *86*, 98-106.

Najm, I., Trussell, R.R. NDMA formation in water and wastewater. AWWA Water Sci. **2001**, *93*(2), 92-99.

Na-Phatthalung, W.; Musikavong, C.; Suttinun, O. The presence of aliphatic and aromatic amines in reservoir and canal water as precursors to disinfection byproducts. J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng. **2016**, *51*(11), 900-913.

Na-Phatthalung., W.; Musikavong, C. Emerging disinfection by-products' formation potential in raw water, wastewater, and treated wastewater in Thailand J. Environ. Sci. Health, Part A. **2019**, *54*(8): 745-758.

Nawrocki, J. Nitrosamines—Troublesome by-products of water disinfection. Ochr. Sr.´ **2007**, *29*, 13-18.

Oya, M., Kosaka, K., Asami, M., Kunikane, S. Formation of Nnitrosodimethylamine (NDMA) by ozonation of dyes and related compounds. Chemosphere. **2008**, 73(11), 1724-1730.

Padhye, L., Luzinova, Y., Cho, M., Mizaikoff, B., Kim, J., Huang, C-. PolyDADMAC and dimethylamine as precursors of N-nitrosodimethylamine during ozonation: reaction kinetics and mechanisms, Environ. Sci. Technol. **2011**, *45*, 4353-4359.

Page, D. W.; VanLeeuwen, J. A.; Spark, K. M.; Mulcahy, D. E. Pyrolysis characterization of plant, humus and soil extracts from Australian catchments. J. Anal. Appl. Pyrol. **2002**, *65*, 269-285.

Pantelaki, I.; Voutsa, D. Formation of iodinated THMs during chlorination of water and wastewater in the presence of different iodine sources. Sci. Total Environ. **2018**, *613-614*, 389-397.

Panyapinyopol, B.; Marhaba, T.F.; Kanokkantapong, V.; Pavasant, P. Characterization of precursors to trihalomethanes formation in bangkok source water. J. Hazard. Mater. **2005**, *120*(1-3), 229-236.

Plewa, M.J.; Wagner, E.D.; Jazwierska, P.; Richardson, S.J.; Chen, P.H.; McKague, A.B. Halonitromethane drinking water disinfection byproducts: chemical characterization and mammalian cell cytotoxicity and genotoxicity. Environ. Sci. Technol. **2004**, *38*, 62-68.

Plewa, M.J.; Wagner, E.D. Quantitative comparative mammalian cell cytotoxicity and genotoxicity of selected classes of drinking water disinfection by-products. Water Research Foundation, Denver, CO, USA, **2009**.

Plewa, M.J., Simmons, J.E.; Richardson, S.D.; Wagner, E.D. Mammalian cell cytotoxicity and genotoxicity of the haloacetic acids, a major class of drinking water disinfection by-products. Environ. Mol. Mutagen. **2010**, *51*(8-9), 871-878.

Quanrud D.M., Lansey K.E., Ela W., Arnold R.G., Fate of organics during soil aquifer treatment: biodegradability, chlorine reactivity, and genotoxicity. J Water Health. **2003** *1*, 33-44.

Ratasuk C, Kositanont C, Ratanatamskul C. 2008. Removal of haloacetic acids by ozone and biologically active carbon. Science Asia. **2008**, *3*4, 293–8.

Richardson, S.D.; Plewa, M.J.; Wagner, E.D.; Schweny, R.; Demarini, D.M. 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. **2007**, *636*, 178-242.

Richardson, S.D.; Fasano, F.; Ellington, J.J.; Crumley, F.G.; Buettner, K.M.; Evans, J.J.; Blount, B.C.; Silva, L.K.; Waite, T.J.; Luther, G.W.; Mckague, A.B.; Miltner, R.J.; Wagner, E.D.; Plewa, P.J. Occurrence and mammalian cell toxicity of iodinated disinfection byproducts in drinking water. Environ. Sci. Technol. **2008**, *42*, 8330-8338.

Rook, J. J. Formation of haloform during chlorination of natural waters, Water. Treat. Exam. **1974**, *23*, 234-243.

Schreiber, I.M.; Mitch, W.A. Occurrence and fate of nitrosamines and nitrosamine precursors in wastewater-impacted surface waters using boron as a conservative tracer. Environ. Sci. Technol. **2006**, *40*, 3203-3210.

Schulten, H.R.; Gleixner, G. Analytical pyrolysis of humic substances and dissolved organic matter in aquatic systems: Structure and origin. Water Res. **1999**, *33*, 2489-2498.

Sierra, M.M.D., Giovanela, M., Parlanti, E., Soriano-Sierra E.J. Fluorescent fingerprint of fulvic and humic acids from varied origins as viewed by single-scan and excitation/emission matrix techniques, Chemosphere. **2005**, *58*: 715-733.

Shah, A.D.; Mitch, W.A. Halonitroalkanes, halonitriles, haloamides, and *N*-nitrosamines: a critical review of nitrogenous disinfection byproduct formation pathways. Environ. Sci. Technol. **2012,** *46*, 119-131.

Shah, A.D.; Liu, Z.-Q.; Salhi, E.; Höfer, T.; Werschkun, B.; von Gunten, U. Formation of disinfection by-products during ballast water treatment with ozone, chlorine, and peracetic acid: influence of water quality parameters. Environ. Sci.: Water Res. Technol. **2015**, *1*(4), 465-480.

Shanks, C.M.; Sérodes, J.B.; Rodriguez, M.J. Spatio-temporal variability of non-regulated disinfection by-products within a drinking water distribution network. Water Res. **2013**, *47*, 3231-3243.

Shi, H., Qiang, Z., Adams, C. Formation of haloacetic acids, halonitromethanes, bromate and iodate during chlorination and ozonation of seawater and saltwater of marine aquaria systems. Chemosphere. **2013**, *90,* 2485-2492.

Sadiq R, Rodriguez MJ. Disinfection by-products (DBPs) in drinking water and predictive models for their occurrence: a review. Science Total Environ. **2004**, *321*, 21– 46.

Singer, P.C.; Bilyk, K. Enhanced coagulation using a magnetic ion exchange resin. Water Res. **2002**. *36*, 4009-4022.

Sinsabaugh, R. L. ; Findlay, S. Dissolved organic matter: Out of the black box into the mainstream. In *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter*; Findlay, S.; Sinsabaugh, R. L., Eds.; Elsevier Science Inc., USA, **2003**, 479-498.

Song, H.; Addison, J.W.; Hu, J.; Karanfil, T. Halonitromethanes formation in wastewater treatment plant effluents. Chemosphere **2010**, *79*, 174-179.

Srimuang, K., Suksaroj, T. T., Suksaroj, C., Musikavong, C. Characterization and reduction ofractionated Dissolved Oraganic Matter in Raw Water Supply from U-Tapao Canal by Enhanced Coagulation. Southest Asian Water Environment. **2013**, 95-100.

Suksaroj, C.; Rattanamanee, P.; Musikavong, C.; Wattanachira, S. The determination of tryptophan and humic and fulvic acid-like substances reduction in raw water from U-Tapao basin Thailand with alum coagulation. Water Practice & Technology. **2009**, *4*(2), 1-9.

Sumpattanavorachai S. , Wongrueng A. Musikavong C. **2014**. Treatment of *N*nitrosodimethylamine precursors in Bangkok source water by PACl coagulation, Nanofiltration, and reverse osmosis processes. The proceeding of Annual Conference on Engineering and Information Technology, March, Tokyo, Japan

Sun, W.L.; Liu, T.T.; Cui, F.; Ni, J.R. Fluorescence evolution of leachates during treatment processes from two contrasting landfills. Environ. Tech. **2008**, *29*(10), 1119-1125.

Teixeira, M.R.; Rosa, S.M.; Sousa, V. Natural organic matter and disinfection by-products formation potential in water treatment. Water Resour. Manag. **2011**, *25*(12), 3005-015.

Tokmak, B.; Capar, G.; Dilek, F.B.; Yetis, U. Trihalomethanes and associated potential cancer risks in the water supply in Ankara, Turkey. Environ. Res. **2004**, *96*, 345-352.

Tongchang, P.; Kumsuvan, J.; Na-Phatthalung, W.; Suksaroj, C.; Wongrueng, A.; Musikavong, C. Reduction by enhanced coagulation of dissolved organic nitrogen as a precursor of *N*-nitrosodimethylamine. J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng. **2018**, *53*, 583-593.

Tingting Gong, Xiangru Zhang. Determination of iodide, iodate and organoiodine in waters with a new total organic iodine measurement approch. Water Res. **2013**, *47*, 6660-6669.

Tugulea, A.M.; Aranda-Rodriguez, R.; Berub, D.; Giddings, M.; Lemieux, F.; Hnatiw, J.; Dabeka, L.; Breton, F. The influence of precursors and treatment process on the formation of Iodo-THMs in Canadian drinking water. Water Res. **2018**, *130*, 215-223.

Urbansky, E.T. Ascorbic acid treatment to reduce residual halogen-based oxidants prior to the determination of halogenated disinfection byproducts in potable water. J. Environ. Monit. **1999**. *1*, 471-476.

US EPA. Enhanced coagulation and enhanced precipitative softening guidance manual, Office of Water, EPA 815-R-99-012, **1999**.

US EPA. Integrated Risk Information System (IRIS). **2011**, Available at http://cfpub.epa.gov/ncea/iris/index.cfm (accessed Mar 2017).

US EPA. National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfectant Byproducts; Final Rule. Part II 40 CFR Parts 9, 141, and 142, **2006**.

Volk, C.; Wood, L.; Johnson, B.; Robinson, J.; Zhu, H.W.; Kaplan, L. Monitoring dissolved organic carbon in surface and drinking waters. J. Environ. Monit. **2002**, *4*, 43-47.

Von Gunten, U., Salhi, E., Schmidt, C.K., Arnold, W.A. Kinetics and mechanisms of N-nitrosodimethylamine formation upon ozonation of N,Ndimethylsulfamide containing waters: bromide catalysis. Environ. Sci. Technol. **2010**, *44*, 5762-5768.

Wang, J.J.; Lafreniere, M.J.; Lamoureux, S.F.; Simpson, A.J.; Gelinas, Y.; Simpson, M.J. Differences in Riverine and pond water dissolved organic matter composition and sources in Canadian High Arctic watersheds affected by active layer detachments. Environ. Sci. Technol. **2018**, *52*, 1062-1071.

Wang, C.; Zhang, X.; Chen, C.; Wang, J. Factors controlling *N*-nitrosodimethylamine (NDMA) formation from dissolved organic matter. Front. Environ. Sci. Eng. **2013**, *7*, 151-157.

Watson, K.; Farré, M.J.; Birt, J.; McGree, J.; Knight, N. Predictive models for water sources with high susceptibility for bromine-containing disinfection by-product formation: implications for water treatment. Environ Sci. Pollut. Res. **2015**, *22*, 1963-1978.

Wei, X.; Chen, X.; Wang, X.; Zheng, W.; Zhang, D.; Tian, D.; Jiang, S.; Ong, C.N.; He, G.; Qu, W. Occurrence of regulated and emerging iodinated DBPs in the Shanghai drinking water. PLoS One **2013a**, *8*(3), e59677.

Wei, Y.; Liu, Y.; Ma, L.; Wang, H.; Fan, J.; Liu, X.; Dai, R. Speciation and formation of iodinated trihalomethanes from microbially derived organic matter during the biological treatment of micro-polluted source water. Chemosphere **2013b**, *92*, 1529-1535.

Weishaar, J.L.; Aiken, G.R.; Bergamaschi, B.A.; Fram, M.S.; Fujii, R.; Mopper, K. Evaluation of specific ultraviolet absorbance as an indicator of the chemical

composition and reactivity of dissolved organic carbon. Environ. Sci. Technol. **2003**, *37*, 4702-4708.

Westerhoff, P.; Mash, H. Dissolved organic nitrogen in drinking water supplies: A review. J Water Supply Res T. **2002**, *51*, 415-488.

WHO. Guidelines for drinking water quality. In *Recommendations*; 3rd Ed.; Vol. 1, World Health Organization, Geneva, Switzerland, **2008**.

WHO. Guidelines for drinking water quality, First addendum to the 3rd ed.; Vol. 1, World World Health Organization. 1996. Guidelines for drinking water quality vol.2 , Health Criteria and Other Supporting Information, 2nd edition, Gerneva, p940. World Health Organization. 2008. N-Nitrosodimethylamine in Drinking-water Health Organization, Geneva, **2006**, pp. 491-492.

World Health Organization. 1996. Guidelines for drinking water quality vol.2 , Health Criteria and Other Supporting Information, 2nd edition, Gerneva, p940. World Health Organization. **2008**. *N*-Nitrosodimethylamine in Drinking-water

Woo, Y.T.; Lai, D.; McLain, J.L.; Manibusan, M.K.; Dellarco, V. Use of mechanism-based structure-activity relationships analysis in carcinogenic potential ranking for drinking water disinfection by-products. Environ. Health Perspect. **2002**, *110*, 75-87.

Xu, B.; Li, D.; Li, W.; Xia, S.; Lin, Y.; Hu, C.; Zhang, C.; Gao, N. Measurements of dissolved organic nitrogen (DON) in water samples with nanofiltration pretreatment. Water Res. **2010**, *44*, 5376-5384.

Xu, B.; Ye, T.; Li, D.P.; Hu, C.Y.; Lin, Y.L.; Xia, S.J.; Tian, F.X.; Gao, N.Y. Measurement of dissolved organic nitrogen in a drinking water treatment plant: Size fraction, fate, and relation to water quality parameters. Sci. Total Environ. **2011**, *409*, 1116-1122.

Yang, X.; Guo, W.; Shen, Q. Formation of disinfection byproducts from chlor(am)ination of algal organic matter. J. Hazard. Mater. **2011**, *197*, 378-388.

Yang, X.; Shen, Q.; Guo, W.; Peng, J.; Liang, Y. Precursors and nitrogen origins of trichloronitromethane and dichloroacetonitrile during chlorination/chloramination. Chemosphere. **2012**, *88*, 25-32.

Yang, M.; Zhang, X. Comparative developmental toxicity of new aromatic halogenated DBPs in a chlorinated saline sewage effluent to the marine polychaete *Platynereis dumerilii*. Environ. Sci. Technol. **2013**, *47*, 10868-10876.

Ye, B.; Wang, W.; Yang, L.; Wei, J. Formation and modeling of disinfection by-products in drinking water of six cities in China. J. Environ. Monit. **2011**, *13*(5), 1271-1275.

Yoon, S., Nakada, N., Tanaka, H. Occurrence and removal of NDMA and NDMA formation potential in wastewater treatment plants. J. Hazard. Mater. **2011**, *190*, 897-902.

Yuanyuan W., Yan L., Luming M., Hongwu W., Jinhong F., Xiang L., Rui-hua D. Speciation and formation of iodinated trihalomethane from microbially derived organic matter during the biological treatment of micro polluted source water. Chemosphere. **2013**, *92*,1529-1535.

Yu, H.; Qu, F.; Sun, L.; Liang, H.; Han, Z.; Chang, H.; Shao, S.; Li, G. Relationship between soluble microbial products (SMP) and effluent organic matter (EfOM): Characterized by fluorescence excitation emission matrix coupled with parallel factor analysis. Chemosphere. **2015**, *121*, 101-109.

