TRIHALOMETHANE FORMATION POTENTIAL OF DOM FRACTIONS IN WATER PRODUCTION BY IN-LINE COAGULATION CERAMIC MEMBRANE MICROFILTRATION

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โอกาสในการก่อตัวของสารไตรฮาโลมีเทนของกลุ่มสารอินทรีย์ละลายน้ำในการผลิต น้ำโดยการโคแอกกูเลชันในเส้นท่อร่วมกับไมโครฟิลเตรชันเซรามิกเมมเบรน

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ภาคภูมิ รักร่วม : โอกาสในการก่อตัวของสารไตรฮาโลมีเทนของกลุ่มสารอินทรีย์ละลายน้ำในการผลิต น้ำโดยการโคแอกกูเลชันในเส้นท่อร่วมกับไมโครฟิลเตรชันเซรามิกเมมเบรน. (TRIHALOMETHANE FORMATION POTENTIAL OF DOM FRACTIONS IN WATER PRODUCTION BY IN-LINE COAGULATION CERAMIC MEMBRANE MICROFILTRATION) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: รศ. ดร.สุรพงษ์ วัฒนะจีระ, 205 หน้า.

งานวิจัยนี้มีจุดประสงค์เพื่อศึกษาโอกาสในการเกิดสารไตรฮาโลมีเทนของกลุ่มสารอินทรีย์ละลายน้ำในน้ำที่ผลิตได้จากกระบวนการโคแอกกูเลชันในเส้นท่อร่วมกับเซรามิกไมโครฟิลเตรชัน น้ำผิวดินที่ใช้ในการทดลองทำการเก็บมาจากแม่น้ำปิงในจังหวัดเชียงใหม่ซึ่งเป็นแหล่งน้ำดิบหลักในการทำน้ำประปาเพื่อใช้ภายในจังหวัด ทำการทดลองกระบวนการโคแอกกูเลชันในเส้นท่อร่วมกับการกรองด้วยเซรามิกเมมเบรนทั้งในแบบกะและแบบต่อเนื่องโดยใช้สารโพลีอลูมิเนียมคลอไรด์เป็นสารโคแอกกูแลนท์ เพื่อศึกษาถึงประสิทธิภาพในการลดสารอินทรีย์ละลายน้ำ (Dissolved organic matter, DOM) ซึ่งเป็นสารตั้งต้นของสารไตรฮาโลมีเทน (Trihalomethane, THMs) สารอินทรีย์ละลายน้ำเป็นสารที่มีโครงสร้างซับซ้อนและสามารถแบ่งแยกประเภทได้มากมายตามขนาดและลักษณะคุณสมบัติต่างๆ ดังนั้นในการศึกษานี้จึงได้ใช้กระบวนการแฟรกชันด้วยเรซินเพื่อแยก DOM ออกเป็นกลุ่มต่างๆตามลักษณะคุณสมบัติทั้งหมด 6 กลุ่มคือไฮโดรฟิลิกที่เป็นกรด (HPIA) ไฮโดรฟิลิกที่เป็นด่าง (HPIB) ไฮโดรฟิลิกที่เป็นกลาง (HPIN) ไฮโดรโฟบิกที่เป็นกรด (HPOA) ไฮโดรโฟบิกที่เป็นด่าง (HPOB) และไฮโดรโฟบิกที่เป็นกลาง (HPON) โดยใช้เรซิน 3 ชนิดคือ DAX-8, WA-10 และ AG-MP-50 นอกจากนี้ยังได้มีการประยุกต์ใช้ไพโรไลซิสจีซีเอ็มเอสเพื่อวิเคราะห์หากลุ่มทางเคมีของ DOM ในน้ำตัวอย่างต่างๆด้วย

จากผลการทดลองพบว่ากระบวนการโคแอกกูเลชันในเส้นท่อร่วมกับการกรองด้วยเซรามิกเมมเบรนสามารถลด DOM จากแหล่งน้ำดิบที่ทำการศึกษาได้โดยประสิทธิภาพในการลด DOM จะมีค่าสูงขึ้นเมื่อใช้สารโคแอกกูแลนท์ในปริมาณที่มากขึ้น เปอร์เซ็นต์ในการลดค่า คาร์บอนละลายน้ำ (Dissolved organic carbon, DOC), การดูดกลืนแสงที่ความยาวคลื่น 254 นาโนเมตร (UV-254) และ โอกาสในการก่อตัวองสารไตรฮาโลมีเทน (Trihalomethane formation potential, THMFP) ที่ความเข้มข้นของสารโคแอกกูแลนท์ที่เหมาะสม (40 มิลลิกรัมต่อลิตร) มีค่าอยู่ในช่วง 40% – 48%, 67% – 75% และ 58% – 68% ตามลำดับ จากการทดลองกระบวนการโคแอกกูเลชันในเส้นท่อร่วมกับการกรองด้วยเซรามิกเมมเบรนในแบบต่อเนื่องพบว่าสามารถเดินระบบแบบต่อเนื่องได้โดยมีประสิทธิภาพที่ค่อนข้างคงที่ตลอดระยะเวลาในการทดลอง ส่วนผลการศึกษาการแยกสารอินทรีย์ละลายน้ำออกเป็นกลุ่มต่างๆด้วยกระบวนการแฟรกชันพบว่า HPIA และ HPOA เป็นกลุ่มที่พบมากที่สุดในน้ำดิบที่ทำการศึกษาโดยมีค่าอยู่ในช่วง 38% - 40% และ 24% - 29% ของ DOM ทั้งหมดตามลำดับ นอกจากนี้ DOM ทั้งสองกลุ่มยังถูกพบว่าเป็นสารตั้งต้นหลักในการเกิดสารไตรฮาโลมีเทนในแหล่งน้ำที่ทำการศึกษา อย่างไรก็ตามผลการศึกษาค่าโอกาสในการเกิดสารไตรฮาโลมีเทนจำเพาะ (specific THMFP) พบว่า HPIB และ HPOB มีค่า specific THMFP สูงที่สุด ซึ่งแสดงว่า DOM ทั้งสองกลุ่มนี้มีความสามารถสูงในการทำปฏิกิริยากับคลอรีนเพื่อเกิดสารไตรฮาโลมีเทน จากการศึกษาการลดลงของ DOM ในกลุ่มต่างๆพบว่ากระบวนการโคแอกกูเลชั่นในเส้นท่อร่วมกับการกรองด้วยเซรามิกเมมเบรนสามารถลด HPOA ได้ดีที่สุด (> 60%) นอกจากนี้ยังสามารถลด HPIB และ HPOB ได้ดีอีกด้วย สำหรับการศึกษาถึงกลุ่มทางเคมีของสารอินทรีย์ละลายน้ำพบว่าอลิฟาติกไฮโดรคาร์บอนเป็นกลุ่มทางเคมีที่พบมากที่สุดในทุกๆกลุ่มของสารอินทรีย์ละลายน้ำ โดยมีค่ามากกว่า 48% ของกลุ่มทางเคมีทั้งหมด อย่างไรก็ตามความสามารถในการทำปฏิกิริยากับคลอรีนเพื่อเกิดสารไตรฮาโลมีเทนมีความแตกต่างกัน โดยอลิฟาติกไฮโดรคาร์บอนที่พบใน HPIA, HPIN, HPOA และ HPON มีความสามารถต่ำในการทำปฏิกิริยากับคลอรีน ในขณะที่อลิฟาติกไฮโดรคาร์บอนที่พบใน HPIB และ HPOB มีความสามารถสูงในการทำปฏิกิริยากับคลอรีน

สาขาวิชา การจัดการสิ่งแวดล้อม	ลายมือชื่อนิสิต ....
ปีการศึกษา 2556	ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก ....

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KEYWORDS: CERAMIC MEMBRANE / DISSOLVED ORGANIC MATTER / TRIHALOMETHANE FORMATION POTENTIAL / RESIN FRACTIONATION / RIVER WATER / IN-LINE COAGULATION

PHARKPHUM RAKRUAM: TRIHALOMETHANE FORMATION POTENTIAL OF DOM FRACTIONS IN WATER PRODUCTION BY IN-LINE COAGULATION CERAMIC MEMBRANE MICROFILTRATION. ADVISOR: ASSOC. PROF. SURAPHONG WATTANACHIRA, D.Eng., 205 pp.

The aims of this research were to investigate the trihalomethane formation potential of DOM fractions in water production by in-line coagulation with ceramic membrane microfiltration. Raw surface water was collected from Ping River water, Chiang Mai, Thailand which utilized as main raw water source for water supply production in this province. In-line coagulation with ceramic membrane filtration was conducted both in batch and continuous experiment. Polyaluminium chloride was used as coagulants. The reduction efficiency of DOM (THMs precursors) by in-line coagulation with ceramic membrane filtration was investigated. DOM is a complex mixture of hydrophilic and hydrophobic organic materials which varies in size, functional groups and reactivity. Thus, the characterization of DOM in water samples was investigated. The fractionation technique was utilized to separate DOM into HPIA, HPIN, HPIB, HPOA, HPOB and HPON fraction by using DAX-8, WA-10 and AG-MP-50 resin. In addition, the chemical classes of DOM in water samples was investigated by using GC/MS pyrolysis technique.

From the results, it was found that in-line coagulation with ceramic membrane filtration can be utilized to reduce DOM from this water source and the reduction efficiency was increased with the increasing of PACl dosage. Percent DOC, UV-254 and THMFP reduction by in-line coagulation with ceramic membrane filtration at the optimal dosage (40 mg/L) was found in the range of 40-48%, 67–75% and 58–68%, respectively. In addition, the results of continuous experiment of in-line coagulation with ceramic membrane filtration showed that this combination processes can be operated in a long term operation without the significantly decreased of performance. For the results of resin fractionation, it was found that HPIA and HPOA fractions were the major fraction (38-40% and 24-29%, respectively) and main precursors of THMs in this water source. However, the highest specific THMFP value was found in HPOB and HPIB fraction which indicates that these two fractions had a high ability to form THMs. In-line coagulation with ceramic membrane filtration was found to reduce DOM mostly in term of HPOA fraction (>60%). Furthermore, it was found to highly reduce HPOB and HPIB fraction which difficult to reduce by conventional coagulation. From the investigation of chemical classes of DOM, it was found that aliphatic hydrocarbon was the major chemical classes in all DOM fractions (>48%). However, chemical classes of DOM in each DOM fraction provided the different ability to form THMs. The results showed that aliphatic hydrocarbon in HPIA, HPIN, HPOA and HPON had a low ability to form THMs but those in HPIB and HPOB fraction had a high ability to form THMs.

Field of Study: Environmental Management　　Student's Signature ....

Academic Year: 2013　　Advisor's Signature ....

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CHAPTER I

INTRODUCTION

1.1 Motivations

In general, the conventional water treatment technologies for surface water was based on physic-chemical process which consisting coagulation, flocculation, sedimentation, filtration and disinfection. These technologies have been used for a long time and their operation is well understood by operators, however, they have been facing some problems such as require larger area for instruction, require higher chemical consumption and low organic removal efficiency. Abeynayaka *et al.* (2012) reported that conventional water treatment which including coagulation-flocculation, sedimentation and rapid sand filtration was ineffective to remove DOM from high DOM water source. DOM which passed through rapid sand filtration can reacts with chlorine to form trihalomethane (THMs) which defined as human carcinogen.

With the limitation of conventional water treatment, stricter standard, higher demand of water supply and higher attention on consumer safety, the advance technologies for water treatment such as membrane filtration technologies are offered. The membrane filtration technologies can reduce the chemical requirement, reduce space to treat a given flow and produce high volume of treated water. One types of membrane filtration widely utilized for surface water treatment is ceramic membrane. They have been providing several advantages including better mechanical strength, resistance to the acidity, produce high permeate water at low pressure, greatly long working operation and easily to clean with extremely chemical.

The ceramic membrane filtration is widely utilized in water treatment and drinking water production and provided the great potential for application especially in developed country such as Japan (Kiyozuka, 2005), Italy (Bottino, 2001) and USA (Lehman *et al*., 2008). As in December 2004, more than 48 plants of municipal potable water in Japan was utilized the ceramic membrane filtration (Hattori *et al*., 2005). However, the operation of ceramic membrane filtration depends on the specific characteristics of surface water sources and other factors such as pH and turbidity. The application of ceramic membrane filtration for the high turbid water source especially in Thailand is rarely studied. Therefore, this research was conducted the ceramic membrane filtration with the high turbid water source which collected from Ping River water, Chiang Mai, Thailand.

Dissolve organic matter (DOM) is primary concern in water treatment and drinking water treatment because it acts as a precursor in the formation of THMs. The formation of THMs is depended on the quantity and characteristics of DOM. The different DOM characteristics are resulted in different ability to form THMs. The quantity of DOM are commonly characterized by measuring DOM surrogate parameters including dissolved organic carbon (DOC), ultraviolet absorbance at wavelength of 254 nm (UV- 254), specific ultraviolet absorption (SUVA) and trihalomethane formation potential (THMFP). For the characteristics of DOM, resin fractionation technique and pyrolysis GC/MS technique can be utilized to characterize DOM. The quantity of DOM in surface water had been investigated by many researchers. Nevertheless, the knowledge on quantity of DOM alone cannot sufficient for the design and selected the appropriate water treatment system due to the different nature of DOM. Resin fractionation technique is commonly applied to separate DOM into DOM fractions. From the past research, it was utilized to fraction DOM in surface water, groundwater and reservoir. However, the information of DOM fractions after filtrated through the ceramic membrane filtration was not been provided. Therefore, the characterization of DOM of filtrated water from ceramic membrane filtration was conducted.

The removal of DOM through the conventional membrane filtration is based on the sieving mechanism alone, the amount of DOM residual in treated water is still of problematic concern. The one process that basically applied to enhance the permeate quality from ceramic membrane filtration would be coagulation/flocculation process. The addition of a coagulant as a pretreatment prior to membrane filtration has been proposed for the purpose of not only improving the removal of DOMs but reducing membrane fouling (Lehman *et al.*, 2005; Wiesner *et al.*, 1989 and Jacangelo *et al.*, 1995). In-line coagulation is the application for coagulation process which applied to small membrane systems. It is referred to the use of coagulation before membrane filtration without a sedimentation step. Korbutowicz (2006) stated that application of in-line coagulation/ultrafiltration process with the use of alum or polyaluminum chloride resulted in improved removal of NOM from treated water and reduced membrane fouling. Thus, this study was investigated the reduction of DOM by using in-line coagulation with ceramic membrane filtration.

1.2 Objectives

The main objective of the study was to investigate the trihalomethane formation potential (THMFP) of DOM fractions in water production by in-line coagulation with ceramic membrane microfiltration. In order to achieve the main objective, the following sub objective should be considered.

1. To investigate the dissolved organic matter reduction efficiency by in-line coagulation with ceramic membrane filtration.

2. To study the long term operation of ceramic membrane filtration and investigate the THMs in filtrated water.

3. To characterize dissolved organic matter into the dissolved organic matter (DOM) fraction and investigate the DOC mass distribution, THMFP distribution and specific THMFP of DOM fractions.

4. To identify the chemical classes, common fragments, major fragment, and prominent major fragments of DOM and their fractions by using pyrolysis gas chromatography/mass spectrometer (GC/MS) technique.

1.3 Hypotheses

1. The using of in-line coagulation with ceramic membrane filtration can reduce DOM fractions that had a high ability to form THMs.

2. The addition of chlorine as pre-chlorination to reduce membrane fouling and disinfection can increase the formation of trihalomethane in filtrated water.

1.4 Scope of Study

1. Ping River, Chiang Mai, Thailand which considered as high turbid surface water was selected as raw surface water. The characteristic of raw surface water was analyzed by measuring various parameters including turbidity, pH, organic matter concentration (DOC, UV-254 and SUVA) and THMFP.

2. Batch experiment of in-line coagulation with ceramic membrane was conducted and studied.

- The optimal coagulants dosage for the in-line coagulation and ceramic membrane filtration was determined by using Jar-test.

- The reduction efficiency of organic matter (DOC and UV-254) and THMFP were investigated.

- The reduction efficiency of DOM fractions and their THMFP were investigated.

3. Continuous experiment of in-line coagulation with ceramic membrane was conducted and studied.

- The experiment was operated continuous and the water quality of filtrated water was investigated.

- The reduction efficiency of organic matter along the experimental periods was investigated.

- The effect of pre-chlorination process to the formation of THMs in filtrated water was determined.

4. The chemical classes of DOM and their fractions of raw surface water and filtrated water from in-line coagulation with ceramic membrane filtration were investigated by using pyrolysis GC/MS technique

CHAPTER II

BACKGROUND AND LITERTURE REVIEW

2.1 Dissolved organic matter

Natural organic matter (NOM), defined as the complex matrix of organic material present in natural waters, affects significantly many aspects of water treatment. NOM in natural is coming from the growth and decay of plant and decomposition of microbe (Dilling and Kaiser, 2002). In general, NOM can be separated from the solubility to dissolved organic matter (DOM) and particulate organic matter (POM). In addition, NOM can be separated to POM, colloid organic matter (COM) and DOM by using the different membrane pore size such as 0.1 μm, 0.45 μm and 1 μm (AWWA, 1993 and Owen *et al*., 1995). In general, POM and DOM can be removed by the water supply process but DOM which can be passed the membrane pore size 0.45 μm is difficult to remove through water supply process (Crozes *et al*., 1995). Dissolved organic matter (DOM) is a complex mixture of hydrophilic and hydrophobic organic materials which varies in size, functional groups and reactivity (Yee *et al*., 2009).

DOM consists of humic substance and non-humic substance. DOM which defined as humic substance is consisting of humic acid, fulvic acid and humine. Whereas, those of non-humic substance are consist of hydrophilic acids, protein, amino acids and carbohydrate. The property of humic substance is hydrophobic organic fraction, HPO while those of non-humic are hydrophilic organic fraction, HPI. Leenheer and Croue (2003) defined DOM as a complex mixture of aromatic and aliphatic hydrocarbon structures with attached amide, carboxyl, hydroxyl, ketone, and various minor functional groups. DOM commonly found in surface water, groundwater and reservoirs. In terms of their chemical properties and implication for water treatment, the humic substance is the most important (Owen *et al*., 1995). DOM in term of humic substance is commonly found in surface water such as river, canal and reservoir at higher concentration than non-humic substance. Martin-mousset *et al*. (1997); Mash *et al*. (2004); and Owen *et al*. (1995) reported that about 45-65% of humic substance was found in surface water, while the non-humic substance was found to have 35-55%. The presence of DOM in natural water depended on the climate, geology and topography.

The presence of DOM creates serious problems include negative effect on the water quality, increased coagulant and disinfectant dose requirements and increased the potential harmful disinfection by product production (Jacangelo *et al*., 1995). Furthermore, DOM is capable of forming complexes with metals such as iron, can serve as a substrate for microbial growth and can exert significant oxidant demand. DOM is serves as the organic precursor which is the major problems of DOM in natural water.

DOM even though present in a tiny quantity in raw water supply, it can react with chlorine during chlorination to form halogenated disinfection by-products (DBPs) such as trihalomethane (THMs) which classified as potential carcinogenic substances, persistent and mobile, and pose a cancer risk to humans. DOM is recognized as precursors for disinfection by-product formation during water treatment disinfection operation (Meyn *et al*., 2012 and Marhaba and Washington 1998). The formation of DBPs depends on the quantity and characteristics of DOM.

2.2 Surrogate parameters of DOM

DOM is commonly characterized by nonspecific or surrogate parameters. The several surrogate parameters must be used to describe DOM because no single surrogate parameter is capable of measuring the widely varied characteristics of DOM. Commonly surrogate parameters used for DOM measurement are include dissolved organic carbon (DOC), ultraviolet absorbance at wavelength of 254 nm (UV- 254), specific ultraviolet absorbance (SUVA) and trihalomethane formation potential (THMFP).

2.2.1 Dissolved organic carbon (DOC)

Dissolved organic carbon (DOC) is defined as the fraction of TOC that dissolved in water and is able to pass through a filter which range of filter size between 0.7 and 0.22 μm. The term of dissolved are defined as the compound which size lower than 0.45 micrometers. DOC is used to represent the presence of dissolved organic matter such as humic substance and non-humic substance (Julie *et al*., 2004)

2.2.2 UV absorbance at wavelength 254-nm (UV-254)

UV-254 is used to provide an indication of the aggregate concentration of UV-absorbing organic constituents, such as humic substances and various aromatic compounds (APHA, AWWA, WEF, 1995). The first surrogate parameter that utilizes to determine the organic matter in raw water is UV absorbance at a wavelength of 254 nm. Organic matter including humic aromatic compounds and molecules with conjugated double bonds can absorb UV light whereas the simple aliphatic acids, alcohol, and sugars do not absorb (Edzwald *et al.* 1985). Hence, the UV-254 absorbance can be used to indicate the presence of aromatic compounds of organic matter in natural water. Eaton (1995) found that the UV absorbance of organic matter in water is very useful to indicate the concentration of DOC and THMs in water because the humic substrates strongly absorb ultraviolet radiation.

2.2.3 Specific Ultraviolet Absorbance (SUVA)

Specific Ultraviolet Absorbance (SUVA) is the ratio between UV absorbance at wavelength 254 nm and dissolved organic carbon (DOC) concentration of a given sample which express in unit of L/mg-m. SUVA is utilized to determine the relative index of humic content and the nature of DOM and its consequent THM formation in raw water (Edzwald, 1993; Owen *et al.,* 1993; Krasner *et al.,* 1996). Furthermore, the SUVA values can be used as an indicator of its coagulation ability to remove organic matter which it THM precursors. Water that having SUVA value higher than 3 L/mg-m has been found to have organic matter mostly in term of humic-like in character, higher in AMW and more readily removed by coagulation. On the other hand, water that having low SUVA (< 3 L/mg-m) has been found to have organic matter mostly in term of fulvic-like in character, lower in AMW and difficult to remove by coagulation. In addition, Edzwald and Tobiason (1999) defined guidelines for SUVA and showed a good correlation between value and the nature of the organic material (as shown in Table. 2.1).

Table 2.1 Guidelines of SUVA value for the nature of NOM (Edzwald and Tobiason, 1999)

SUVA	Composition
> 4	Mostly aquatic NOM. High hydrophobicity, high molecular weight
2-4	Mixture of aquatic NOM and other NOM. Mixture of hydrophobic
< 2	Mostly non-humic substances. Low hydrophobicity. Low molecular weight

2.2.4 Trihalomethane Formation Potential (THMFP)

THMFP is the potential of DOM to form THMs when contacted with chlorine under the extreme condition of chlorination. Standard method (1995) recommended that the chlorination condition for THMFP test as follow: the incubation time is seven days, the free chlorine residual at the end of incubation time should be range between 3 to 5 mg/L, the pH should be 7.0± 0.2 with phosphate buffer and the incubation temperature should be maintain at 25 ± 2°C. Total trihalomethane (TTHMs) is the sum of all four compound concentration including chloroform, dichlorobromomethane, dibromochloromethane and bromoform. THM_0 is the total THMs concentration at the time of sampling. The value of THM_0 is depended on the chlorine concentration of water. It can be range from zero to hundred micrograms per liter. $TTHM_7$ is the total concentration of all four compounds that form after the sample is incubated over a 7-days at temperature 25± 2°C in the presence of excess free chlorine under the recommended chlorination conditions for THMFP (Standard Methods, 1995).

THMFP or ΔTHMFP is the difference between the final $TTHM_7$ concentration and the initial concentration $TTHM_0$. In case of sample do not contain chlorine at the time of sampling, the initial concentration TTHM0 is almost zero. So, the term of THMFP is used as shown in Figure 2.1. However, if the sample contains chlorine at a time of sampling, the initial concentration TTHM0 is detected. Thus, the term of ΔTHMFP may be used as shown in Figure 2.2.

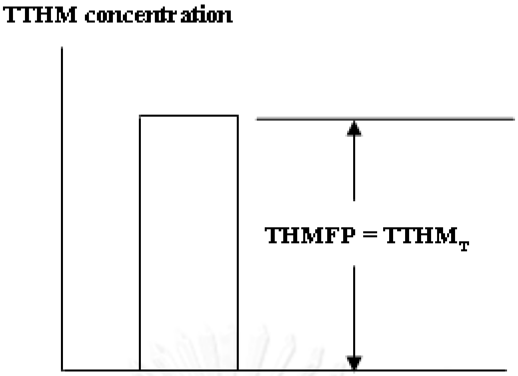


Figure 2.1 Definition used in the formation potential test of a sample without free chlorine at the time of sampling

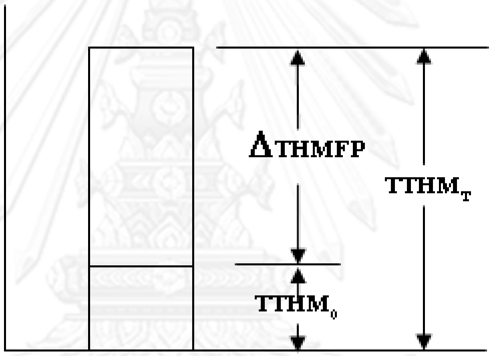


Figure 2.2 Definition used in the formation potential test, of a sample with free chlorine at the time of sampling

2.3 Disinfection By-Products (DBPs)

The addition of chlorine in the disinfection process of water supply production can cause of the formation of Disinfection By-Products (DBPs). Disinfection By-Products (DBPs) are formed when free chlorine is added to water and reacts with the natural organic matter (NOM) in water. The most dominant DBPs which commonly found is trihalomethane (THMs) followed by HAAs (Krasner *et al*., 1989; Marhaba and Van, 1999; Owen *et al*., 1995; and Grenier *et al*., 1992). THMs and HAAs were identified as potential adverse health effect agents. The generalized equation describing the formation of chlorine halogenated DBPs is shown in Equation (2.1) (Marhaba and Washington, 1998):

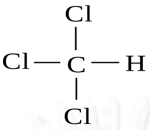
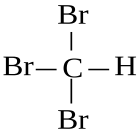
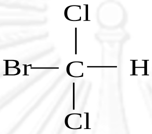
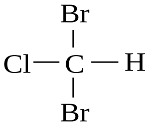
$$\text{Organic matter + free chlorine} \longrightarrow \begin{array}{c}\text{Disinfection By-products}\\ \text{(THMs+HAAs+HANs)}\end{array} \qquad (2\text{-}1)$$

2.3.1 Trihalomethane (THMs)

Trihalomethanes (THMs) commonly found in water supply and water treatment plant when chlorine reacted with natural organic matter such as humic or fulvic substances. Rook (1974) and Bellar *et al*. (1974) reported that the disinfection by-products (DBPs) such as THMs are generated from reaction between DOM and chlorine. Symon *et al.* (1975) described a survey of halogenated organic compounds from 80 water supply plants. THMs have been found to be the most widespread organic contaminants in drinking water, and occur at higher concentrations than other disinfection by-products. THMs concentration occurred in various stages of the water treatment process, especially in finished water, which contained 41.70-54.50 μg/L (El-Shahat *et al*., 1998; 2001). THMs are persistent and mobile, and pose a cancer risk to humans (Munro and Travis, 1986; Pereira, 1983).

Trihalomethanes (THMs) are a part of organic chemicals that contain one carbon atom, one hydrogen atom and three halogen atoms. Normally, halogen atoms are fluorine, iodine, chlorine and bromine. However, bromine and chlorine are the most common halogen atoms to form THMs in water (Rook, 1977). Classes of THMs can be characterized based the replacing of the hydrogen atoms by halogen atoms. Four THMs species actually occur in water supplies including chloroform, bromodichloroform, dibromochloroform and bromoform which the structures of these species are shown in Table 2.2. In the source of water with highly organic content such as surface water, THMs in four form including chloroform, bromodichloromethane, dibromochloromethane and bromoform are formed when chlorine-based disinfectants are added. Chloroform are commonly found at the highest concentration in water supply and drinking water process followed by dibromochloromethane.

Table 2.2 Chemical formulas of the four most common trihalomethanes

Individual, DBPs	**Structure**	**Individual, DBPs**	**Structure**
Trichloromethane or Chloroform ($CHCl_3$or TCM)	 $\begin{matrix} & \mathrm{Cl} & \\ \mathrm{Cl}- & \mathrm{C} & -\mathrm{H} \\ & \mathrm{Cl} & \end{matrix}$	Tribromomethane or Bromoform **(**$CHBr_3$ or TBM**)**	 $\begin{matrix} & \mathrm{Br} & \\ \mathrm{Br}- & \mathrm{C} & -\mathrm{H} \\ & \mathrm{Br} & \end{matrix}$
Bromodichloromethane ($CHBrCl_2$ or BDCM)	 $\begin{matrix} & \mathrm{Cl} & \\ \mathrm{Br}- & \mathrm{C} & -\mathrm{H} \\ & \mathrm{Cl} & \end{matrix}$	Dibromochlromethane ($CHBr_2Cl$ or DBCM)	 $\begin{matrix} & \mathrm{Br} & \\ \mathrm{Cl}- & \mathrm{C} & -\mathrm{H} \\ & \mathrm{Br} & \end{matrix}$

Source: Rook, (1977).

THMs can be taken in by ingestion from drinking water and food and inhalation during showering. Capece (1998) reported that people who use a showering for 10 minutes get the THMs equal to people who drink the water which contained THMs only 5 glasses. After taken in the human or animal, THMs are metabolized into less-toxic form. However, some of them are transformed to reactive substance when exposed to high concentration. THMs can be absorbed by human and animals after exposure and the highest tissue concentrations are attained in the fat, liver and kidneys. Chloroform and bromodichloromethane are influences cancer in the liver and kidneys after exposure to high concentration. The toxicity of THMs in all species is shown in Table 2.3.

Table 2.3 Toxicity of THMs compound

THMs compound	**Effect to Health**
Chloroform	Effect to central nervous system, tumors and cancer in livers, kidneys and large intestine.
Bromodichloromethane	Effect to tumors and cancer in livers, kidneys
Dibromochloromethane	Effect to central nervous system, tumors in livers kidneys
Bromoform	Effect to central nervous system and cancer in livers, kidneys and large intestine.

Sources: USEPA (1999); IPCS (2000)

Due to the various effects of THMs, the US Environmental Protection Agency (USEPA) in the National Interim Primary Drinking Water Regulation was set the maximum contaminant level (MCL) of the disinfection by product rule (D/DBP Rule) for stage 1 at 80 μg/L and for stage 2 at lower than 40 μg/L (USEPA, 1998).

In Thailand, the standard of THMs was set according to the standard of THMs from World Health Organization (WHO) which set the overall guideline value of THMs should lower than 1. The guideline value can be calculated from Eq. 2.2.

$$\frac{C_{\text{bromoform}}}{GV_{\text{bromoform}}} + \frac{C_{\text{DBCM}}}{GV_{\text{DBCM}}} + \frac{C_{\text{BDCM}}}{GV_{\text{BDCM}}} + \frac{C_{\text{chloroform}}}{GV_{\text{chloroform}}} \leqslant 1 \qquad (2\text{-}2)$$

Where C is the surveyed concentration of each THM, and GV is the WHO guideline value. WHO (2006) have been established GV value separately at 300 mg/L for chloroform, 100 mg/L for each of bromoform and dibromochloromethane (DBCM), and 60 mg/L for bromodichloromethane (BDCM).