Zepp, R.G.; Sheldon, W.M.; Moran, M.A. Dissolved organic fluorophores in southeastern US coastal waters: correction method for eliminating Rayleigh and Raman scattering peaks in excitation–emission matrices. Mar. Chem. **2004**, *89*(1-4), 15-36.

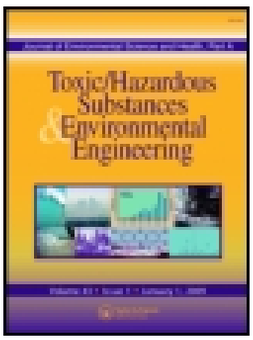
Zhang, J.; Chen, D.D.; Li, L.; Li, W.W.; Mu, Y.; Yu, H.Q. Role of NOM molecular size on iodo-trihalomethane formation during chlorination and chloramination. Water Res. **2016**, *102*, 533-541.

Zhang, T.Y.; Xu, B.; Hu, C.Y.; Lin, Y.L.; Lin, L.; Ye, T.; Tian, F.X. A comparison of iodinated trihalomethane formation from chlorine, chlorine dioxide and potassium permanganate oxidation processes. Water Res. **2015**, *68*, 394-403.

Zhang, H.; Zhang, K.; Jin, H.; Gu, L.; Yu, X. Variations in dissolved organic nitrogen concentration in biofilters with different media during drinking water treatment. Chemosphere **2015**, *139*, 652-658.

Zhou, S.; Zhu, S.; Shao, Y.; Naiyun, Gao. Characteristics of C-, N-DBPs formation from algal organic matter: Role of molecular weight fractions and impacts of pre-ozonation. Water Res. **2015**, *72*, 381-390.

Appendix



Taylor & Francis
Taylor & Francis Group

Journal of Environmental Science and Health, Part A
Toxic/Hazardous Substances and Environmental Engineering

ISSN: 1093-4529 (Print) 1532-4117 (Online) Journal homepage: https://www.tandfonline.com/loi/lesa20

Emerging disinfection by-products' formation potential in raw water, wastewater, and treated wastewater in Thailand

Warangkana Na Phatthalung & Charongpun Musikavong

To cite this article: Warangkana Na Phatthalung & Charongpun Musikavong (2019): Emerging disinfection by-products' formation potential in raw water, wastewater, and treated wastewater in Thailand, Journal of Environmental Science and Health, Part A, DOI: 10.1080/10934529.2019.1592532

To link to this article: https://doi.org/10.1080/10934529.2019.1592532

JOURNAL OF ENVIRONMENTAL SCIENCE AND HEALTH, PART A
https://doi.org/10.1080/10934529.2019.1592532

Emerging disinfection by-products' formation potential in raw water, wastewater, and treated wastewater in Thailand

Warangkana Na Phatthalung [a,b] and Charongpun Musikavong[a,b]

[a]Department of Civil Engineering, Faculty of Engineering, Environmental Assessment and Technology for Hazardous Waste Management Research Center, Prince of Songkla University, Kho Hong, Hatyai, Songkhla, Thailand; [b]Center of Excellence on Hazardous Substance Management (HSM), Bangkok, Thailand

ABSTRACT

Raw water (RW) from the Bangkok and Sing Buri water treatment plants located on the Chao Phraya River, river water, domestic wastewater (WW), and treated wastewater (TWW) from two wastewater treatment plants in Thailand were collected three times to investigate disinfection by-products' (DBPs) formation potential (FP) including trihalomethane FP (THMFP), iodo-THMFP (I-THMFP), haloacetonitriles FP (HANFP), and trichloronitromethane FP (TCNMFP). High THMFP levels were observed in river water, WW, and TWW. Considering average value, the THMFP of TWW was about two times higher than that of RW. Relatively high levels of I-THMFP were found in WW and TWW. The I-THMFP of TWW was three to seven times higher than that of RW. The HANFP of TWW was one to three times higher than that of RW. High levels of TCNMFP were found in WW and TWW. TCNMFP of TWW was six to thirteen times higher than that of RW. The discharge of TWW to RW must be prevented and controlled. The moderately positive linear relationship was obtained between dissolved organic carbon and TCNMFP in TWW. Considering measured weight concentration, THMFP was found as the highest DBPs. The highest lethal concentration 50-weighted and lowest cytotoxicity-weighted concentrations of DBPs were determined for HANFP.

ARTICLE HISTORY
Received 25 September 2018
Accepted 26 February 2019

KEYWORDS
DOC/DON; trihalomethanes; iodo-trihalomethanes; haloacetonitriles; trichloronitromethane

Introduction

Dissolved organic matter (DOM) in source water mostly originates from ecological impacts and human activities at the specific location. A conventional water treatment process including coagulation, sedimentation, and filtration slightly removes DOM. A certain amount of DOM, therefore, can pass through a conventional process. Disinfection by chlorine is commonly employed after the conventional water treatment process. A reaction between DOM and chlorine can cause potentially harmful substances, also known as disinfection by-products (DBPs). DBPs in water are undesirable because of their toxicity to water consumers.[1] Health risks may arise from the consumption of water contaminated with DOM and its DBPs. Currently, the investigation of DBPs' formation from different types of water sources is very important.

A surrogate parameter for DOM is dissolved organic carbon (DOC), which reacts with chlorine resulting in the formation of carbonaceous DBPs (C-DBPs). Trihalomethanes (THMs) are the most dominant species in chlorinated waters[2] and traditionally used as a surrogate parameter for C-DBPs.[3] Four THMs species are often measured namely chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform. The United States Environmental Protection Agency (US EPA) has classified chloroform, BDCM, and bromoform as probable human carcinogens, while DBCM is classified as a possible human carcinogen.[4]

Levels of THMs are regulated by many environmental protection agencies worldwide. The European Community has set a limit for maximum THMs concentration to 100 μg/L[5] in drinking water, and the US EPA has set a regulation level for THMs in drinking water of 80 μg/L.[6] The World Health Organization (WHO) has regulated the health-related guideline values for bromoform (100 μg/L), DBCM (100 μg/L), BDCM (60 μg/L), and chloroform (300 μg/L) in drinking water.[7] Also, the WHO suggested that the sum of the ratios of the THM concentrations to its respective guideline value should not exceed one.[7] In Thailand, the levels of THMs in the water supply are regulated based on the WHO guideline values.

Recently, researchers have identified many emerging DBPs in water. These emerging DBPs may have greater toxicity than the regulated chloro- and bromo-THMs. Iodo-trihalomethanes (I-THMs) is an emerging class of C-DBPs that have higher cytotoxicity than THMs, except chlorodiiodomethane (CDIM).[8] I-THMs can be formed in the disinfected water from raw water, sea water intrusion with bromide or iodide concentration.[9] Five common I-THMs

CONTACT Charongpun Musikavong mcharongpun@eng.psu.ac.th; charongpun@gmail.com Department of Civil Engineering, Faculty of Engineering, Prince of Songkla University, Kho Hong, Hatyai, Songkhla 90112, Thailand

Supplemental data for this article is available online at https://doi.org/10.1080/10934529.2019.1592532.

species, namely iodoform or triiodomethane (TIM), dichloroiodomethane (DCIM), bromochloroiodomethane (BCIM), bromodiiodomethane (BDIM), and CDIM have been identified in drinking water.[2,8] The I-THMs have also been detected in treated wastewater effluents.[10] The increase in iodide concentration in source water may enhance the formation of I-THMs during disinfection.[11] Currently, the guideline value for I-THMs in drinking water is not currently regulated by the WHO.

Nitrogenous DBPs (N-DBPs) are one group of DBPs that are more toxic to human health than regulated C-DBPs.[12] N-DBPs may form in water from water sources with a high level of dissolved organic nitrogen (DON), especially when water sources are polluted by wastewater and algae organic matter.[13] Haloacetonitriles (HANs), *N*-nitrosamines, halonitromethanes (HNMs), and haloacetamides are emerging N-DBPs that have been recently reported.[2,8]

Among N-DBPs, HANs have been frequently reported and studied. Research on other N-DBPs in drinking waters is infrequently carried out. Previous studies have suggested that four HANs species, namely trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), bromochloroacetonitrile (BCAN), and dibromoacetonitrile (DBAN) were often detected after chlorination of bromide-containing water.[14] WHO recommends drinking water guideline values for DCAN of 20 μg/L and DBAN of 70 μg/L.[15] HNMs have been reported as extremely cytotoxic and genotoxic compared with regulated C-DBPs.[16] Chloropicrin or trichloronitromethane (TCNM) was primarily found as HNM species in drinking water and produced water from drinking water treatment plants during chlorination/chloramination.[17] The regulation for emerging HNMs has not been promulgated. Currently, there is no regulation or guideline values for I-THMs as well as HANs and HNMs in water supply in Thailand. A well-managed water treatment plant for reducing the N-DBPs' formation is of critical importance.

Bangkok, the capital city of Thailand, has a registered population of about 8 million people. The Bangkhen water treatment plant (WTP), the largest WTP in Thailand, provides a water supply of about 3.7 million m^3 per day to the majority of Bangkok's population and the vicinity of Bangkok. The Chao Phraya River is the major source of raw water for the Bangkhen WTP and other WTPs. The Chao Phraya River is located in Chao Phraya watershed. Approximately 69% of the total area in the Chao Phraya watershed is utilized for agricultural activities including paddy fields (60% of the total area), field crop (30%), perennial and fruit trees (5%), and other agriculture areas (5%). Other areas are community areas and buildings (15%), forests (10%), water (3%) and others (3%).[18] The Chao Phraya River has been markedly polluted by wastewater and treated wastewater discharge from domestic properties, industries, and agricultural activities which are located at an upstream location.

The iodide concentration in seawater varied from sub-μg/L and up to 60 μg/L levels.[19,20] Due to the sea level rise sometimes, the raw water from the Chao Phraya River is also exposed to high levels of iodide contamination from sea water. When raw water from the Chao Phraya River that is polluted by sea water, wastewater, and treated wastewater react with chlorine in the water treatment process, emerging C-DBPs and N-DBPs can be formed in the water supply.

Emerging C-DBPs' and N-DBPs' formation has been a concern. To date, few studies have focused on the occurrence of I-THMs and HNMs in water. In addition, the study on the emerging DBPs' formation of raw water, wastewater, treated wastewater in Thailand is not thoroughly investigated. This work is aimed at investigating the formation potentials of four THMs (chloroform, BDCM, DBCM, and bromoform), five I-THMs (TIM, DCIM, BCIM, BDIM, and CDIM), four HANs (TCAN, DCAN, BCAN, and DBAN) and one HNM (TCNM) in raw water of Bangkhen WTP. The weight measured the concentration of DBPs, lethal concentration 50-weighted, and lowest cytotoxicity-weighted concentrations of DBPs of raw water were determined.

In addition, the raw water of one WTP from the Chao Phraya River from an upstream location was investigated for their DBPs' formation and toxicity. Wastewater and treated wastewater from two domestic wastewater treatment plants (WWTP) were also studied as the sources of discharged DOM. The water sample at a downstream location of the Chao Phraya River was selected as the water that was polluted by sea water. The obtained results could provide a better understanding of the formation of emerging C-DBPs and N-DBPs in the water supply that could cause a health effect. In addition, the results can be used by policy makers to establish the plan for controlling the level of DOM discharged and DBPs' formation in the water supply.

Materials and methods

Sampling sites and sample collection

In this work, the raw water from two WTPs, river water at a downstream location of the Chao Phraya River, and wastewater and treated wastewater from two domestic WWTPs were collected three times from each source waters. The location of sampling sites is illustrated in Figure 1. Water samples were collected in October 2016, May 2017, and February 2018 as the representative of emerging C-DBPs' and N-DBPs' formation during the rainy season, summer, and winter, respectively. Raw waters from the Chao Phraya River were collected from the pumping station of Bangkhen WTP (BK WTP) at a downstream location (RW-1) and Singburi WTP (SB WTP) at an upstream location (RW-2).

Water samples from the river were obtained from the Siriraj sampling site, which is located downstream of the Chao Phraya River after the BK WTP. This sample stands for water with seawater, treated and untreated wastewater contamination. Domestic wastewater before (WW-1) and after treated wastewater (TWW-1) were collected from the WWTP in Ang Thong (AT) province. In addition, domestic wastewater before (WW-2) and treated wastewater (TWW-2) were obtained from the WWTP in Ayutthaya (AY) province. These two WWTPs are located in the upstream location of the Chao Phraya River. The wastewater and treated wastewater represent the sources of contamination from

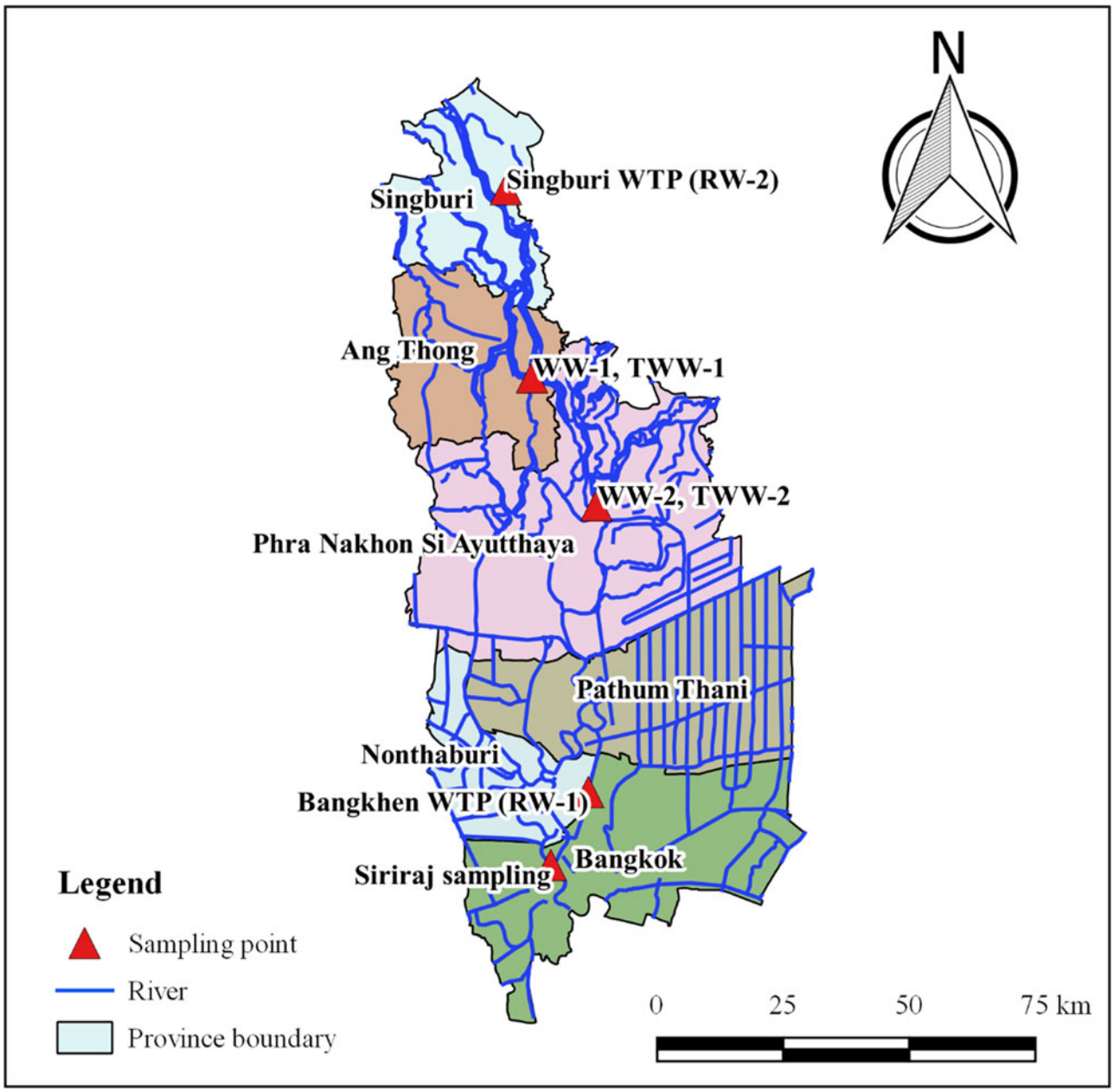


Fig. 1. The location of sampling sites. Source: http://thaigis.net/thailand-gis-resources/, http://www.diva-gis.org/gdata and Author.

human activities. All samples were stored at a temperature of 4 °C until analysis.