The standard of THMs in water from different country are shown in Table 2.4

Table 2.4 Standard of THMs in water from different country

Country	Products	Maximum contaminant level, MCL (μg/L)	Reference
US-EPA	THMs	80	Mallika and Pongsri (2006)
Japan	$CHCl_3$	60	Wang *et al*. (2007)
	$CHCl_2Br$	30	
	$CHClBr_2$	10	
	$CHBr_3$	90	
Italy	THMs	30	Roccaro *et al*. (2005)
Germany	THMs	50	
Thailand	$CHCl_3$	300	Metropolitan Waterworks Authority, (2013)
	$CHCl_2Br$	60	
	$CHClBr_2$	100	
	$CHBr_3$	100	

2.3.2 Factors Influencing THM Formation

The formation of THMs is depended on various factor including chlorine concentration, NOM concentration, contact time, temperature and pH. Each of factors for THMs formation is explained as follow:

2.3.2.1 Chlorine Dosage

The chlorine concentration is the one of factor that affected the formation of THMs. Kavanaugh *et al*., 1980 stated that the THMs level rises with the increasing of chlorine dose. The linear relationship between chlorine consumption and THMs formation was found to be greater than or equal to unity. Natural Environmental Board (1984) investigated the relationship between chloroform level and chlorine dose in water distribution system and reported that the chloroform level increased from 20 to 220 µg/L at the various chlorine dosage from 4 to 30 mg/L. The highest chloroform level was found at chlorine dosage of 22 mg/L.

2.3.2.2 Precursor Concentration

Natural organic matter (NOM) is the major precursor of THMs formation. NOM is considered to contain many of precursors that effect to the formation of THMs such as humic and non-humic material. The concentration of THMs was increased with increasing of NOM in water. The concentration of THMs was in the range of 1-250 μg/L when the TOC concentration was in the range of 1-11 mg/L (Natural Environmental Board, 1984). The relationship between NOM concentration and THMs formation was quite good which led to use the concentration of NOM to estimate the formation of THMs.

2.3.2.3 Contact time

The formation of THMs increase with the increasing of reaction time. When chlorine was added, the rapid THMs formation was occurred at the initial few hours. After that the rate of THMs formation was decreased. Jinfeng *et al*., (2009) found that the formation of THMs was rapidly increasing after added chlorine to water in the first 48 hour. After that the formation of THMs was decreasing between 48 - 72 hour. Furthermore, Faust and Aly (1997) found that the formation of THMs was rapidly occur after added chlorine to water for 4 hour and the completed reaction was found after 20 hour.

2.3.2.4 Water temperature and pH

The temperature was affected the formation of THMs. The formation of THMs increase with the increasing of temperature (AWWARF 1991, Siddiqui and Amy, 1993). Carlson and Hardy, 1998 reported that the impact of temperature on THMs formation was highest at the longer contact time. Furthermore, pH was found to affect the formation of THMs. Normally, the charge of NOM are negative charge which can combined together to form colloids. When the pH value increased, the negative charge of NOM are increasing which led the NOM is stable and difficult to reduce NOM via coagulation process. Natural Environmental Board (1984) investigated the effect of pH on chloroform production at constant temperature, TOC and chlorine dosage and found that chloroform concentration decreased when pH was decreased.

2.3 Resin fractionations

DOM is a heterogeneous mixture which could be separated into DOM fractions by using resin fractionation process (Hua *et al*., 2008). Resin fraction process is utilized to characterize DOM and separate organic matter based on the similarity of their chemical (AWWA, 1993). The fractionation of DOM is developed to characterize DOM and investigate the effect of each DOM fraction. The resin fractionation process could be help to gain better understanding of DOM on the formation of DBPs by conducting THMFP test on DOM fractions. The ability of each DOM fractions to react with chlorine to form THMs was evaluated (Musikavong, 2006).

Leenheer (1981) proposed the use DAX-8 resin to isolate DOM into hydrophobic and hydrophilic fractions and developed the resin fractionation process to separate DOM into six DOM fraction including hydrophobic neutral (HPON), hydrophobic base (HPOB), hydrophobic acid (HPOA), hydrophilic base (HPIB), hydrophilic acid (HPIA) and hydrophilic neutral (HPIN) by using a series of three resin (DAX-8, AG-MP-50 and Duolite A7). Later on, Marhaba *et al*. (2003) was modified the resin fractionation which proposed by Leenheer (1981) by replacing Duolite A7 resin with WA-10 resin as shown in Figure 2.3.

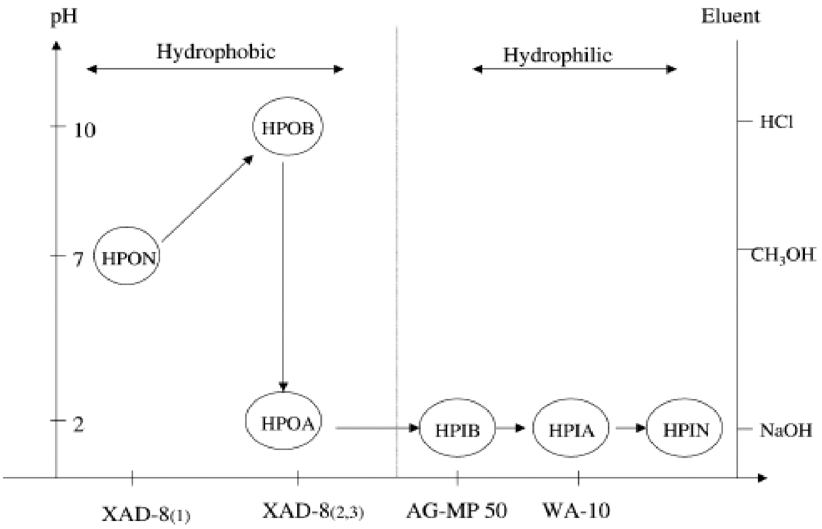


Figure 2.3 Resin fractionation process (Marhaba *et al.,* 2003)

The characteristics and chemical group of six DOM fractions are illustrated in Table. 2.5.

Table 2.5 Characteristics and chemical group of DOM fractions

DOM fractions	Characteristics and chemical group
Hydrophilic	
Acids	Humic acid, fulvic acid and high MW alkyl monocarboxylic and dicarboxylic acids
Base	Proteins, aromatic amines and high MW alkyl amines
Neutrals	Hydrocarbon, aldehydes, furan and high MW methyl ketones and alkyl alcohols
Hydrophobic	
Acids	Hydroxy acids, sugars, sulfonics and low MW alkyl monocarboxylic and dicarboxylic acids
Base	Amino acids, purines and low MW alkyl amine
Neutrals	Polysaccharides, aldehydes and ketones

Many researchers utilized resin fractionation technique to characterize DOM in various water source such as surface water (Day 1991; Marhaba and Van, 1999; Croue *et al*., 2000; Marhaba and Van, 2000; Imai *et al.* 2001; Kimura *et al*. 2004, and Panyapinyopol *et al.,* 2005), reservoir and lake waters (Imai *et al*., 2001; Imai *et al.*, 2003; and Janhom *et al.,* 2005) and groundwater (Swietlik *et al.,* 2004).

Marhaba and Van (2000) isolated water from the Passaic River in New Jersey and found that it comprised of hydrophilic higher than 50% and DBPs test showed that the THMFP created from hydrophilic fraction was high at 69% while those of hydrophobic fractions was only 6%. Whereas, Liang and Singer (2003) reported that hydrophobic fractions was the major contributor to THMs formation.

Panyapinyopol *et al*. (2005) utilized the resin fractionation with three resin including DAX-8, AG-MP-50 and WA-10 to fraction DOM from raw water of water supply production at Bang Khen, Bangkok, Thailand into six fraction. The results showed that the DOC concentration of six DOM fraction from high to low were hydrophilic neutral (HPIN), hydrophobic acid (HPOA), hydrophilic acid (HPIA), hydrophobic neutral (HPON), hydrophilic base (HPIB) and hydrophobic base (HPOB). The HPIN and HPOA fractions were the two main precursors for THMs production.

Phumpaisanchai (2005) conducted the resin fractionation technique with reservoir water from Mae Hia, Chiang Mai and Phumiphol Dam, Tak of Thailand. DOM in raw water was separated into hydrophilic (HPI) and hydrophobic (HPO) fractions. The results showed that HPI fraction was found at higher percent mass distribution than HPO fraction both of water samples.

Srimuang (2011) applied the resin fractionation technique to separate DOM from U-tapao canal to hydrophilic (HPI), hydrophobic (HPO) and transphilic (TPI) fractions by using DAX-8 and XAD-4 resins. The results showed that DOM in raw water collected from U-tapao canal was mostly in HPO fraction (42%) followed by HPI fraction (31%) and transphilic fraction (27%), respectively.

Krutklom (2013) using the resin fractionation technique to fraction DOM in Ping River water to hydrophilic (HPI) and hydrophobic (HPO) fraction. The results showed that hydrophilic fraction was the major DOM fraction in Ping River water.

Homklin (2004) investigated the DOM fraction in raw water from Ang Kaew reservior, Mae Kuang reservior and Mae Sa river, Chiang Mai, Thailand. The results found that HPO fraction was found at the highest percent DOC distribution in the range of 53% - 69% of all water source.

2.4 Pyrolysis GC/MS Analysis

Pyrolysis GC/MS is the analytical technique that has been commonly utilized to identify the structure of complex organic macromolecules. Pyrolysis is the method which uses the thermal to separate organic molecule into volatile fragments. Then, it was separated by gas chromatography and identified the fragment by mass spectroscopy (MS). Pyrolysis GC/MS provided the fragments or fingerprint of organic matter which can be used to characterize the organic matter. The advantages of pyrolysis GC/MS were it required small amount of sample (only few milligram) for analysis and the preparation of sample was not difficult. Furthermore, it is capable to provide the detail molecular weight information (Saiz-Jimenez, 1994). Recently, the pyrolysis GC/MS has been utilized to identify the original mixture of DOM in water. The pyrolysis GC/MS provide the pyrolysis fragment or fingerprint which could be used to determine the chemical classes of DOM in water (Gray *et al*., 1996). Many researchers were utilized pyrolysis GC/MS to identify the chemical classes of DOM.

Bruchet *et al*. (1990) apply the GC/MS pyrolysis to investigate the characteristics of organic matter in term of biopolymer such as polysaccharide, polyhydroxyl aromatic, amino sugars and protein. The pyrochromatogram of a mixture of biopolymer and the pyrolysis fragment of each pyrochromatogram which obtained from the pyrolysis GC/MS are shown in Figure 2.4 and Table 2.6, respectively.

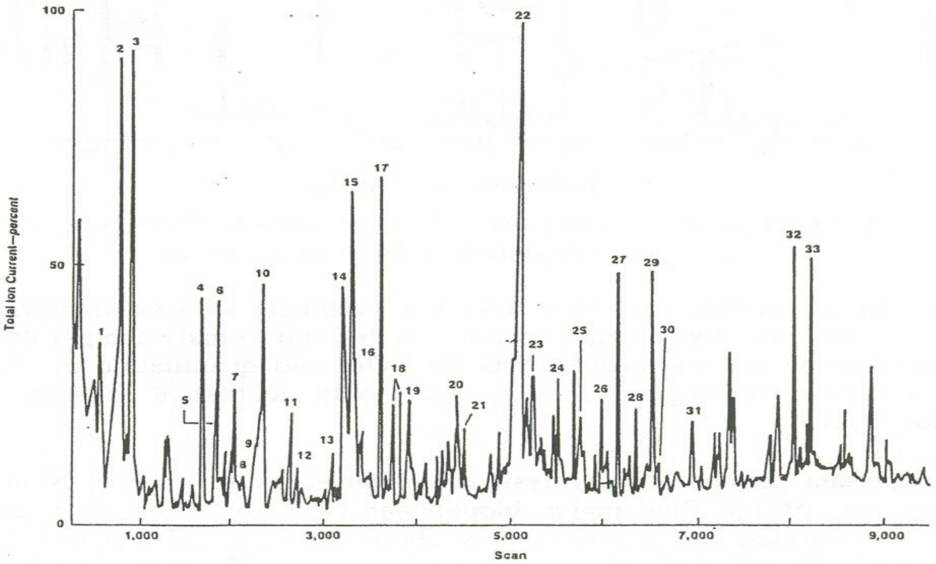


Figure 2.4 Pyrochromatogram of a mixture of biopolymer obtained from pyrolysis

Table 2.6 Pyrolysis fragment from a mixture of biopolymers (bovine serum albumin, cellulose acetate, fluka humic acid, and chitin) for pyrochromatograms shown in Figure 2.4 (Bruchet *et al.,* 1990)

Peak	Pyrolysis fragment	Biopolymer type*	Peak	Pyrolysis fragment	Biopolymer type*
1	Benzene	PH	18	Methypyrrole	Pr
2	Acetronitrile	Pr, As	19	Methylfurfural	Ps
3	Toluene	Pr	20	Acetophenone	
4	Pyridine	Pr	21	Furfuryl alcohol	Ps
5	2-Methylfuran	Ps	22	Acetamide	As
6	Methylpyridine	Pr	23	Methylnaphthalene	
7	Styrene	Pr	24	N-methylacetamide	As
8	polysaccharide fragment	Ps	25	Phenylacetronitrile	Pr
			26	Levoglucosenone	Ps
9	Methylpiridine	Pr	27	Phenol	PH, Pr
10	Hydroxypropanone	Ps	28	Unknown chitin fragment	As
11	2-Cyclopenten-1-one	Ps	29	p-cresol	Pr, PH
12	2-Cyclopenten-1-one-3-methyl	Ps	30	m-cresol	PH
			31	C2-Phenol	PH
13	Furfural	Ps	32	Indole	Pr
14	Acetic acid	Ps, As	33	Methylindole	Pr
15	2-Furaldehyde	Ps			
16	2-Acetylfuran	Ps			
17	Pyrrole	Pr			

Remark: *Pr = protein, Ps = polysaccharide, PH = polyhydroxy aromatic, As = amino sugar

Widrig *et al.* (1996) studied the reduction of algal-derived organic material by using preozonation and coagulation. The results showed that the aromatic nitrogen-containing fragment was the major substance of algal-devired organic material both in water before and after coagulation with ferric chloride.

Sirivedhin and Dallbauman (2004) investigated the characteristics of organic matter by using GC/MS pyrolysis. The results showed that the chemical classes of organic matter are consisting of nitrogen, aromatic and aliphatic.

Ritter et al. (1999) characterized DOM in raw water by using pyrolysis GC/MS and found that the percent distribution of polysaccharide, protein, amino sugars, polyhydroxyl aromatic and other class were 21%, 3%, 41%, 14% and 21%, respectively.

Cunha *et al.* (2000) used pyrolysis GC/MS to characterize riverine particulate organic matter. Particulate matter samples were collected in the mountainous section and river mouth at the Tech River basin, south France, during flood (December 1996) and summer (September 1997). The 23 identified pyrolysis fragments were found and can be classified into five main biopolymer; amino sugars, aromatic hydrocarbons, polysaccharides, phenols and nitrogeneuous compounds.

White *et al.* (2003) determined the nature of natural organic matter (NOM) contributing to DBPs in Alaskan water supplies using pyrolysis GC/MS. It was found that a phenolic compound was the major NOM to contribute the DBPs formation.

Musikavong and Wattanachira (2013) investigate the chemical classes of DOM in two reservoirs and upstream and midstream of canal, and raw water supply during rainy and summer season in Songkla, Thailand by using pyrolysis GC/MS technique. The chemical classes of DOM can be characterized into aliphatic hydrocarbon, aromatic hydrocarbon, phenolic compound, organic nitrogen, aldehydes and ketones, ester and alcohols, carboxylic acid and unknown. The results showed that aliphatic hydrocarbon was the major chemical classes of DOM in all water samples with percent distribution in the range of 30% -55% and 34% - 46% in rain and summer, respectively.

Musikavong (2006) utilized the pyrolysis GC/MS to investigate the chemical classes of DOM in wastewater collected from central wastewater treatment plant of the Northern-Region Industrial Estate, Lamphun province, Thailand. The chemical classes of DOM was characterized to aliphatic hydrocarbon, carboxylic acids, aromatic hydrocarbon, organic nitrogen, phenol, aldehydes and ketones, alcohol and unknown based on the similar chemical characteristics. The results showed that aliphatic hydrocarbon was dominant chemical classes in the influent wastewater and treated water.

2.5 Membrane filtration

2.5.1 Ceramic membrane filtration

Membrane filtration technology is widely used both for water and wastewater treatment all over the world. The membrane filtration has gained interest in the field of water supply or drinking water over the conventional coagulation. The use of membrane filtration has rapidly increased with the stricter regulation of water quality, the decreasing of cost and the improving of membrane materials (Choi and Dempsey, 2004). In addition, it can offered many advantages including require lower space to treat a given flow, require lower chemical consumption, easy to operate and maintenance and provided the better water quality (Nakatsuka *et al*., 1996). Furthermore, membrane filtration is ecologically friendly and more favorable than other separation technologies.

In recent years, ceramic membranes are increasingly being used in a field of water and wastewater treatment, especially for surface water treatment. Ceramic membranes provided the several advantages over polymeric membranes such as produce high permeate, stable to chemically, thermally and mechanically, easy to cleaning with strong acid/base or backwashing with high pressure and less water loss produce (Abeynayaka *et al*., 2012). Furthermore, the membrane modules can withstand elevated temperatures, extremes of pH (0 to 14), and high operating pressures up to 10 bar (145 psi) without concern for membrane compaction, delamination or swelling. In addition, ceramic membranes are ideal for in-place chemical cleaning at high temperatures, while using caustic, chlorine, hydrogen peroxide, ozone and strong inorganic acids, and/or by using steam sterilization. So, this membrane is suitable for many applications where polymeric and other inorganic membranes cannot be used. The advantages and disadvantages of ceramic membrane are presented in Table 2.7.

Table 2.7 The advantages and disadvantages of ceramic membrane

Advantages	Disadvantages
1. Ceramic membrane cans resistance at higher temperature (300 °C) than polymer membrane.	1. Cost of ceramic membrane is still high.
2. Ceramic membrane is resistance with strong acid, base and other chemical solution for cleaning.	2. Broken easier
3. Provide high permeate production at low pressure.	3. Range of molecular rejection was low compare to polymer membrane.
4. Excellent mechanical and ease to cleaning.	
5. Long life cycle more than 3-5 years.	

Ceramic membranes are available in various pore sizes including microfiltration, ultrafiltration and nanofiltration. Ceramic membranes normally have an asymmetrical structure composed of at least two or mostly three layers. Generally, there are two main layers assembled in ceramic membrane including of separation layer and support layer, as illustrated in Figure 2.5.

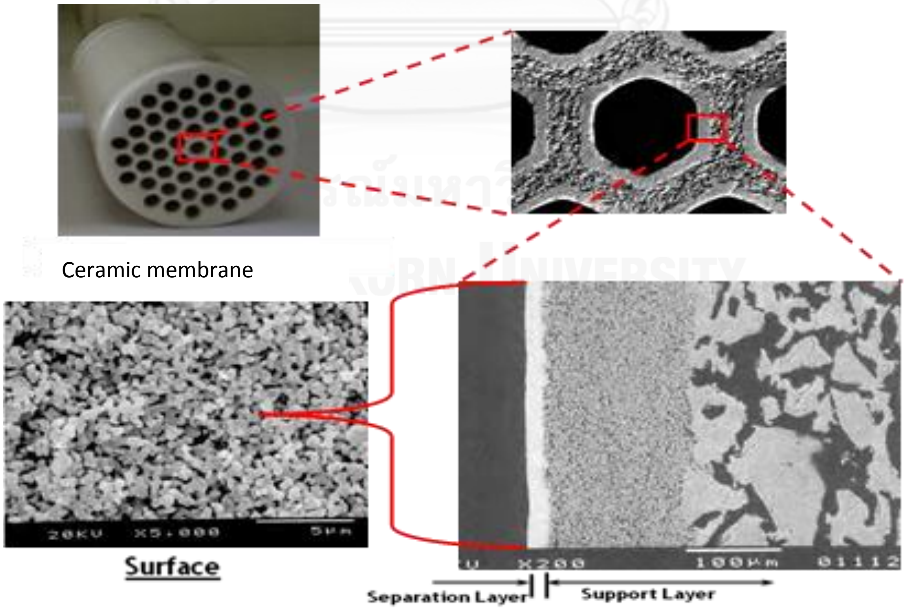


Figure 2.5 The structure of ceramic membrane (Source: Meta Water Co., Ltd. Confidential Report, 2008)

For the treatment of surface water, the membrane filtration process is highly effective due to its high efficiency of suspended solids removal and its compactness compared to the conventional coagulation and rapid filtration processes. Watanabe *et al*. (2005) reported that the ceramic membrane filtration is effective for stable removal of suspended solids from highly turbid water and also concluded that among all kinds of membrane, the ceramic membrane has the highest durability, which leads to lower maintenance cost and lower life cycle cost.

2.5.2 Combination system of ceramic membrane and coagulation

The combination of ceramic membrane filtration and coagulation process was utilized to enhance the DOM removal from water. Generally, the removal mechanism of ceramic membrane is size separation. However, the lower pressure membrane such as microfiltration has larger pore size than DOM. Then, the DOM removal efficiency was limited. The using of membrane filtration alone is not effective to remove DOM with lower percent DOC removal (Laine *et al.*, 1990). The coagulation process was applied to increase the DOM removal efficiency by using the aggregation mechanism with coagulants such as adsorption, entrapment and charge neutralization (Jarvis *et al*., 2004). The addition of coagulants during the coagulation process can be increased the size of DOM to have larger than the membrane pore size (Matsushita *et al*., 2005). The combination of coagulation process with membrane filtration can enhances the DOM removal efficiency (Konieczny, 2006; Loi-Brugger *et al*., 2006 and Shirasaki *et al*., 2010). In addition, the addition of coagulants before membrane filtration has been proposed for the purpose of not only improving the DOM removal but also reducing membrane fouling (Pikkarainen *et al*., 2003; Wiesner *et al.*, 1989; and Jacangelo *et al.*, 1995). Many researchers was studied the efficiency of DOM removal by using the combination of membrane filtration with coagulation process. Hata *et al*. (2009) shows that the ceramic membrane filtration process with coagulation is effective for removing suspended solids from several river water samples in Southeast Asia. In addition, Kabsch-Korbutowicz (2005) studied the surface water treatment by using coagulation (alum, $NaAlO_2$ and PACl) combine with ultrafiltration process. The results indicated that the coagulation with ultrafiltration provided the highest percent NOM removal in the range of 60-70% when studied at pH 6-8. Li *et al*. (2011) indicated that the hybrid coagulation-ceramic microfiltration could remove DOC with higher percent removal than coagulation or membrane filtration alone.

The in-line coagulation process is refer to the use of coagulation without removal of sediment or coagulated solid prior to membrane filtration (Choi and Dempsey, 2004). The using of in-line coagulation with ceramic membrane filtration has been rapidly utilized to treatment of high DOM surface water (Meyn *et al.*, 2012). The advantages of in-line coagulation were need shorter coagulation time and require lower dosages of coagulants (Lehman and Liu, 2009). The precoagulation (PC) with either ferric or aluminium coagulants also improve DOM removal and lead to reduced trihalomethane (THM) formation (Judd *et al.,* 2001).

Many researchers were investigated the efficiency of in-line coagulation with membrane filtration. Guigui *et al.* (2002) reported that the better performance and filtrated water quality of in-line coagulation with UF membrane depended on the good coagulation condition including coagulant type, dose and pH. While Wang *et al*. (2006) reported that a hybrid process of in-line coagulation with ultrafiltration can greatly enhanced the removal of natural humic acids compared to ultrafiltration alone. The precoagulation at pH 7 can increased the DOC removals from 28% to 53%. Furthermore, the in-line coagulation also reduced the rate of membrane fouling with lead to constant of permeate flux and slightly increase of transmembrane pressure during filtration.

Krutklom (2013) investigated the efficiency of in-line coagulation with ceramic membrane filtration to reduce DOM from Ping River water, Chiang Mai, Thailand by using alum as coagulants. The results showed that in-line coagulation with ceramic membrane filtration at alum dosage 60 mg/L can reduce DOC concentration with percent reduction 26%.

Chaimongkol (2008) studied the efficiency of in-line coagulation with microfiltration ceramic membrane to remove DOM from Ping River water, Chiang Mai, Thailand. At the optimal dosage of PACl, in-line coagulation with ceramic membrane filtration can remove DOC concentration from raw water with percent reduction 18.1%.

2.6 Coagulation process

2.6.1 Conventional coagulation

Coagulation and flocculation are the adding of chemical reagent to destabilize of colloid particles which it can easier to combine together. Normally, the surface charges of colloid particles are negative which cannot combine together.

Thus, the adding of chemical can be neutralized the surface charge of colloid particles which it easier to agglomerate. Coagulation referred to the addition of coagulants and rapid mixing which cause of destabilization of the colloid particles. Then, the destabilization colloid particles were agglomerated. While flocculation is the slow mixing which the destabilization colloid particles can be aggregate to form floc. Subsequently, the floc was removed by sedimentation or filtration.

2.6.2 Mechanisms of coagulation

Four mechanisms can be used to explain the particle destabilization: (1) double layer compression, (2) adsorption or charge neutralization, (3) enmeshment in a precipitation, and (4) adsorption and antiparticle bridging. Normally, the coagulation is the process of particles charge destroyed. The mechanism which related was double layer compression and charge neutralization. While the enmeshment and bridging is related to flocculation process (Benefield *et al*., 1982).

2.6.2.1 Double Layer Compression

Double layer compression are involves the electrostatic repulsion. It occurs when the counter ions is added as coagulants. The highest concentration of counter ions is found at the surface of particles and decreases at the outer boundary of diffusion layer. The compression of diffusion layer can lead the destabilized of particles by counter ions. It can decrease the electrostatic repulsive forces between similar particles and the zeta potential is mitigated. Therefore, the particles are bind together with the attractive forces (van der Waals forces).

2.6.2.2 Charge Neutralization

Charge neutralization occurs when a colloid particle is destabilized by the coagulant ions. When the coagulants dissolves in water, the positive charged of coagulants ions neutralizes the negative charge of colloid particles. Thus, the charge of particle is reduced to the level that particles are destabilized. Then, the colloid particles can be adsorbed together.

2.6.2.3 Sweep Coagulation

Sweep coagulation involves the formation of a solid precipitate. This mechanism occurs when the enough concentration of coagulants was added. The crystal of coagulants is covering the colloid particles. So, the negative charge of colloids particles is enmeshed to the precipitates.

2.6.2.4 Interparticle Bridging

Destabilized particles can be aggregated by bridging with a polymer. Interparticulate bridging refers to the interaction between the polymer and the reactive groups on the destabilized particles. When a high molecular weight polymer comes into contact with a colloidal particle, some of the reactive groups in the polymer adsorb at the particle surface and leaving other portions of the molecule extending into the solution (AWWA, 1990).

2.6.3. Factor influence coagulation process

2.6.3.1 Characteristics of natural organic matter (NOM)

Characteristics of NOM in water are depended on the origination and geology. Thus, NOM characteristics in various place or country are different which affect the coagulation process. Kim and Yu (2005) and Sharp *et al*. (2006) reported that NOM which defined as hydrophobic were easier to remove than hydrophilic and the high molecular of NOM are higher remove by coagulation than small molecular of NOM.

2.6.3.2 Types and concentration of coagulants

There are many types of coagulants. The different types of coagulants provided the different ability to remove NOM in water. Many researchers investigated the performance of different coagulants for NOM removal. Uyak and Ismail (2007) studied the NOM removal by using AL^{3+} and Fe^{3+} and found that Fe^{3+} can remove NOM better than AL^{3+}. In addition, Musikavong (2005) studied the removal of NOM and THMFP by using alum and $FeCl_3$ and reported that both Alum and FeCl3 can remove NOM with percent removal 35% at coagulants concentration 40 mg/L.

2.6.3.3 pH

The variation of pH of water was found to affect the coagulation process. Many researcher including Kabsch-Korbutowicz (2005); Qin *et al*. (2006) and Uyak and Ismail (2007) were studied the effect of pH on the coagulation process and concluded that the different of pH was affected to the performance of coagulation process.

2.6.4 Polyaluminium Chloride (PACl)

Polyaluminium chloride (PACl) is increasingly used in water treatment. Its showing the various advantages compared to use of aluminium sulphate (alum). PACL (formula is $Al_n(OH)_mCl_{3n-m}$) was prepared by reaction between aluminium (Al_2O_3) and HCl at high temperature. PACL are the synthetic polymers which can be dissolved in water and formed insoluble aluminium poly-hydroxides which precipitate in a large volumetric of flocs. Thus, the flocs can absorb pollutants in the water and precipitated with PACL floc which easily to remove. PACL can be applied to all field treatment such as water treatment, drinking water and wastewater treatment.

The advantages of using PACl are as follow:

- Require lower dosage
- No need to add any neutralizing agent such as soda or lime
- Flocculation time are shorter
- Produce smaller amount of sludge
- Provide better quality of treated water

2.6.5 Removal of organic matter by coagulation process

Coagulation process is utilized in water supply process. It can remove both turbidity and dissolved organic matter which defined as a precursor of THMs (Krasner *et al*., 1995; and Huang and Shiu, 1996). Many researchers utilize coagulation process with PACl to remove DOM as precursors of THMs from natural waters.

Rizzo (2005) studied the efficiency of alum, PACl and $FeCl_3$ for NOM reduction. The results showed that the using PACl as coagulants can remove turbidity with highest percent removal compared to alum and $FeCl_3$. The range of percent removal of turbidity, TOC and UV-254 of all coagulants were 73-96%, 29-42% and 48-56%, respectively.

Zhonglian *et al*. (2010) used the coagulation process with alum and PACl to remove NOM from surface water. The results showed that the using of PACl as coagulants provided the higher percent NOM removal than using alum. The percent removal of turbidity, DOC and UV-254 of coagulation with PACl were 94.5%, 34.8% and 53.5%, respectively. Furthermore, it was found that the using of PACl as coagulants has the residual aluinium after treatment lower than using of alum.

Thongnak (2010) studied the removal of NOM by using coagulation process with PACl, alum and $FeCl_3$. The results showed that the coagulation with PACl provided the higher percent removal of turbidity, TOC, DOC, UV-254 and THMFP than alum and $FeCl_3$. Percent removal of turbidity, TOC, DOC, UV-254 and THMFP by using PACl coagulation were 94.55%, 56.36%, 49.15%, 42.22% and 48.14%, respectively.