Reagents

A standard THM mixture (chloroform ($CHCl_3$), BDCM ($CHBrCl_2$), DBCM ($CHBr_2Cl$), and bromoform ($CHBr_3$)) containing 1,000 μg/mL of each compound in methanol was purchased from Supelco (Bellefonte, PA, USA). Separate neat standards for I-THMs analysis, including DCIM ($CHCl_2I$), BCIM (CHBrClI), BDIM ($CHBrI_2$), and CDIM ($CHClI_2$), were purchased from CanSyn Chem. Corp. (New Westminster, Canada), and TIM was purchased from Supelco (Bellefonte, PA, USA). Separate standard solutions for four HANs species, namely TCAN (CCl_3CN), DCAN (Cl_2CHCN), BCAN ($C_2HBrClN$), and DBAN (C_2HBr_2N) and one HNM species (TCNM or chloropicrin; CCl_3NO_2) were purchased from AccuStandard (New Haven, USA). The 4-bromofluorobenzene (1,000 μg/mL in methanol, purity >97.5%) as the internal standard solution was purchased from Supelco (Bellefonte, PA, USA).

Experimental and analytical methods

Physicochemical water parameters

The pH of water samples was directly measured by a Hach pH meter (accuracy of ±0.01 pH unit). Concentrations of ammonia, nitrate, and nitrite were measured with a Hatch DR 2700 Portable Spectrophotometer. Ammonia was analyzed following the Standard Methods 8038 (Nessler Method) and 10031 (Salicylate Method). Nitrite (NO_2^-) was measured using the diazotization method (Hach Method

8507), and nitrate (NO_3^-) was analyzed using the cadmium reduction method (Hach Method 8192).

DOM surrogate parameters

The water samples for analyzing their DOC, ultraviolet absorption at 254 nm (UV-254), specific UV absorption (SUVA), and DON were filtered by a precombusted (550 °C, 2 h) 0.7 μm filter before measurement. The filtered water samples were acidified with sulfuric acid (H_2SO_4) to pH ~2 for preservation and stored at 4 °C until analysis.

DOC concentrations in water samples were determined by a combustion method (Standard Method 5310D)[21] on a total organic carbon analyzer (TOC-V CSN, Shimadzu, Japan). The DOC is usually represented as a complex mixture of aromatic and aliphatic carbon-rich compounds of natural DOM in water.[22] UV-254 was measured by the Standard Method 5910B using a Genesys 10S UV/VIS spectrophotometer (Thermo Electron Corp. Madison, WI, USA). UV-254 can be used as a quantitative indicator of the DOM with aromatic rings in the water.[23] SUVA was calculated using the UV-254 absorbance normalized to the mg/L DOC concentration. The SUVA is a useful surrogate for DOC aromaticity in the natural organic matter of water.[24]

DON concentrations in water samples were calculated directly by subtracting the concentrations of dissolved inorganic nitrogen (DIN) species (NH_4^+, NO_3^-, NO_2^-) from the total dissolved nitrogen (TDN) concentration. High DIN levels could become a concentration error of DON in the water sample. To reduce the DON measurement error, pretreating the water sample before TDN and DIN analysis was performed using a nanofiltration (NF) method as developed by Xu et al.[25] The TDN was analyzed using a TOC/total nitrogen analyzer (Analytik Jena, Germany). Duplication was carried out for DOC, DON, and UV-254 analysis.

Iodide and bromide analysis

Iodide concentration in water samples was determined using the Standard Method 4500-I^- B. (leuco crystal violet method) for high concentration of iodide (50 to 6,000 μg/L) and the Standard Method 4500-I^- C. (catalytic reduction method) for low concentration of iodide (<80 μg/L). Bromide concentration in water samples was analyzed by ion chromatography with an Alltech liquid chromatograph equipped with an Allsep anion column (100 mm length × 4.6 mm ID × 7 μm particle diameter, USA). Each sample was analyzed in duplicate.

DBPs' formation potential (DBPFP)

The water samples were filtered using GF/F (Whatman GF/F, 0.7 μm) and analyzed for their DBPFP. The DBPs analyzed in this study included four THM species (chloroform, BDCM, DBCM, and bromoform); five I-THM species (TIM, DCIM, BCIM, BDIM, and CDIM); four HAN species (TCAN, DCAN, BCAN, and DBAN); and one HNM species (TCNM).

The DBPs formation potential test was conducted under controlled conditions including pH, temperature, and free chlorine residual to determine the highest DBPs' formation.

It must be noted that the DBPs' formation potential could not be used to represent the DBPs levels of water samples in their natural environment. The highest formation potential of THMs was measured according to the 7–day chlorine test procedure (the Standard Methods 5710B).[21] For I-THMs, HANs, and HNM, the highest formation potential of DBPs occurred during a 24-h chlorination reaction period with a hypochlorite reagent as determined in previous studies.[26–29] In summary, the formation potential experiments for I-THMs, HANs, and HNM were conducted with a 24-h incubation period, but 7-day incubation for THMs.

Briefly, a water sample was neutralized by a phosphate buffer (pH 7.0 ± 0.2) prior to chlorination using a Cl_2 sodium hypochlorite solution in amber bottles with a screw cap. The samples were then incubated in the dark at 25 ± 2 °C. Samples had a remaining free chlorine residual of 3–5 mg/L as Cl_2 after the incubation period. Free residual chlorine was measured using the Standard Method 4500-Cl G. (DPD colorimetric method) with a Hach spectrophotometer. Each chlorinated sample was quenched with sodium thiosulfate after the end of the reaction. It was reported that sodium thiosulfate could have an effect on HANs degradation.[30] In this work, the extraction process was shortly carried out after dechlorination of water samples to prevent the HAN degradation.

Analysis of DBPFP

The DBPs were extracted with methyl *tert*-butyl ether (MTBE); purity 99.9% with 4-bromofluorobenzene as an internal standard following US EPA Method 551.1.[31] The extraction conditions were based on a previously reported procedure with some modifications.[29] Briefly, 35 mL of water samples were analyzed by liquid–liquid extraction using MTBE (2 mL) with 4-bromofluorobenzene as the internal standard (50 μg/L).

All extracts were analyzed using a gas chromatograph (GC) with a micro-electron capture detector (Agilent 6890N). The analytical column was HP-5ms (5% diphenyl/95% dimethyl polysiloxane as stationary phase, 30 m length, 0.32 mm inside diameter × 0.25 mm film thickness). The injection was conducted in the split mode of 1 μL with a split ratio of 5:1 at 225 °C with helium carrier gas at a flow rate of 10 mL/min. The GC oven temperature was 35 °C for 8 min and ramped to 50 °C at 5 °C/min and held for 5 min, then ramped at 25 °C/min to 180 °C and held for 1 min. The detector temperature was maintained at 260 °C. Nitrogen at 60 mL/min was used as the make-up gas. Duplication was carried out for DBPFP analysis.

Results and discussion

Characteristics of water

pH, UV-254, and SUVA of water samples are presented in Supplementary Table S1. The pH levels of all water samples

Table 1. DOC, DON, and DOC/DON.

	DOC (mg C/L)				DON (mg N/L)				DOC/DON			
Samples	1st	2nd	3rd	Ave.±SD	1st	2nd	3rd	Ave.±SD	1st	2nd	3rd	Ave.±SD
Raw water												
RW-1	4.6	3.2	3.7	3.8 ± 0.7	0.16	0.44	0.25	0.28 ± 0.14	29	7	15	17 ± 11
RW-2	4.8	4.1	2.4	3.8 ± 1.2	0.18	0.28	0.12	0.19 ± 0.08	27	15	20	21 ± 6
River water	5.1	3.9	5.4	4.8 ± 0.8	0.09	0.32	0.33	0.25 ± 0.14	57	12	16	28 ± 25
Wastewater												
WW-1	7.3	5.6	3.0	5.3 ± 2.2	2.62	1.39	0.47	1.49 ± 1.08	3	4	6	4 ± 2
WW-2	7.4	7.0	7.9	7.4 ± 0.5	0.39	1.21	0.63	0.74 ± 0.42	19	6	13	13 ± 7
Treated wastewater												
TWW-1	5.3	6.8	7.0	6.4 ± 0.9	0.20	2.58	1.16	1.31 ± 1.20	27	3	6	12 ± 13
TWW-2	5.6	6.3	4.8	5.6 ± 0.8	1.22	0.65	0.36	0.74 ± 0.44	5	10	13	9 ± 4

Remark: DOC is dissolved organic carbon; DON is dissolved organic nitrogen.
SD = standard deviation.

ranged from 7.0 to 8.2, which were nearly neutral. RW-1, RW-2, and river water had similar range of UV-254 values: 0.12–0.14 cm^{-1} for RW-1, 0.09–0.16 cm^{-1} for RW-2, and 0.11–0.19 cm^{-1} for river water at the downstream location. UV-254 values of WW-1 and WW-2 ranged from 0.07 to 0.93 cm^{-1} and 0.18 to 0.34 cm^{-1}, respectively. For treated wastewater, UV-254 of 0.12–0.16 cm^{-1} for TWW-1 and 0.10–0.17 cm^{-1} for TWW-2 were determined. UV-254 in wastewater varied according to the sampling period. In almost every case, the UV-254 in wastewater is higher than that of raw water and river water.

SUVA of DOM ranges from 1.0 to 6.0 L/(mg·m) in surface waters[32] which was related to aromatic carbon content in DOM.[24] Ranges of SUVA of 3.0–4.1 L/(mg·m) for raw water and 2.7–3.7 L/(mg·m) for river water were similar. The seasonal variations can affect the quality of raw water and river water. According to the standard deviation (SD) values in Supplementary Table S1, the changes of season had little effect on the pH, UV-254, and SUVA of raw water and river water. The ranges of SUVA value of 2.2–12.7 L/(mg·m) for wastewater and 1.8–2.7 L/(mg·m) for treated wastewater were determined. In almost all cases, the SUVA of wastewater and treated wastewater was lower than that of raw water and river water, except WW-1 and WW-2 at the first sampling. When the SUVA was higher than 2 L/(mg·m), coagulation was suitable for reducing SUVA.[33] The raw water, river water, and wastewater (WW-1 and WW-2) at the first sampling had a high possibility of using coagulation for reducing DOM. Because of the low SUVA value of some wastewater samples and all treated wastewater samples, coagulation may not be suitable for reducing DOM.

Organic precursors

DOC as the precursor of C-DBPs

DOC is used as a surrogate parameter for a complex mixture of aromatic and aliphatic carbons in water. DOC is considered as the precursor of THMs' formation.[34] In Table 1, DOC in the RW-1 and RW-2 ranged from 3.2 to 4.6 mg C/L and 2.4 to 4.8 mg C/L, respectively. These ranges are rather low compared with DOC of river water at the downstream location (3.9 to 5.4 mg C/L). Regarding the standard deviation of DOC (Table 1). It appears that seasonal variations have a minor effect on the DOC of raw and river water samples.

A relatively high range of DOC from 7.0 to 7.9 mg C/L was detected in WW-2, while DOC of WW-1 ranged from 3.0 to 7.3 mg C/L. For treated wastewater, ranges of DOC of TWW-2 and TWW-1 were from 4.8 to 6.3 mg C/L and 5.3 to 7.0 mg C/L, respectively. Treated wastewater is one of the major discharged DOM to a raw water source. The average value of DOC of treated wastewater was 1.5 to 1.7 times higher than that of raw water. When more treated wastewater is discharged into a raw water stream, more DOC must be removed by water treatment plants to reduce the possibility of C-DBPs' formation.

In comparison with the previous study, DOC can vary according to types of water. DOC in raw water of RW-1 of the BK WTP from a previous study was determined at 4.2 mg C/L,[35] which was similar to the detected DOC in this current study. River waters contained more organic carbon and generally had DOC in the range from 2 to 12 mg C/L.[36,37] DOC in the domestic wastewater in Nanjing, China ranged from 18.2 to 24.6 mg C/L, with an average of 20.3 mg C/L.[38] DOC in the wastewater after primary treatment and the final effluent from the Nine Springs WWTP in Madison, Wisconsin, USA were determined as 28.4 and 8.5 mg C/L, respectively.[39] The range of DOC in domestic wastewater and the treated wastewater from the municipal WWTPs at the Chao Phraya River was lower than those of domestic wastewater in the USA and China.

DON as the precursor of N-DBPs

High DON levels in water may cause a problem of algal growth and anthropogenic nitrogen. In addition, DON in water had a probability of contributing to the formation of emerging N-DBPs.[40,41] DON from 0.16 to 0.44 mg N/L and 0.12 to 0.28 mg N/L were detected in RW-1 and RW-2, respectively (Table 1). The range of DON in the river water was 0.09 to 0.33 mg N/L and was comparable to that of RW-1 and RW-2. During summer, high DON in raw water (the second sampling) was found compared to during the rainy season and winter. The highest DON level in the river water (the third sampling) at downstream was found during winter. These observations showed the effect of seasonal variations on the nature of DON in raw water and river water.

The WW-1 and WW-2 had high ranges of DON 0.47 to 2.62 mg N/L and 0.39 to 1.21 mg N/L, respectively. For treated wastewater, ranges of DON of TWW-1 and TWW-2 were from 0.2 to 2.58 mg N/L and 0.36 to 1.22 mg N/L, respectively. Water with a low DON is easier to manage in comparison to water with a high DON. A high amount of DON precursors in water tends to increase the risk of N-DBPs' formation and could lead to the formation of several toxic N-DBP species.[13] The average value of DON in treated wastewater was three to seven times higher than that of raw water. The water treatment plant that uses raw water contaminated with treated wastewater or wastewater must seriously consider and remove DON prior to chlorination for prevention of N-DBPs' formation. Investigations on advanced water treatment technologies such as adsorptions, advanced oxidation processes, and membrane filtrations for removing DOC and DON from raw water contaminated with treated wastewater must be conducted and employed for operating and controlling water treatment plants.

DON in raw water and wastewater is a major precursor of N-DBPs. These include HANs, HNMs, cyanogen chloride (CNCl), and *N*-nitrosodimethylamine (NDMA).[13,42] The DON in surface waters (e.g., wastewater discharge, river, raw water) ranged from <0.1 to >10 mg N/L with the median at about 0.3 mg/L.[43–45] DONs from 0.37 to 0.70 mg N/L have been detected in the raw water of a Kinmen Tai Lake WTP in Taiwan.[46] In the United States, an average DON of 0.19 mg N/L was detected in the raw waters from 28 WTPs.[47] DONs from 0.2 to 0.4 mg N/L were determined in the raw waters from the Huron River, the Salt River, and the Harwood reservoir for WTPs in Virginia, USA.[48] A relatively high DON level of 0.53 mg N/L has been measured from the raw water of the Pinghu WTP, China.[49] According to the DON in surface water from the literature data and obtained result in this current work, ranges of DON in surface water were from 0.09 to 0.53 mg N/L.

Average DON concentration of 6.13 mg/L in influent wastewater from two municipal WWTPs in Beijing, China was reported.[50] The DON of treated wastewater in municipal WWTPs ranged from 0.23 to 1.33 mg N/L.[46,50] The high DON levels in treated wastewater were determined because treated wastewater may contain mostly recalcitrant nitrogenous substances. With regard to the results obtained from this work and previous studies, it can be concluded that the ranges of the levels of DON in domestic wastewater and treated wastewater were from 0.39 to 6.13 mg N/L and 0.20 to 2.58 mg N/L, respectively.

DOC/DON ratio

A DOC/DON ratio can be used as an indicator of N-DBP formation.[51]A low DOC/DON value probably provides high N-DBP formation such as NDMA and HNMs.[52,53] In addition, a low DOC/DON ratio typically represents the nature of autochthonous natural organic matter (NOM), while a high DOC/DON ratio indicates the presence of allochthonous NOM.[54] RW-1, RW-2, and river water had DOC/DON ratios ranging from 7 to 29, 15 to 27, and 12 to 57, respectively. The variations of DOC/DON ratio in raw water and river water are caused by the variations of DON (Table 1). The variation of DOC/DON ratios may be caused by the variation in the seasonal factor that correlated with algal growth and the generation of soluble microbial products such as tryptophan, tyrosine, and protein in water.[55]

DOC/DON ratios of WW-1 and WW-2 ranged from 3 to 6 and 6 to 19, respectively. For treated wastewater, ranges of DOC/DON ratios of TWW-1 from 3 to 27 and TWW-2 from 5 to 13 were detected, respectively. When the DOC/DON ratio was lower than 20, it had a tendency to form high N-DBPs.[40] The DOC/DON ratio typically varied from 8 to 11 mg C/mg N in WWTP effluents.[43] In natural waters, the DOC/DON ratios are generally high within the range of 10 to 21.[45,47,48] With reference to the DOC/DON ratio in this study and previous works, wastewater and treated wastewater had a greater probability of forming N-DBPs than raw water and river water.

The presence of bromide and iodide ions

The levels of bromide (Br^-) and iodide (I^-) in the water samples are presented in Table 2.

Br^- C μg/L and <10 to 51 μg/L were detected in RW-1 and RW-2, respectively (Table 2). The range of Br^- in the river water was <10 to 27 μg/L and was lower than that of RW-1 and RW-2. Br^- from 785 to 4,273 μg/L and 2,150 to 7,844 μg/L were detected in WW-1 and WW-2, respectively (Table 2). The range of Br^- in the treated wastewater was <10 to 5,050 μg/L and <10 to 3,630 μg/L in TWW-1 and TWW-2, respectively. In almost all cases, the levels of Br^- treated wastewater were extremely higher than that of raw water and river water.

I^- from < 0.1 to 16.9 μg/L and < 0.1 to 8.3 μg/L were detected in RW-1 and RW-2, respectively (Table 2). The range of I^- in the river water was 0.2 to 19.5 μg/L and was comparable to that of RW-1 and RW-2. I^- from 1.2 to 846 μg/L and <0.1 to 56.2 μg/L were detected in WW-1 and WW-2, respectively (Table 2). The range of I^- in the treated wastewater was 0.9 to 270 μg/L and 0.2 to 224 μg/L in TWW-1 and TWW-2, respectively. In almost all cases, the levels of I^- in treated wastewater were relatively higher than that of raw water and river water.

According to the results obtained in this work, the main discharged source of Br^- and I^- into the river water could originate from the wastewater and treated wastewater. To minimize the formation of brominated and iodinated DBPs, when the river water is utilized as raw water and is contaminated with high Br^- and I^- level from the upstream discharged, the water treatment plant needs to install advanced treatment technologies to remove Br^- and I^-.

The others option is to minimize the level of Br^- and I^- in treated wastewater from the WWTP nearby the raw water sources by a tertiary treatment process prior discharging treated wastewater.

Table 2. Bromide (Br^-) and iodide (I^-) concentrations.

	Br^- (μg/L)				I^- (μg/L)			
Samples	1st	2nd	3rd	Ave.±SD	1st	2nd	3rd	Ave.±SD
Raw water								
RW-1	48	43	16	36 ± 17	3.2	16.9	<0.1	10.1
RW-2	51	32	<10	42	4.1	8.3	<0.1	6.2
River water	27	10	<10	19	3.1	19.5	0.2	7.6 ± 10.4
Wastewater								
WW-1	1,320	785	4,273	2,126 ± 1,879	846	76.8	1.2	308± 467
WW-2	2,540	2,150	7,844	4,178 ± 3,181	41	56.2	<0.1	48.6
Treated wastewater								
TWW-1	5,050	254	<10	2,652	270	6.3	0.9	92.4 ± 154
TWW-2	3,630	23	<10	1,827	224	1.7	0.2	75.3 ± 129

Formation potential of C-DBPs

THMs' formation

THMFP, the ratio of THMFP to the WHO guideline, and I-THMFP for raw water, river water, domestic wastewater, and treated wastewater are presented in Figure 2. THMFP ranged from 121 to 265 μg/L and 103 to 210 μg/L for the raw water from the BK WTP (RW-1) and SB WTP (RW-2), respectively. For the river water at downstream, the THMFP ranged from 204 to 449 μg/L. The level of THMFP in raw and river water varies with seasonally (Supplementary Table S2). As previously reported by Musikavong et al.[34] the THMFP of the U-Tapao canal water in Hatyai, Songkhla, Thailand ranged from 165 to 729 μg/L. A THMFP ranging from 150 to 300 μg/L has been detected in the Ohio River basin, USA.[56] The formation of THM in river waters varied according to geographical location.

The THMFP ranged from 220 to 463 μg/L, and from 390 to 536 μg/L were determined for the domestic wastewater of the WW-1 and WW-2, respectively. For the TWW-1 and TWW-2, the THMFP ranged from 373 to 472 μg/L and 267 to 633 μg/L, respectively. The highest THMFP level of 633 μg/L was observed in the TWW-2 at the second sampling, possibly due to the high level of THM precursors in the water. An increase in the soluble humic material, chloride, and bromide in water may cause an increase in THM formation.[57] The average value of THMFP of treated wastewater was 2.3 to 2.5 times higher than that of raw water. The river water, wastewater, and treated wastewater sources had a high potential to form THMs over the maximum contamination level set by the US EPA of 80 μg/L[6] and the level in the European Union standard of 100 μg/L.[5]

The percent distribution of each THMFP species is tabulated in Table S3. Chloroform ($CHCl_3$) was the major THMFP species detected in all water samples. The chloroform accounted within the range from 74 to 96%, 73 to 95%, 81 to 98%, and 56 to 91% of the total THMFP for the raw water, river water, domestic wastewater, and treated wastewater, respectively. Chloroform was more frequently observed than other THM species in chlorinated water.[58] The obtained result in this current study corresponds well with earlier studies.

Brominated THM species including BDCM, DBCM, and bromoform are considerably more toxic than their chlorinated analogs.[59] BDCM had a higher proportion in RW-1 from the BK WTP (6–21%) than in RW-2 from the SB WTP (4–9%). The BDCM accounted within the range from 5 to 22%, 2 to 15%, and 8 to 29% of the total THMFP in river water, domestic wastewater, and treated wastewater samples, respectively. The high percent distribution of DBCM was observed only in treated wastewater (1 to 14% of the total THMFP). For other water samples, the DBCM was detected <6% of the total THMFP. Among these four THMFP species, bromoform was not detected (N.D.) or detected only for 1.1%.

Bromoform in the chlorination of bromide-rich water has been found in a high concentration compared with that of DBCM, BDCM, and chloroform.[60] It was suggested that the yield of THM species in chlorinated water could depend on the type of their precursors such as bromide ions, DOC, and Br/DOC ratio.[61] The increase in levels of brominated species of THMs in chlorinated water should be seriously considered due to its greater toxicity.

The THMFP/WHO ratio of RW-1 and RW-2 ranged from 0.6 to 1.1 and 0.5 to 0.8, respectively. The RW-1 had the potential to form THMs with slightly higher than the standard guideline of ≤1 whereas RW-2 had a tendency to form THMs with lower than the standard guideline. In general, THMFP of raw water represents the highest possible THMs' formation without removing the precursors. A high chlorine dosage was used in the experiment. In practice, the water treatment plant can remove some amount of DOM, and a low amount of chlorine was used that can reduce the amount of THMs' formation and THM/WHO ratio.

The values of the THMFP/WHO guidelines for the river water at downstream ranged from 1.0 to 2.7. In treated wastewater from WWTPs, the THMFP/WHO values were detected in a relatively high range from 1.4 to 3.1 compared with that of 1.2 to 2.1 of wastewater samples. When the treated wastewater was discharged to a raw water source, the high ratio of THMFP/WHO in the treated wastewaters can contribute to the influence of organic loading and the formation of THMs. A good management practice of the water treatment plant must be proposed as a key to reduce and control THMs' formation.

I-THMs formation

I-THMs are much more toxic and potentially more carcinogenic than THMs.[62] I-THMs are considered as emerging C-DBPs. From Figure 2, the low levels of I-THMFP (sum of five I-THMFP species) in the RW-1 (raw water of BK WTP) and RW-2 (raw water of SB WTP) were detected in the

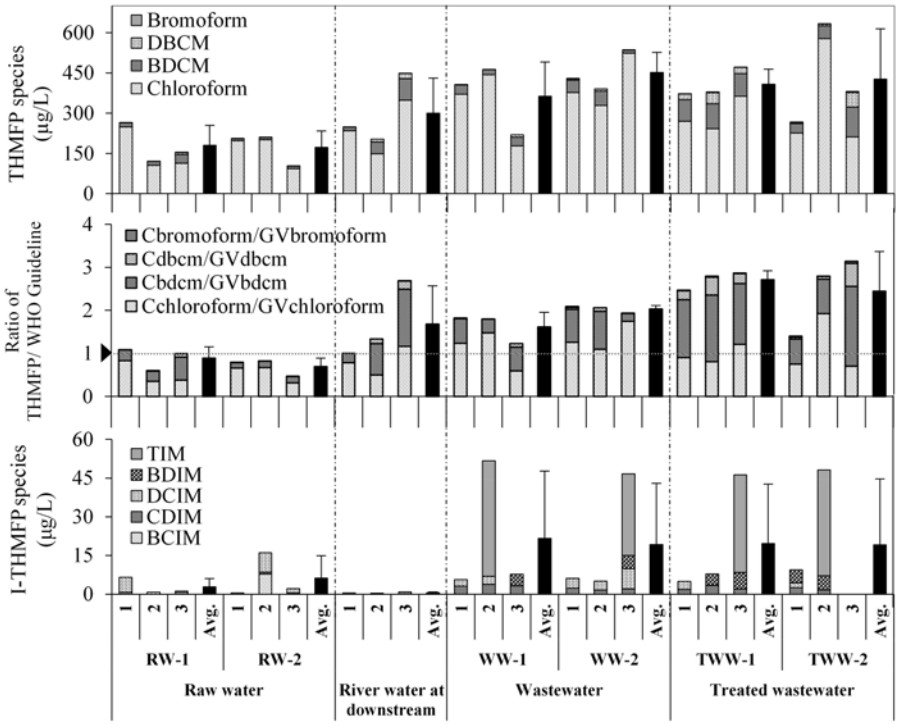


Fig. 2. THMFP, the ratio of THMFP to the WHO guideline and I-THMFP for raw water, river water, domestic wastewater, and treated wastewater.

range from 1 to 7 and 1 to 16 µg/L, respectively. The variations of I-THMFP in raw water could be affected by the seasonal changes and geographical location of the raw water sources (Table S2). The river water at the downstream location formed the lowest value within the range from 0.4 to 1 µg/L. The precursors of I-THMs in raw water and river water reveal the low potential to form I-THMs.

Relatively high levels of I-THMFP ranging from 6 to 52 µg/L for WW-1 and 5 to 47 µg/L for WW-2 were found. For treated wastewater, ranges of I-THMFP from 5 to 46 µg/L for TWW-1 and ND to 48 µg/L for TWW-2 were found. A wide range of I-THMFP in wastewater and treated wastewater was determined. This may be due to the variation of I-THMs precursors that originated from the sources of wastewater. The average value of I-THMFP of treated wastewater was 3.2 to 6.7 times higher than that of raw water.

For RW-1, DCIM and CDIM accounted for N.D. to 91.7% and 8.3 to 100%, respectively. BCIM, BDIM, and TIM were not detected (Supplementary Table S3). The percent distribution of BCIM, CDIM, and DCIM of RW-2 ranged from N.D. to 48.4%, N.D. to 100%, and N.D. to 77.3%, respectively. I-THMFP species that contained one bromide compound was detected in RW-2. BDIM and TIM were not detected. Only CDIM was found in river water at the downstream location.

For wastewater and treated wastewater, four I-THMFP species were detected. Percent distribution of CDIM, DCIM, BDIM, and TIM for WW-1 ranged from 7.4 to 55.4%, N.D. to 44.6%, N.D. to 58.4%, and N.D. to 86.7%, respectively. For WW-2, CDIM, DCIM, BDIM, and TIM ranged from 4.5 to 39.3%, 16.7 to 66.0%, N.D. to 10.9%, and N.D. to 67.8%, respectively. For TWW-1, CDIM, DCIM, BDIM, and TIM ranged from 4.5 to 43.6%, N.D. to 61.2%, N.D. to 56.4%, and N.D. to 81.8%, respectively. CDIM, DCIM, BDIM, and TIM for TWW-2 ranged from N.D. to 27.7%, N.D. to 19.1%, N.D. to 53.2% and N.D. to 85.2%, respectively. BCIM was not detected for wastewater and treated wastewater.