Phumpaisanchai, A. (2005) studied the reduction of DOC and SUVA from two reservoir water including Mae Hia, Chiang Mai and Phumiphol Dam, Tak, Thailand by alum coagulation with the varied of coagulants dosage and pH. The results showed that coagulation by alum at the optimal condition can reduce DOM from both raw water with percent reduction higher than 40%.

Srimuang, K. (2011) studied the reduction of DOM in U-Tapao canal by using PACl coagulation and the results showed that coagulation process with PACl at dosage 40 mg/L can reduce DOC with percent reduction 57%. In addition, PACl coagulation at dosage 40 mg/L can reduce UV-254 with 52% reduction.

Krutklom (2013) studied the efficiency of alum coagulation for reduce DOM form Ping River water, Chiang Mai, Thailand. The alum dosage and pH was varied. The results showed that the optimal dosage was selected at alum dosage 60 mg/L and controlled pH 7.7 which can reduce DOC concentration about 33%.

CHAPTER III

METHODOLOGY

3.1 Studied Site and Sampling point

Ping River is the main river of Chiang Mai basin in northern Thailand and is one of the main contributories of Chao Phraya River. It originates at Doi Chiang Dao in Chiang Dao district, Chiang Mai Province. This river is currently a majority raw water source for water supplied production in urban and local area of Chiang Mai city. In general, turbidity of Ping River varies due to seasonal changes. However, it typically contains high turbidity value between 50 - 220 NTU and high as 300 NTU in rainy season (Hata *et al.* 2009). The selected sampling point is situated at N 18°51’7”, E 98°58’57.9” which about 10 kilometers-upstream far from Chiang Mai municipal area as shown in Figure 3.1 and 3.2. The sampling point was selected in upstream to avoid the contamination from human activities.

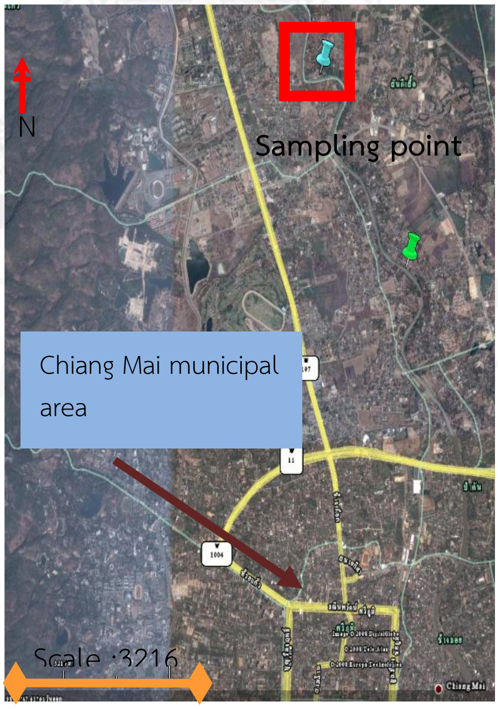


Figure 3.1 Sampling point in Ping River, Chiang Mai Province

Figure 3.2 Ping River, Chiang Mai Province

3.2 Sample Collection and Preservation

Raw surface water was collected from Ping River by pumping up from the depth of about 30 centimeters below water surface at the sampling point. Because of the water quality is varied with the seasonal change. Thus, water samples were collected three times in December 2011, April 2012 and August 2012 for represented the nature of dissolved organic matter (DOM) in winter, summer and rainy seasons, respectively. All water samples were stored in winter room at temperature 4 °C until analysis.

3.3 Experimental Framework

This research was divided into three parts. In the first part, the batch experiment of in-line coagulation with ceramic membrane filtration was conducted. The optimal conditions of ceramic membrane filtration were determined by using Jar test. The second part was focused on the continuous ceramic membrane experiment and aims to investigate the performance of ceramic membrane filtration to produce potable water. The membrane flow rate and the formation of THMs in filtrated water were investigated. The last part was focused on the characterization of DOM by using resin fractionation method and pyrolysis GC/MS technique. The chemical classes of DOM fraction and their relationship with the formation of THMs were determined. Figure 3.3 shows the experimental framework of the study. First, Ping River, raw surface water, was collected and characterized both in physical (Turbidity,

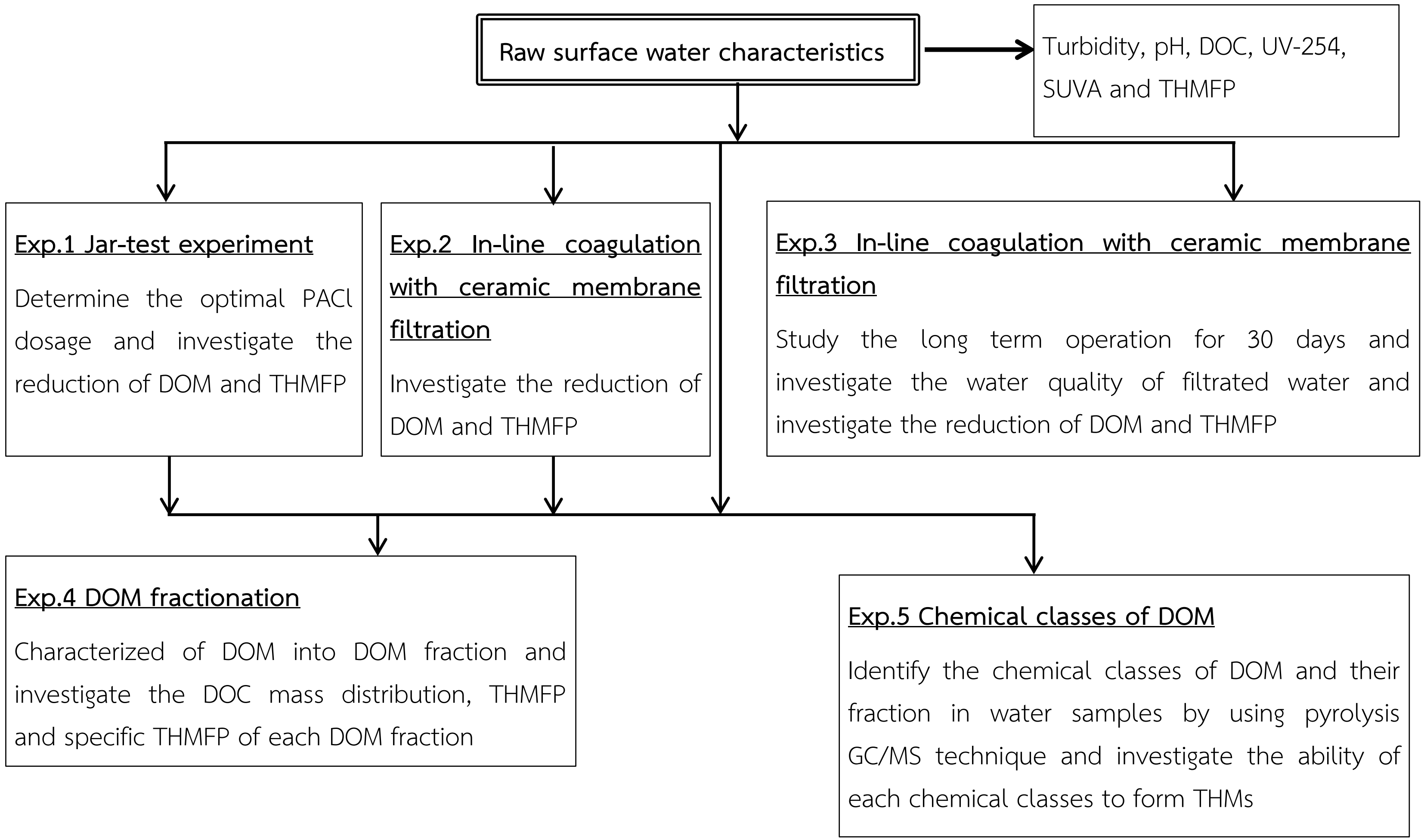


Figure 3.3 Experimental Framework

suspended solids and pH) and chemical (organic matter and THMFP) characteristics. After that Ping River was used as raw surface water for the further experiment. In the experiment 1, Jar-test experiment was conducted with varied PACl concentration to determine the optimal coagulants dose. The efficiency of PACl coagulation process to reduce organic matter was investigated. After that the experiment 2 was conducted to study the performance of in-line coagulation with ceramic membrane filtration process to reduce organic matter. Three optimal dosages of PACl from the result in experiment 1 were used in this experiment. The performance of in-line coagulation with ceramic membrane to reduce organic matter was investigated by measuring the DOC, UV-254 and THMFP in raw surface water and filtrated water. The results of both experiments can be used to achieve objective 1. In the continuous experiment, the long term operation of in-line coagulation with ceramic membrane was conducted. The operating condition was applied from the results in the batch experiment. This experiment was operated continuous to study the water quality of filtrated water and filtration rate. The results of this experiment were used to complete the objective 2. In the experiment 3, the resin fractionation process was conducted with raw surface water, coagulated water and filtrated water to study the composition of organic matter by separating into organic fraction. In addition, the trihalomethane formation potential (THMFP) of each fraction were studied. The relationship of each DOM fraction with the formation of THMs was investigated. The results were used to attain objective 3. After that the experiment 4 was studied. This experiment was mainly focused on the identification of chemical classes of DOM. The common fragments, major fragments and prominent major fragments of DOM of raw surface water, coagulated water, filtrated water and fractionated water were investigated. This result was used to attain objective 4.

3.4 Experimental Procedure

3.4.1 Raw surface water characteristics

Raw surface water from Ping River was directly collected by pumping from the river and analyzed for water characteristic. The physical and chemical characteristics including pH, turbidity, dissolved organic carbon, UV absorbance at 254 nm and THMFP of raw surface water in different season were analyzed in order to investigate the characteristics of Ping River in each season.

3.4.2 Coagulation Experiment

The coagulation experiment was performed by using Jar-test experiment. Poly aluminium chloride (PACl) was used as coagulants. In this experiment, the stock solution of PACl was prepared by diluting from PACl in liquid with concentration of 1,214 g/L. The coagulants dosage was varied at 0, 10, 20, 30, 40 and 50 mg/L. The jar-test experiment was conducted with rapid mixing at 150 rpm for 1 minutes follow by the slow mixing at 30 rpm for 20 minutes. The suspension was left undisturbed for 60 minutes. After settling, the supernatant was collected and filtrated with 0.45 μm GF/C filter paper before analyzed for turbidity, pH, organic matter concentration (DOC and UV-254) and THMFP. The optimal condition for coagulation process in term of coagulants dose was determined. The jar-test apparatus are shown in Figure 3.4.

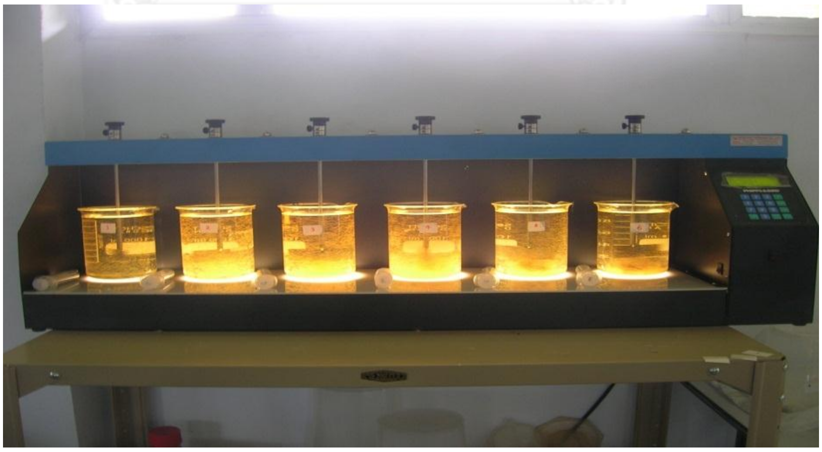


Figure 3.4 Jar test apparatus

3.4.3 The in-line coagulation with ceramic membrane filtration experiment

This experiment was conducted by using the batch ceramic membrane experiment and aims to investigate the efficiency of the in-line coagulation with ceramic membrane filtration process to reduce organic matter in raw surface water. First, raw surface water was mixed with three dosage of PACl (20, 30 and 40 mg/L) which obtained from the results in section 3.4.2 by using Jar-test to perform rapid mixing at 150 rpm for 1 minutes. Then, the coagulated water was poured to pressurized tank immediately. By the controlled pressure at 0.2 MPa, the coagulated water in pressurized tank was allowed to pass 7-meters nylon tube prior flowing to the bottom of the ceramic membrane module and filtrate through 0.1 μm ceramic membrane. The filtrated water was collected and measured for their turbidity, DOC, UV-254 and THMFP.

The diagram of in-line coagulation with ceramic membrane filtration is shown in Figure 3.5. Ceramic membranes was provided by METAWATER Co., Ltd., Japan which the lab-scale ceramic membrane modules with 0.1 μm pore size. The dimension of ceramic membrane module is 3 centimeters in diameter, 10 centimeters height and 55 tubular channels. The filtration surface area was 0.042 m^2.

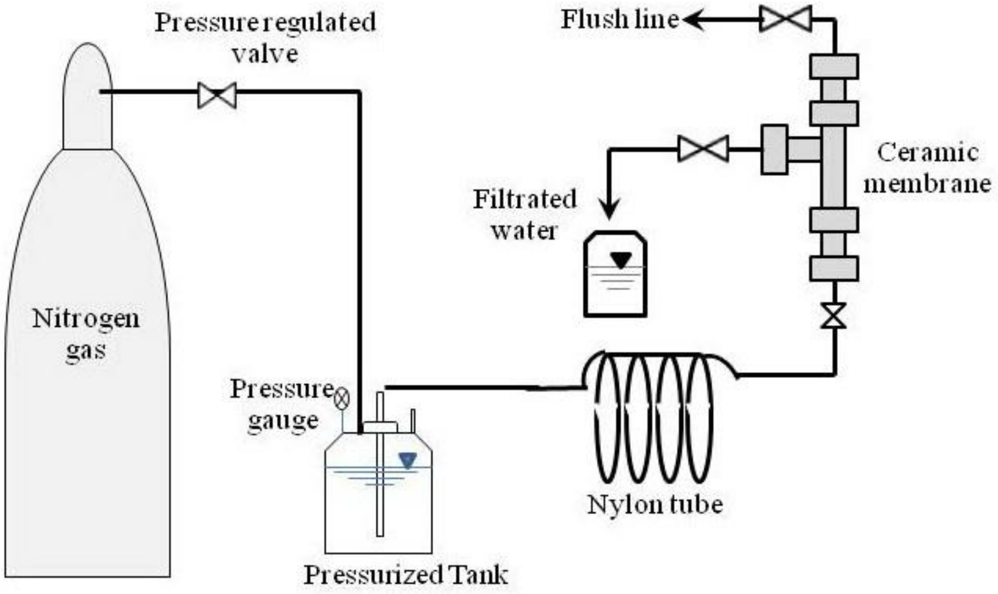


Figure 3.5 The diagram of in-line coagulation with ceramic membrane filtration

3.4.4 Continuous ceramic membrane filtration experiment

The continuous ceramic membrane filtration experiment was conducted by using the membrane module as shown in Figure 3.6. Raw surface water from Ping River water was pumped directly to the membrane module. The coagulants (PACl) and chlorine (NaOCl) were added to the system before filtration. The coagulant was contacted with raw surface water and flow through the system as the in-line coagulation process. The NaOCl was added to the system as pre-chlorination which can acts as chemical cleaning for ceramic membrane and disinfection process for microbial removal. After that raw surface water was filtrated by ceramic membrane. Water quality of raw surface water and filtrated water was analyzed with various parameters including turbidity, DOC concentration, UV-254 absorbance and THMs. Furthermore, the performance of long term ceramic membrane filtration in term of filtration flux was investigated.

Figure 3.6 The unit of ceramic membrane filtration for continuous operation system

3.4.5 Resin fractionation procedure

Resin fractionation method was utilized to characterize DOM of water samples into organic fraction including two fractions (hydrophobic, HPO and hydrophilic, HPI fractions) and six fractions, namely hydrophobic neutral (HPON), hydrophobic base (HPOB), hydrophobic acid (HPOA), hydrophilic neutral (HPIN), hydrophilic base (HPIB) and hydrophilic acid (HPIA) fractions.

3.4.5.1 Six fractions resin fractionation procedures

The bulk DOM can be separate into six DOM fractions (HPON, HPOB, HPOA, HPIN, HPIB and HPIA fractions) based on their physical and chemical properties by using resin fractionation technique with three different types of resins including DAX-8, AG-MP-50 and WA-10 resin. The three resins used in this procedure were prepared as described follows:

1. DAX-8

The DAX-8 resin is nonionic resin with a porosity of 0.6. It was prepared by refine in 0.1 N of NaOH for 24 hrs. and rinse with milli-Q water to remove NaOH. After that it was purify by using a set of Soxhlet extraction apparatus with acetone for 24 h follow by hexane for 24 h as shown in Figure 3.7. After finished the extraction, the resin was rinse by methanol until it free from hexane. The purified resin in slurry methanol was transferred into the column with glass wool packed at the bottom of column as shown in Figure 3.8. The glass wool packed must be purifying by using the set of Soxhlet extraction apparatus before used with the same chemical as resin purification. The packed column was rinsed by using 0.1 N of NaOH and 0.1 N of HCl for 2.5 bed volume (BV) or 250 ml, respectively, followed by Milli-Q water until the DOC or conductivity of the effluent were lower than 0.2 mg/L and 10 μs/cm, respectively.

2. AG-MP-50

The AG-MP-50 is a strong acid cation exchange resins with porosity of 0.3 - 0.5 and the effective surface area was 35 square meters per dry gram. This resin was purified with methanol for 24 h by using a set of Soxhlet extraction apparatus. The purified resin was transferred into the column with glass wool packed. The packed column was rinsed with 1 N of NaOH and 2 N of HCl for 2 BV or 200 ml, respectively followed by Milli-Q water until the DOC and conductivity of the effluent water is less than 0.1 mg/L and 10 μs/cm, respectively.

3. WA-10 (SUPELCO):

The WA-10 is the weak anionic resin. It was purified by soaked in methanol for 24 h. The purified resin was transferred into the column with glass wool packed. The packed column was rinsed by 1 N of HCl for 1 BV (100 ml) and 1 N of NaOH for 2.5 BV (250 ml), respectively. After that it was rinsed by Milli-Q water until DOC and conductivity of the effluent water is less than 0.1 mg/L and 10 μs/cm, respectively

Figure 3.7 Soxhlet extraction apparatus

Figure 3.8 Resin column with glass wool packed

The resin fractionation technique was followed the resin fractionation method which developed by Leenheer (1981) and Marhaba *et al* (2003). The diagram of resin fractionation procedure is illustrated in Figure 3.9 and can be described as follows:

1. First, water samples were filtrated through 0.7 μm GF/F filters and adjusted pH to 7 before fractionation. Water sample was pumped through the first DAX-8 resin column with a flow rate less than 12 BV/h or 0.33 ml/s. After that it was displaced quickly with 1 BV (100 ml) of Milli-Q water. The HPON fraction was adsorbed in DAX-8 resin and eluted from resin by using methanol (CH_3OH). The

rotary evaporator was utilized to extract methanol from the extracted sample. Then, the HPON fraction was obtained.

2. The effluent sample from first DAX-8 resin column in step 1 was adjusted pH to 10 by NaOH. After that it was pumped through the second DAX-8 resin column with the flow rate of less than 12 BV/h (0.33 ml/s). Then, it was displaced quickly with 1 BV (100 ml) of Milli-Q water. The HPOB fraction was retained in resin. The 0.1 N of HCl (0.25 BV or 25 ml) and 0.01 N of HCl (150 ml) were used to elude the HPOB fraction from DAX-8 resin with flow rate of less than 2 BV/h (3.3 ml/min). Then, the HPOB was obtained.

3. The effluent sample from the second DAX-8 resin column in step 2 was acidified to pH 2 and pumped through the last DAX-8 resin column with the flow rate less than 12 BV/h (0.33 ml/s). After that it was displace quickly with 1 BV (100ml) of Milli-Q water. HPOA fraction was adsorbed on DAX-8 resin which can be eluted by using 0.1 N of NaOH (0.25 BV or 25 ml) and 0.01 N of NaOH (1.25 BV or 125 ml) at a flow rate of less than 2 BV/h (3.3 ml/min), respectively. Then, the HPOA fraction was obtained.

4. The effluent sample from the last DAX-8 resin column in step 3 was pumped through the AG-MP-50 resin column with the flow rate of less than 5 BV/h (8.33 ml/min). After that it was displace quickly with 1 BV (100 ml) of Milli-Q water. The HPIB was retained in resin and can be eluted by using 1 N of NaOH (1 BV or 100 ml) at the flow rate of less than 2 BV/h (3.3 ml/min). Then, the HPIB was obtained.

5. The effluent sample from AG-MP-50 resin column in step 4 was pumped through the WA-10 resin column with a flow rate of less than 8 BV/h (13.33 ml/min). Then, it was displace quickly with 1 BV (100 ml) of Milli-Q water. The effluent sample from WA-10 resin column was contained HPIN fraction while HPIA fraction was retained in WA-10 resin. The HPIA fraction can be eluted from resin by using 0.1 N of NaOH (1.5 BV or 150 ml) and 0.01 N of NaOH (1 BV or 100 ml) at a flow rate of less than 4 BV/h (6.67 ml/min).

The fractionated water of all fractions was collected and analyzed for DOC concentration, UV-254 absorbance and THMFP. All fractionated samples were adjusted pH to 7 by using NaOH and H_2SO_4 and filtrated with 0.45 μm GF/C filter paper prior to measurement DOC, UV-254 and THMFP. Figure 3.10 showed the resin fractionation apparatus.

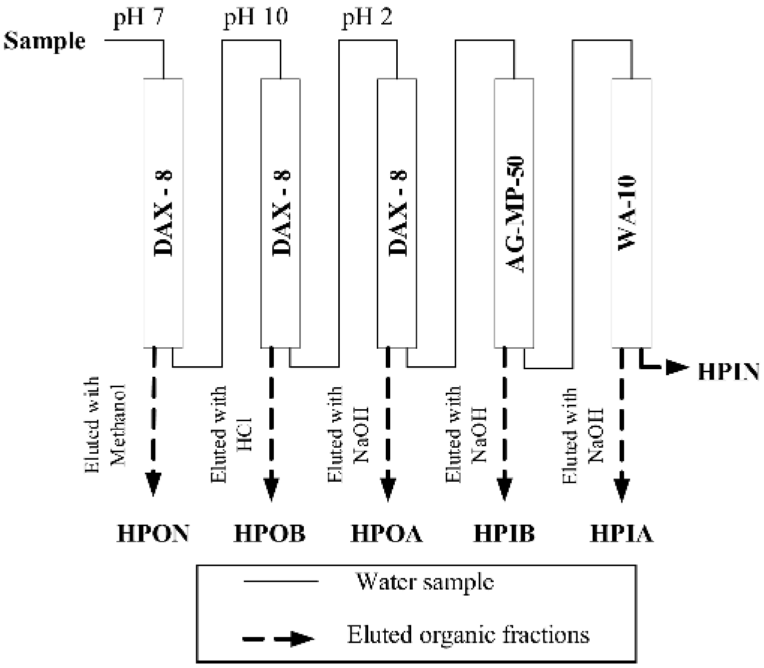


Figure 3.9 Fractionation procedures (Kanokkantapong, 2006)

Figure 3.10 Resin fractionation apparatus

3.4.5.2 Two fractions resin fractionation procedures

Resin adsorption procedure was employed to fractionate three liters of water samples into two organic fractions by using a series of DAX-8 resin

(Leenheer, 1981). The diagram of the resin fractionation procedure is presented in Figure 3.11. First, water samples were acidified to pH 2 and passed through the columns which containing DAX-8 resin with a flow rate of less than 12 BV/h (0.33 ml/s). The effluent water from DAX-8 resin column was contained the HPI fraction. While the HPO fraction was adsorbed on the DAX-8 resin which can be eluted from resin by using 0.1 N of NaOH (5 BV or 50 ml) and 0.01 N of NaOH (25 BV or 250 ml), respectively with flow rate of less than 2 BV/h (3.3 ml/min). Fractionated samples of each fraction were adjusted pH to 7 and filtrated with 0.45 μm GF/C filter paper before analyzed for their organic fractions in term of UV-254, DOC and THMFP.

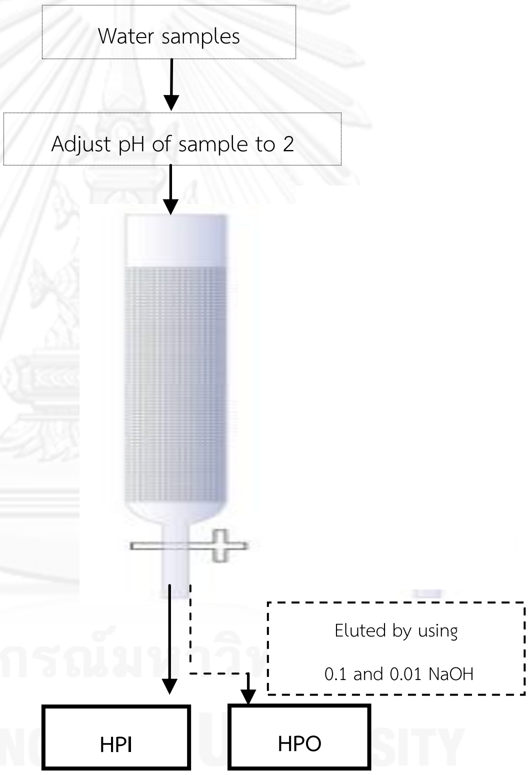


Figure 3.11 Diagram of resin fractionation method

3.4.6 GC/MS pyrolysis analysis

The pyrolysis fragment and chemical classes of DOM of water samples were identified by using the pyrolysis GC/MS technique. First, water samples were poured into special grass bottles, as shown in Figure 3.12, which were resistant to the Freeze-Drying unit. After that it was placed in a pre-freeze unit at temperature (-20) ˚C for more than 12 hr. Then, it was placed in a freeze-drying unit which operate at temperature (-57) °C and pressure 0.004 bar for 24 hr. (Figure 3.13). After finished the freeze-drying process, the uniform fine powder of samples were obtained as shown in Figure 3.14 and can be used to determine the chemical classes of DOM in water samples by using pyrolysis GC/MS technique.

Figure 3.12 Special grass bottles for pyrolysis GC/MS sample preparation

Figure 3.13 Freeze-drying unit

Figure 3.14 The uniform powder of water samples

For the procedure of chemical classes analysis by using pyrolysis GC/MS technique, a few milligrams of uniform powder of water sample was placed in platinum buckets and attached to a sample holder of the pyrolyzer of GC/MS (As shown in Figure 3.15). When the analysis started, sample was pyrolysed at temperature 700 °C for 10 s. After that it was transferred to GC/MS process from the injection port of a Shimadzu GC/MS QP-5050 which attached to pyrolyzer. The operating time of GC/MS process was around 86.0 minutes for one sample. The results of GC/MS were provided the pyrochromatograms of sample as shown in Figure 3.16.

Figure 3.15 Platinum buckets and sample holder of the pyrolyzer of GC/MS

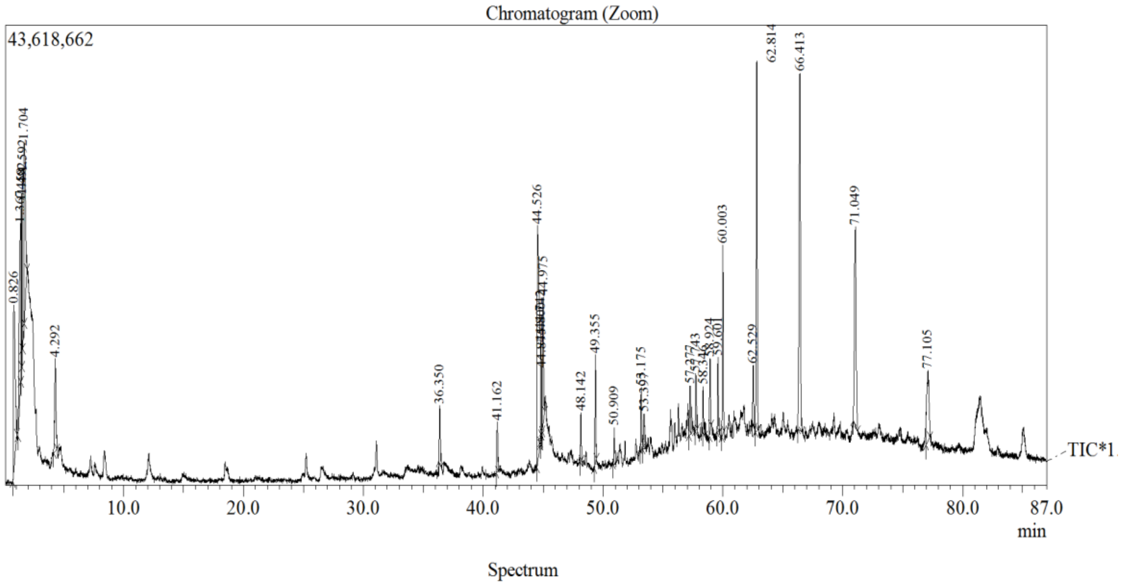


Figure 3.16 The pyrochromatograms of sample obtained from GC/MS pyrolysis

The operating condition for pyrolyzer, GC and MS are shown as follows:

1. Pyrolysis Conditions

- Pressure: 150 psi

- Spilt flow: 8 cm/s

- Intermediate temp: 220 ˚C

- Initial temperature: 220 ˚C

- Final temperature: 700 ˚C, final time 10 second

- Gas type: Helium

2. GC Conditions

- Initial temp: 40 ˚C

- Ramp#1: Rate 2.0 ˚C/min, final temperature 80 ˚C

- Ramp#2: Rate 3.0 ˚C/min, final temperature 140 ˚C

- Ramp#3: Rate 5.0 ˚C/min, final temperature 220 ˚C, final time 30 min

- Run time: 86.0 min

3. MS Condition

- Acquisition mode: Scan

- Interface Temp: 220 ˚C

- Solvent cut time: 0.1 min

- Detector voltage: Relative to turning results

- Start time: 0.1 min

- End time: 86.0 min

- Start (m/z): 40

- End (m/z): 650

- Scan speed: 2000

3.5 Analytical method

3.5.1 Turbidity

The HACH Turbidity meter Model 2100 was used to measure the turbidity of water samples.

3.5.2 pH

pH of water samples was directly measured by using a Model F-21 Horibra pH-meter with an accuracy of ± 0.01 pH unit. The pH-meter was daily calibrated with buffer solutions at pH 4.00, 7.00 and 9.00.