The three I-THMFP species (DCIM, CDIM, and BCIM) detected in this study were the most frequently occurring in raw waters of the WTPs, similar to the description of total I-THM levels in drinking water from surveys in other countries.[8,63,64] In Scotland, DCIM and BCIM were detected ranging from N.D. to 3.7 µg/L, with median 0.9 µg/L in chloraminated and chlorinated water from seven drinking WTPs.[63] In the USA and Canada, DCIM and BCIM were detected ranging from 0.09 to 7.8 µg/L in chloraminated and chlorinated water from 23 cities in drinking WTPs.[8] In China, DCIM of 1.42 ± 0.05 µg/L and TIM ranging from 0.01 to 1.25 µg/L were detected in water after the chloramination process from drinking WTPs.[64,65]

In the case of iodoform (or TIM), it was the dominant species of I-THMFP detected at relatively high levels (N.D. to 44.8 µg/L) in the wastewater and treated wastewater samples at WWTPs, while a lower level of iodoform (<21.66 µg/L) was present in the effluent water after disinfection at drinking WTPs in the findings of other studies.[2,9,65] The greater formation of I-THMs may possibly be because of the different characteristics of organic precursors in water sources. The previous studies have indicated that some waters with high bromide, iodide, and ammonium concentrations were associated with the formation of I-THMs.[9,66]

Formation potential of N-DBPs

HANs' formation

Four HANFP species, namely, DBAN, BCAN, DCAN, and TCAN were detected in all water samples (Fig. 3). The range

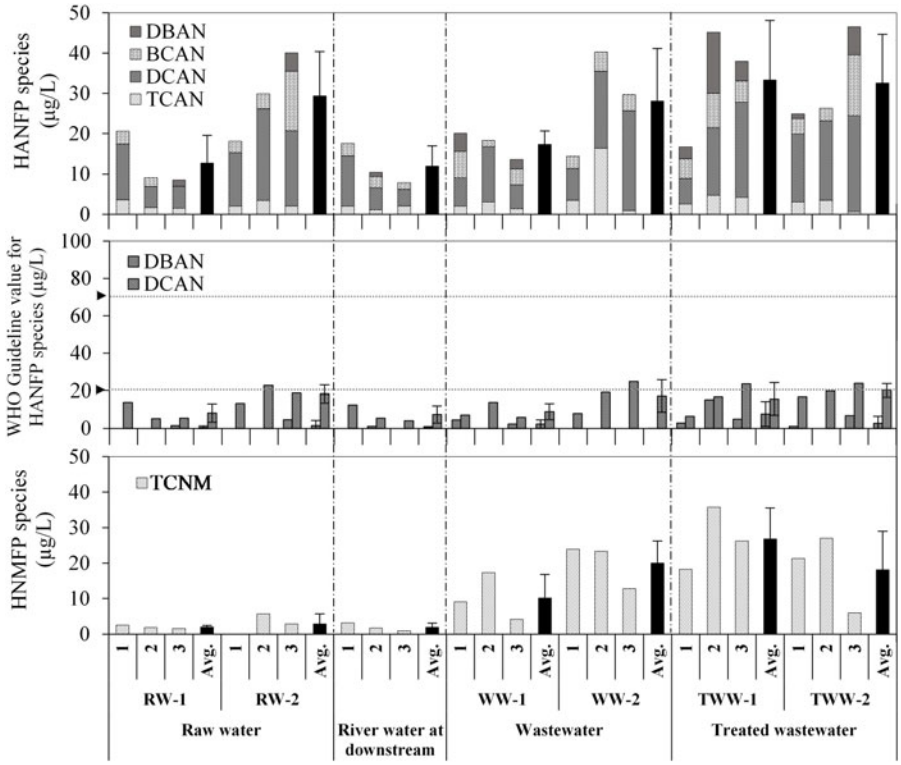


Fig. 3. HANFP and HNMFP for raw water, river water, domestic wastewater, and treated wastewater.

of HANFP from 9 to 21 μg/L in RW-1 of the BK WTP was lower than that of RW-2 of the SB WTP from the upstream location (18–40 μg/L). For the river at the downstream location, the HANFP ranged from 8 to 18 μg/L. During the rainy season, the high HANFP level in RW-1 and river water at the downstream location (the first sampling) was found in compared to during summer and winter. The highest HANFP level in RW-2 (the third sampling) at the upstream location was found during winter. These observations showed the effect of seasonal variations and location of water sources on the formation of HANs in raw water and river water. The HANFP levels of raw water from four WTPs in Korea have been reported in the range of 10.3 to 33.6 μg/L,[67] HANFP of about 17 μg/L was detected in raw water from the Dez River in Iran.[68] The range of HANFP values of raw water found in this current work was similar to that of raw water from other studies.[67,68]

The HANFP level of WW-1 and WW-2 ranged from 14 to 20 and 14 to 40 μg/L, respectively. HANFP levels ranging from 17 to 45 μg/L for TWW-1 and 25 to 47 μg/L for TWW-2 were determined. The average value of HANFP of treated wastewater was 1.1 to 2.5 times higher than that of raw water. A number of precursors such as carboxylic acid functional groups, amino acids, proteins, polypeptides, and carbohydrates which produce high levels of HANs have been identified.[69] The presence of untreated HANs' precursors in the discharge of treated wastewater to raw water source may influence HANs' formation in the water supply.

The formation of HANFP species is presented in Supplementary Table S3. Among four HANFP species, DCAN concentration was the most abundant in raw waters (46–76% of the total HANFP), river waters (52–71%), wastewaters (35–84%), and treated wastewaters (37–75%). BCAN (8–33%) and TCAN (1–41%) were the other HANFP species found in both wastewater and treated wastewater samples. The BCAN (N.D. to 37%) and TCAN (5–27%) in raw and river waters were detected as a lower portion than those in wastewater and treated wastewater. DBAN (N.D. to 34%) was the dominant HAN species in treated wastewater rather than in other water sources. As reported previously, DCAN, BCAN, and DBAN were the most frequently found species in treated water samples from drinking WTPs in England.[70] The detected HANs species in this study corresponded with previous work.

The concentration of DBAN and DCAN species should not exceed their guideline values of 70 and 20 μg/L, respectively.[15] The total HANFP of river water was lower than the standard guideline (Fig. 3). The values of the DCAN for the raw water were lower than the guideline value, except for the RW-2 of the SB WTP at the second sampling. The DCAN values were slightly higher in some samples from wastewater and treated wastewater, which could represent the greater potential to form HANs higher than the WHO guideline value.

HNM formation

HNM is considered as an emerging N-DBP. In this work, the trichloronitromethane (TCNM) species was detected at a low concentration from 2 to 3 μg/L for RW-1 (BK WTP) and N.D. to 6 μg/L for RW-2. In the case of river water at the downstream location, TCNM ranged from 1 to 3 μg/L (Fig. 3). The level of TCNMFP in raw and river water has

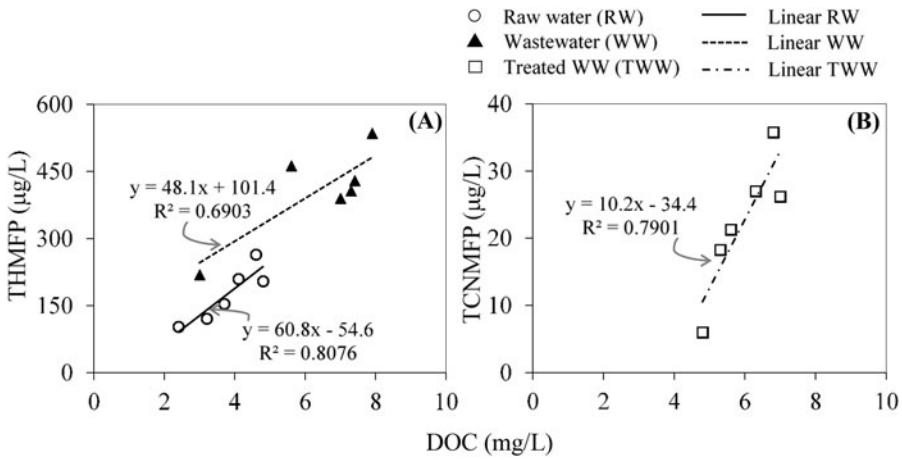


Fig. 4. Relationship between DOC of raw water, domestic wastewater and treated wastewater samples and THMFP and TCNMFP.

slightly varied with the changes of season (Supplementary Table S2). TCNM was typically detected at a lower level (ng/L to µg/L) in natural surface waters. For drinking water in the USA WTPs, TCNM ranged from N.D. to 2.0 µg/L in finished water.[2] A low concentration of TCNM was reported from N.D. to 7.6 µg/L with a median of 0.5 µg/L in finished water of surveyed plants.[71] The TCNM concentrations detected in raw water and river water in this study had similar levels to that of other survey studies.[2,71]

For domestic wastewaters, the WW-1 and WW-2 gave high TCNM levels from 4 to 17 and 13 to 24 μg/L, respectively. The high level of TCNM from 18 to 36 and 6 to 27 µg/L for TWW-1 and TWW-2 still occurred in the treated wastewaters. The TCNM level obtained in this study was higher than that of the level of TCNM from 0.9 to 1.5 µg/L in a municipal WWTP effluent in the US.[29] The average value of HNMFP of treated wastewater was 6 to 13.5 times higher than that of raw water. The high level of some reactive HNM precursors in the municipal WWTP effluents may cause an increase in the level of TCNM formation. Previous studies showed that organic nitrogen compounds (e.g., tryptophan and alanine), and algal cells with high organic nitrogen content could be the major sources for TCNM during the chlorination process.[72,73] In general, tryptophan was detected in treated wastewater[74] and was the dominant N-DBPs precursor.

The relationship between DBPFP and DOC concentration, DBPFP and bromide, and DBPFP and iodide

The correlation and regression between each DBPFP (4 THMs, 5 I-THMs, 4 HANs and TCNM) and DOM surrogate parameters (DOC, DON, and DOC/DON) for each water source are presented in Supplementary Table S4. According to AWWA,[75] it has been recognized that correlation levels were divided in four categories as a correlation coefficient (R^2)>0.9 was considered a good correlation, 0.7<R^2<0.9 a moderate correlation, 0.5<R^2<0.7 a fair correlation, and R^2<0.5 a poor correlation. In this study, DOC was a good surrogate parameter for DOM to predict THMs and TCNM.

The positive relationship between THMFP and DOC for raw water and domestic wastewater is shown in Figure 4A. A moderate correlation was obtained from the relationship between THMFP and DOC with R^2 of 0.8076 for raw water whereas a fair (R^2=0.6903) correlation was obtained from the relationship between THMFP and DOC for wastewater (Supplementary Table S4). There was no consistent pattern between DOC and THMFP concentration for treated wastewater. A moderate correlation was observed for the relationship between TCNMFP and DOC with R^2 of 0.7901 of treated wastewater (Fig. 4B). In summary, a DOM surrogate parameter like DOC was the most positively correlated parameter with the occurrence of THMFP in the raw water and TCNMFP in the treated wastewater in this study.

The correlation and regression between DBPFP species and the Br^- and I^- concentrations for each water source are presented in Supplementary Table S5. For almost all water sources, poor correlations were found between DBPFP species and Br^- and DBPFP species and I^-. In the case of raw water, only a fair correlation was obtained from the relationship between $CHBrCl_2FP$ and Br^- with a R^2 of 0.6200 and a moderate correlation (R^2=0.7343) was obtained from the relationship between $CHBr_2ClFP$ and Br^-. This presents the negative relationship between the $CHBrCl_2FP$ and $CHBr_2ClFP$ and the Br^- concentration. A moderate correlation was observed for the relationship between $CHClI_2FP$ species and I^- in raw water with a R^2 equal to 0.8303 (Supplementary Table S5). The $CHClI_2FP$ decreased with an increasing I^- concentration.

In the case of treated wastewater, only a fair correlation was observed between the $CHBrI_2$ species and Br^- with a R^2 of 0.5392. The $CHBrI_2FP$ decreased when increased Br^- concentration. Two HANFP species (CCl_3CN and Cl_2CHCN) were negatively correlated with Br^- with a R^2>0.60. The total concentration of HANFP decreased when Br^- concentration of treated wastewater increased. This work analyzed 14 DBPs species. Negative relationships may occur for some species, although some positive relationships may form for

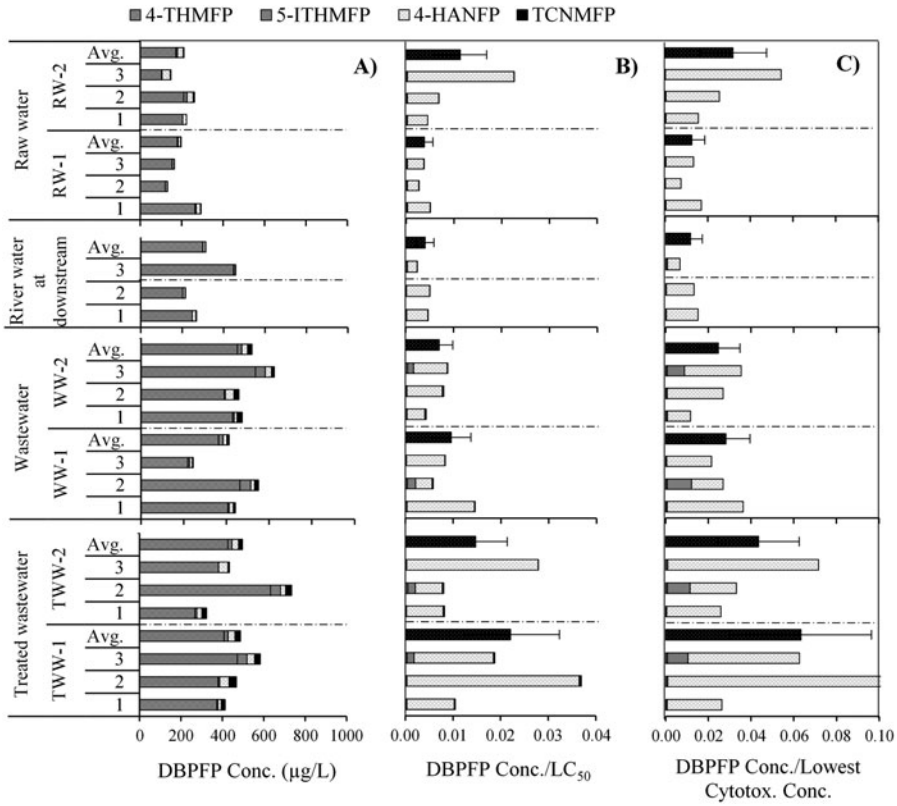


Fig. 5. Weight measured concentration (A), lethal concentration 50-weighted (B), and lowest cytotoxicity-weighted concentrations (C) of DBPs.

other species. This could not, however, significantly be determined in this work.

Evaluation of cytotoxicity risk caused by C-DBPs and N-DBPs

The cytotoxicity index is typically expressed as the LC_{50} value of all of the individual compounds of a single class of DBPs. The LC_{50} represents the DBP concentration that induced a 50% reduction of cell growth as compared with the cell growth in the concurrent negative controls. The cytotoxicity values of several DBP chemical classes using a Chinese hamster ovary cells assay have been investigated and used to determine the level of toxicity in this study.[8,12,16,41] This work used the LC_{50} and lowest cytotoxicity of THMs,[41] I-THMs,[8] HANs,[12] and LC_{50} of TCNM[16] in the analysis.

The results of weight measured concentration and the toxicity-weight basis among C-DBPs and N-DBPs chemical classes (4 THMFP, 5 I-THMFP, 4 HANFP, and 1 HNMFP) in different water sources are shown in Figure 5. Based on a mass basis of the DBP concentrations (Fig. 5A), the THMFP is considered more unsafe than the other DBPs classes because it had much greater cumulative concentration than the others and exceeded the US.EPA maximum contaminant level of 80 μg/L in all the water sources. With considering the average value, weight measured the concentration of C-DBPs and N-DBPs of RW-1 of the BK WTP and RW-2 of the SB WTP from high to low was THMFP > HANFP > I-THMFP > TCNMFP. For the river waters, wastewaters, and treated wastewaters, the rank order of these DBPs on a mass concentration basis was THMFP > HANFP > TCNMFP > I-THMFP.

For the toxic risk, the value of the LC_{50}-weighted concentration of C-DBPs and N-DBPs in water sources is shown in (Fig. 5B). The rank order for toxic risk caused by these DBPs was HANFP > THMFP > TCNMFP > I-THMFP in raw waters and river waters. For wastewater, the rank order for toxic risk was HANFP > THMFP > I-THMFP > TCNMFP. Treated wastewaters contained highly toxic HANFP, followed by I-THMFP, THMFP, and TCNMFP. The average value of the LC_{50}-weighted HANFP concentration of treated wastewater was 1.2 to 5.7 times higher than that of raw water.

Considering the value of the lowest cytotoxicity-weighted concentration of C-DBPs and N-DBPs in water sources (Fig. 5C), the rank order for toxic risk caused by these DBPs was HANFP > THMFP > I-THMFP in raw waters and river waters. For wastewaters and treated wastewaters, the rank order of these DBPs was HANFP > I-THMFP > THMFP. The average value of the lowest cytotoxicity-weighted HANFP concentration of treated wastewater was 1.2 to 4.8 times higher than that of raw water. Based on the toxicity-weighted basis, the most cytotoxic in all the water sources were HANFP. The HANFP is considered the least safe because it features higher concentrations of the toxicity drivers. A similar level of HANFP concentration was also found in polluted source waters.[76] Thus, the toxic risk class of HANs cannot be ignored with other DBPs as it may cause adverse effects on human health through water consumption.

Conclusion

This study collected water samples from the raw water of Bangkhen and Sing Buri WTPs located in the Chao Phraya River, river water, domestic wastewater, and final treated wastewater of two municipal WWTPs. The formation potential for THMs, I-THMs, HANs, and HNM and their individual species were determined. The levels of DOC and DON in the wastewater and treated wastewater were slightly higher than those in the raw and river water. The river water, wastewater, and treated wastewater had potential to form THMs which exceed the THMFP/WHO guideline value of $\leq$1. The average value of THMFP of treated wastewater was about two times higher than that of raw water. Relatively high levels of I-THMFP were found in wastewater and treated wastewater. The average value of I-THMFP of treated wastewater was three to seven times higher than that of raw water. Iodoform was the dominant species of I-THMFP detected at high level in the wastewater and treated wastewater, while BCIM, CDIM, and DCIM were identified in most of the samples in the raw water. HANFP was detected in all water sources. The average value of HANFP of treated wastewater was one to three times higher than that of raw water. DCAN was the most abundant species for HANFP in all the water sources. For HNM species, the TCNM levels mainly remain in the treated wastewater samples at a relatively high level. The average value of TCNMFP of treated wastewater was six to thirteen times higher than that of raw water. The discharge of TWW to RW must be prevented and controlled. In linear regression analysis, only moderate associations were obtained for the correlations between DOC and THMFP in the raw water samples and TCNMFP in the treated wastewater samples. THMs were the most prevalent class of DBPs and their formation potential was above the US EPA maximum contaminant level of 80 μg/L. However, the HANs and I-THMs were considered the least safe because they feature higher concentrations of the toxicity drivers. Considering the weight measured concentration of C-DBPs and N-DBPs, THMFP was found as the highest DBPs. The highest LC_{50}-weighted and lowest cytotoxicity-weighted concentrations of C-DBPs and N-DBPs were determined for HANFP.

Funding

This research was funded by the Thailand Research Fund (TRF) under contract number RSA5980047, with bilateral support by the PSU-Postdoctoral fellowship, Prince of Songkla University.

References

[1] Butterworth, B. E. Science-Based Risk Assessments For Drinking Water Disinfection By-Products. *Environ. Res.* **2005**, *98*, 276–278. DOI: 10.1016/j.envres.2004.06.009.

[2] Krasner, S. W.; Weinberg, H. S.; Richardson, S. D.; Pastor, S. J.; Chinn, R.; Sclimenti, M. J.; Onstad, G. D.; Thruston, A. D. Occurrence of a New Generation of Disinfection Byproducts. *Environ. Sci. Technol.* **2006**, *40*, 7175–7185.

[3] Shanks, C. M.; Sérodes, J. B.; Rodriguez, M. J. Spatio-Temporal Variability Of Non-Regulated Disinfection by-Products within a Drinking Water Distribution Network. *Water Res.* **2013**, *47*, 3231–3243. DOI: 10.1016/j.watres.2013.03.033.

[4] US EPA. Integrated Risk Information System (IRIS). **2011**. Available at http://cfpub.epa.gov/ncea/iris/index.cfm (Accessed March 2017).

[5] EECD. Council Directive 98/83/EC of 3 November 1998 on the Quality of Water Intended for Human Consumption. *Off. J. Eur. Commun.* **1998**, *L330*, 32–54.

[6] US EPA. National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfectant Byproducts; Final Rule. *Part II 40 CFR Parts* **2006**, *9*, 141–142.

[7] WHO. Guidelines for Drinking Water Quality, First Addendum to the 3rd ed.; Vol. 1; World Health Organization: Geneva, **2006**; pp. 491–492.

[8] Richardson, S. D.; Fasano, F.; Ellington, J. J.; Crumley, F. G.; Buettner, K. M.; Evans, J. J.; Blount, B. C.; Silva, L. K.; Waite, T. J.; Luther, G. W.; et al. Occurrence and Mammalian Cell Toxicity Of Iodinated Disinfection Byproducts in Drinking Water. *Environ. Sci. Technol.* **2008**, *42*, 8330–8338. DOI: 10.1021/es801169k.

[9] Tugulea, A. M.; Aranda-Rodriguez, R.; Berub, D.; Giddings, M.; Lemieux, F.; Hnatiw, J.; Dabeka, L.; Breton, F. The Influence of Precursors and Treatment Process on the Formation of Iodo-THMs in Canadian Drinking Water. *Water Res.* **2018**, *130*, 215–223. DOI: 10.1016/j.watres.2017.11.055.

[10] Gong, T.; Zhang, X. Detection, Identification and Formation of New Iodinated Disinfection Byproducts in Chlorinated Saline Wastewater Effluents. *Water Res.* **2015**, *68*, 77–86. DOI: 10.1016/j.watres.2014.09.041.

[11] Zhang, T. Y.; Xu, B.; Hu, C. Y.; Lin, Y. L.; Lin, L.; Ye, T.; Tian, F. X. A Comparison of Iodinated Trihalomethane Formation from Chlorine, Chlorine Dioxide and Potassium Permanganate Oxidation Processes. *Water Res.* **2015**, *68*, 394–403. DOI: 10.1016/j.watres.2014.09.040.

[12] Muellner, M. G.; Wagner, E. D.; McCalla, K.; Richardson, S. D.; Woo, Y. T.; Plewa, M. J. Haloacetonitriles vs. Regulated Haloacetic Acids: Are Nitrogen-Containing DBPs More Toxic? *Environ. Sci. Technol.* **2007**, *41*, 645–651. DOI: 10.1021/es0617441.

[13] Lee, W.; Westerhoff, P. Dissolved Organic Nitrogen Removal During Water Treatment by Aluminium Sulfate and Cationic Polymer Coagulation. *Water Res.* **2006**, *40*, 3767–3774. DOI: 10.1016/j.watres.2006.08.008.

[14] Chen, B.; Westerhoff, P. Predicting Disinfection By-Product Formation Potential in Water. *Water Res.* **2010**, *44*, 3755–3762. DOI: 10.1016/j.watres.2010.04.009.

[15] WHO. Guidelines for Drinking Water Quality. In *Recommendations*; 3rd ed.; World Health Organization: Geneva, Switzerland, **2008**; Vol. 1.

[16] Plewa, M. J.; Wagner, E. D.; Jazwierska, P.; Richardson, S. J.; Chen, P. H.; McKague, A. B. Halonitromethane Drinking Water Disinfection Byproducts: Chemical Characterization and Mammalian Cell Cytotoxicity and Genotoxicity. *Environ. Sci. Technol.* **2004**, *38*, 62–68. DOI: 10.1021/es030477l.

[17] Jia, A.; Wu, C.; Duan, Y. Precursors and Factors Affecting Formation of Haloacetonitriles and Chloropicrin during Chlor(Am)Ination of Nitrogenous Organic Compounds in Drinking Water. *J. Hazard. Mater.* **2016**, *308*, 411–418. DOI: 10.1016/j.jhazmat.2016.01.037.

[18] LDD. Land Development Department (LDD), Ministry of Agriculture and Cooperatives **2017**. http://www.ldd.go.th/www/lek_web/web.jsp?id=18907 (accessed Jan, 2019).

[19] Ito, K.; Ichihara, T.; Zhuo, H.; Kumamoto, K.; Timerbaev, A. R.; Hirokawa, T. Determination of Trace Iodide in Seawater by Capillary Electrophoresis following Transient Isotachophoretic Preconcentration: Comparison with Ion Chromatography. *Anal Chim. Acta* **2003**, *497*, 67–74.

[20] Chandramouleeswaran, S.; Vijayalakshmi, B.; Kartihkeyan, S.; Rao, T. P.; Iyer, C. S. P. Ion-Chromatographic Determination

of Iodide in Sea Water with UV Detection. *Mikrochim. Acta* **1998**, *128*, 75–77. DOI: 10.1007/BF01242193.

[21] APHA. *Standard Methods for the Examination of Water and Wastewater*, 20th Ed.; American Public Health Association, AWWA and WEF: Washington DC, **1998**.

[22] Sinsabaugh, R. L.; Findlay, S. Dissolved Organic Matter: Out of the Black Box into the Mainstream. In *Aquatic Ecosystems: Interactivity of Dissolved Organic Matter;* Findlay, S.; Sinsabaugh, R. L., Eds.; Elsevier Science Inc., USA, **2003**; pp 479–498.

[23] Hong, H. C.; Huang, F. Q.; Wang, F. Y.; Ding, L. X.; Lin, H. J.; Liang, Y. Properties of Sediment NOM Collected from a Drinking Water Reservoir in South China, and Its Association with THMs and HAAs Formation. *J. Hydrol.* **2013**, *476*, 274–279. DOI: 10.1016/j.jhydrol.2012.10.040.

[24] Weishaar, J. L.; Aiken, G. R.; Bergamaschi, B. A.; Fram, M. S.; Fujii, R.; Mopper, K. Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon. *Environ. Sci. Technol.* **2003**, *37*, 4702–4708. DOI: 10.1021/es030360x.

[25] Xu, B.; Li, D.; Li, W.; Xia, S.; Lin, Y.; Hu, C.; Zhang, C.; Gao, N. Measurements of Dissolved Organic Nitrogen (DON) in Water Samples with Nanofiltration Pretreatment. *Water Res.* **2010**, *44*, 5376–5384. DOI: 10.1016/j.watres.2010.06.034.

[26] Pantelaki, I.; Voutsa, D. Formation of Iodinated THMs during Chlorination of Water and Wastewater in the Presence of Different Iodine Sources. *Sci. Tot. Environ.* **2018**, *613–614*, 389–397. DOI: 10.1016/j.scitotenv.2017.09.072.

[27] Zhang, J.; Chen, D. D.; Li, L.; Li, W. W.; Mu, Y.; Yu, H. Q. Role of NOM Molecular Size on Iodo-Trihalomethane Formation during Chlorination and Chloramination. *Water Res.* **2016**, *102*, 533–541. DOI: 10.1016/j.watres.2016.07.007.

[28] Bougeard, C. M. M.; Goslan, E. H.; Jefferson, B.; Parsons, S. A. Comparison of the Disinfection by-Product Formation Potential of Treated Waters Exposed to Chlorine and Monochloramine. *Water Res.* **2010**, *44*, 729–740. DOI: 10.1016/j.watres.2009.10.008.

[29] Song, H.; Addison, J. W.; Hu, J.; Karanfil, T. Halonitromethanes Formation in Wastewater Treatment Plant Effluents. *Chemosphere* **2010**, *79*, 174–179. DOI: 10.1016/j.chemosphere.2010.01.001.

[30] Urbansky, E. T. Ascorbic Acid Treatment to Reduce Residual Halogen-Based Oxidants Prior to the Determination of Halogenated Disinfection Byproducts in Potable Water. *J. Environ. Monit.* **1999**, *1*, 471–476. DOI: 10.1039/a904574k.

[31] Munch, D. J.; Hautman, D. P. *Method 551.1, Determination of Chlorinated Disinfection Byproducts, Chlorinated Solvents, and Halogenated Pesticides/Herbicides in Drinking Water by Liquid/Liquid Extraction and Gas Chromatography with Electron Capture Detection;* USEPA: Cincinnati, OH, **1995**.

[32] Hansen, A. M.; Kraus, T. E. C.; Pellerin, B. A.; Fleck, J. A.; Downing, B. D.; Bergamaschi, B. A. Optical Properties of Dissolved Organic Matter (DOM): Effects of Biological and Photolytic Degradation. *Limnol. Oceanogr.* **2016**, *61*, 1015–1032. DOI: 10.1002/lno.10270.

[33] US EPA. Enhanced Coagulation and Enhanced Precipitative Softening Guidance Manual, Office of Water, EPA 815-R-99-012, **1999**.

[34] Musikavong, C.; Srimuang, K.; Suksaroj, T. T.; Suksaroj, C. Formation of Trihalomethanes of Dissolved Organic Matter Fractions in Reservoir and Canal Waters. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* **2016**, *51*, 782–791. DOI: 10.1080/10934529.2016.1178033.

[35] Tongchang, P.; Kumsuvan, J.; Phatthalung, N.; Suksaroj, W.; Wongrueng, C.; Musikavong, A. C. Reduction by Enhanced Coagulation of Dissolved Organic Nitrogen as a Precursor of *N*-Nitrosodimethylamine. *J. Environ. Sci. Health A Tox. Hazard. Subst. Environ. Eng.* **2018**, *53*, 583–593. DOI: 10.1080/10934529.2018.1428270.

[36] Volk, C.; Wood, L.; Johnson, B.; Robinson, J.; Zhu, H. W.; Kaplan, L. Monitoring Dissolved Organic Carbon in Surface and Drinking Waters. *J. Environ. Monit.* **2002**, *4*, 43–47. DOI: 10.1039/b107768f.

[37] Wang, J. J.; Lafreniere, M. J.; Lamoureux, S. F.; Simpson, A. J.; Gelinas, Y.; Simpson, M. J. Differences in Riverine and Pond Water Dissolved Organic Matter Composition and Sources in Canadian High Arctic Watersheds Affected by Active Layer Detachments. *Environ. Sci. Technol.* **2018**, *52*, 1062–1071. DOI: 10.1021/acs.est.7b05506.

[38] Liu, X.; Chen, Q.; Zhu, L. Improving Biodegradation Potential of Domestic Wastewater by Manipulating the Size Distribution of Organic Matter. *J. Environ. Sci.* **2016**, *47*, 174–182. DOI: 10.1016/j.jes.2016.02.004.

[39] Maizel, A. C.; Remucal, C. K. The Effect of Advanced Secondary Municipal Wastewater Treatment on the Molecular Composition of Dissolved Organic Matter. *Water Res.* **2017**, *122*, 42–52. DOI: 10.1016/j.watres.2017.05.055.

[40] Dotson, A.; Westerhoff, P.; Krasner, S. W. Nitrogen Enriched Dissolved Organic Matter (DOM) Isolates and Their Affinity to Form Emerging Disinfection By-Products. *Water Sci. Technol.* **2009**, *60*, 135–143. DOI: 10.2166/wst.2009.333.

[41] Plewa, M. J.; Wagner, E. D. *Quantitative Comparative Mammalian Cell Cytotoxicity and Genotoxicity of Selected Classes of Drinking Water Disinfection by-Products*; Water Research Foundation: Denver, CO, USA, **2009**.

[42] Krasner, S. W.; Westerhoff, P.; Chen, B.; Rittmann, B. E.; Nam, S. N.; Amy, G. Impact of Wastewater Treatment Processes on Organic Carbon, Organic Nitrogen, and DBP Precursors in Effluent Organic Matter. *Environ. Sci. Technol.* **2009**, *43*, 2911–2918. DOI: 10.1021/es802443t.