3.5.3 DOM surrogate parameter

3.5.3.1 DOC

DOC of water samples were measured in accordance with Standard Method 5310 Total Organic Carbon (TOC); section 5310 C Persulfate-Ultraviolet Oxidation Method by using O.I. analytical 1010 TOC Analyzer. The samples were filtered through a 0.45 μm filter prior to measurement. Milli-Q water (ELGA) was used on every sample for clean system and blank sample preparation. The analysis of DOC was conducted with two replications for each sample.

3.5.3.2 UV-254

UV-254 was analyzed in accordance with Standard Method 5910B Ultraviolet Absorption Method. The samples were filtered through a 0.45 μm filter prior to measurement. UV-254 of water samples was analyzed by using Perkin-Elmer Model Lambda 25, UV/VIS spectrophotometer: a Jasco V-350 spectrophotometer at 253.7 nm with matched quartz cells that provided a path length of 10 mm. The UV-254 analysis was performed with two replication for each sample.

3.5.3.3 Specific ultraviolet absorption (SUVA)

SUVA of water samples was calculated from the ratio of UV absorbance at 254 nm to DOC value in mg/L.

3.5.3.4 THMs and THMFP

THMFP measurements were conducted according to Standard Method 5710B. The phosphate solution was used as buffer solution before incubation at 25 ± 2 °C in amber bottles with PTFE liners. At the end of 7-day reaction period, the remaining free chlorine in water samples should between 3 to 5 mg/L. The residual chlorine was measured according to the Standard Method 4500-Cl G. The chlorine concentration was represented by the light absorbance at 515 nm using a spectrophotometer with matched quartz cells that provided a path length 10 mm. THMs were extracted with pentane in accordance with Standard Method 6232B. Agilent Gas Chromatography-6890 with an electron capture detector (ECD) was utilized for measure THMs in water samples under the operating conditions as shown in Table 3.1.

THMFP analysis was conducted with two replication for each sample and Milli-Q water was used for dilutions, chemical preparation and final glassware cleaning. All of analytical methods were summary and illustrated in Table 3.2.

Table 3.1 The operating condition for THMs measurement by using Gas Chromatography

Model	HP 6890 GC
Inlet conditions	Mode: Split Initial temp: 225 ˚C Pressure: 31.14 psi Split ratio: 10.1 and Split flow: 96.4 ml/min Total flow 108.7 ml/min Gas type: Helium
Column	HP-5 5% phenyl Methyl Siloxane Length: 30 m and Diameter: 320 µm Film thickness: 0.25 µm Mode: constant flow Initial flow: 9.6 ml/min Initial pressure: 31.15 psi
Detector	ECD : Temperature: 320 ℃ Mode: Constant make up flow Make up flow: 60.0 ml/min Make up Gas type: Nitrogen
Injection temperature	225 ˚C
Initial temperature	60 ˚C initial time 1.00 min
Temperature program	10 ˚C/min to 100 ˚C for 1 minute 10 ˚C/min to 130 ˚C for 1 minute 10 ˚C/min to 180 ˚C for 1 minute
Final time duration	16 minutes

Table 3.2 Analytical methods and instrument

Parameter	Analytical method	Standard	Analytical Instrument
Turbidity	Direct measurement	-	HACH, 2100 Turbidity Meter
pH	Direct measurement	-	pH Meter, Model F-21, Horibra
DOC	Wet Oxidation Method	Standard method 5310C*	O.I. analytical 1010 TOC Analyzer
UV-254	Ultraviolet Absorption Method	Standard method 5910B*	UV/VIS Spectrophotometer, Model Lambda 25
Free chlorine residual	Colorimetric Method	Standard method 4500Cl G*	Spectrophotometer 6400, Jenway
THMs and THMFP	Formation of Trihalomethane and Other Disinfection By-Products and Liquid-Liquid Extraction Gas Chromatography Method	Standard method 5710 and 6232B*	Agilent 6890 Series Gas Chromatography with ECD detector
Pyrolysis GC/MS analysis	-	-	Shimadzu GC/MS QP-5050

CHAPTER IV

REDUCTION OF DISSOLVED ORGANIC MATTER AND THMFP BY IN-LINE COAGULATION WITH CERAMIC MEMBRANE AND CONVENTIONAL COAGULATION

4.1 Introduction and Objective

Dissolved organic matter (DOM) is a complex mixture which varies in size, functional groups and reactivity (Yee *et al*., 2009). DOM commonly presented in natural water including groundwater, surface water and reservoir which the main water source for water supply in Thailand. DOM was affected the water treatment by required higher coagulants dose and fouling in membrane filtration. Furthermore, the presence of DOM in raw water source can be reacts with chlorine during chlorination of water supply production to form halogenated disinfection by-products (DBPs) such as trihalomethane (THMs) which classified as potential carcinogenic substances, persistent and mobile, and pose a cancer risk to humans. Marhaba and Washington (1998) reported that dissolved organic matter (DOM) contains precursors for disinfection by-product formation during water treatment disinfection operation. The formation of DBPs depends on the quantity and characteristics of DOM. Normally, the quantity of DOM is characterized by surrogate parameters including dissolved organic carbon (DOC), ultraviolet absorbance at wavelength of 254 nm (UV-254), specific ultraviolet absorption (SUVA) and trihalomethane formation potential (THMFP) (USEPA, 1999).

In Thailand, conventional coagulation was commonly employed to reduce DOM from raw water source in water supply process. It is used for produce potable water for a long time and the operator are well understood for design, operation and maintenance. However, it required the larger area for instruction and it is ineffective to remove higher concentration of DOM. Thus, DOM in coagulated water can be react with chlorine during chlorination process to form THMs. Abeynayaka *et al*. (2012) reported that the removal efficiency of DOM from a high DOM water source by conventional coagulation was lower than 30%.

With the limitation of coagulation to produce potable water to meet the stricter standard or increasing of attention of consumer, the new advance technology such as filtration is interested. Nowadays, ceramic membranes application systems for DOM removal in water supply or water treatment are still being developed to replace or enhance conventional treatment processes. It have gained the popularity because they can offer several advantages over their organic counterparts, such as the better mechanical strength, resistance to the acidity, superior thermal and chemical stability, narrow pore size distribution, and little pollution to the environment (Yingchao *et al*., 2006)(Rishi Sondhi, 2003 #43;Abeynayaka, 2012 #67) (Rishi Sondhi et al., 2003) (Rishi Sondhi, Ramesh Bhave et al. 2003).

Ceramic membrane filtration alone cannot remove DOM effectively because the reduction mechanism of ceramic membrane based on the pore size. DOM which particles size lower than pore size of ceramic membrane filtration are passed the filtration process and presented in filtrated water. So, the addition of pretreatment such as coagulation process is necessary to improve the performance of ceramic membrane filtration. The addition of a coagulant as a pretreatment prior to membrane filtration has been proposed for the purpose of not only improving the removal of DOMs but reducing the rate of membrane fouling (Wiesner *et al*., 1989; Jacangelo *et al*., 1995). In-line coagulation is the application of coagulation process which applied to small membrane systems. It is referred to the use of coagulation before membrane filtration without a sedimentation step. Korbutowicz (2006) stated that application of in-line coagulation/ultrafiltration process with the use of alum or polyaluminum chloride resulted in improved the removal of NOM from treated water and reduced membrane fouling.

Ping River is the main river in Chiang Mai province. It is currently the main water source utilized to produce water supply for Chiang Mai City. The turbidity and DOM were relatively high especially in rainy season. The presence of DOM in Ping River was provided the problematic of THMs when its react with chlorine during chlorination process in water supply system. The villagers that utilize this water source without appropriate treatment technology are risk to the health problems.

Thus, this chapter was aimed at investigating the reduction of DOM from Ping River water by using in-line coagulation with ceramic membrane filtration. The reduction efficiency of DOM by in-line coagulation with ceramic membrane filtration and conventional coagulation was compared.

4.2 Material and Methods

Raw surface water was collected from Ping River at the sampling station in the upstream of Ping Rive which 10 kilometers far from Chiang Mai municipal area. Raw surface water was collected three times in December 2011, April 2012 and August 2012 for represented the characteristics of DOM in winter, summer and rainy season. Water samples were measured for pH, turbidity, temperature and suspended solids. For the measurement of DOM surrogate parameters (DOC concentration and UV-254), water samples were filtrated through GF/C Whatman 0.45 μm before analyzed. While, the THMFP test was conducted for 7 days periods and the remaining free chlorine residual should be 3-5 mg/L at end of periods.

Raw surface water was divided into two portions. A first portion was used to perform the conventional coagulation by Jar-Test apparatus. A second portion was used to conduct the in-line coagulation with ceramic membrane filtration. The pore size of ceramic membrane was 0.1 μm. The conditions of Jar-Test apparatus and in-line coagulation with ceramic membrane filtration are shown in Table 4.1. The coagulants dosage for in-line coagulation with ceramic membrane filtration was selected based on the results of optimal dosage which obtained from the Jar-test apparatus. Coagulated water and filtrated water were collected and measured for their DOC, UV-254 and THMFP. Detailed of the experiment procedure of conventional coagulation and in-line coagulation with ceramic membrane experiment and analytical method for DOC, UV-254 and THMFP are presented in Chapter III.

Table 4.1 The experimental conditions

Experiment	Coagulant	Coagulant Dosage (mg/L)
Conventional coagulation	PACl	0, 10, 20, 30, 40 and 50 mg/L
In-line coagulation with ceramic membrane filtration	PACl	0, 20, 30 and 40 mg/L

4.3 Results and discussions

4.3.1 Characteristics of raw surface water

Water quality and DOM surrogate parameter of raw surface water from Ping River in rainy, winter and summer season are shown in Table 4.2. The pH values of raw surface water of all season were close to neutral (7.6 - 7.8). The turbidity of raw surface water was varied due to seasonal changes. In rainy season, turbidity was high at 291.0 NTU and decrease to 57.1 and 94.0 NTU in winter and summer, respectively. From the results of turbidity, it can be indicated that this water source cannot utilize directly for potable water. The standard of turbidity of water supply was set at 5 NTU by Provincial Waterworks Authority, Thailand (PWA, 2013). Therefore, this water source is necessary to treat by appropriate process for turbidity reduction prior use this water as potable water.

Table 4.2 Raw surface water characteristics of Ping River in winter, summer and rainy season

Parameters	Rainy (August 2012)	Winter (December 2011)	Summer (April 2012)
Turbidity (NTU)	291	57.1	94
pH	7.6	7.7	7.8
DOC (mg/L)	2.3	2.0	2.2
UV 254 (cm^{-1})	0.076	0.086	0.066
SUVA (L/mg-m)	3.3	4.4	3.0
THMFP (μg/L)	330	258	302

The values of DOC, UV-254, SUVA and THMFP of raw surface water in rainy season were 2.3 mg/L, 0.076 cm^{-1}, 3.3 L/mg-m and 330 μg/L, respectively. Whereas those of winter season were 2.0 mg/L, 0.086 cm^{-1}, 4.4 L/mg-m and 258 μg/L, respectively, and those of summer season were 2.2 mg/L, 0.066 cm^{-1}, 3.0 L/mg-m and 302 μg/L, respectively. The value of DOC in water is used to indicate the aromatic and aliphatic hydrocarbons in water. DOC concentration in raw surface water was not significantly different in all season. It was found in the range of 2.0 -

2.3 mg/L in all season. The highest DOC concentration was found at 2.3 mg/L in rainy season. However, Hata *et al.*, 2009 found that the DOC concentration of Ping River were high at 5.7 mg/L in rainy season. The different of DOC values of Ping River was depended on the seasonal change, collection times and also the rainfall in each year.

Northern meteorological department (2014) reported that rainfall amount of Chiang Mai province during the samples collection in December 2011, April 2012 and August 2012 were 0.6 mm, 75.9 mm and 185.1 mm. The heavy rain in August 2012 may leach the DOM from ground or non-point source to the Ping River which resulted in the highest DOM concentration in this month.

SUVA values is calculated from the ratio of UV-254 absorbance and DOC values and used to indicate the presence of humic in water. The results showed that the SUVA value of raw surface water was relatively high in the range of 3.0 - 4.4 L/mg-m which indicated that DOM of raw surface water was contained more humic. USEPA (1999) stated that the water that SUVA value lower than 3 L/mg-m was contain more non-humic. While the water that SUVA value around 4-5 L/mg-m was contain more humic. In addition, the higher value of SUVA was indicated that DOM in this water source was easily removed by coagulation process. Water that contains SUVA value higher than 3 mg/L is possibility to remove organic carbon with the coagulation method (USEPA, 1999). From the results, it can be indicating that this water source was containing more humic or aromatic and possible to reduce by coagulation process. This results was related to the various investigation of many researchers which indicated that DOM in surface water is mainly composed of humic substances in the range of 50%-65% (Leenheer and Croue, 2003; Marhaba and Van, 2000 and Leenheer *et al*., 2001).

The results of THMFP showed that THMFP values of raw surface water were higher than 250 μg/L in all season. Thus, this water source must be treated by effectively method for reduction of organic matter (THMs precursors) prior to utilize as raw water supply or contact with chlorine. The THMFP values obtained in these results was compared with other raw water source in Thailand (Table 4.3).

Trihalomethane (THMs) are classified as potentially carcinogenic substances which U.S. Environmental Protection Agency (USEPA) proposed the drinking water standard under the Disinfection By-Products (DBPs) Rule with a THMs Maximum Contaminant Level (MCL) of 80 μg/L for stage 1 and 40 μg/L for stage 2. As known that THMs in water are found in many forms including Chloroform ($CHCl_3$), Dichloromethane ($CHCl_2Br$), Dibromochlrinemethane ($CHClBr_2$) and Bromoform ($CHBr_3$). Thus, the World Health has set the guideline values for $CHCl_3$ at 300 μg/L, $CHCl_2Br$ at 60 μg/L, $CHClBr_2$ and $CHBr_3$ at 100 μg/L (WHO, 2006).

Table 4.3 THMFP and THMs species in raw surface water of this study and other water sources in Thailand

Water source	Sampling Times	THMFP (μg/L)	CHCL3-FP (μg/L)	CHBrCl2-FP (μg/L)	CHBr2Cl-FP (μg/L)	CHBr3-FP (μg/L)
The Chao Phraya River, Bangkok, Thailand (Panyapinyopol et al., 2005)	August, 2003	313	262 (84%)*	43.8 (14%)	6.9 (2%)	ND
Mae-Sa River, Chiang Mai, Thailand (Homklin, 2004)	February, 2005	113	94 (83%)	11.7 (10%)	7.0 (7%)	ND
Mae-Hae Reservoir, Chiang Mai, Thailand (Pumpaisanchai, 2005)	November, 2004	482	462 (95%)	20 (5%)	ND	ND
The Ping River, Chiang Mai, Thailand (Chaimongkol, 2008)	November, 2008	239	223 (93%)	14 (6%)	2 (0.8%)	ND
The Ping River, Chiang Mai, Thailand of this study in winter season	December, 2011	258	233 (90%)	22 (8%)	2 (0.8%)	ND
The Ping River, Chiang Mai, Thailand of this study in summer season	April, 2012	302	282 (93%)	18 (6%)	2 (0.7%)	ND
The Ping River, Chiang Mai, Thailand of this study in rainy season	August,2012	330	301 (91%)	26 (8%)	2 (0.6%)	ND

Remark: ( )* = percent distribution and ND = Not detected

From the results of raw surface water, three forms of THMs ($CHCl_3$, $CHCl_2Br$ and $CHClBr_2$) were found in this water source. The results showed that the values of THMFP in rainy season were 301 μg/L, 26 μg/L and 2 μg/L for $CHCl_3$, $CHCl_2Br$ and $CHClBr_2$, respectively. Whereas, those values in winter and summer were 233 μg/L, 22 μg/L, 2 μg/L and 282 μg/L, 18 μg/L, 2 μg/L for $CHCl_3$, $CHCl_2Br$ and $CHClBr_2$, respectively. In addition, the results indicating that chloroform ($CHCl_3$) was the major THM species in this water source. These results was well corresponded with the results of Chaimongkol, 2008 which reported that chloroform was the dominant THM species in Ping River water at 93%. The chloroform was found to be the major THMFP species in natural water source with 73% - 83% (Inthanuchit, 2009; Teksoy *et al*., 2008 and Srimuang, 2011). When compared the results of chloroform in this study with the WHO standard of THMs, it was found that chloroform in rainy season was higher than standard. Thus, this water source might be risk to villagers that utilized this water directly.

The THMs species in water source of Thailand that illustrated in Table 4.3 showed that the dominant THMs species in river water and reservoir were chloroform which found in higher percent (83% - 93% in river water and 92% - 97% in reservoir) than other THMs species. Dichloromethane were found in the range of 6% - 14% in river water and 3% - 8% in reservoir. While Dibromochlrinemethane were found at lower than 10% in water source. The results indicated that the THMs species of Ping river water was related to those of other water source. However, the concentration of each THMs species was different based on the various conditions such as seasonal changes and geological.

4.3.2 Reduction of DOM by conventional coagulation

The reduction of DOM was investigated by considered the reduction of DOM surrogate parameters including DOC, UV-254 and THMFP. The reduction of DOC, UV-254 and THMFP by conventional coagulation was investigated and discussed separately in the following sections.

4.3.2.1 Reduction of DOC and UV-254

The results of DOC and UV-254 reduction by conventional coagulation in rainy season are shown in Figure 4.1. The results from Figure 4.1 (a) showed that the DOC concentration was reduced from 2.3 mg/L in raw surface water to 2.2, 1.9, 1.6, 1.4 and 1.3 mg/L at PACl dosage 10, 20, 30, 40 and 50 mg/L, respectively. Percent DOC reduction were 3.0%, 16.4%, 31.3%, 41.1% and 43.7% at PACl dosage

10, 20, 30, 40 and 50 mg/L, respectively. From the results, it can be indicated that percent DOC reduction was increased with PACl dosage increasing. While, the results of UV-254 reduction in Figure 4.1 (b) showed that the conventional coagulation can reduce UV-254 from 0.076 cm^{-1} in raw surface water to 0.074, 0.059, 0.030, 0.025 and 0.022 cm^{-1}. Percent UV-254 reduction was 2.2%, 22.5%, 60.3%, 66.6% and 70.7% at PACl dosage 10, 20, 30, 40 and 50 mg/L, respectively.

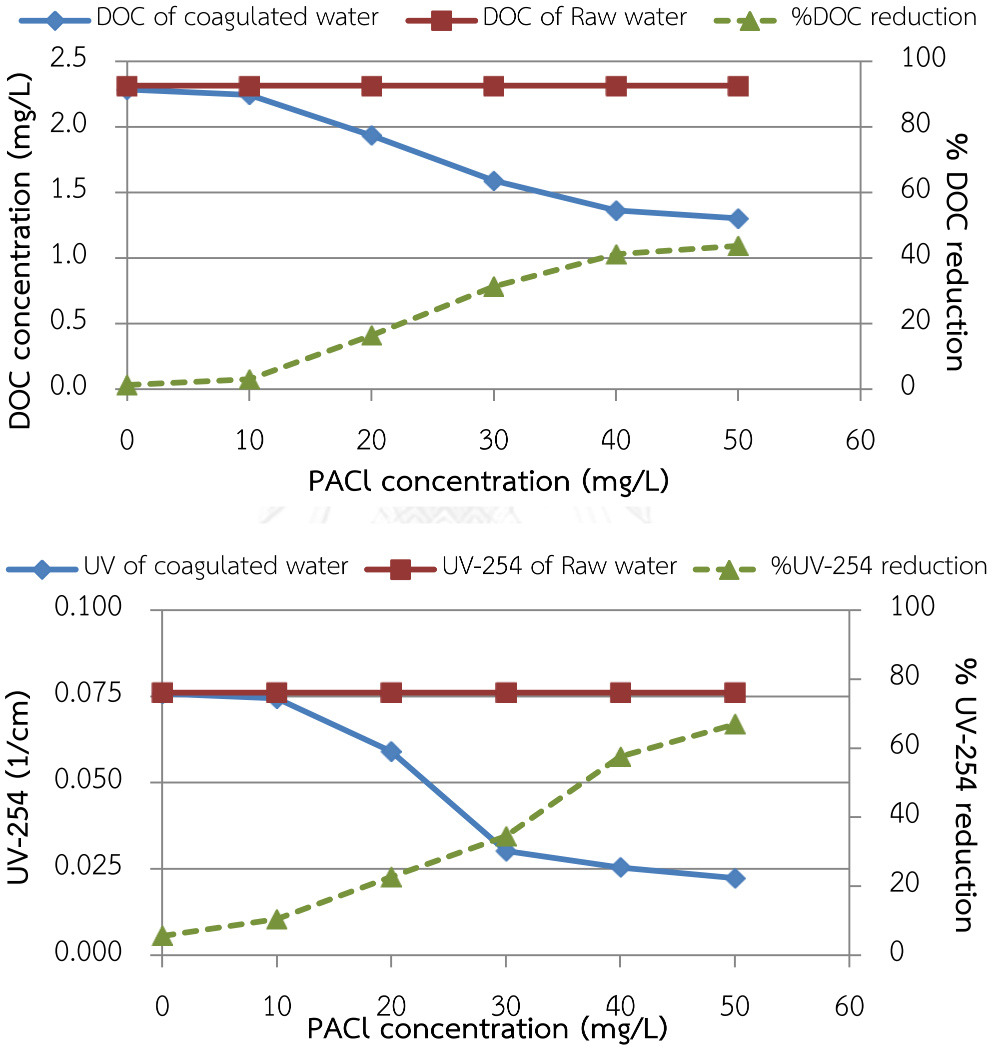


Figure 4.1 Reduction of DOC and UV-254 and their percent reduction by conventional coagulation in rainy season

The reductions of DOC and UV-254 by conventional coagulation in winter and summer season are shown in Figure 4.2 and 4.3, respectively. In winter season, the conventional coagulation can reduce DOC concentration from 2.0 mg/L in raw surface water to 1.8, 1.7, 1.5, 1.3 and 1.3 mg/L at PACl dosage 10, 20, 30, 40 and 50 mg/L, respectively. Whereas those of summer, DOC concentration was reduced from 2.2 mg/L to 2.0, 1.8, 1.7, 1.5 and 1.4 mg/L at PACl dosage 10, 20, 30, 40 and 50 mg/L, respectively. The highest percent DOC reduction was 32.3% and 33.9% at PACl dosage 50 mg/L for winter and summer season, respectively.

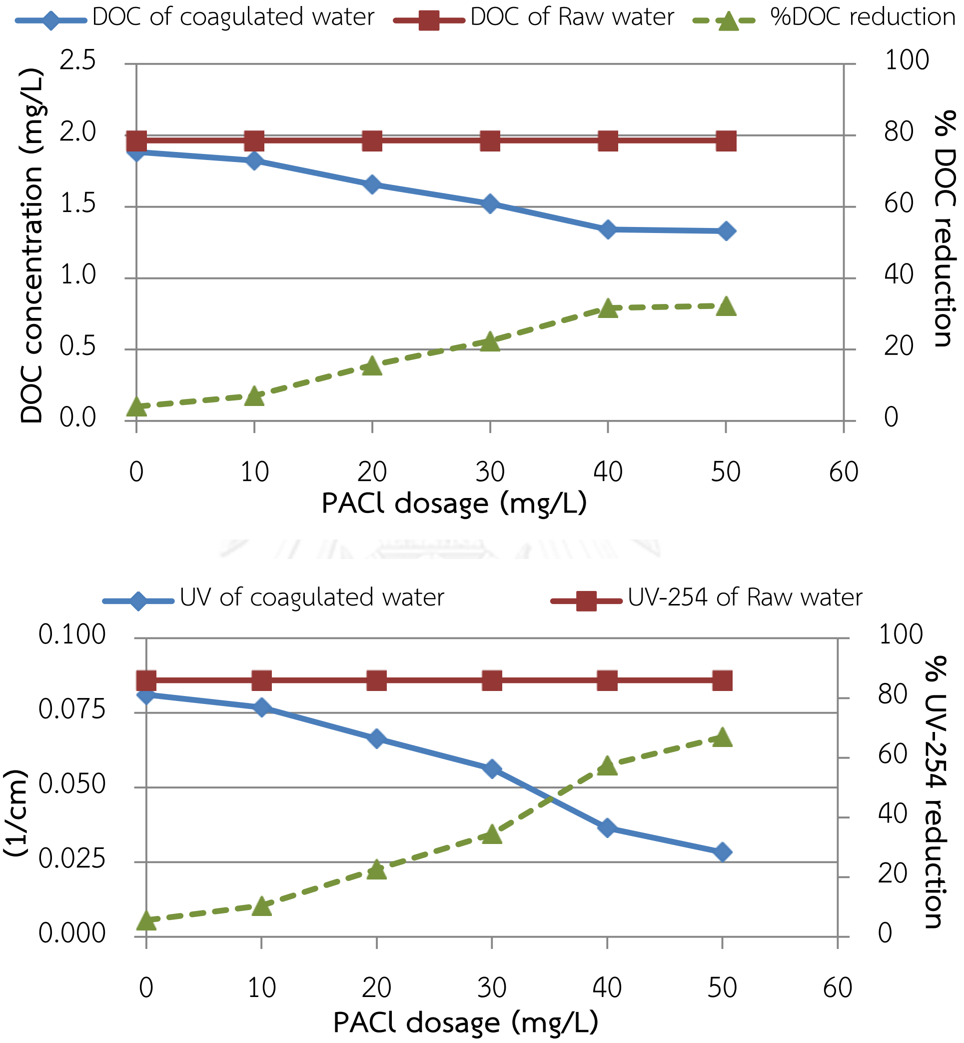


Figure 4.2 Reduction of DOC and UV-254 and their percent reduction by conventional coagulation in winter season

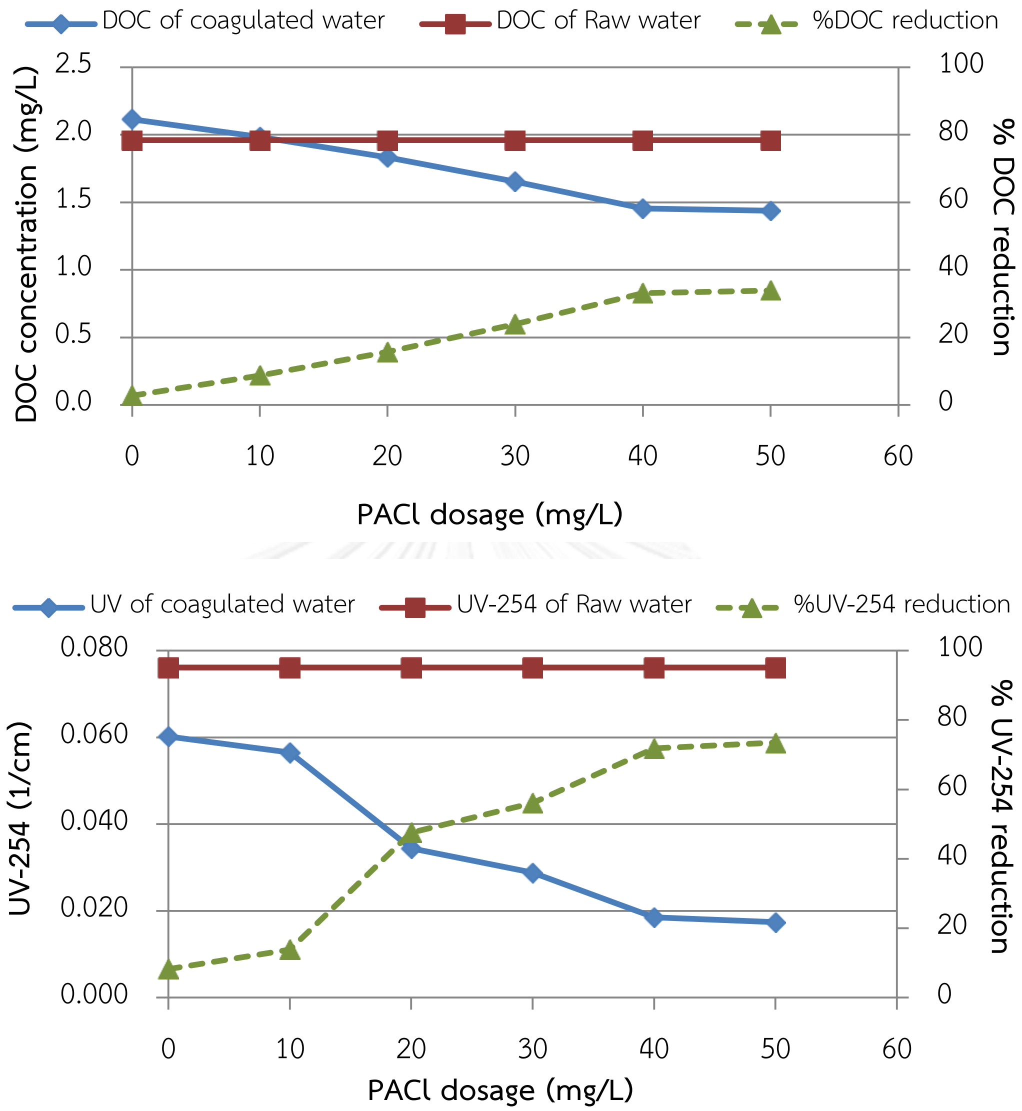


Figure 4.3 Reduction of DOC and UV-254 and their percent reduction by conventional coagulation in summer season

In case of UV-254 reduction, conventional coagulation can reduce UV-254 from 0.086 cm^{-1} of raw surface water in winter season to 0.077, 0.066, 0.056, 0.037 and 0.028 cm^{-1} at PACl dosage 10, 20, 30, 40 and 50 mg/L, respectively. While those of summer, UV-254 was reduced from 0.066 cm^{-1} of raw surface water in summer season to 0.057, 0.034, 0.029, 0.019 and 0.017 cm^{-1} at PACl dosage 10, 20, 30, 40 and 50 mg/L, respectively. The highest percent UV-254 reduction were found at 66.9% and 73.5% at PACl dosage 50 mg/L in winter and summer season, respectively.

The results in Figure 4.1, 4.2 and 4.3 showed that the percent DOC and UV-254 reduction was increased with the increment of PACl dosage. The optimal PACl dosage was selected at 40 mg/L for water in all season because the increment of PACl dosage from 40 mg/L to 50 mg/L was resulted in slight increase of DOC and UV-254 reduction. This results was well corresponded with the results Iriarte-Velasco *et al*. (2007) which reported that the addition of PACl coagulant higher than 40 mg/L does not result in any significant improvement in water quality. The results indicated that the using of PACl in coagulation process at dosage 40 mg/L can provided the percent DOC and UV-254 reduction in the range of 31.7% - 41.1% and 57.5% - 71.8%, respectively. These observation were well corresponded to the results of Musikavong *et al*. (2013) which reported that the PACl coagulation at the optimal condition (dosage 40 mg/L and pH 7) can reduce DOC concentration and UV-254 from U-Tapao canal, Songkla, Thailand about 55% and 52%, respectively. In addition, Alvarez-Uriarte *et al*. (2010) reported that the PACl coagulation at 40 mg/L can reduced DOC and UV-254 with percent reduction 30.9% and 59.7%, respectively and Thongnak (2010) which found that PACl coagulation at pH 7 can reduce DOC and UV-254 from river water with percent reduction 34.8% and 44.9%, respectively. From the review of literature, the coagulation with PACl was found to have the highest percent DOM reduction when compared to the using of other coagulants such as alum and $FeCl_3$. Iriarte-Velasco *et al*. (2007) stated that the coagulation with PACl provided the better efficiency for precursors removal than alum.