[43] Dotson, A.; Westerhoff, P.; Chen, B.; Lee, W. Organic Nitrogen Occurrence and Characterization. In *Disinfection By-Products in Drinking Water: occurrence, Formation, Health Effects, and Control;* Karanfil, T.; Krasner, S. W.; Westerhoff, P.; Xie, Y., Eds.; American Chemical Society: Washington, DC, **2008**, pp 274–288.

[44] Westerhoff, P.; Mash, H. Dissolved Organic Nitrogen in Drinking Water Supplies: A Review. *J. Water Supply: Res. Technol. AQUA* **2002**, *51*, 415–488. DOI: 10.2166/aqua.2002.0038.

[45] Xu, B.; Ye, T.; Li, D. P.; Hu, C. Y.; Lin, Y. L.; Xia, S. J.; Tian, F. X.; Gao, N. Y. Measurement of Dissolved Organic Nitrogen in a Drinking Water Treatment Plant: Size Fraction, Fate, and Relation to Water Quality Parameters. *Sci. Tot. Environ.* **2011**, *409*, 1116–1122. DOI: 10.1016/j.scitotenv.2010.12.016.

[46] Chang, H.; Wang, G. Fractionation of Nitrogen-Enriched Dissolved Organic Matter in Water. *Sep. Purif. Technol.* **2013**, *117*, 89–97. DOI: 10.1016/j.seppur.2013.04.027.

[47] Lee, W.; Westerhoff, P.; Esparza-Soto, M. Occurrence and Removal of Dissolved Organic Nitrogen in US Water Treatment Plants. *J. Am. Water Works Assoc.* **2006**, *98*, 102–110. DOI: 10.1002/j.1551-8833.2006.tb07782.x.

[48] Lee, W.; Westerhoff, P.; Croue, J. P. Dissolved Organic Nitrogen as a Precursor for Chloroform, Dichloroacetonitrile, *N*-Nitrosodimethylamine, and Trichloronitromethane. *Environ. Sci. Technol.* **2007**, *41*, 5485–5490. DOI: 10.1021/es070411g.

[49] Zhang, H.; Zhang, K.; Jin, H.; Gu, L.; Yu, X. Variations in Dissolved Organic Nitrogen Concentration in Biofilters with Different Media during Drinking Water Treatment. *Chemosphere* **2015**, *139*, 652–658.

[50] Huo, S.; Xi, B.; Yu, H.; Qin, Y.; Zan, F.; Zhang, J. Characteristics and Transformations of Dissolved Organic Nitrogen in Municipal Biological Nitrogen Removal Wastewater Treatment Plants. *Environ. Res. Lett.* **2013**, *8*, 044005–0449pp. DOI: 10.1088/1748-9326/8/4/044005.

[51] Chu, W.; Gao, N.; Yin, D.; Krasner, S. W. Formation and Speciation of Nine Haloacetamides, an Emerging Class of Nitrogenous DBPs, during Chlorination or Chloramination. *J.*

Hazard. Mater. **2013**, *260*, 806–812. DOI: 10.1016/j.jhazmat.2013.06.044.

[52] Karanfil, T.; Hu, J.; Jones, D. B.; Addison, J. W.; Song, H. *Formation of Halonitromethanes and Iodo-Trihalomethanes in Drinking Water*; Water Research Foundation: Denver, CO, USA, **2011**.

[53] Wang, C.; Zhang, X.; Chen, C.; Wang, J. Factors Controlling *N*-Nitrosodimethylamine (NDMA) Formation from Dissolved Organic Matter. *Front. Environ. Sci. Eng.* **2013**, *7*, 151–157. DOI: 10.1007/s11783-013-0482-7.

[54] Aiken, G.; Cotsaris, E. Soil and Hydrology: their Effect on NOM. *J. Am. Water Works Assoc.* **1995**, *87*, 36–45. DOI: 10.1002/j.1551-8833.1995.tb06299.x.

[55] Fan, Z.; Zhang, H.; Xu, X.; Liu, B.; Zhang, D.; Yu, X. Dissolved Organic Nitrogen (DON) in Full Scale Two-Stage O_3-BAC with Nitrate as Sole Inorganic Nitrogen Source. *Int. J. Environ. Res.* **2012**, *6*, 985–994.

[56] Jack, J.; Sellers, T.; Bukaveckas, P. A. Algal Production and Trihalomethane Formation Potential: An Experimental Assessment and Inter-River Comparison. *Can. J. Fish. Aquat. Sci.* **2002**, *59*, 1482–1491. DOI: 10.1139/f02-121.

[57] Adin, A.; Katzhendler, J.; Alkaslassy, D.; Rav-Acha, C. Trihalomethanes Formation in Chlorinated Drinking Water: A Kinetic Model. *Water Res.* **1991**, *25*, 797–805. DOI: 10.1016/0043-1354(91)90159-N.

[58] Tokmak, B.; Capar, G.; Dilek, F. B.; Yetis, U. Trihalomethanes and Associated Potential Cancer Risks in the Water Supply in Ankara, Turkey. *Environ. Res.* **2004**, *96*, 345–352. DOI: 10.1016/j.envres.2003.11.005.

[59] Yang, M.; Zhang, X. Comparative Developmental Toxicity of New Aromatic Halogenated DBPs in a Chlorinated Saline Sewage Effluent to the Marine Polychaete *Platynereis Dumerilii*. *Environ. Sci. Technol.* **2013**, *47*, 10868–10876. DOI: 10.1021/es401841t.

[60] Basu, M.; Gupta, S. K.; Singh, G.; Mukhopadhyay, U. Multi-Route Risk Assessment from Trihalomethanes in Drinking Water Supplies. *Environ. Monit. Assess.* **2011**, *178*, 121–134. DOI: 10.1007/s10661-010-1677-z.

[61] Watson, K.; Farré, M. J.; Birt, J.; McGree, J.; Knight, N. Predictive Models for Water Sources with High Susceptibility for Bromine-Containing Disinfection By-Product Formation: implications for Water Treatment. *Environ. Sci. Pollut. Res.* **2015**, *22*, 1963–1978. DOI: 10.1007/s11356-014-3408-4.

[62] Cemeli, E.; Wagner, E. D.; Anderson, D.; Richardson, S. D.; Plewa, M. J. Modulation of the Cytotoxicity and Genotoxicity of the Drinking Water Disinfection Byproduct Iodoacetic Acid by Suppressors of Oxidative Stress. *Environ. Sci. Technol.* **2006**, *40*, 1878–1883. DOI: 10.1021/es051602r.

[63] Goslan, E. H.; Krasner, S. W.; Bower, M.; Rocks, S. A.; Holmes, P.; Levy, L. S.; Parsons, S. A. A Comparison of Disinfection By-Products Found in Chlorinated and Chloraminated Drinking Waters in Scotland. *Water Res.* **2009**, *43*, 4698–4706. DOI: 10.1016/j.watres.2009.07.029.

[64] Wei, X.; Chen, X.; Wang, X.; Zheng, W.; Zhang, D.; Tian, D.; Jiang, S.; Ong, C. N.; He, G.; Qu, W. Occurrence of Regulated and Emerging Iodinated DBPs in the Shanghai Drinking Water. *PLoS One* **2013**, *8*, e59677. DOI: 10.1371/journal.pone.0059677.

[65] Wei, Y.; Liu, Y.; Ma, L.; Wang, H.; Fan, J.; Liu, X.; Dai, R. Speciation and Formation of Iodinated Trihalomethanes from Microbially Derived Organic Matter during the Biological Treatment of Micro-Polluted Source Water. *Chemosphere* **2013**, *92*, 1529–1535.

[66] Ioannou, P.; Charisiadis, P.; Andra, S. S.; Makris, K. C. Occurrence and Variability of Iodinated Trihalomethanes Concentrations within Two Drinking-Water Distribution Networks. *Sci. Tot. Environ.* **2016**, *543*, 505–513. DOI: 10.1016/j.scitotenv.2015.10.031.

[67] Kim, J.; Chung, Y.; Shin, D.; Kim, M.; Lee, Y.; Lim, Y.; Lee, D. Chlorination by-Products in Surface Water Treatment Process. *Desalination* **2003**, *151*, 1–9. DOI: 10.1016/S0011-9164(02)00967-0.

[68] Ahmadi, M.; Ramavandi, B. The Formation Potential of Haloacetonitriles in the Dez River Water, Iran. *Environ. Technol.* **2014**, *35*, 2347–2355. DOI: 10.1080/09593330.2014.903301.

[69] Chu, W.; Gao, N.; Krasner, S. W.; Templeton, M. R.; Yin, D. Formation of Halogenated C-, N-DBPs from Chlor(Am)Ination and UV Irradiation of Tyrosine in Drinking Water. *Environ. Pollut.* **2012**, *161*, 8–14. DOI: 10.1016/j.envpol.2011.09.037.

[70] Bond, T.; Templeton, M. R.; Kamal, N. H. M.; Graham, N.; Kanda, R. Nitrogenous Disinfection Byproducts in English Drinking Water Supply Systems: Occurrence, Bromine Substitution and Correlation Analysis. *Water Res.* **2015**, *85*, 85–94. DOI: 10.1016/j.watres.2015.08.015.

[71] Mitch, W. A.; Krasner, S. W.; Westerhoff, P.; Dotson, A. *Occurrence and Formation of Nitrogenous Disinfection by-Products*; Water Research Foundation: Denver, CO, USA, **2009**.

[72] Yang, X.; Guo, W.; Shen, Q. Formation of Disinfection Byproducts from Chlor(Am)Ination of Algal Organic Matter. *J. Hazard. Mater.* **2011**, *197*, 378–388. DOI: 10.1016/j.jhazmat.2011.09.098.

[73] Yang, X.; Shen, Q.; Guo, W.; Peng, J.; Liang, Y. Precursors and Nitrogen Origins of Trichloronitromethane and Dichloroacetonitrile during Chlorination/Chloramination. *Chemosphere* **2012**, *88*, 25–32. DOI: 10.1016/j.chemosphere.2012.02.035.

[74] Lee, S.; Ahn, K. H. Monitoring of COD as an Organic Indicator in Waste Water and Treated Effluent by Fluorescence Excitation–Emission (FEEM) Matrix Characterization. *Water Sci. Technol.* **2004**, *50*, 57–63. DOI: 10.2166/wst.2004.0488.

[75] AWWA. Characterization of Natural Organic Matter and its Relationship to Treatability, 1st ed.; AWWARF and AWWA: USA, **1993**.

[76] Bond, T.; Huang, J.; Templeton, M. R.; Graham, N. Occurrence and Control of Nitrogenous Disinfection By-products in Drinking Water: A Review. *Water Res.* **2011**, *45*, 4341–4354. DOI: 10.1016/j.watres.2011.05.034.

SUPPORTING MATERIALS

Table S1. The pH, UV-254, and SUVA of raw water (RW), river water, domestic wastewater (WW), and treated wastewater (TWW) for the three sampling times.

Parameter		BK WTP	SB WTP	River	AT		AY	
		RW-1	RW-2	At downstream	WW-1	TWW-1	WW-2	TWW-2
pH	1st	7.8	7.9	7.6	8.2	7.9	7.7	7.8
	2nd	7.5	7.0	7.2	7.4	7.8	7.3	7.4
	3rd	7.3	7.1	7.0	7.0	8.0	7.0	7.1
	Ave.± SD	7.5±0.3	7.3±0.5	7.3±0.3	7.5±0.6	7.9±0.1	7.3±0.4	7.4±0.4
UV-254	1st	0.14	0.16	0.19	0.93	0.12	0.34	0.10
(cm^{-1})	2nd	0.13	0.14	0.11	0.12	0.13	0.19	0.17
	3rd	0.12	0.09	0.15	0.07	0.16	0.18	0.12
	Ave.± SD	0.13±0.01	0.13±0.04	0.15±0.04	0.37±0.48	0.14±0.02	0.24±0.09	0.13±0.04
SUVA	1st	3.0	3.3	3.7	12.7	2.3	4.6	1.8
(L/mg·m)	2nd	4.1	3.5	2.7	2.2	2.0	2.7	2.7
	3rd	3.2	3.9	2.9	2.4	2.3	2.3	2.6
	Ave.± SD	3.4±0.6	3.6±0.3	3.1±0.5	5.8±6.0	2.2±0.2	3.2±1.2	2.4±0.5

Remark: BK WTP = Bangkhen Water Treatment Plant, SB WTP = Sing Buri Water Treatment Plant, AT = Ang Thong, AY = Ayutthaya

Table S2. DBPFP of raw water (RW), river water, domestic wastewater (WW), and treated wastewater (TWW) for the three sampling times.

Samples	THMFP (µg/L)				I-THMFP (µg/L)				HANFP (µg/L)				TCNMFP (µg/L)			
	1st	2nd	3rd	Ave.± SD	1st	2nd	3rd	Ave.± SD	1st	2nd	3rd	Ave.± SD	1st	2nd	3rd	Ave.± SD
Raw water																
RW-1	265	121	154	180±75	7	1	1	3±3.2	21	9	9	13±7	3	2	2	2±0.5
RW-2	205	210	103	173±60	1	16	2	6±8.6	18	30	40	29±11	N.D.	6	3	3±2.9
River water	249	204	449	300±130	1	0.4	1	1±0.3	18	10	8	12±5	3	2	1	2±1.2
Wastewater																
WW-1	407	463	220	363±127	6	52	8	22±26	20	18	14	17±3	9	17	4	10±6.6
WW-2	430	390	536	452±75	6	5	47	19±24	14	40	30	28±13	24	23	13	20±6.2
Treated wastewater																
TWW-1	373	379	472	408±56	5	8	46	20±23	17	45a	38	33±15	18	36	26	27±8.8
TWW-2	267	633	381	427±187	9	48	N.D.	19±26	25	26	47	33±12	21	27	6	18±10.9

N.D. is not detected

Table S3. Percent distribution of THMFP, I–THMFP, and HANFP species of raw water, river water, domestic wastewater and treated wastewater

Water sources		4-THMFP, %				5-ITHMFP, %					4-HANFP, %			
		Chloroform	BDCM	DBCM	Bromoform	BCIM	CDIM	DCIM	BDIM	TIM	TCAN	DCAN	BCAN	DBAN
Raw water														
RW-1	1st	94.1	5.7	0.2	N.D.	N.D.	12.3	87.7	N.D.	N.D.	17.5	67.0	15.5	N.D.
(BK WTP)	2nd	87.4	11.5	1.1	N.D.	N.D.	N.D.	100	N.D.	N.D.	18.7	57.1	24.2	N.D.
	3rd	73.9	20.7	5.2	0.1	N.D.	91.7	8.3	N.D.	N.D.	17.6	64.7	N.D.	17.6
	Avg.	85.1	12.7	2.2	0.03	N.D.	34.7	65.3	N.D.	N.D.	17.9	62.9	13.2	5.9
RW-2	1st	96.0	3.9	0.1	N.D.	N.D.	100	N.D.	N.D.	N.D.	11.0	73.5	15.5	N.D.
(SB WTP)	2nd	95.6	4.3	0.1	N.D.	48.4	4.3	47.2	N.D.	N.D.	11.4	76.3	12.4	N.D.
	3rd	90.9	8.7	0.4	N.D.	22.7	N.D.	77.3	N.D.	N.D.	5.2	46.4	36.9	11.5
	Avg.	94.2	5.6	0.2	N.D.	23.7	34.8	41.5	N.D.	N.D.	9.2	65.4	21.6	3.8
River water at downstream														
	1st	94.5	5.2	0.2	N.D.	N.D.	100	N.D.	N.D.	N.D.	11.4	71.0	17.6	N.D.
	2nd	73.2	21.6	5.2	N.D.	N.D.	100	N.D.	N.D.	N.D.	10.6	52.9	26.9	9.6
	3rd	77.8	17.8	4.2	0.1	N.D.	100	N.D.	N.D.	N.D.	26.6	51.9	21.5	N.D.
	Avg.	81.8	14.9	3.2	N.D.	N.D.	100	N.D.	N.D.	N.D.	16.2	58.6	22.0	3.2
Domestic wastewater														
WW-1	1st	91.1	8.4	0.5	N.D.	N.D.	55.4	44.6	N.D.	N.D.	10.0	35.3	32.3	22.4
(AT)	2nd	95.7	4.1	0.2	N.D.	N.D.	7.4	6.0	N.D.	86.7	16.4	75.4	8.2	N.D.
	3rd	81.1	15.0	3.9	N.D.	N.D.	41.6	N.D.	58.4	N.D.	10.3	43.4	29.4	16.9
	Avg.	89.3	9.2	1.5	N.D.	N.D.	34.8	16.9	19.5	28.9	12.2	51.4	23.3	13.1
WW-2	1st	87.7	10.7	1.2	0.4	N.D.	39.3	60.7	N.D.	N.D.	24.3	54.9	20.8	N.D.
(AY)	2nd	84.3	13.6	2.1	N.D.	N.D.	34.0	66.0	N.D.	N.D.	40.7	47.4	11.9	N.D.
	3rd	97.8	2.1	0.1	N.D.	N.D.	4.5	16.7	10.9	67.8	3.0	83.5	13.5	N.D.
	Avg.	90.0	8.8	1.1	0.1	N.D.	26.0	47.8	3.6	22.6	22.7	61.9	15.4	N.D.

Table S3. (Con't) Percent distribution of THMFP, I–THMFP, and HANFP species of raw water, river water, domestic wastewater and treated wastewater.

Water sources		4-THMFP, %				5-ITHMFP, %					4-HANFP, %			
		Chloroform	BDCM	DBCM	Bromoform	BCIM	CDIM	DCIM	BDIM	TIM	TCAN	DCAN	BCAN	DBAN
Treated wastewater														
TWW-1	1st	72.4	21.7	5.6	0.2	N.D.	38.8	61.2	N.D.	N.D.	15.0	38.3	29.3	17.4
(AT)	2nd	63.8	24.5	10.9	0.7	N.D.	43.6	N.D.	56.4	N.D.	10.4	37.2	18.8	33.6
	3rd	76.9	18.0	4.8	0.3	N.D.	4.5	N.D.	13.6	81.8	11.1	62.1	13.9	12.9
	Avg.	71.1	21.4	7.1	0.4	N.D.	29.0	20.4	23.3	27.3	12.1	45.9	20.7	21.3
TWW-2	1st	84.6	13.1	1.6	0.7	N.D.	27.7	19.1	53.2	N.D.	12.0	67.9	15.7	4.4
(AY)	2nd	91.4	7.6	1.1	N.D.	N.D.	3.5	N.D.	11.2	85.2	13.3	74.9	11.8	N.D.
	3rd	55.6	29.1	14.1	1.1	N.D.	N.D.	N.D.	N.D.	N.D.	1.3	51.4	32.5	14.8
	Avg.	77.2	16.6	5.6	0.6	N.D.	10.4	6.4	21.5	28.4	8.9	64.7	20.0	6.4

Remark: BK WTP = Bangkhen Water Treatment Plant, SB WTP = Sing Buri Water Treatment Plant, AT = Ang Thong, AY = Ayutthaya, Avg. = Average, N.D. is not detected

Table S4. Linear correlation coefficients (R^2) between DBPFP and DOM surrogate parameters of raw water, domestic wastewater, and treated wastewater.

Water sources	Regression parameter				N	R^2	Sig. level	Correlation level
	Dependent variables (y)	Independent variables (x)	Slope (m)	Intercept (C)				
Raw water								
DOC 2.4-4.8 mg C/L	THMFP	DOC	60.8	-54.6	6	0.8076	0.01	Moderate
DON 0.12-0.44 mg N/L	THMFP	DON	-	-	6	0.0798	Not	Poor
DOC/DON 7-29	THMFP	DOC/DON	-	-	6	0.4309	Not	Poor
	I–THMFP	DOC	-	-	6	0.0627	Not	Poor
	I–THMFP	DON	-	-	6	0.0002	Not	Poor
	I–THMFP	DOC/DON	-	-	6	0.0001	Not	Poor
	HANFP	DOC	-	-	6	0.1172	Not	Poor
	HANFP	DON	-	-	6	0.3616	Not	Poor
	HANFP	DOC/DON	-	-	6	0.0870	Not	Poor
	HNMFP	DOC	-	-	5	0.0528	Not	Poor
	HNMFP	DON	-	-	5	0.0074	Not	Poor
	HNMFP	DOC/DON	-	-	5	0.0017	Not	Poor
Wastewater								
DOC 3.0-7.9 mg C/L	THMFP	DOC	48.1	101.4	6	0.6903	0.04	Fair
DON 0.39-2.62 mg N/L	THMFP	DON	-	-	6	0.0160	Not	Poor
DOC/DON 3-19	THMFP	DOC/DON	-	-	6	0.1077	Not	Poor
	I–THMFP	DOC	-	-	6	0.0103	Not	Poor
	I–THMFP	DON	-	-	6	0.0098	Not	Poor
	I–THMFP	DOC/DON	-	-	6	0.0010	Not	Poor
	HANFP	DOC	-	-	6	0.2260	Not	Poor
	HANFP	DON	-	-	6	0.0134	Not	Poor
	HANFP	DOC/DON	-	-	6	0.0176	Not	Poor
	HNMFP	DOC	-	-	6	0.3137	Not	Poor
	HNMFP	DON	-	-	6	0.0317	Not	Poor
	HNMFP	DOC/DON	-	-	6	0.2090	Not	Poor
Treated Wastewater								
DOC 4.8-7.0 mg C/L	THMFP	DOC	-	-	6	0.1707	Not	Poor
DON 0.20-2.58 mg N/L	THMFP	DON	-	-	6	0.0357	Not	Poor
DOC/DON 3-27	THMFP	DOC/DON	-	-	6	0.0002	Not	Poor
	I–THMFP	DOC	-	-	5	0.2605	Not	Poor
	I–THMFP	DON	-	-	5	0.0707	Not	Poor
	I–THMFP	DOC/DON	-	-	5	0.0590	Not	Poor
	HANFP	DOC	-	-	6	0.0448	Not	Poor
	HANFP	DON	-	-	6	0.2293	Not	Poor
	HANFP	DOC/DON	-	-	6	0.3216	Not	Poor
	HNMFP	DOC	10.2	-34.4	6	0.7901	0.01	Moderate
	HNMFP	DON	9.0	13.2	6	0.6051	0.06	Fair
	HNMFP	DOC/DON	-	-	6	0.0204	Not	Poor

Remark: Regression equation is $y = mx+C$; Regression analysis was not carried out for $R^2 < 0.5$. Hence, slope (m) and intercept (C) for equation were not computed; DBPFP was dependent variable whereas DOC, DON and DOC/DON were independent variables; N = Sample size; Sig. = Significant

Table S5. Linear correlation coefficients (R^2) between DBPFP species and the bromide ion (Br^-) and iodide ion (I^-) of raw water, domestic wastewater, and treated wastewater.

Water sources	Regression parameter				N	R^2	Sig. level	Correlation level
	Dependent variables (y)	Independent variables (x)	Slope (m)	Intercept (C)				
Raw water	**THMFP**							
Br^- 16-51 µg/L	(1) $CHCl_3FP$	Br^-	-	-	5	0.2835	Not	Poor
	(2) $CHBrCl_2FP$	Br^-	-53.3	35.9	5	0.6200	0.11	Fair
	(3) $CHBr_2ClFP$	Br^-	-20.4	9.8	5	0.7343	0.06	Moderate
	(4) $CHBr_3FP$	Br^-	-	-	1	NA	NA	NA
	Total (1)+(2)+(3)	Br^-	-	-	5	0.1608	Not	Poor
	I–THMFP							
	(1) CHBrClIFP	Br^-	-	-	1	NA	NA	NA
	(2) $CHClI_2FP$	Br^-	-	-	4	0.3553	Not	Poor
	(3) $CHCl_2IFP$	Br^-	-	-	4	0.0042	Not	Poor
	(4) $CHBrI_2FP$	Br^-	-	-	0	NA	NA	NA
	(5) CHI_3FP	Br^-	-	-	0	NA	NA	NA
	Total (1)+(2)+(3)	Br^-	-	-	5	0.0156	Not	Poor
	HANFP							
	(1) CCl_3CNFP	Br^-	-	-	5	0.0923	Not	Poor
	(2) $Cl_2CHCNFP$	Br^-	-	-	5	0.0366	Not	Poor
	(3) $C_2HBrClNFP$	Br^-	-	-	4	0.4850	Not	Poor
	(4) C_2HBr_2NFP	Br^-	-	-	1	NA	NA	NA
	Total (1)+(2)+(3)+(4)	Br^-	-	-	5	0.0565	Not	Poor
I^- 3.2-16.9 µg/L	**I–THMFP**							
	(1) CHBrClIFP	I^-	-	-	1	NA	NA	NA
	(2) $CHClI_2FP$	I^-	-0.06	0.9	4	0.8303	0.03	Moderate
	(3) $CHCl_2IFP$	I^-	-	-	4	0.0006	Not	Poor
	(4) $CHBrI_2FP$	I^-	-	-	0	NA	NA	NA
	(5) CHI_3FP	I^-	-	-	0	NA	NA	NA
	Total (1)+(2)+(3)	I^-	-	-	5	0.0014	Not	Poor
Wastewater	**THMFP**							
Br^- 785-7,844 µg/L	(1) $CHCl_3FP$	Br^-	-	-	6	0.0601	Not	Poor
	(2) $CHBrCl_2FP$	Br^-	-	-	6	0.2377	Not	Poor
	(3) $CHBr_2ClFP$	Br^-	-	-	6	0.0083	Not	Poor
	(4) $CHBr_3FP$	Br^-	-	-	1	NA	NA	NA
	Total (1)+(2)+(3)+(4)	Br^-	-	-	6	0.0374	Not	Poor
	I–THMFP		-	-				
	(1) CHBrClIFP	Br^-	-	-	0	NA	NA	NA
	(2) $CHClI_2FP$	Br^-	-	-	6	0.1882	Not	Poor
	(3) $CHCl_2IFP$	Br^-	-	-	5	0.3404	Not	Poor
	(4) $CHBrI_2FP$	Br^-	-	-	2	NA	NA	NA
	(5) CHI_3FP	Br^-	-	-	2	NA	NA	NA
	Total (2)+(3)+(4)+(5)	Br^-	-	-	6	0.0882	Not	Poor

Remark: Regression equation is y = mx+C; Regression analysis was not carried out for $R^2 < 0.5$. Hence, slope (m) and intercept (C) for equation were not computed; DBPFP was dependent variable whereas Br^- and I^- were independent variables; N = Sample size; Sig. = Significant; NA is not available

Table S5. (cont.) Linear correlation coefficients (R^2) between DBPFP species and the bromide ion (Br^-) and iodide ion (I^-) of raw water, domestic wastewater, and treated wastewater.

Water sources	Regression parameter				N	R^2	Sig. level	Correlation level
	Dependent variables (y)	Independent variables (x)	Slope (m)	Intercept (C)				
Wastewater	**HANFP**							
	(1) CCl_3CNFP	Br^-	-	-	6	0.0950	Not	Poor
	(2) $Cl_2CHCNFP$	Br^-	-	-	6	0.2936	Not	Poor
	(3) $C_2HBrClNFP$	Br^-	-	-	6	0.0028	Not	Poor
	(4) C_2HBr_2NFP	Br^-	-	-	2	NA	NA	NA
	Total (1)+(2)+(3)+(4)	Br^-	-	-	6	0.0354	Not	Poor
I^- 1.2-846 µg/L	**I–THMFP**							
	(1) CHBrClIFP	I^-	-	-	0	NA	NA	NA
	(2) $CHClI_2FP$	I^-	-	-	6	0.0673	Not	Poor
	(3) $CHCl_2IFP$	I^-	-	-	5	0.0346	Not	Poor
	(4) $CHBrI_2FP$	I^-	-	-	2	NA	NA	NA
	(5) CHI_3FP	I^-	-	-	2	NA	NA	NA
	Total (2)+(3)+(4)+(5)	I^-	-	-	6	0.0984	Not	Poor
Treated Wastewater	**THMFP**							
Br^- 23-5,050 µg/L	(1) $CHCl_3FP$	Br^-	-	-	4	0.3030	Not	Poor
	(2) $CHBrCl_2FP$	Br^-	-	-	4	0.0052	Not	Poor
	(3) $CHBr_2ClFP$	Br^-	-	-	4	0.0646	Not	Poor
	(4) $CHBr_3FP$	Br^-	-	-	4	0.0007	Not	Poor
	Total (1)+(2)+(3)+(4)	Br^-	-	-	4	0.4005	Not	Poor
	I–THMFP							
	(1) CHBrClIFP	Br^-	-	-	0	NA	NA	NA
	(2) $CHClI_2FP$	Br^-	-	-	4	0.0733	Not	Poor
	(3) $CHCl_2IFP$	Br^-	-	-	2	NA	NA	NA
	(4) $CHBrI_2FP$	Br^-	-0.07	5.3	3	0.5392	0.26	Fair
	(5) CHI_3FP	Br^-	-	-	1	NA	NA	NA
	Total (2)+(3)+(4)+(5)	Br^-	-	-	4	0.3868	Not	Poor
	HANFP							
	(1) CCl_3CNFP	Br^-	-0.03	4.1	4	0.6956	0.16	Fair
	(2) $Cl_2CHCNFP$	Br^-	-0.19	19.2	4	0.6562	0.19	Fair
	(3) $C_2HBrClNFP$	Br^-	-	-	4	0.0650	Not	Poor
	(4) C_2HBr_2NFP	Br^-	-	-	3	0.1514	Not	Poor
	Total (1)+(2)+(3)+(4)	Br^-	-0.4	36.2	4	0.5423	0.27	Fair
I^- 0.2-270 µg/L	**I–THMFP**							
	(1) CHBrClIFP	I^-	-	-	0	NA	NA	NA
	(2) $CHClI_2FP$	I^-	-	-	5	0.0381	Not	Poor
	(3) $CHCl_2IFP$	I^-	-	-	2	NA	NA	NA
	(4) $CHBrI_2FP$	I^-	-	-	4	0.1166	Not	Poor
	(5) CHI_3FP	I^-	-	-	2	NA	NA	NA
	Total (2)+(3)+(4)+(5)	I^-	-	-	5	0.1983	Not	Poor

Remark: Regression equation is y = mx+C; Regression analysis was not carried out for $R^2 < 0.5$. Hence, slope (m) and intercept (C) for equation were not computed; DBPFP was dependent variable whereas Br^- and I^- were independent variables; N = Sample size; Sig. = Significant; NA is not available