The absorbance of UV-254 was used to indicate the presence of aromatic hydrocarbon in water. The obtained results showed that the reduction of UV-254 was higher than DOC reduction at the same PACl dosage of coagulation. This can be indicated that PACl coagulation has potential to reduce more aromatic hydrocarbon from water. The results was related to the results of Li *et al*. (2011); Iriarte-Velasco *et al*. (2007); Guigui *et al*. (2002) and Bian *et al*. (2000) which reported that coagulation is more efficient to remove UV-254 than DOC. In addition, AWWA (1993) found that PACl coagulation reduced aromatic hydrocarbon 50% of water samples from various river, lake and groundwater in USA.

SUVA values are the ratio between UV absorbance at wavelength 254 nm and dissolved organic carbon (DOC) concentration of a given sample. The results of SUVA values in coagulated water at various coagulants concentration are shown in Figure 4.4.

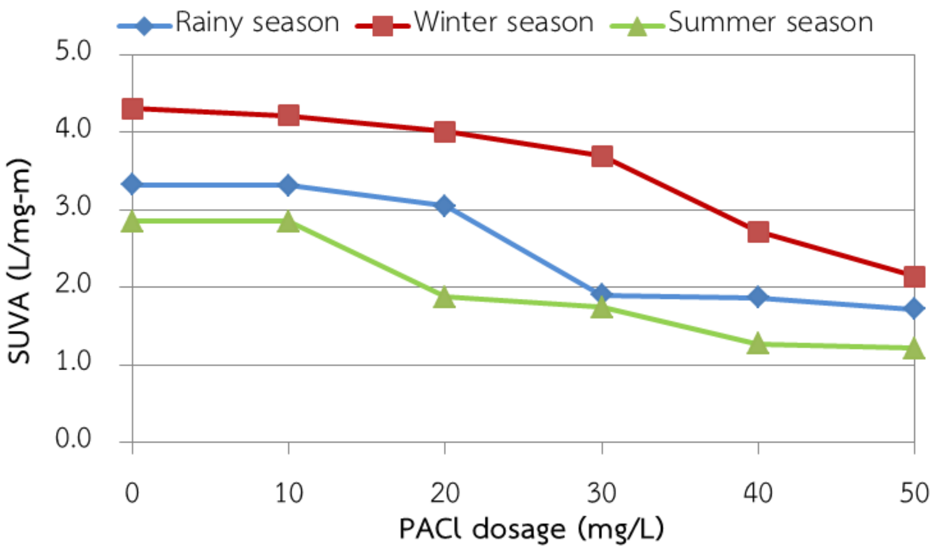


Figure 4.4 SUVA values of coagulated water at various concentration of PACl

The results of SUVA values of rainy season showed that the increment of PACl dosage from 10 to 30 mg/L resulted in higher decreasing of SUVA values. However, when adding more concentration of PACl, the SUVA values were nearly constant. Based on the results, it can be indicated that the using of PACl dosage between 10-30 mg/L can reduce DOM mostly in term of humic acids but the increasing of PACl dosage to 40 and 50 mg/L can reduced DOM mostly in term of fulvic acids. These results are related to the studied of Musikavong *et al*. (2005) which reported that the increment of coagulants can remove only fulvic acids based on the constant of SUVA values in coagulated water. For the summer season, the results of SUVA values were similar to those results in rainy season. The higher decreasing of SUVA value was found when using PACl dosage from 10 to 30 mg/L and nearly constant at PACl dosage 40 to 50 mg/L. As for winter season, the results of SUVA values were seem different. The SUVA values were gradually decreased from PACl dosage 10 mg/L to 50 mg/L because the percentage of UV-254 reduction was higher than that of DOC. The obtained result was contradicted with the studied of Musikavong *et al*. (2013) which found that the SUVA after PACl coagulation was slightly increased.

4.3.2.2 Reduction of THMFP

The reduction of THMFP by conventional coagulation in rainy, winter and summer season are shown in Figure 4.5, 4.6 and 4.7, respectively. In rainy season, conventional coagulation can reduce THMFP from 330 μg/L in raw surface water to 265, 231, 211, 189 and 176 μg/L at PACl dosage 10, 20, 30, 40 and 50 mg/L, respectively. The highest THMFP reduction (47%) was found at the highest PACl dosage (50 mg/L). This result was related to the results of DOC reduction which the highest percent reduction (44%) was obtained at the same PACl dosage.

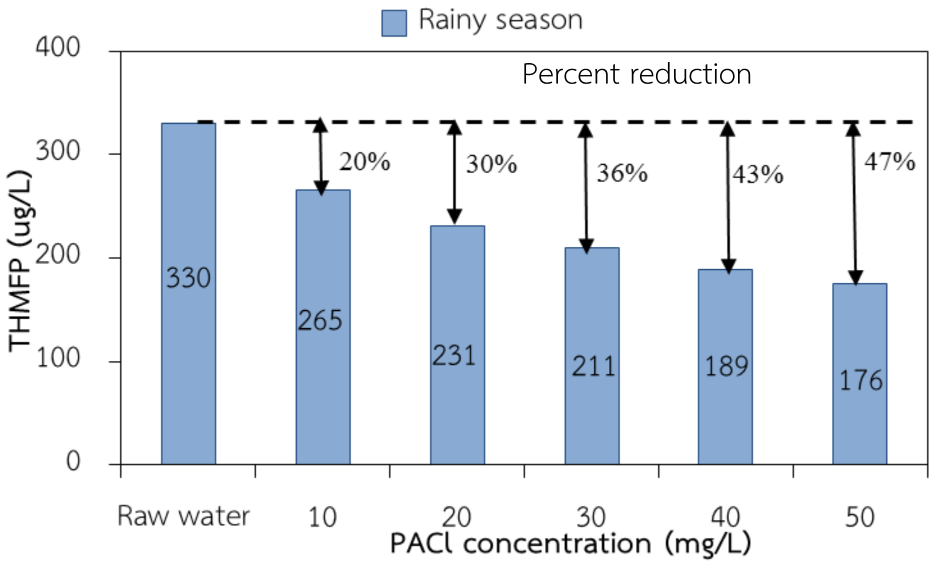


Figure 4.5 Reduction of THMFP by conventional coagulation in rainy season

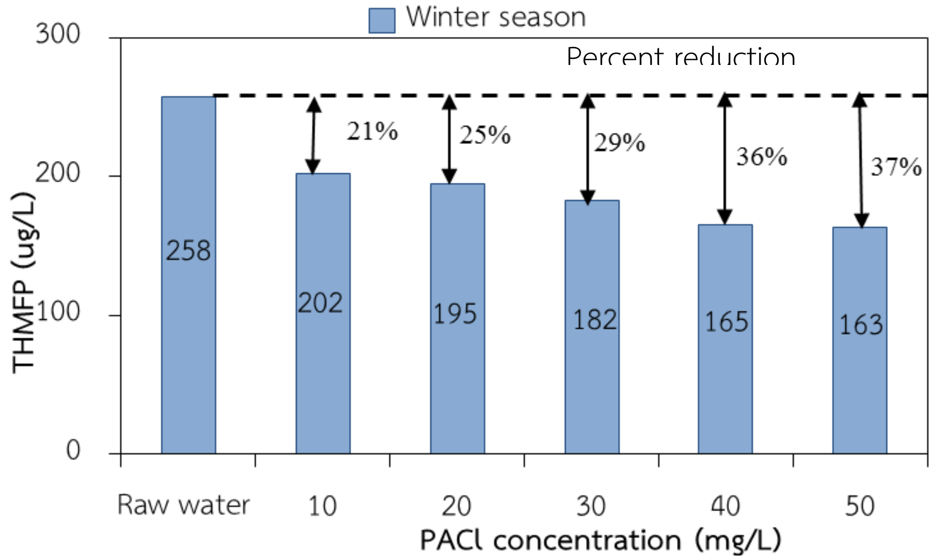


Figure 4.6 Reduction of THMFP by conventional coagulation in winter season

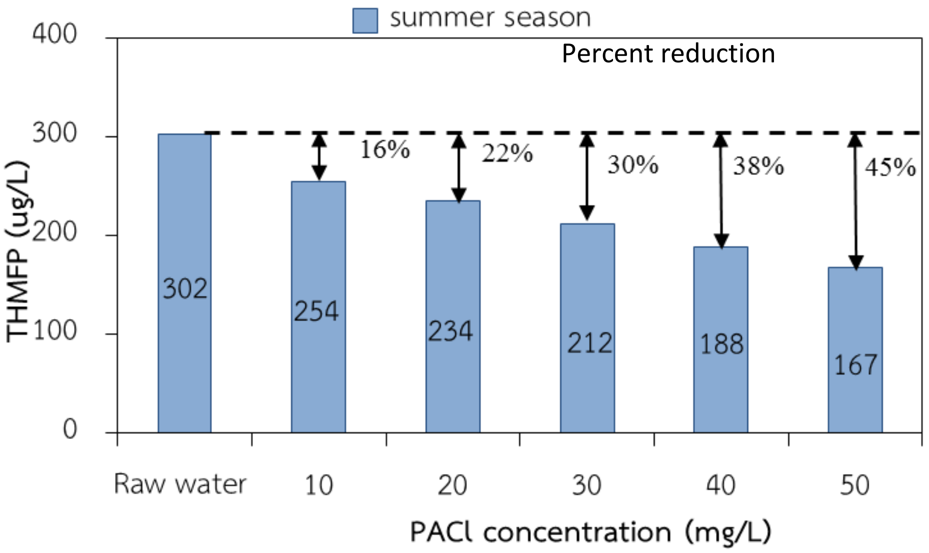


Figure 4.7 Reduction of THMFP by conventional coagulation in summer season

In winter season, the THMFP in raw surface water at 258 μg/L was reduced to 202, 195, 182, 165 and 163 μg/L at PACl dosage 10, 20, 30, 40 and 50 mg/L, respectively. The highest percent reduction (37%) was obtained at PACl dosage 50 mg/L. Whereas in summer season, THMFP at 302 μg/L in raw surface water was reduced to 254, 234, 212, 188 and 167 μg/L at PACl dosage 10, 20, 30, 40 and 50 mg/L, respectively. Coagulation at the highest PACl dosage 50 mg/L was provided the highest THMFP reduction at 45%.

The results of THMFP reduction by conventional coagulation showed that the percent THMFP reduction was increased with the increasing of PACl dosage. From the obtained results, it can be stated that the highest percent THMFP reduction was found PACL dosage at 50 mg/L of PACl for all season. However, the results showed that the increasing of PACl dosage from 40 mg/L to 50 mg/L resulted in slight increase of percent THMFP reduction. This results was well corresponded with the results Iriarte-Velasco *et al*. (2007) which reported that the addition of PACl coagulant higher than 40 mg/L does not result in any significant improvement in water quality. Therefore, the optimal PACl dosage for THMFP reduction was selected at PACl 40 mg/L for all season. From the literature review, the using of PACl coagulation for THMFP reduction was provided the better efficiency than other coagulants such as alum and $FeCl_3$. Srimuang (2011) reported that coagulation with PACl dosage 40 mg/L can reduced THMFP in raw water in rainy and summer season by 46% and 51%, respectively. While Musikavong *et al.* (2005) reported that alum and $FeCl_3$ at 80 mg/L can reduce THMFP from treated wastewater with 25.2% and 27.7%, respectively.

The reduction of THMFP by conventional coagulation was related to the reduction of DOC concentration which defined as the precursors for THMs. From the results, it was found that the THMFP reduction was increased when the percent DOC reduction increased. As known that DOM in water are defined as precursors for THMs, the decreasing of DOM concentration was led to the lower THMs formation potential in water. However, the formation of THMs in water was not only depending on the concentration of DOM but also the characteristics of DOM in water. Thus, the specific THMFP of raw water and coagulated water in all season were investigated.

4.3.2.3 Specific THMFP

The specific THMFP is the ratio between THMFP and DOC of each water sample. It is used to indicate the potential of the organic matter to react with chlorine to form THMs. The specific THMFP values of raw surface water and coagulated water at various PACl dosages are shown in Table 4.4.

Table 4.4 Specific THMFP of raw surface water and coagulated water

Specific THMFP (μg/mg)	Raw water	PACl dosage (mg/L)				
		10	20	30	40	50
Winter	131	111	117	120	123	123
Rainy	143	118	120	133	139	135
Summer	139	128	128	128	130	116

The specific THMFP in raw surface water was 131, 143 and 139 μg/mg in winter, rainy and summer season, respectively. The results showed that the specific THMFP in coagulated at all PACl dosage was lower than those of in raw surface water. From the results, it can be indicated that the potential of DOM to form THMs was reduced by PACl coagulation. The decreasing of specific THMFP indicates that DOM which was reduced by PACl coagulation was high ability to form THMs. However, the results showed that specific THMFP was slightly increased with the PACl dosage increasing.

4.3.2.4 THMs species

Three species of THMs including chloroform, dichlorobromoform and dibromochloroform were found in raw surface water and coagulated water for all season. The THMs species of raw surface water and coagulated water in rainy, winter and summer are illustrated in Figure 4.8, 4.9 and 4.10, respectively.

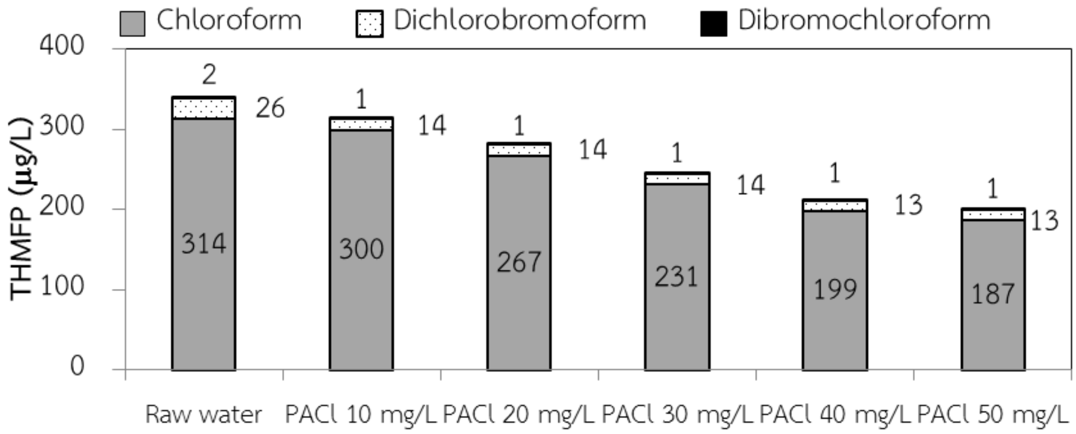


Figure 4.8 THMs species of raw surface water and coagulated water in rainy season

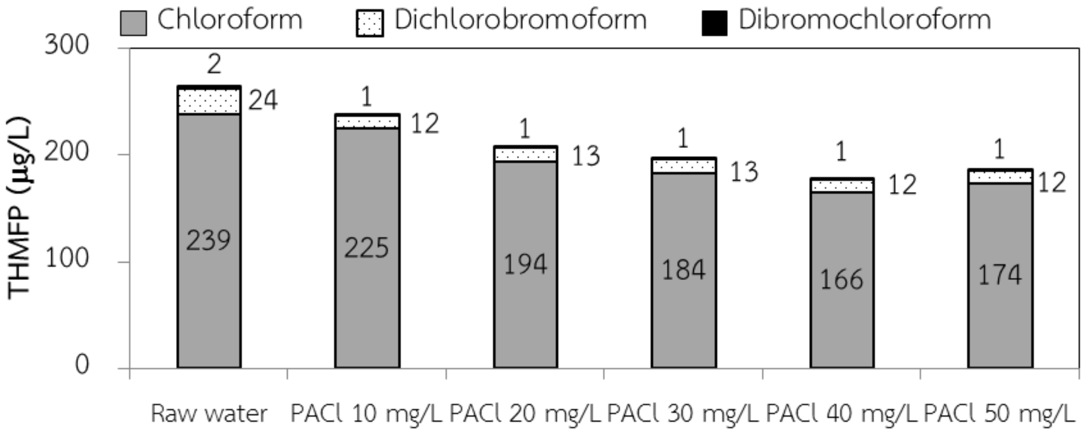


Figure 4.9 THMs species of raw surface water and coagulated water in winter season

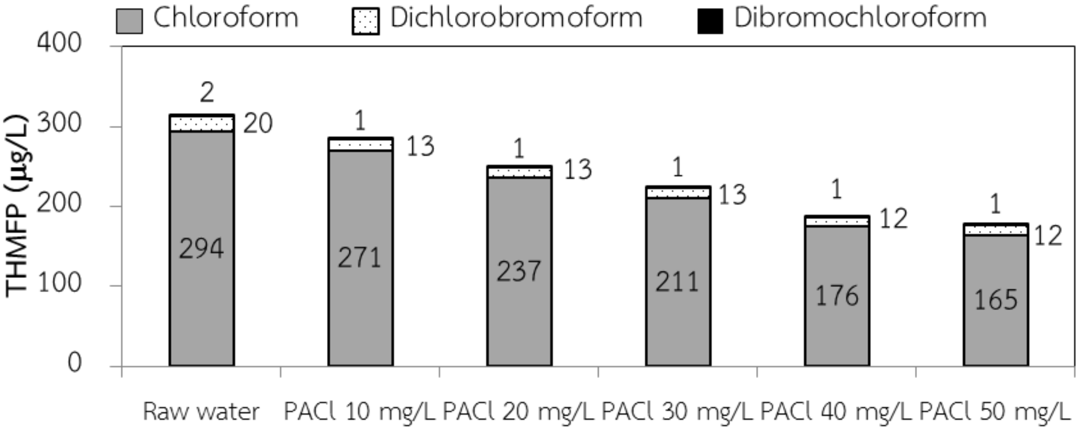


Figure 4.10 THMs species of raw surface water and coagulated water in summer season

The obtained results showed that chloroform was the major THMs species in raw surface water and coagulated water in all season. Chloroform was found to highly decrease with the increasing PACl dosage from 10 mg/L to 40 mg/L. On the other hand, it was found to slightly decrease when the PACl dosage was increased from 40 mg/L to 50 mg/L. These results indicated that the increasing of PACl dosage from 40 mg/L to 50 mg/L was not affected the reduction of chloroform. While the results of dichlorobromoform showed that the slight decrease of dichlorobromoform was observed at the increment of PACl dosage from 10 mg/L to 50 mg/L. According to the standard of THMs in tap water of Metropolitan Waterworks Authority which followed the guideline from WHO (2006), the maximum level of chloroform, dichlorobromoform and dibromochloroform were 300 μg/L, 60 μg/L and 100 μg/L, respectively. From the results, it can be stated that THMFP in coagulated water was met the standard of Metropolitan Waterworks Authority.

4.3.3 Reduction of DOM by in-line coagulation with ceramic membrane filtration

In the previous section, the studied was focus on the efficiency of conventional coagulation process for DOM reduction which commonly utilize for water supply production in Thailand. However, the performance of conventional coagulation for DOM removal was limited and require larger area for constructed. Thus, the combination of coagulation process and membrane filtration is increasing used for enhance or replace the conventional coagulation for water treatment and water supply process. Then, this section aimed at investigating the efficiency of in-line coagulation with ceramic membrane filtration for DOM reduction. PACl was used as coagulants and varied dosage at 20, 30 and 40 mg/L based on the results of conventional coagulation process in section 4.3.2.

4.3.3.1 Reduction of DOC and UV-254

The results of DOC and UV-254 reduction by in-line coagulation with ceramic membrane filtration of rainy season are illustrated in Figure 4.11. The results showed that the in-line coagulation with ceramic membrane filtration can reduce DOC concentration from 2.3 mg/L in raw surface water to 1.7, 1.3 and 1.2 mg/L at PACl dosage 20, 30 and 40 mg/L, respectively. The highest percent DOC reduction was 48% which obtained at PACl dosage 40 mg/L. While the results of UV-254 reduction showed that the UV-254 was decreased from 0.076 cm^{-1} to 0.026, 0.023 and 0.022 cm^{-1} at PACl dosage 20, 30 and 40 mg/L, respectively.

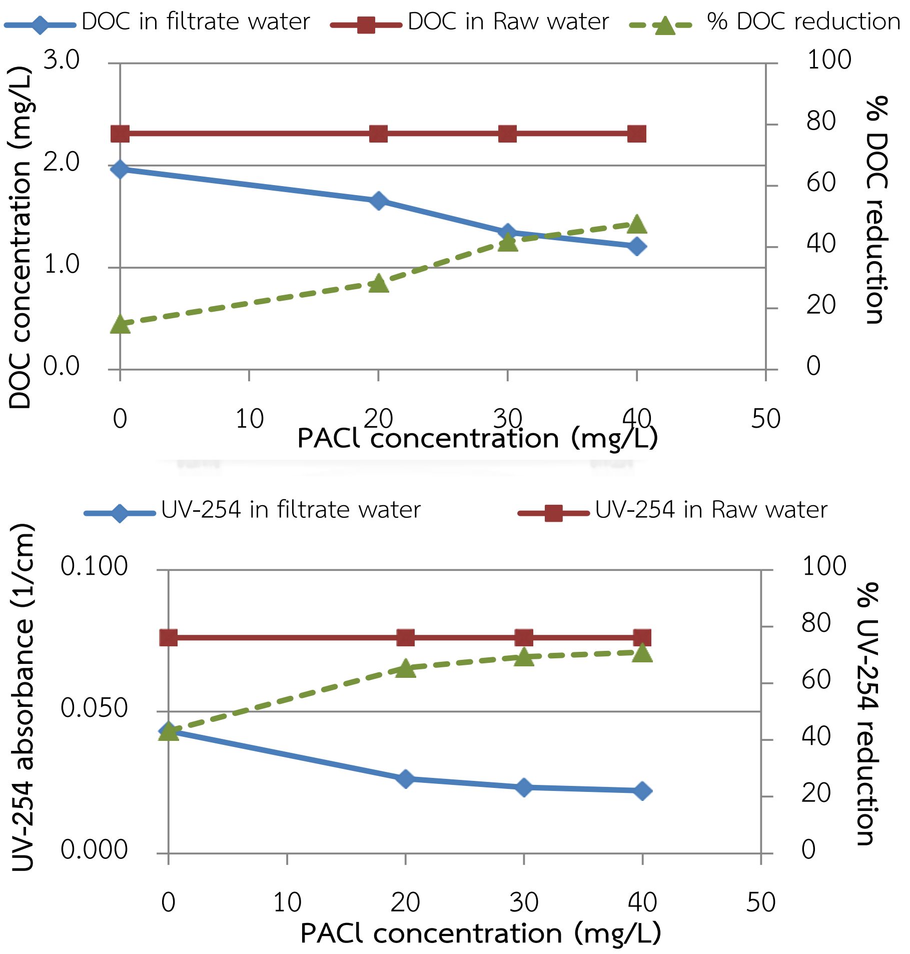


Figure 4.11 Reduction of DOC and UV-254 and their percent reduction by in-line coagulation with ceramic membrane filtration in rainy season

In case of raw surface water in winter and summer season, the results was provided the same trends with the raw surface water in rainy season as shown in Figure 4.12 and 4.13.

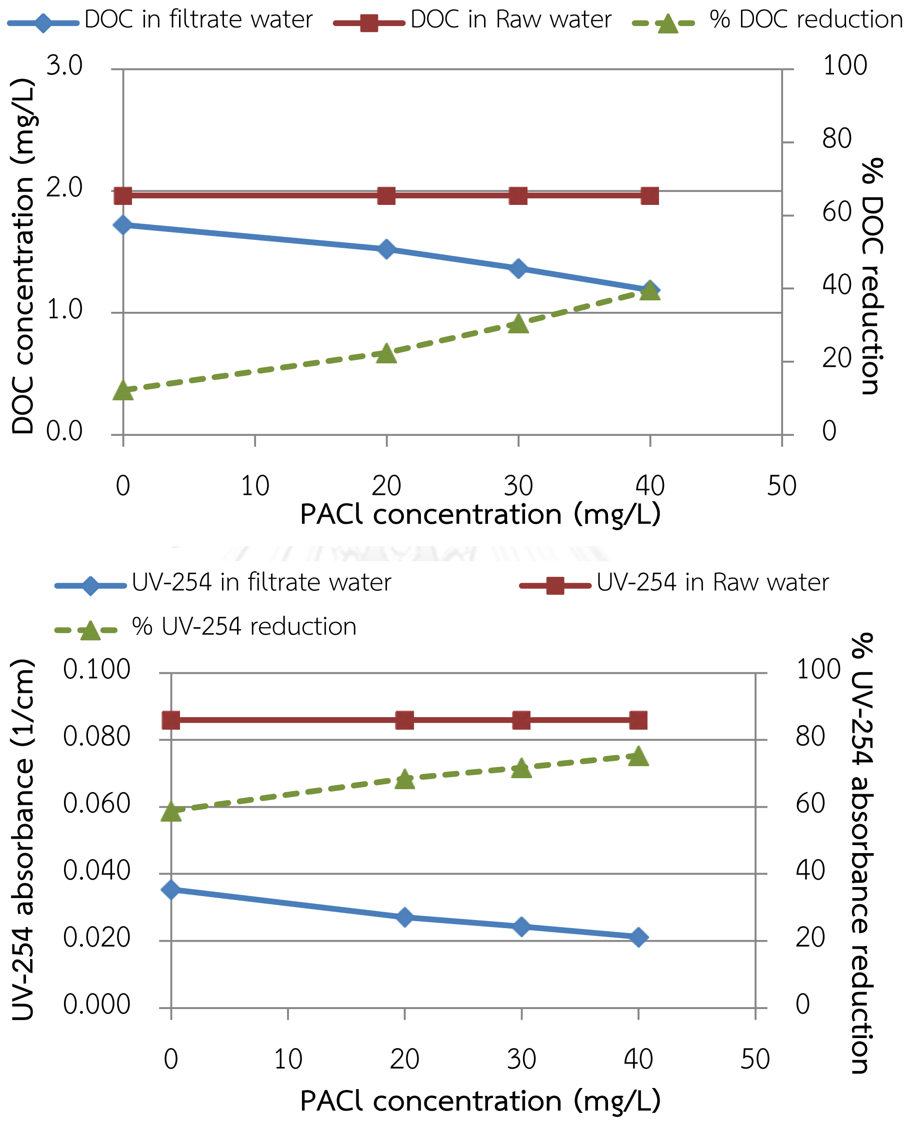


Figure 4.12 Reduction of DOC and UV-254 and their percent reduction by in-line coagulation with ceramic membrane filtration in winter season

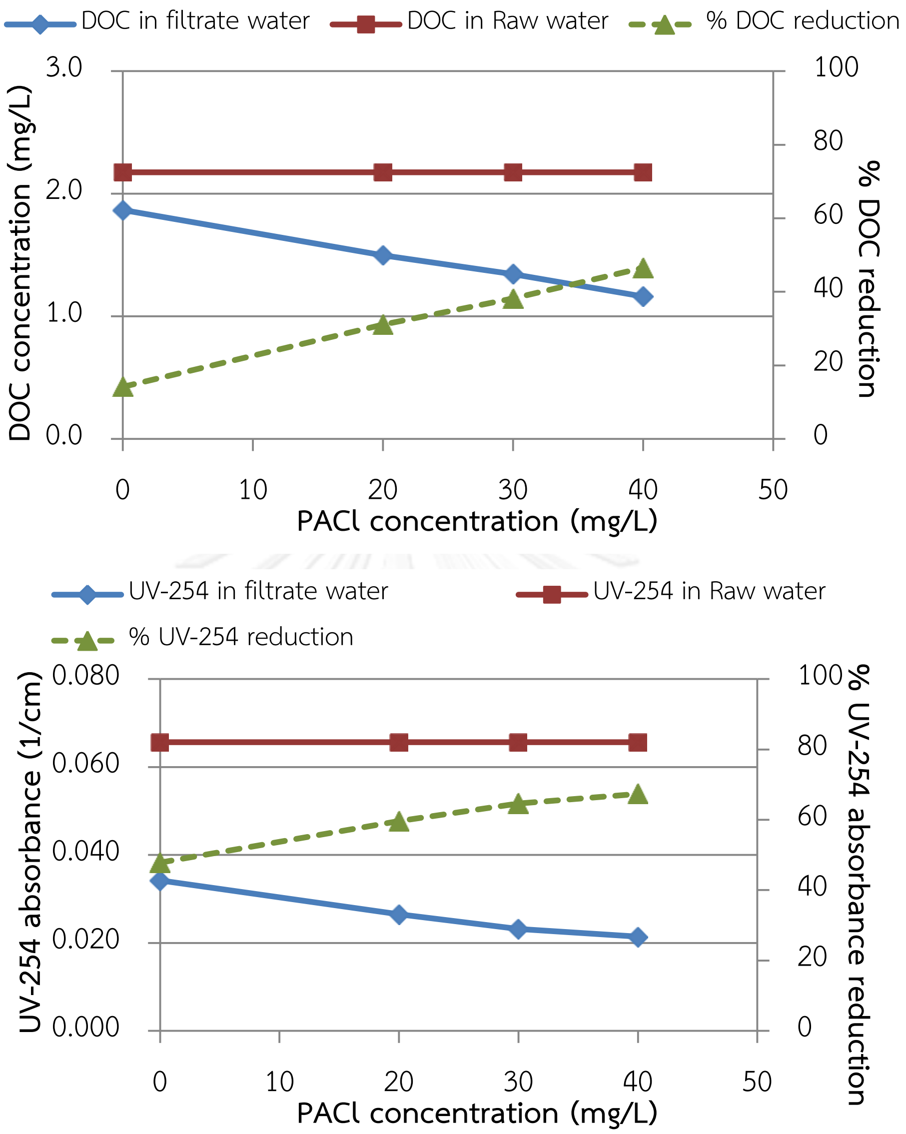


Figure 4.13 Reduction of DOC and UV-254 and their percent reduction by in-line coagulation with ceramic membrane filtration in summer season

From the results in Figure 4.12, the in-line coagulation with ceramic membrane filtration can reduce DOC values from 2.0 mg/L of raw surface water in winter season to 1.5, 1.4 and 1.2 mg/L at PACl dosage 20, 30 and 40 mg/L, respectively. The highest percent DOC reduction was 40% which obtained at PACl dosage 40 mg/L. Whereas, those in summer season, the DOC values was reduced from 2.2 mg/L to 1.5, 1.3 and 1.2 mg/L at PACl dosage 20, 30 and 40 mg/L, respectively. The highest percent DOC reduction was 47% which obtained at PACl dosage 40 mg/L.

As for the UV-254 reduction, the in-line coagulation with ceramic membrane filtration can decrease UV-254 values from 0.086 cm^{-1} of raw surface water in winter season to 0.027, 0.024 and 0.021 cm^{-1} at PACl dosage 20, 30 and 40 mg/L, respectively. While, those in summer season, the UV-254 values decrease from 0.066 cm^{-1} to 0.027, 0.023 and 0.021 cm^{-1} at PACl dosage 20, 30 and 40 mg/L, respectively. The highest percent UV-254 reduction was 75% and 67% which obtained at PACl dosage 40 mg/L of winter and summer season, respectively. The results showed that the reduction of UV-254 was higher than those of DOC concentration. This can be indicated that in-line coagulation with ceramic membrane filtration has potential to reduce more aromatic hydrocarbon from water. Many researchers reported that coagulation is more efficient to remove UV-254 than DOC (Li *et al*. 2011; Iriarte-Velasco *et al*. 2007; Guigui *et al*. 2002 and Bian *et al*. 2000). Thus, it can be indicated that the higher reduction of UV-254 by in-line coagulation with ceramic membrane filtration might be due to the PACl coagulation.

The efficiency of in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L for DOC and UV-254 reduction was compared with the efficiency of ceramic membrane filtration alone (without PACl coagulation). The results showed that the DOC reduction efficiency by using ceramic membrane filtration alone were in the range of 12.2 - 15.0%. The DOC reduction efficiency was increased to the range of 39.5 - 47.6% by using the combination of coagulation with ceramic membrane filtration at PACl dosage 40 mg/L. The increasing of percent reduction of DOC and UV-254 by using in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L compared to use ceramic membrane filtration alone are shown in Table 4.5.

Table 4.5 The increasing of percent reduction of DOC and UV-254 by using in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L

Reduction efficiency (%)	Increasing of percent reduction		
	Rainy	Winter	Summer
DOC	32.6	27.3	32.3
UV-254	27.8	16.5	19.5

From the results, it can be indicated that the using of in-line coagulation with ceramic membrane filtration provided the higher percent reduction efficiency of DOC and UV-254 than using ceramic membrane filtration alone in water of all season. The increasing of reduction efficiency of DOC by in-line coagulation with ceramic membrane compared to ceramic membrane filtration alone were approximately 30% in all season. The results was corresponded well with the results of Abeynayaka *et al*. (2012) which reported that the combination of coagulation with ceramic membrane can increased the DOC removal from 20% in case of without coagulation to 45% and studied of Li *et al*. (2011) which reported that the hybrid coagulation-ceramic microfiltration could remove DOC more efficiency than coagulation or membrane filtration alone.

SUVA values are the ratio between UV absorbance at wavelength 254 nm and dissolved organic carbon (DOC) concentration of a given sample. The results of SUVA values in filtrated water at various coagulants concentration are shown in Figure 4.14 which found that SUVA values were nearly constant when the PACl dosage increases from 0 to 40 mg/L.

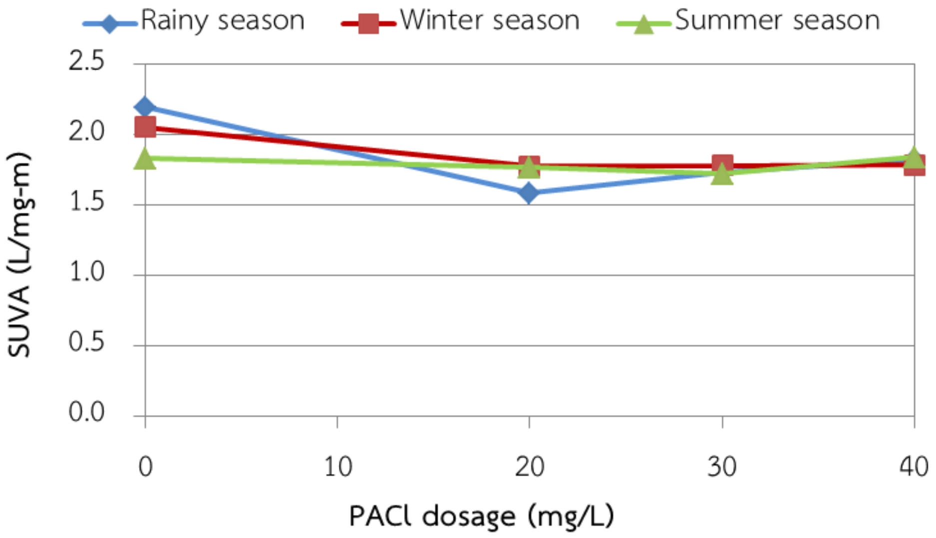


Figure 4.14 SUVA values of filtrated water at various PACl dosages

4.3.3.2 Reduction of THMFP

DOM is defined as THMs precursors. So, the reduction of DOM is led to the THMFP reduction. The results of THMFP reduction by in-line coagulation with ceramic membrane filtration in rainy, winter and summer season are shown in Figure 4.15, 4.16 and 4.17.

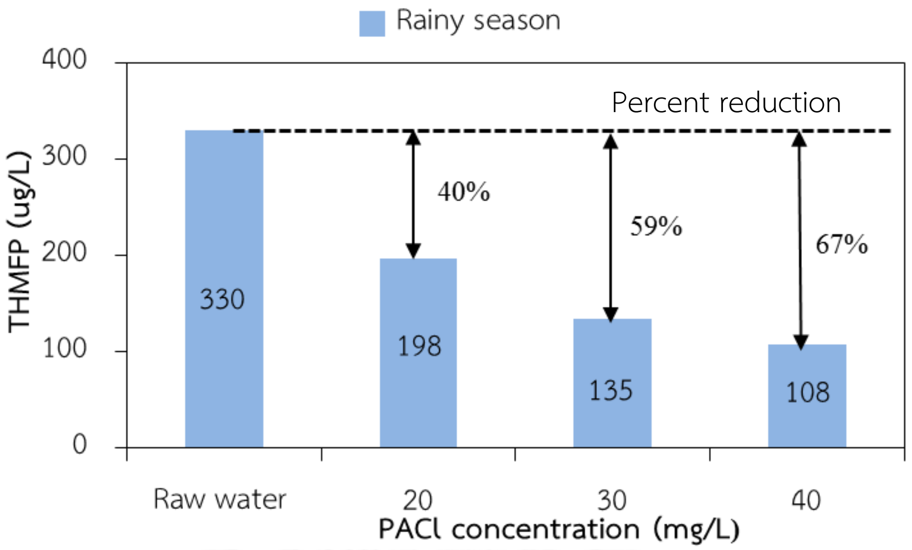


Figure 4.15 Reduction of THMFP by in-line coagulation with ceramic membrane filtration in rainy season

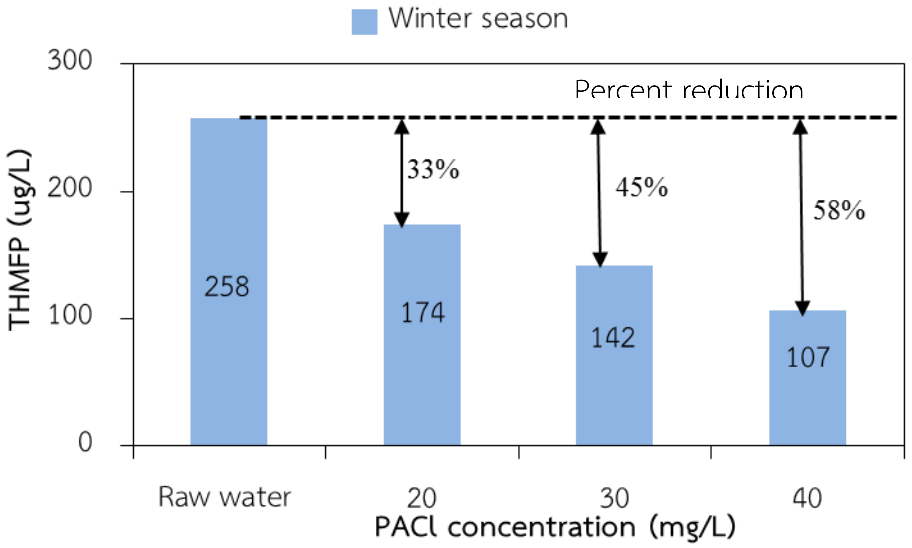


Figure 4.16 Reduction of THMFP by in-line coagulation with ceramic membrane filtration in winter season

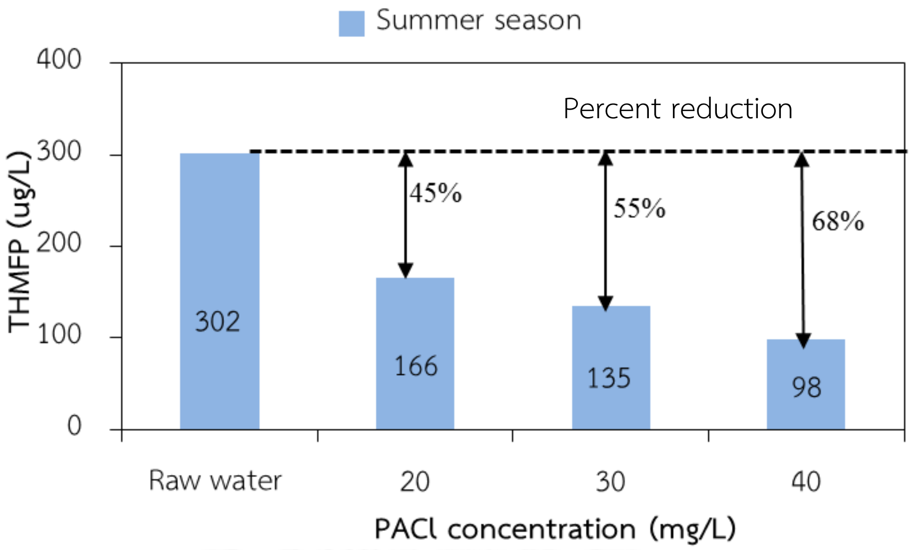


Figure 4.17 Reduction of THMFP by in-line coagulation with ceramic membrane filtration in summer season

In rainy season, the in-line coagulation with ceramic membrane filtration can reduce THMFP from 330 μg/L in raw surface water to 198, 135 and 108 μg/L at PACl dosage 20, 30 and 40 mg/L, respectively. In winter and summer season, the results were corresponded well with those results in rainy season. THMFP of 258 μg/L in raw surface water of winter season was reduced to 174, 142 and 107 μg/L at PACl dosage 20, 30 and 40 mg/L, respectively. While those in summer, THMFP at 302 μg/L was reduced to 166, 135 and 98 μg/L at PACl dosage 20, 30 and 40 mg/L, respectively. The highest percent THMFP reduction obtained at PACl dosage 40 mg/L were 65%, 58% and 68% in rainy, winter and summer, respectively.

The efficiency of in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L for THMFP reduction was compared with the efficiency of ceramic membrane filtration alone (without PACl coagulation). The results of THMFP reduction by in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L and ceramic membrane filtration alone are shown in Table 4.6.

Table 4.6 Percent THMFP reduction by in-line coagulation with ceramic membrane filtration and ceramic membrane filtration alone

% Reduction efficiency	In-line coagulation with ceramic membrane			Ceramic membrane filtration alone		
	Rainy	Winter	Summer	Rainy	Winter	Summer
THMFP	67.4	58.4	67.6	21.3	25.8	30.3

The results of THMFP reduction showed that in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L provided the percent THMFP reduction in the range of 58.4% - 67.6% which higher than those of reduction from ceramic membrane alone (21.3% - 30.3%). The results indicated that the using of in-line coagulation with ceramic membrane can increase the percent THMFP reduction about 46.1%, 32.6% and 37.3% in rainy, winter and summer, respectively. The obtained results related to the studied of Abeynayaka *et al.* (2012) which concluded that hybrid ceramic microfiltration can provide the lower THMFP in treated water under the surface water with high DOM concentration.

4.3.3.3 Specific THMFP

Specific THMFP is the ratio between THMFP and DOC of each water sample and use to indicate the potential of organic matter to react with chlorine to form THMs. The specific THMFP of raw surface water and filtrated water are shown in Table 4.7.

Table 4.7 Specific THMFP of raw surface water and filtrated water

Specific THMFP (μg/mg)	Raw water	PACl dosage (mg/L)		
		20	30	40
Winter	131	114	104	107
Rainy	143	119	100	89
Summer	139	111	100	84

The specific THMFP in raw surface water were 131, 143 and 139 μg/mg in winter, rainy and summer season, respectively. After filtrated by in-line coagulation with ceramic membrane, the specific THMFP was lower than that of in raw surface water at all conditions. It can be indicated that the potential of DOM to form THMs in filtrated was decreased by using in-line coagulation with ceramic membrane. The decreasing of specific THMFP in filtrated water can be indicated that in-line coagulation with ceramic membrane filtration can reduce DOM which has high potential to form THMs. In addition, the increased of PACl dosage was resulted in lower specific THMFP in filtrated water. When compared the specific THMFP of filtrated water by in-line coagulation with ceramic membrane and coagulated water by conventional coagulation, it was found that the specific THMFP in filtrated water were lower than those of coagulated water. This indicated that the using of in-line coagulation with ceramic membrane can reduced DOM which high potential to form THMs better than using conventional coagulation.

4.3.3.4 THMs species

Three species of THMs including chloroform, dichlorobromoform and dibromochloroform were found in raw surface water and filtrated water for all season. The THMs species of raw surface water and filtrated water in rainy, winter and summer are illustrated in Figure 4.18, 4.19 and 4.20, respectively.

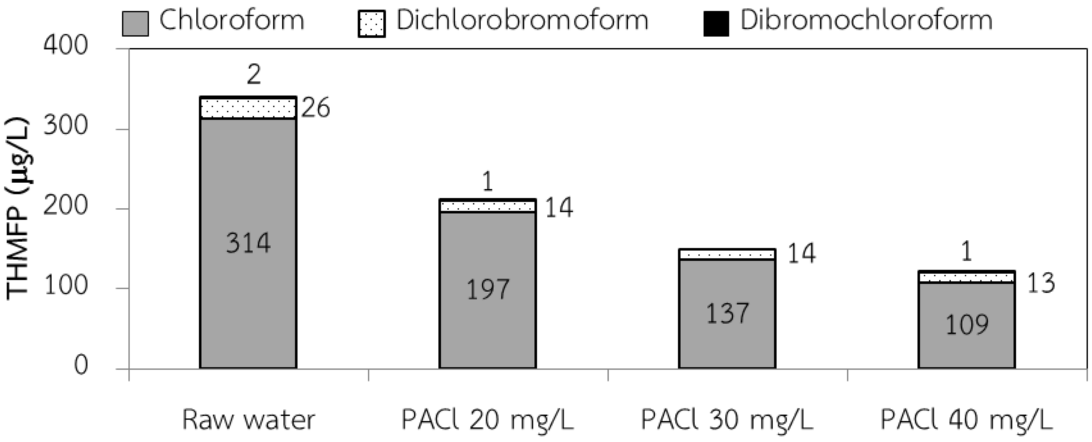


Figure 4.18 THMs species of raw surface water and filtrated water in rainy season

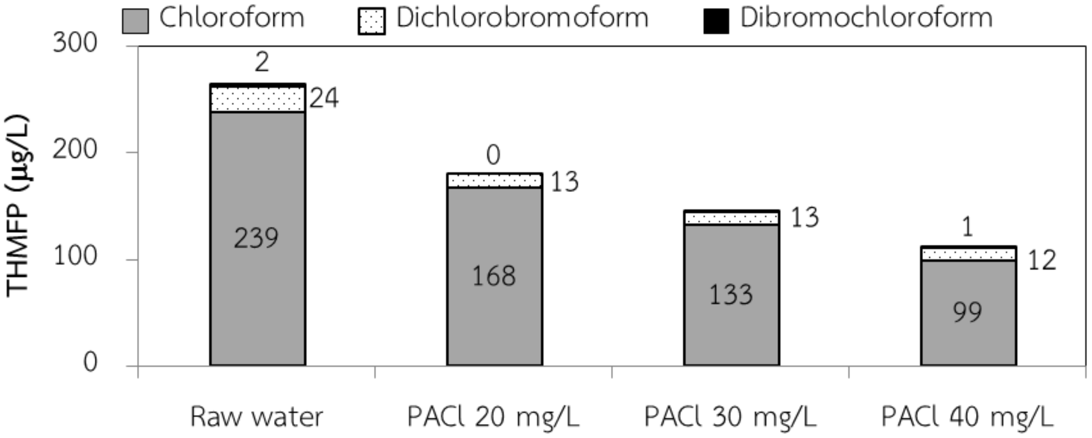


Figure 4.19 THMs species of raw surface water and filtrated water in winter season

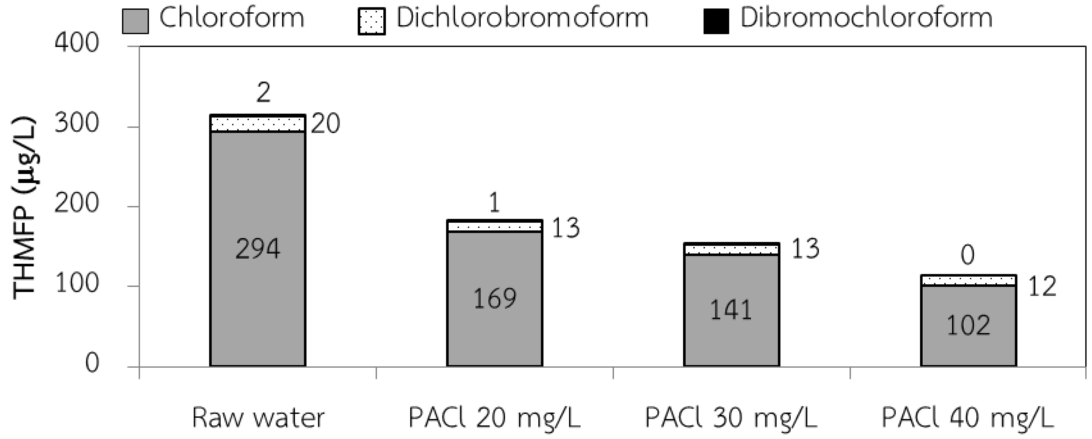


Figure 4.20 THMs species of raw surface water and filtrated water in summer season

The obtained results showed that chloroform was the major THMs species in raw surface water and filtrated water in all season. Chloroform was found to highly reduce with the increasing of PACl concentration from 20 mg/L to 40 mg/L. While Dichlorobromoform was highly reduced at PACl dosage 20 mg/L and nearly constant with the increment of PACl dosage from 20 mg/L to 40 mg/L. This indicated that the increasing of PACl dosage from 20 mg/L to 40 mg/L was not affected the reduction of dichlorobromoform. According to the standard of THMs in tap water of Metropolitan Waterworks Authority which followed the guideline from WHO (2006), the maximum level of chloroform, dichlorobromoform and dibromochloroform were 300 μg/L, 60 μg/L and 100 μg/L, respectively. From the results, it can be stated that THMFP in filtrated water by using PACl met the standard of Metropolitan Waterworks Authority. When compared the results of THMs species in filtrated water by in-line coagulation with ceramic membrane and those results by PACl coagulation. It was found that the in-line coagulation with ceramic membrane provided the higher percent of THMFP reduction in all species than PACl coagulation.

4.4 Water quality of filtrated water by in-line coagulation with ceramic membrane filtration

As stated earlier, the conventional coagulation which consists of coagulation, flocculation, sedimentation and filtration was commonly used as water treatment in water supply process. However, the new promising technology as membrane filtration was increasing used in the field of water treatment and water supply. Thus, the water quality of filtrated water by in-line coagulation with ceramic membrane filtration was investigated and compared with the water quality of treated water which collected from supernatant water in Jar-test apparatus and filtrated with 0.45 μm GF/C filter paper. This water was used to represent the water quality of conventional coagulation water treatment. Table 4.8 showed the water quality (DOC, UV-254 and THMFP) of treated water by conventional coagulation and filtrated water by in-line coagulation with ceramic membrane filtration.

The results in Table 4.8 showed that the water quality in term of DOC and UV-254 of both water samples was nearly the same. However, water quality in term of turbidity of filtrated water might be better than those in treated water by conventional coagulation. This might due to the ceramic membrane pore size (0.1 μm) is lower than filter paper that used to filtrate supernatant water from coagulation process. Then, turbidity might be highly reduced. Furthermore, in case of THMFP, the results showed that THMFP of filtrated water by in-line coagulation with ceramic membrane filtration was lower than those of treated water by conventional coagulation. The high decreasing of THMFP in filtrated water might be related to the DOM that had the particles size in the range of 0.1 -0.45 μm which it can passes the filter paper during conventional coagulation but it can remove through ceramic membrane filtration. When consider the results of DOC concentration in both water samples, it seems nearly the same but the THMFP was highly different. Thus, it might be related to the characteristics of DOM which it was investigated and discuss in the Chapter V.

Table 4.8 Water quality of treated water from conventional coagulation and filtrated water by in-line coagulation with ceramic membrane filtration

Processes	Optimal condition	Seasonal	Turbidity (NTU)	DOC (mg/L)	UV-254 (1/cm)	THMFP (μg/L)
Conventional coagulation	PACl dosage 40 mg/L	Rainy	6.84	1.4	0.025	189
In-line coagulation with CMF			0.01	1.2	0.022	108
Conventional coagulation	PACl dosage 40 mg/L	Winter	1.01	1.3	0.037	165
In-line coagulation with CMF			0.02	1.2	0.021	107
Conventional coagulation	PACl dosage 40 mg/L	Summer	1.01	1.5	0.019	188
In-line coagulation with CMF			0.01	1.2	0.021	98

(CMF = ceramic membrane filtration)

From the obtained results, it can be proved that the in-line coagulation with ceramic membrane filtration was the effective technology in field of water treatment and can be used to replace or enhance the conventional coagulation in field of water supply in Thailand.

4.5 Continuous experiment of in-line coagulation with ceramic membrane filtration

The efficiency of in-line coagulation with ceramic membrane filtration for organic matter reduction was investigated in the previous section. The results of batch experiment indicated that the in-line coagulation with ceramic membrane filtration can be utilized to replace or enhance conventional coagulation for organic matter reduction. Thus, this section was aimed at investigating the performance of in-line coagulation with ceramic membrane filtration for potable water production. The water quality of filtrated water including organic matter and THMs was investigated. The membrane filtration performance in term of filtration flux was studied.

The continuous experiment of in-line coagulation with ceramic membrane filtration was conducted by using the ceramic membrane module and the condition that described in Chapter 3 section 3.4.4. Raw surface water was collected from Ping River water on August, December and March to represent the water quality in rainy, winter and summer season, respectively. The experiment was run continuous for 30 days and the filtration flux was determined every day. Water quality of raw surface water and filtrated water in term of turbidity, DOC concentration, UV-254 and THMs were analyzed.

4.5.1 Water quality of raw surface water and filtrated water

Water quality of raw surface water and filtrated water from in-line coagulation with ceramic membrane filtration in each season was investigated. Many parameters including turbidity, DOC concentration, UV 254 absorbance, trihalomethanes concentration (THMs) and chlorine residual were investigated.

4.5.1.1 Turbidity

Turbidity is the important parameters in water supply production. The standard of turbidity of water supply was set at 5 NTU by Provincial Waterworks Authority, Thailand (PWA, 2013). During the experimental periods, turbidity of raw surface water and filtrated water was measured every day. The results of turbidity of raw surface water and filtrated water from in-line coagulation with ceramic membrane filtration are shown in Figure 4.21.

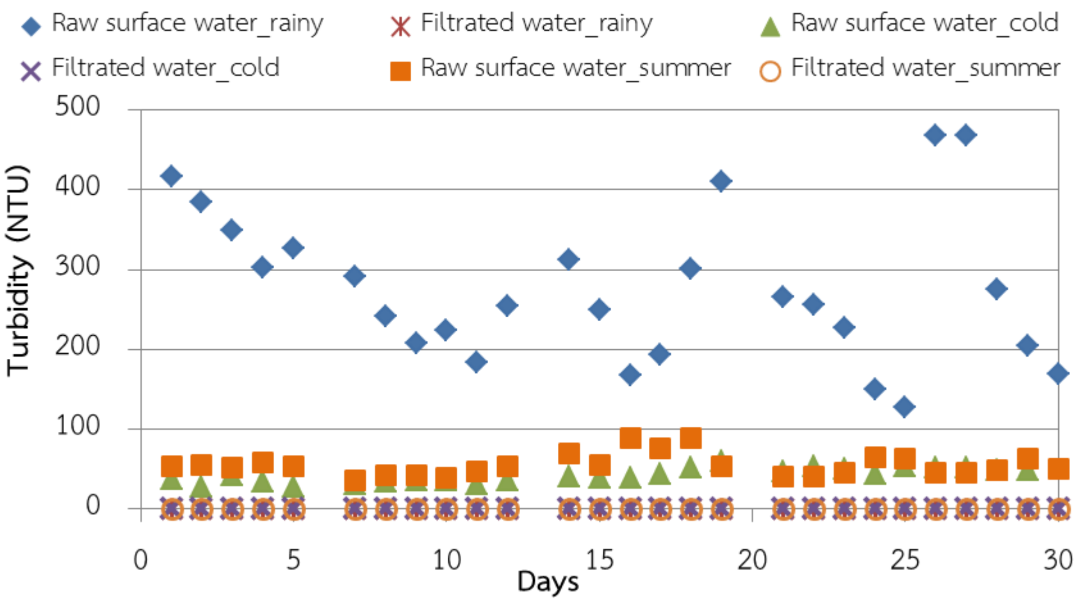


Figure 4.21 Turbidity of raw surface water and filtrated water during continuous experiment

From the results in Figure 4.21, it was found that turbidity of raw surface water was varied with seasonal changes. Turbidity of raw surface water in rainy season was fluctuated in the range of 100 – 500 NTU depended on the rainfall in each day. The heavy rain was affected the turbidity of raw surface water. The average turbidity of raw surface water in rainy season was 275 NTU. For winter and summer season, the turbidity of raw surface water was nearly constant during the experiment. The average turbidity of raw surface water in winter and summer season was 42.0 and 54.5 NTU, respectively.

After the raw surface water was filtrated by using in-line coagulation with ceramic membrane filtration for 30 days, turbidity of filtrated water in all season was decreased to lower than 0.2 NTU. Turbidity of filtrated water was nearly constant and varied between 0.10 to 0.17 NTU during the experiment periods. The average turbidity of filtrated water in rainy, winter and summer were 0.12, 0.11 and 0.11 NTU, respectively. From the results, it can be indicated that the in-line coagulation with ceramic membrane filtration can produce filtrated water that meet the standard of turbidity of water supply (5 NTU). In addition, the varied of turbidity of raw surface water during the experimental periods did not affected the reduction efficiency of turbidity by in-line coagulation with ceramic membrane filtration.

4.5.1.2 DOC and UV-254

Water quality of raw surface water and filtrated water in term of organic matter concentration was analyzed by measuring DOM surrogates parameters including DOC concentration and UV-254 absorbance. The DOC concentration and UV-254 absorbance of raw surface water and filtrated water were analyzed two times per week. The results of DOC concentration and UV-254 absorbance of raw surface water and filtrated water in all season are shown in Figure 4.22 and Figure 4.23.

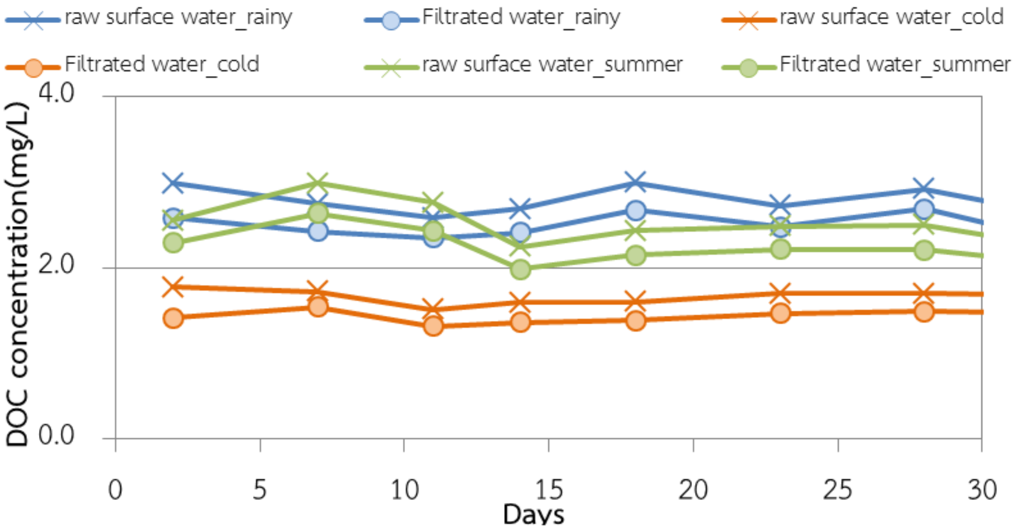


Figure 4.22 DOC concentrations of raw surface water and filtrated water during the experimental periods in all season

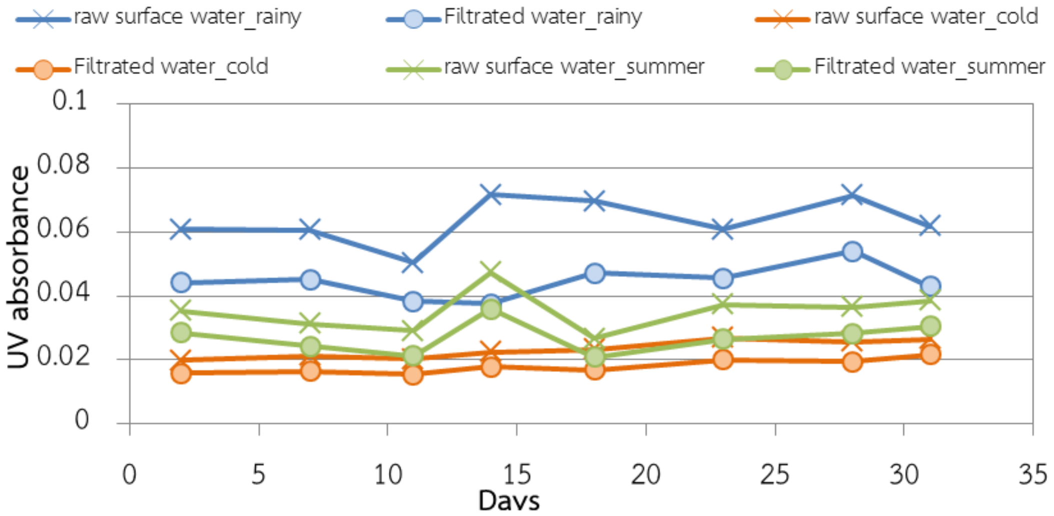


Figure 4. 23 UV-254 absorbance of raw surface water and filtrated water during the experimental periods in all season

The results of DOC concentration of raw surface water showed that the DOC concentration was nearly constant during the experimental periods in all season. The average DOC concentration of raw surface water in rainy, winter and summer season was 2.8, 1.7 and 2.6 mg/L, respectively. The DOC concentration of raw surface water in winter season was found at the lowest concentration which related to the lower turbidity of raw surface water in this season. The DOC concentration in filtrated water was nearly constant and depended on the DOC concentration of raw surface water during the experimental periods. The average DOC concentration of filtrated water in rainy, winter and summer was 2.5, 1.4 and 2.3 mg/L, respectively. Percent DOC reduction of in-line coagulation with ceramic membrane filtration during the experimental periods was investigated. The results showed that the percent DOC reduction was nearly constant during the experimental periods for all season. The average percent DOC reduction by in-line coagulation with ceramic membrane filtration was 10.3%, 13.6% and 11.4% in rainy, winter and summer season, respectively. The results indicated that the filtration process by using in-line coagulation with ceramic membrane filtration can maintained the reduction efficiency of DOC for 30 days without significantly decreased of DOC reduction efficiency.

The results of UV-254 showed the same trends as the results of DOC concentration. The UV-254 absorbance of raw surface water was nearly constant during the experimental periods in all season. The average UV-254 absorbance of raw surface water was 0.0634, 0.0233 and 0.0348 cm^{-1} in rainy, winter and summer season, respectively. After filtration with in-line coagulation with ceramic membrane filtration, UV-254 absorbance of filtrated water was nearly constant and depended on the UV-254 absorbance of raw surface water during the experimental periods. The average UV-254 absorbance of filtrated water was 0.0444, 0.0179 and 0.0265 cm^{-1} in rainy, winter and summer season, respectively. Percent UV-254 reduction by in-line coagulation with ceramic membrane filtration during the experimental periods was investigated. The results showed that the average percent UV-254 reduction by in-line coagulation with ceramic membrane filtration was 29.6%, 22.8% and 23.9% in rainy, winter and summer season, respectively. The results indicated that the filtration process by using in-line coagulation with ceramic membrane filtration can maintained the reduction efficiency of UV-254 for 30 days without significantly decreased of UV-254 reduction efficiency.

4.5.1.3 THMs

THMs is commonly found in water supply process when the chlorine which used for disinfection process are react with organic matter. In the continuous experiment of in-line coagulation with ceramic membrane filtration, chlorine was utilized for both microbial or virus disinfection and control fouling which commonly occurred during membrane filtration. However, the addition of chlorine can cause the formation of trihalomethanes (THMs) in filtrated water. Thus, the THMs concentration in filtrated water was investigated. THMs of raw surface water and filtrated water were measured once per week during the experimental periods. The average THMs of raw surface water and filtrated water are shown in Figure 4.24.

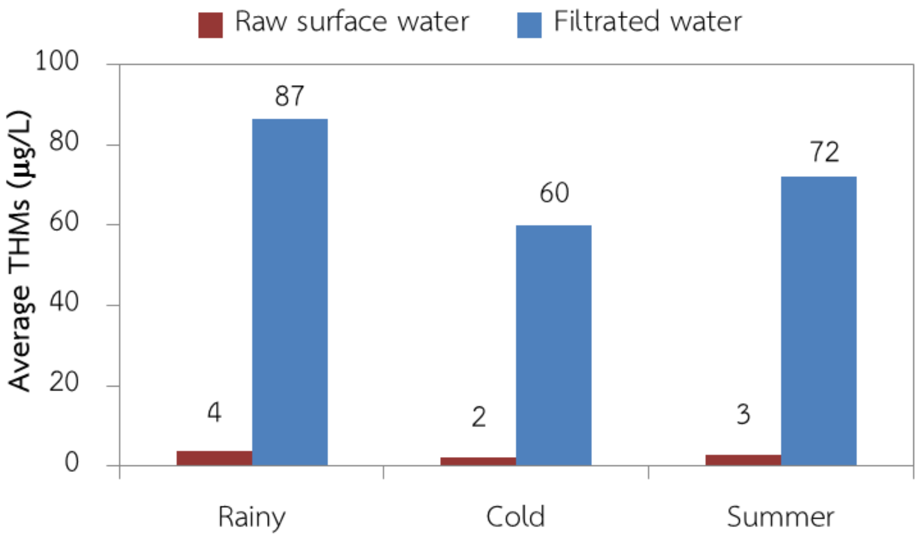


Figure 4.24 Average THMs of raw surface water and filtrated water in each season

The results in Figure 4.24 showed that the average THMs of raw surface water was found in very low concentration at 3.79, 2.03 and 2.67 μg/L in rainy, winter and summer season, respectively. However, the THMs were increased to 86.6, 59.9 and 72.0 μg/L in filtrated water of rainy, cod and summer season, respectively. From the results, it can be indicated that the addition of chlorine as pre-chlorination during the in-line coagulation with ceramic membrane filtration experiment can increased the THMs concentration in filtrated water. When compared the THMs in filtrated water with the standard of THMs for stage 1 which set at 80 μg/l by USEPA, It was found that THMs in filtrated water in rainy season was higher than the standard. Thus, it can be indicated that the pre-chlorination during the in-line coagulation with ceramic membrane filtration can created THMs in filtrated water higher than the standard of THMs and it not suitable to utilize for this water source.

4.5.2 Performance of ceramic membrane filtration

Performance of in-line coagulation with ceramic membrane filtration in term of filtration flux was investigated. The results of filtration flux in each season are shown in Figure 4.25.

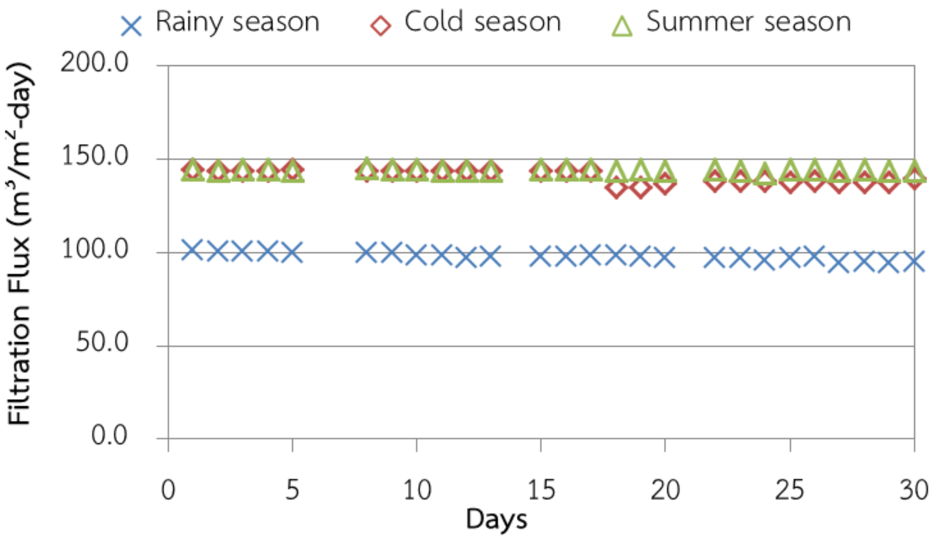


Figure 4.25 Filtration flux of ceramic membrane during experimental periods in rainy, winter and summer season

The results of filtration flux during the experimental periods showed that the filtration flux was gradually decreased with time. The initial flux of ceramic membrane in rainy season was 101.0 m^3/m^2-day. After 30 days of filtration, it was decreased to 94.8 m^3/m^2-day. For winter and summer season, the initial flux was 144.4 m^3/m^2-day and 144.8 m^3/m^2-day, respectively. After filtration for 30 days, the filtration flux was decreased to 140.1 m^3/m^2-day and 144.2 m^3/m^2-day in winter and summer season, respectively. From the results, it can be indicated that the in-line coagulation with ceramic membrane filtration can be utilized to filtrate raw surface water in all season without the significantly reduction in filtration flux during the 30 days of filtration periods.

4.6 Concluding Remarks

The using of in-line coagulation with ceramic membrane filtration provides the higher efficiency for DOM reduction than conventional coagulation process at all PACl dosage. The results of DOM reduction efficiency by both process of raw surface water in each season showed the same trends. Percent reduction of DOM was increased with PACl dosage increasing both in conventional coagulation and in-line coagulation with ceramic membrane filtration.

The use of conventional coagulation for reduction of DOM provided the highest percent DOM reduction at PACl dosage 50 mg/L. However, the optimal condition was selected at PACl dosage 40 mg/L because it utilized lower chemical concentration and the efficiency was not significantly different when compared with the results of PACl dosage 50 mg/L. At the optimal condition, the conventional coagulation can reduce DOC, UV-254 and THMFP by 41%, 67% and 43% in rainy season, respectively. While the other season (Winter and summer), it can reduce DOC, UV-254 and THMFP in the range of 31 - 33%, 58 - 72% and 36 - 38%, at the optimal condition, respectively.

The use of in-line coagulation with ceramic membrane filtration provided the highest efficiency at PACl dosage 40 mg/L at all season. In rainy season, the in-line coagulation with ceramic membrane filtration can reduce DOC, UV-254 and THMFP by 48%, 71% and 67% at the optimal condition (PACl dosage 40 mg/L), respectively. Whereas, in winter and summer season, DOC, UV-254 and THMFP were reduced in the range of 40 - 47%, 67 -75% and 58 - 68% at the optimal condition by in-line coagulation with ceramic membrane filtration, respectively. Furthermore, the in-line coagulation with ceramic membrane filtration can reduce the specific THMFP from 143 mg/mg of raw surface water in rainy season to 89 mg/mg in filtrated water at PACl dosage 40 mg/L. When compared the results of specific THMFP in filtrated water and coagulated water, it was found that the specific THMFP of filtrated water was lower than those in coagulated water. This result indicated that the in-line coagulation with ceramic membrane can reduced DOM which high potential to form THMs better than conventional coagulation.

From the obtained results, it can be stated that the in-line coagulation with ceramic membrane can be utilized to reduce the DOM from water source. It was provided the higher efficiency for DOM reduction than the conventional coagulation which commonly used for DOM reduction in water supply process of Thailand.

The results of continuous experiment of in-line coagulation with ceramic membrane showed that in-line coagulation with ceramic membrane filtration can be operated in long term operation at least 30 days without the significantly decreased of filtration flux. The reduction efficiency of organic matter and turbidity was nearly constant during the experimental periods. Furthermore, the addition of chlorine can increase the THMs concentration in filtrated water and it was higher than the THMs standard which set by US EPA. Thus, the pre-chlorination did not suitable to utilize for this water source.

In this chapter, the efficiency of in-line coagulation with ceramic membrane filtration to reduce DOM in term of quantity was investigated. However, the seriously problems from the presence of DOM in natural water such as precursors for THMs was depend on the quantity and the characteristics of DOM. Thus, the next chapter was mainly studied the reduction of DOM in term of DOM characteristics by in-line coagulation with ceramic membrane filtration.

CHAPTER V

CHARACTERIZATION AND REDUCTION OF DOM FRACTIONS AND THEIR THMFP IN RAW SURFACE WATER, COAGULATED WATER AND FILTRATED WATER

5.1 Introduction and Objective

Dissolved organic matter (DOM) is a complex mixture of hydrophilic and hydrophobic organic materials which varies in size, functional groups and reactivity (Yee *et al.*, 2009). DOM in natural water can react with chlorine during chlorination process to form disinfection by-products (DBPs) such as THMs which defined as carcinogenic substances. The formation of THMs depends on quantity and characteristics of DOM. To gain a better understanding of the formation of THMs from organic matter, characteristics of DOM should be investigated by grouping DOM into different groups according to the physical and chemical properties. The resin fractionation technique has been successfully employed to isolate bulk DOM into DOM fractions that are chemically similar (AWWA, 1993). DOM can be characterized to DOM fraction namely hydrophilic (HPI) and hydrophobic (HPO) fraction by using the DAX-8 resins. In addition, Leenheer (1981) conducted a resin fractionation technique with three resin (DAX-8, WA-10 and AG-MP-50) to separate DOMs into six DOM fractions, namely hydrophobic acid (HPOA), hydrophobic neutral (HPON), hydrophobic base (HPOB), hydrophilic acid (HPIA), hydrophilic neutral (HPIN) and hydrophilic base (HPIB). The fractionation allows a thorough investigation of the formation of THMs from organic matter in water sources and can provide a better understanding of the relationship between each DOM fraction and the formation of THMs. The ability of each DOM fraction to form THMs is the important information for design and selects the appropriate treatment technique to reduce THMs from water.

This chapter was aimed at investigating the characteristics of DOM fractions in raw surface water from Ping River, coagulated water from PACl coagulation and filtrated water by using in-line coagulation with ceramic membrane filtration. The ability of each DOM fraction to form THMs was investigated by determine the THMFP and specific THMFP values of each DOM fraction. Furthermore, the reduction efficiency of DOM fractions and their THMFP by in-line coagulation with ceramic membrane filtration and conventional coagulation was determined.

5.2 Material and Methods

Water samples including raw surface water in all season, coagulated water by Jar-test apparatus at PACl dosages 10, 20, 30, 40 and 50 mg/L and filtrated water from in-line coagulation with ceramic membrane filtration at PACl dosages 20, 30 and 40 mg/L were collected and analyzed for DOM fractions by using resin fractionation method. The resin fractionation was conducted with DAX-8 resin to separate DOM in water samples into hydrophilic (HPI) and hydrophobic (HPO) fraction. Water samples were filtered through a pre-combusted (550°C) GF/F 0.7 μm filter before fractionation. After fraction, each DOM fraction of water samples was collected. The unfractionated water and fractionated water (HPI and HPO) was filter through 0.45 μm GF/C filter paper before analyzed for their DOC and THMFP.

In addition, the fractionation of DOM into six DOM fractions namely HPIA, HPIN, HPIB, HPOA, HPON and HPOB was conducted. Raw surface water was collected from Ping River at the same sampling station as described in Chapter III. Raw surface water was collected two times in July 2012 and December 2012 to represent the nature of DOM in rainy and dry season, respectively. Based on the obtained results from Chapter IV, water quality of this water source can be characterized into two seasons and the optimal PACl dosage was 40 mg/L for in-line coagulation with ceramic membrane filtration. Thus, this experiment was conducted for raw surface water in two seasons. Raw surface water was used to conduct the in-line coagulation with ceramic membrane filtration at the condition of PACl dosage 40 mg/L. Before fractionated, water samples (raw surface water and filtrated water) were filtered through a pre-combusted (550°C) GF/F 0.7 μm filter. About 3 L of water samples were fractionated by using a series of three resins (DAX-8, WA-10 and AG-MP-50) and followed the resin fractionation procedure as proposed by Marhaba *et al.* (2003). After fractionation, each DOM fraction of all water samples were collected and filtrated through 0.45 μm GF/C filter paper before analyze for DOC and THMFP. The detailed of fractionation procedure were illustrated in Chapter III, Section 3.4.5.1.

5.3 Results and discussions

5.3.1 Characterization of DOM into hydrophilic (HPI) and hydrophobic (HPO) fractions

Water samples including raw surface water, coagulated water and filtrated water were collected and fractionated DOM into HPI and HPO fractions. THMFP values of each fraction were investigated. In addition, the reduction efficiency of DOM fraction by in-line coagulation with ceramic membrane filtration was investigated and compared with the reduction efficiency obtained from conventional coagulation.

5.3.1.1 Characteristics of DOM fractions and their THMFP in raw surface water

Raw surface water which collected from Ping River during winter, rainy and summer season was fractionated by using DAX-8 resin fractionation procedure to isolate DOM into two fractions (HPI and HPO). All water samples (raw surface water before fractionated, HPI and HPO fraction) were collected and analyzed for DOC concentration and THMFP values. The results of fractionation process are reported in Table 5.1.

The results in Table 5.1 showed that percent different between water samples before fraction and total of fractionated water (HPI + HPO) were ±8.9%, ±3.4%, and ±0.5% in winter, rainy, and summer season, respectively. This weight surplus may have come from resin bleeding during the elution process (Leenheer, 1981). While the loss of DOC mass might be occur during elution process (Srimuang, 2011). The percent different obtained from this results were acceptable. Day *et al*. (1991) and Marhaba and Pipada (2000) stated that the level of inaccuracy in the range of 10-15% was acceptable for the fractionation technique. The percent different were reported at 8% - 12% by Croue *et al*. (1993), 9.7% by Janhom (2006) and 5.8% by Srimuang (2011).

The results of fractionation showed that the DOC concentration of HPI fraction was higher than those in HPO fraction in all season. This indicates that the hydrophilic fraction was the major fraction in this water source. The obtained result was related to the studied of Day *et al*. (1991) which reported that hydrophilic fraction were higher than hydrophobic fraction in almost natural waters.

Table 5.1 Characteristics of DOM fractions and their THMFP in raw surface water

Season	Parameter	Fractionated water		HPI + HPO	Unfractionated water	%Diff
		HPI	HPO			
Winter	DOC (mg/L)	1.24	0.94	2.18	1.98	±8.9
	Mass DOC (mg)	3.73	2.80	6.53	5.95	-
	% Mass DOC	57	43	100	-	-
	THMFP (μg/L)	127	194	321	265	-
	% THMFP	40	60	100	-	-
Rainy	DOC (mg/L)	1.26	0.99	2.25	2.32	±3.4
	Mass DOC (mg)	3.78	2.96	6.74	6.97	-
	% Mass DOC	56	44	100	-	-
	THMFP (μg/L)	129	247	376	341	-
	% THMFP	34	66	100	-	-
Summer	DOC (mg/L)	1.18	0.99	2.17	2.18	±0.5
	Mass DOC (mg)	3.55	2.96	6.51	6.54	-
	% Mass DOC	55	45	100	-	-
	THMFP (μg/L)	117	232	350	316	-
	% THMFP	34	66	100	-	-

In general, the result of fractionation process was reported in term of percent mass distribution in each fraction. Therefore, percent mass DOC distribution of DOM fractions in each season were determined and illustrated in Figure 5.1.

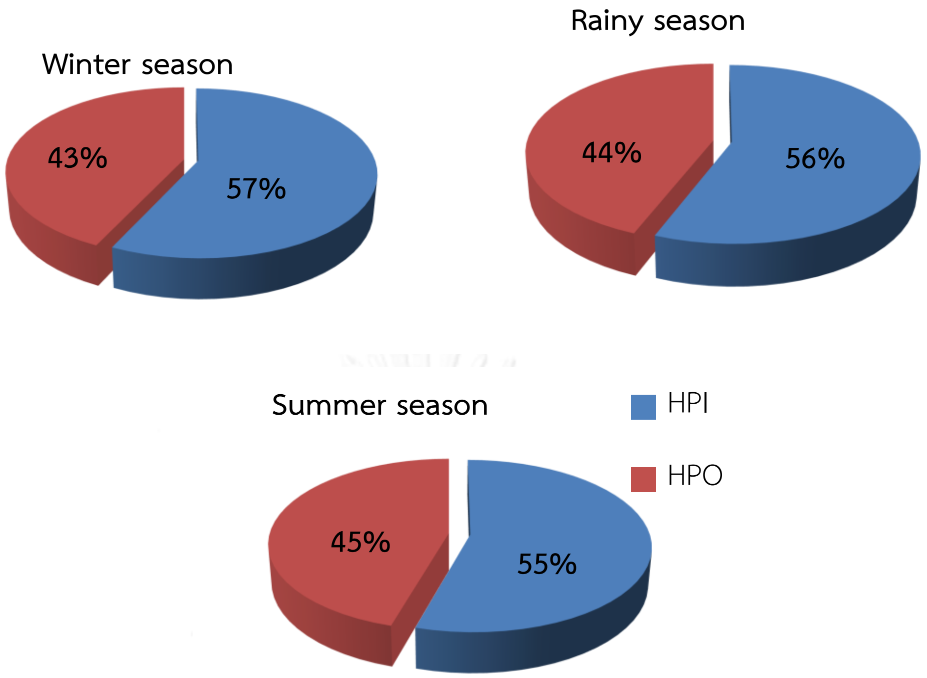


Figure 5.1 Percent mass DOC distribution in each DOM fraction of raw surface water in winter, rainy and summer season

The results in Figure 5.1 showed that the HPI fraction was found to have percent mass DOC distribution higher than HPO fraction in all season. Percent mass DOC distribution of HPI fraction were 57%, 56% and 55% in raw surface water in winter, rainy and summer season, respectively. While those of HPO fraction were 43%, 44% and 45% in raw surface water in winter, rainy and summer season, respectively. The results indicate that the DOM in raw surface water had more HPI fraction than HPO fraction. The DOC mass distribution of raw surface water obtained in this studied was compared with that distribution of other water source as shown in Table. 5.2

Table 5.2 Percent mass DOC distribution of raw surface water in this study was compared with other water sources

Water source	DOC (mg/L)	Percent distribution		References
		HPI	HPO	
Ang Kaew reservoir, Chiang Mai	2.4	47	53	Homklin,2004
Mae Kuang reservoir, Chiang Mai	2.0	40	60	
Mae Sa river, Chiang Mai	1.8	31	69	
Mae Hia reservoir, Chiang Mai	6.4	51	49	Phumpaisanchai, 2005
Choa Phraya river, Bangkok	4.7	60	40	Panyapinyopol *et al,2005*
U-Tapao canal in rainy season Songkla	10.7	54	46	Inthanuchit,2009
U-Tapao canal in dry season, Songkla	6.9	52	48	
Ping river, Chiang Mai	4.4	58	42	Khutklom, 2013
Ping river in rainy season, Chiang Mai	2.3	56	44	This studied
Ping river in winter season, Chiang Mai	2.0	57	43	
Ping river in summer season, Chiang Mai	2.1	55	45	

The presence of DOM in water source is one of the factors for the THMs formation. Thus, the THMFP test on DOM fractions was conducted. The results of THMFP created from each DOM fraction are shown in Table 5.2. The results showed that THMFP in raw surface water created from HPI fraction were 127, 129 and 117 μg/L in winter, rainy and summer season, respectively. While, those of created from HPO fraction were 194, 247 and 232 μg/L in winter, rainy and summer, respectively. Percent THMFP distribution of DOM fraction in each season is shown in Figure 5.2.

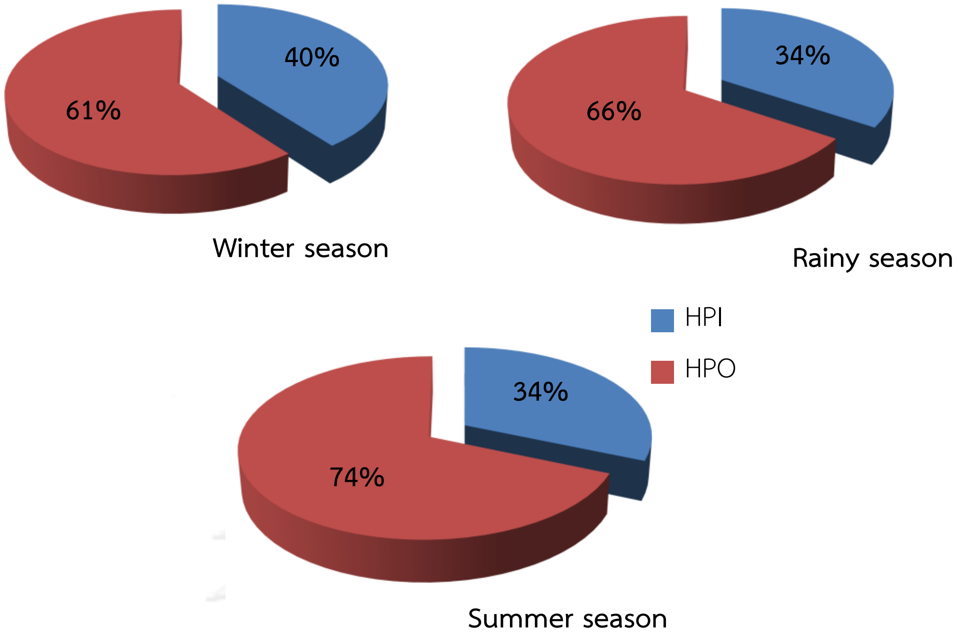


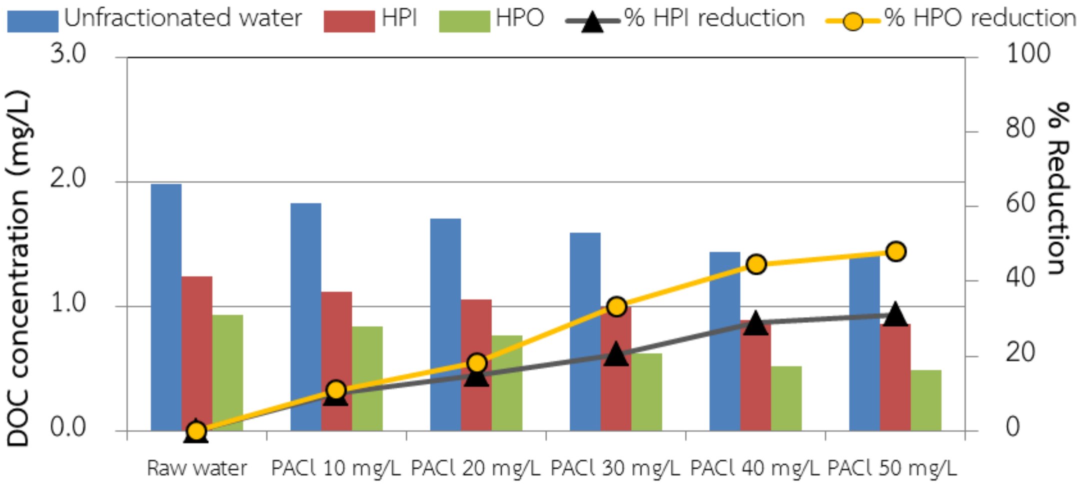
Figure 5.2 THMFP of DOM fraction of raw surface water in winter, rainy and summer season

The results in Figure 5.2 showed that THMFP of HPI fraction were in the range of 34% - 40% while those of HPO fraction were in the range of 60% - 66% in winter, rainy, summer season. From the results, it can be indicated that THMFP created from HPO fraction were higher than those in HPI fraction. The results of THMFP were contrasted with the results of DOC mass distribution. HPO fraction, low mass DOC distribution, was created higher THMFP than HPI fraction, large mass DOC distribution. This indicates that the formation of THMs was not only depended on the quantity of organic matter but also the characteristics of organic matter. From the results, it can be stated that HPO fraction was higher ability to form THMs when contacted with chlorine than HPI fraction. Thus, the HPO fraction should be concerned and reduced from raw surface water by appropriated technique before utilize as raw water supply.

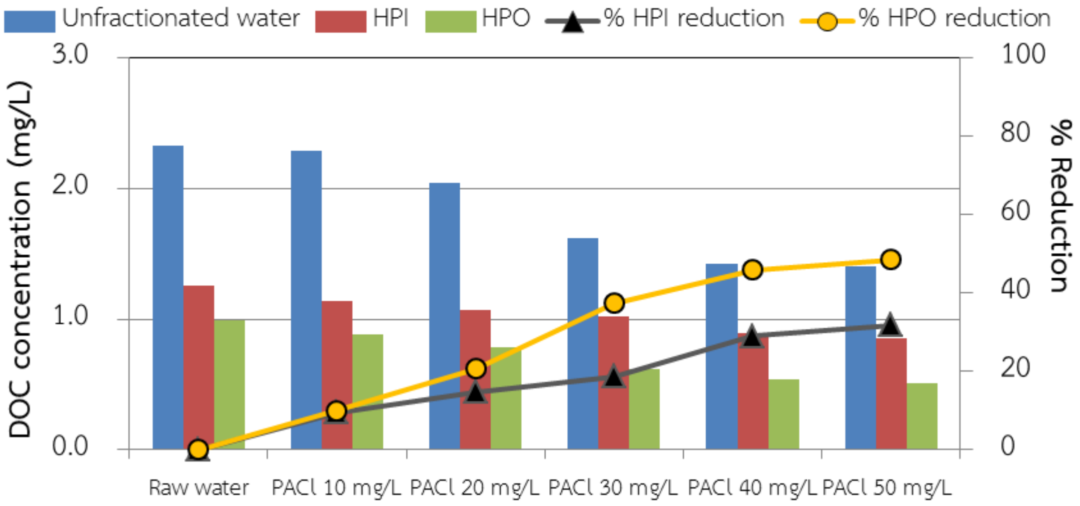
5.3.1.2 Reduction of DOM fractions and their THMFP by coagulation process

Coagulated water at all PACl dosages were collected and fractionated by resin fractionation process. DOM in coagulated water was fractionated into two fraction; HPI and HPO. The reduction efficiency of each DOM fraction in term of DOC concentration by coagulation process was investigated and the results are shown in Figure 5.3 (a) - (c).

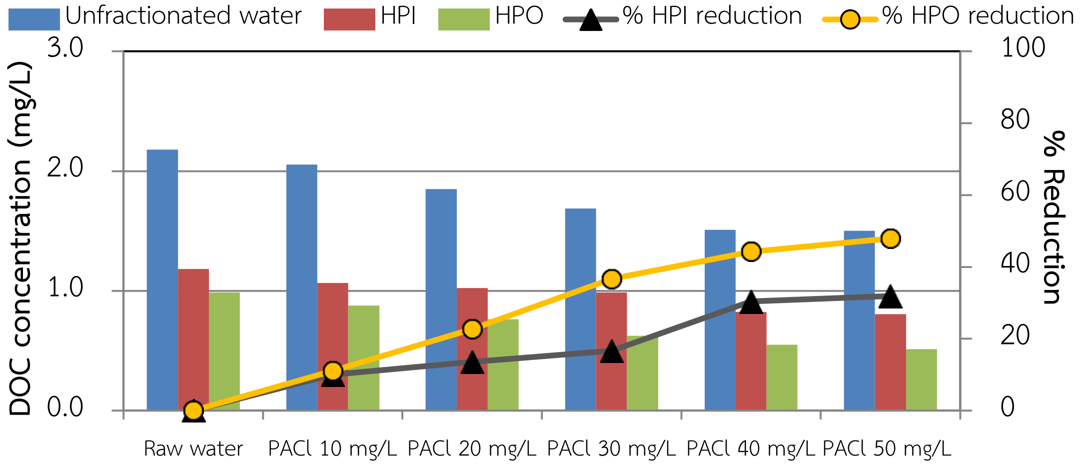
The results from Figure 5.3 showed that the DOC concentration of HPI and HPO fraction were decreased with increasing PACl dosages from 10 mg/L to 50 mg/L. For raw surface water in winter season, the coagulation process with PACl can reduced DOM in term of HPI fraction from 1.24 mg/L in raw surface water to 1.12, 1.06, 0.99, 0.89, and 0.86 mg/L at PACl dosages 10, 20, 30, 40, and 50 mg/L, respectively. While, those of HPO fraction was reduced from 0.94 mg/L in raw surface water to 0.83, 0.77, 0.62, 0.52, and 0.49 mg/L at PACl dosages 10, 20, 30, 40, and 50 mg/L, respectively. The reduction results of raw surface water in rainy and summer season showed the same trends as the results of raw surface water in winter season. The results of coagulation at PACl dosage 10 mg/L showed that percent reduction of HPI and HPO fraction was almost same. However, when using PACl dosage higher than 10 mg/L, percent reduction of HPO fraction was highly increased and higher than those of HPI fraction. This result indicated that HPO fraction was easily removed by coagulation than HPI fraction. The highest percent DOC reduction of HPI and HPO fraction was found at PACl dosages 50 mg/L. The highest percent DOC reduction of HPI fraction were 31%, 32%, and 32% in winter, rainy and summer season, respectively. Whereas, the highest percent DOC reduction of HPO fraction were 47.9%, 48.6%, and 48.0% in winter, rainy, and summer season, respectively.



(a) Winter season



(b) Rainy season

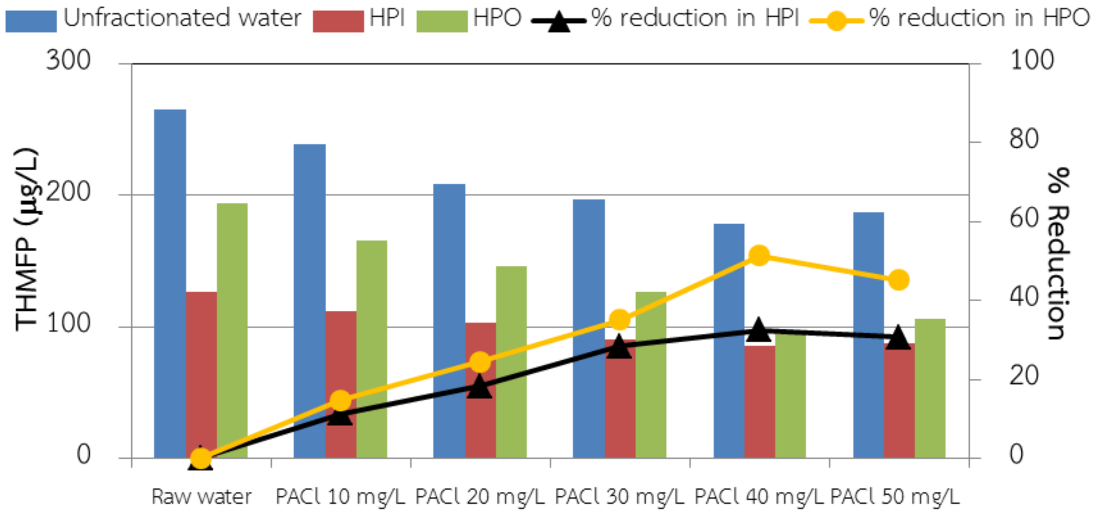


(c) Summer season

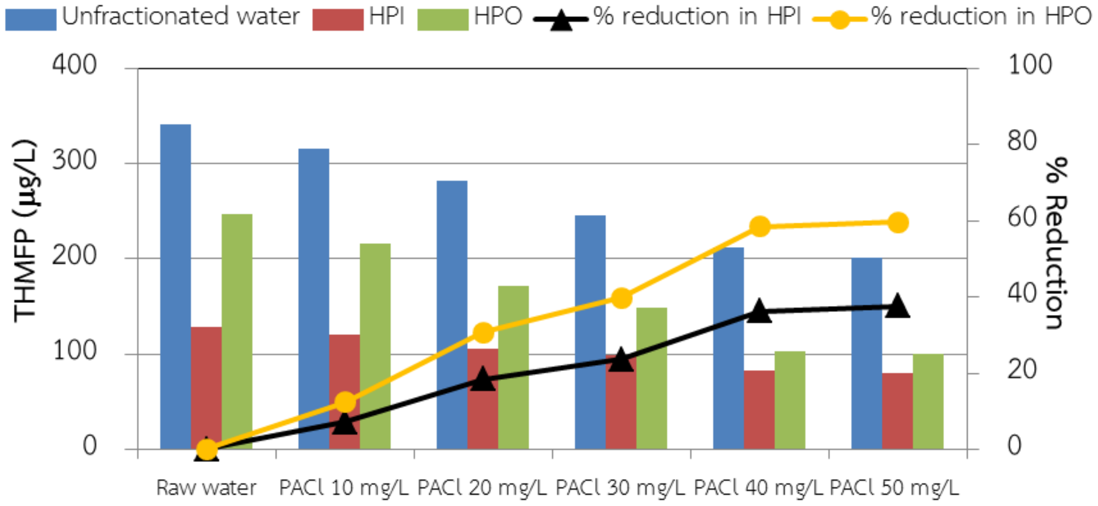
Figure 5.3 Reduction of DOM fraction in term of DOC concentration by coagulation process of raw surface water in (a) winter, (b) rainy, and (c) summer season

From the results, it can be stated that coagulation process with PACl can reduced DOM in term of HPO fraction more than HPI fraction. The obtained results was similar to the results of Srimuang (2011) and Musikavong *et al.* (2013) which reported that PACl coagulation process may easily remove HPO fraction and difficulty to remove HPI fraction. In addition, Marhaba and Pipada (2000); Marhaba and van (2000); Tan *et al*. (2005); Kim *et al*. (2006) and Ji *et al*. (2008) reported that hydrophobic fraction (high molecular weight organic matter) was easily reduced by coagulation than hydrophilic fraction (low molecular weight organic matter).

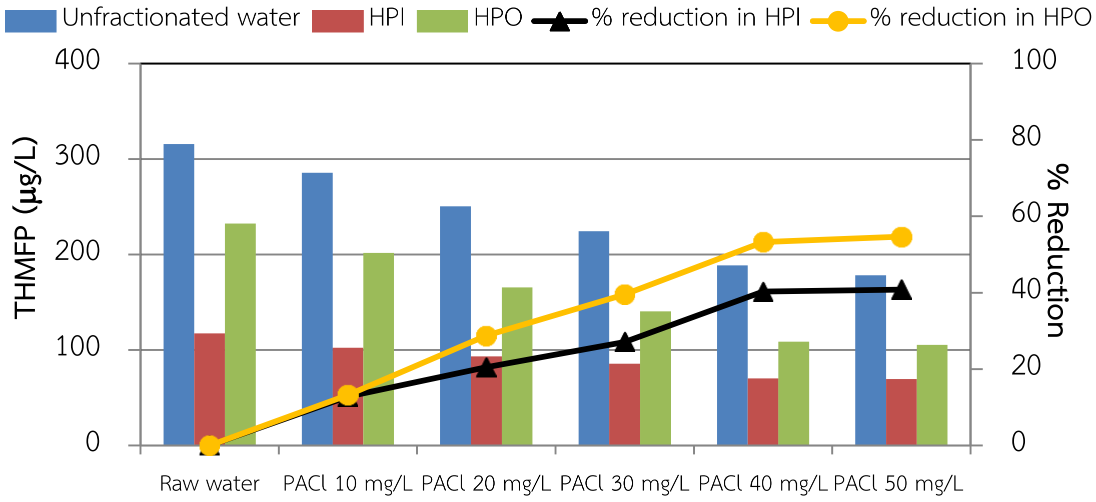
THMFP in each DOM fraction of coagulated water was investigated and the reduction of THMFP by coagulation process was determined. The reductions of THMFP in each DOM fraction by coagulation process at various PACl dosages are shown in Figure 5.4 (a) - (c).



(a) Winter season



(b) Rainy season



(c) Summer season

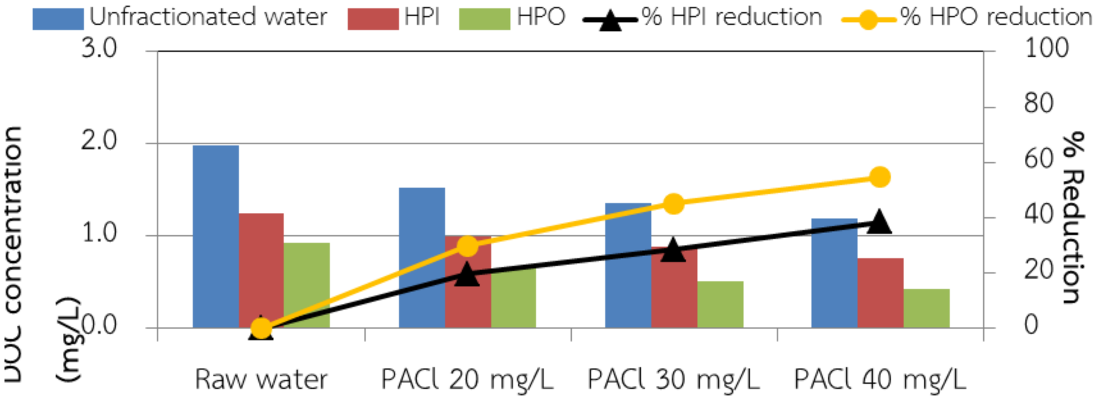
Figure 5.4 Reduction of THMFP in DOM fractions by coagulation process of raw surface water in (a) winter, (b) rainy, and (c) summer season

The results in Figure 5.4 showed that the formation potential of THMs in HPI and HPO fraction were decreased with increasing of PACl dosages from 10 to 50 mg/L which related to the reduction of DOM in term of DOC concentration in the results of previous section. The trends of the reduction were the same for raw surface water in all season. In winter season, the coagulation process with PACl can decreased THMFP of HPI fraction from 127 μg/L in raw surface water to 112, 103, 91, 85, and 88 μg/L at PACl dosage 10, 20, 30, 40 and 50 mg/L, respectively while those of HPO fraction, it was decreased from 194 μg/L in raw surface water to 165, 146, 126, 95, and 106 μg/L, respectively. The highest percent reduction of THMFP in HPI and HPO fraction of raw surface water in winter season was found at 32.5%, and 51.3%, respectively, at PACl dosage 40 mg/L. For the raw surface water in rainy and summer season, the highest percent reduction of THMFP in all water samples were found at PACl dosage 50 mg/L. However, it was slightly increase when compared with those obtained at PACl dosage 40 mg/L. Percent reduction of THMFP in HPI and HPO fraction of rainy season by coagulation at PACl dosage 40 mg/L were 36.3% and 58.5%, respectively. While those in summer season were 40.3% and 54.6%, respectively.

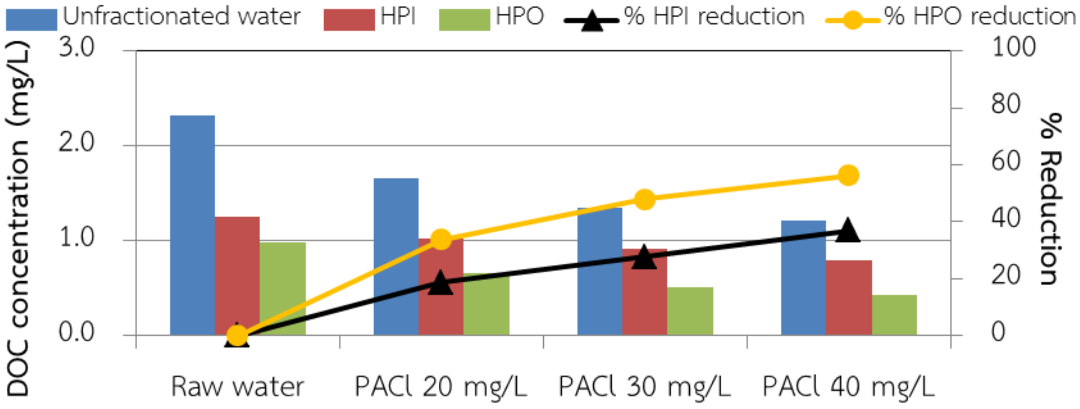
From the obtained results, it was found that the THMFP in HPO fraction were higher than those in HPI fraction in all conditions. This can be indicated that DOM in term of HPO fraction was higher ability to create THMs than DOM in term of HPI fraction. In addition, the results of reduction by coagulation process showed that coagulation with PACl can reduced THMFP in HPO fraction higher than those in HPI fraction. This results was well corresponded with the study of Srimuang (2011) and Musikavong *et al.* (2013) which reported that THMFP of HPO fractions was reduced by coagulation more than THMFP of hydrophilic fractions. This result confirmed that the coagulation process with PACl can be utilized for reduced HPO fraction which found to have high ability to form THMs from this water source.

5.3.1.3 Reduction of DOM fractions and their THMFP by in-line coagulation with ceramic membrane filtration

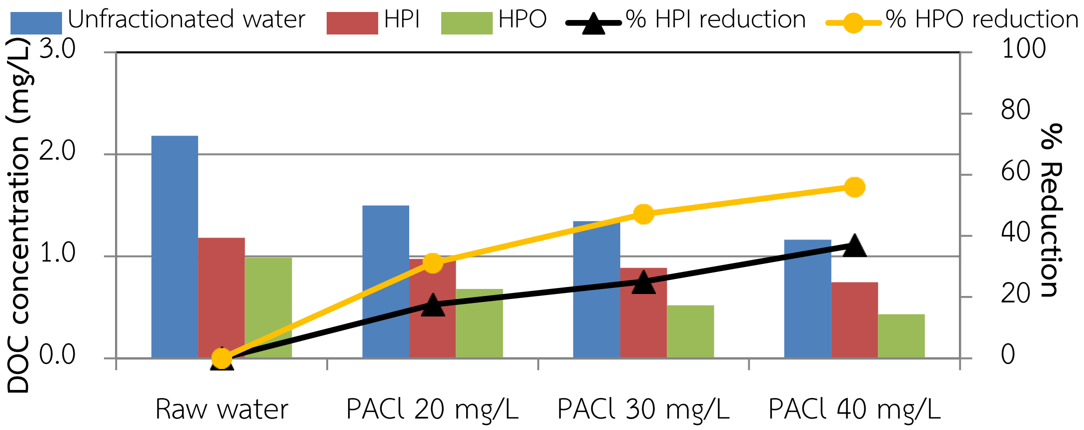
The filtrated water from the in-line coagulation with ceramic membrane filtration at PACl dosages 20, 30 and 40 mg/L were collected and fractionated by using resin fractionation process. DOM in filtrated water was fractionated into two fraction; HPI and HPO. The reduction efficiency of each DOM fraction in term of DOC concentration was investigated and illustrated in Figure 5.5 (a) - (c).



(a) Winter season



(b) Rainy season

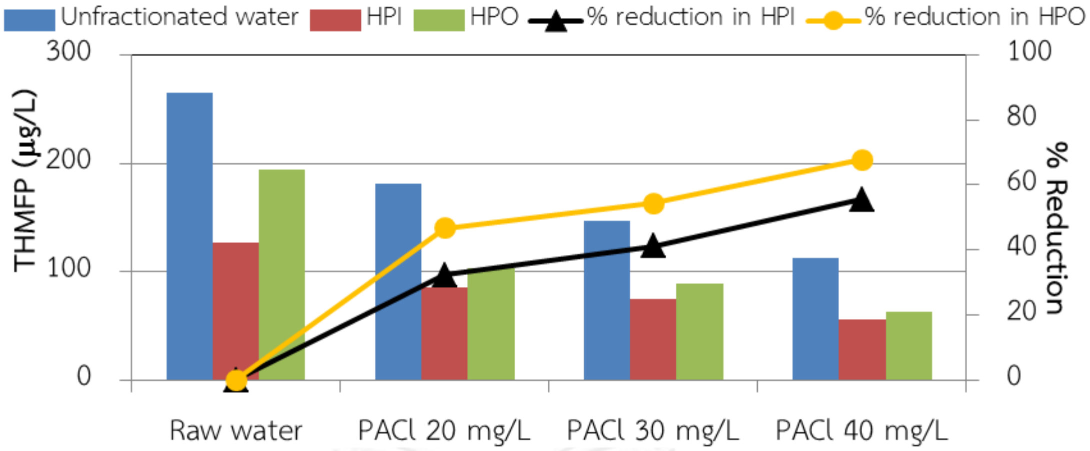


(c) Summer season

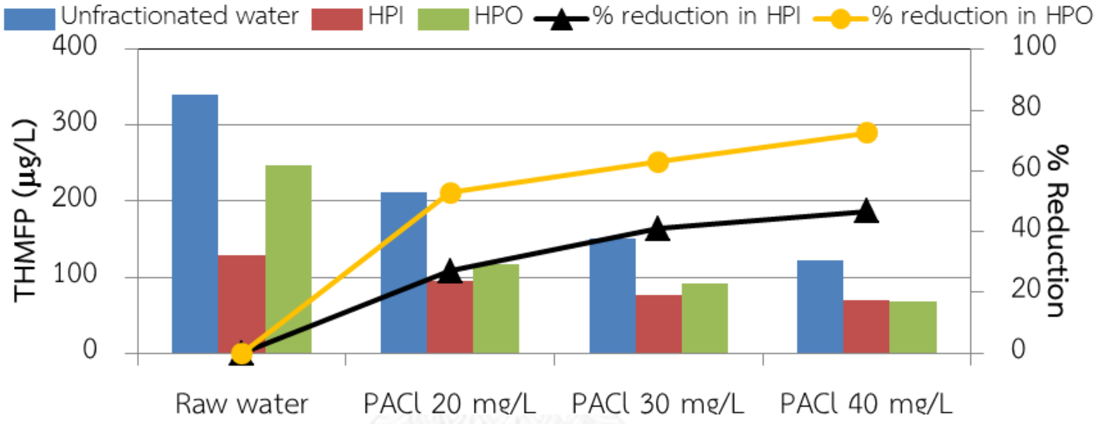
Figure 5.5 Reduction of DOM fractions in term of DOC concentration by in-line coagulation with ceramic membrane filtration at various PACl dosages in (a) winter, (b) rainy, and (c) summer season

From the results in Figure 5.5, it was found that the in-line coagulation with ceramic membrane filtration can reduced DOM fraction both in HPI and HPO fractions. The DOC concentration in filtrated water was decreased with increasing PACl dosages from 20 mg/L to 40 mg/L. The trends of reduction were the same for raw surface water in winter, rainy and summer season. The highest DOC reduction was found at PACl dosage 40 mg/L in raw surface water of all season. The in-line coagulation with ceramic membrane filtration at PACl dosages 20, 30, and 40 mg/L can decreased DOC concentration in HPI fraction of raw surface water in rainy season from 1.26 mg/L to 1.02, 0.91, and 0.80 mg/L, respectively, while those in HPO fraction, it was decreased from 0.99 mg/L to 0.65, 0.51, and 0.43 mg/L, respectively. The highest percent DOC reduction in HPI fractions were 38.5%, 36.9% and 37.0% in winter, rainy and summer season, respectively, which found at PACl dosage 40 mg/L. While those of HPO fraction were 54.8%, 56.3% and 56.1%, in winter, rainy and summer season, respectively. From the results, it can be concluded that in-line coagulation with ceramic membrane filtration can be reduced DOM mostly in term of HPO fraction.

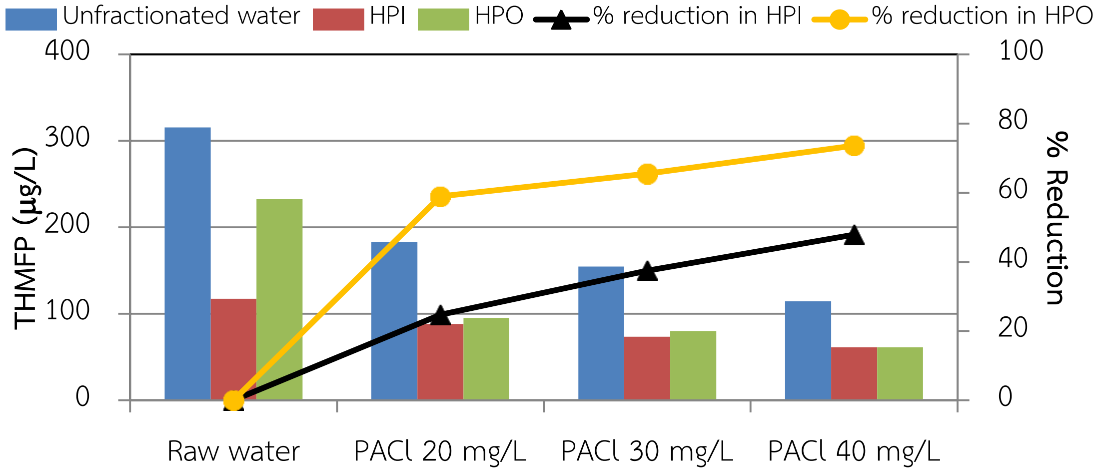
The formation potential of THMs in each DOM fraction of filtrated water was studied and the reduction of THMFP by in-line coagulation with ceramic membrane filtration was also investigated. The reductions of THMFP in each DOM fraction of filtrated water at various PACl dosages are shown in Figure.5.6 (a) - (c).



(a) Winter season



(b) Rainy season



(c) Summer season

Figure 5.6 Reduction of THMFP in DOM fraction by in-line coagulation with ceramic membrane at various PACl dosages of raw surface water in (a) winter, (b) rainy, and (c) summer season

From the results of THMFP in Figure 5.6, it was found that in-line coagulation with ceramic membrane filtration can decreased THMFP both in HPI and HPO fractions. THMFP in DOM fraction was decreased with increasing PACl dosages. The trends of reduction of THMFP in DOM fraction were the same for raw surface water in all season. Percent reduction of THMFP in HPI fraction at PACl dosage 40 mg/L were 55.6%, 46.7%, and 47.9% in winter, rainy, and summer season, respectively. While, those of HPO fraction were 67.8%, 72.6%, and 73.6%, respectively. From the results, it was found that THMFP in HPO fraction was mostly reduced by in-line coagulation with ceramic membrane filtration. This result was related to the higher percent reduction of DOM in term of HPO fraction as shown in Figure.5.5.

5.3.1.4 The reduction efficiency of DOM fractions and their THMFP by in-line coagulation with ceramic membrane filtration and conventional coagulation

The reduction efficiency of DOM fraction (HPI and HPO fraction) and their THMFP by conventional coagulation and in-line coagulation with ceramic membrane filtration were investigated. The results in previous chapter indicated that the optimal PACl dosage of conventional coagulation and in-line coagulation with ceramic membrane filtration was 40 mg/L. Thus, the reduction of DOM fraction and their THMFP by conventional coagulation with PACl 40 mg/L and in-line coagulation with ceramic membrane filtration at PACl 40 mg/L were considered. The results are illustrated in Table 5.3.

Table 5.3 Percent reduction of DOM fraction and their THMFP by conventional coagulation and in-line coagulation with ceramic membrane filtration

Processes	Optimal condition	Seasonal	Reduction efficiency (%)				Increasing in reduction efficiency (%)			
			HPI		HPO		HPI		HPO	
			DOC	THMFP	DOC	THMFP	DOC	THMFP	DOC	THMFP
Conventional coagulation	PACl dosage 40 mg/L	Rainy	29	36	46	59	-	-	-	-
Inline coagulation with CM filtration			37	47	56	73	8	11	10	14
Conventional coagulation	PACl dosage 40 mg/L	Winter	29	33	45	51	-	-	-	-
Inline coagulation with CM filtration			39	56	55	68	10	23	10	17
Conventional coagulation	PACl dosage 40 mg/L	Summer	30	40	44	53	-	-	-	-
Inline coagulation with CM filtration			37	48	56	74	7	8	12	21

The results in Table 5.3 showed that the in-line coagulation with ceramic membrane filtration was provided the higher percent reduction of DOC and THMFP in HPI and HPO fraction than conventional coagulation in all season. It might due to the fact that the pore size of ceramic membrane was 0.1 μm which lower than the pore size of filter paper (0.45 μm) used in conventional coagulation. From the obtained results, the using of in-line coagulation with ceramic membrane filtration can increased the percent reduction of DOC and THMFP in HPI fraction in the range of 8-10% and 8-23%, respectively. Whereas, those in HPO fraction, it was increased in the range of 10-12% and 14-21%, respectively. From the results, it was found that the increasing of percent reduction of THMFP by using in-line coagulation with ceramic membrane filtration was higher than those of DOC concentration. This indicates that DOM which removed by in-line coagulation with ceramic membrane filtration had a high ability to form THMs.

5.3.2. Characterization of DOM into six DOM fractions

For the better understanding of DOM characteristics and their THMFP of DOM fractions, the resin fractionation with three different resins was utilized to fraction bulk DOM into six DOM fractions. Water samples including raw surface water and filtrated water from in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L were collected and fractionated. Fractionated water was analyzed for DOM concentration by measuring DOC concentration and THMFP. Percent distribution of DOC and their THMFP in each DOM fraction of raw surface water and filtrated water were investigated. Furthermore, the reduction efficiency of each DOM fraction by in-line coagulation with ceramic membrane filtration was investigated.

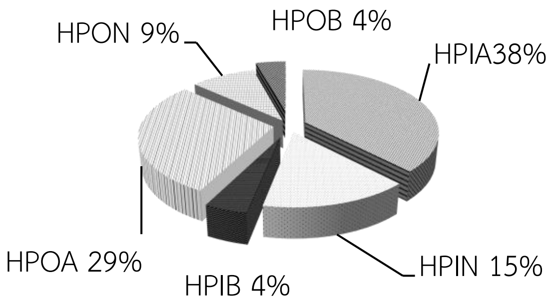
5.3.2.1 Characteristics of six DOM fractions and their THMFP in raw surface water

Raw surface water was collected two times in July and December 2012 for represent DOM in rainy and dry season. The results of six DOM fractionation of raw surface water in rainy and dry season are illustrated in Table 5.4.

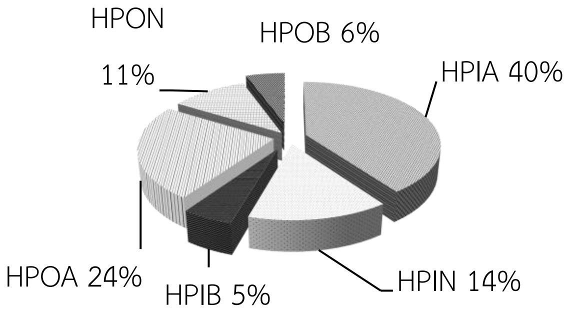
Table 5.4 Characteristics of six DOM fractions of raw surface water in rainy and dry season

Season	Parameter	Fractionated water						Total	Unfractionated water	%Diff
		HPIA	HPIN	HPIB	HPOA	HPON	HPOB			
Rainy	DOC (mg/L)	0.89	0.36	0.10	0.69	0.22	0.10	2.363	2.132	±9.8
	Mass DOC (mg)	2.68	1.09	0.31	2.06	0.65	0.30	7.09	6.4	
	% Mass DOC	38	15	4	29	9	4	100		
	THMFP (ug/L)	81.8	56.1	65.8	89.4	25.1	68.5	386.7	325.0	
	% THMFP	21	15	17	23	6	18			
Dry	DOC (mg/L)	0.903	0.323	0.117	0.542	0.241	0.125	2.251	2.041	±9.3
	Mass DOC (mg)	2.71	0.97	0.35	1.63	0.72	0.38	6.76		
	% Mass DOC	40	14	5	24	11	6	100		
	THMFP (ug/L)	82.9	52.4	75.0	76.4	34.1	73.1	393.9	275.1	
	% THMFP	21	13	19	19	9	19			

The results in Table 5.4 showed that percent different between water samples before fraction and total of fractionated water were ±9.8%, and ±9.3% in rainy, and dry season, respectively. This weight surplus may have come from resin bleeding during the elution process (Leenheer, 1981). From the review of literature, the percent different obtained from this results was acceptable. Day *et al*. (1991) and Marhaba and Pipada (2000) stated that the level of inaccuracy in the range of 10-15% was acceptable for the fractionation technique. The percent different were reported at 8% - 12% by Croue *et al*. (1993) and 9.7% by Janhom (2006). The results in Table. 5.4 showed the DOC concentration and THMFP on each DOM fraction of raw surface water. However, the fractionation was commonly reported in term of percent mass DOC distribution. Thus, the percent mass DOC distribution of each fraction of raw surface water was determined and illustrated in Figure 5.7.



(a) Rainy season



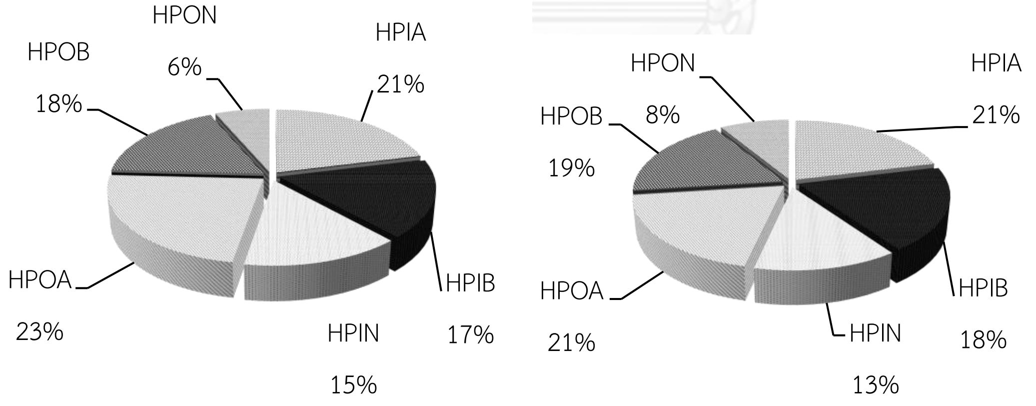
(b) Dry season

Figure 5.7 Percent mass DOC distribution of each DOM fraction of raw surface water in rainy and dry season

From the Figure 5.7, percent mass DOC distribution of each DOM of raw surface water in rainy season from high to low were; HPIA, HPOA, HPIN, HPON, HPIB and HPOB fractions, respectively. While, those in dry season were; HPIA, HPOA, HPIN, HPON, HPOB and HPIB fractions, respectively. The total of HPI fractions (HPIA + HPIB + HPIN) in rainy and dry season were 57% and 59%, respectively. Whereas, the total of HPO fractions (HPOA + HPOB + HPON) in rainy and dry season were 43% and 41%, respectively. It can be indicated that DOM in raw surface water had more HPI fraction than HPO fraction which related to the results of DOM fractionation into two fractions from the previous section.

The hydrophilic acid (HPIA) were found at high percent distribution (38% and 40% in rainy and dry season) followed by hydrophobic acid (HPOA) at percent distribution 29% and 24% in rainy and dry season, respectively. These two fractions were found to be the highest percent distribution of hydrophilic and hydrophobic group. The percent distribution of hydrophilic neutral (HPIN) and hydrophobic neutral (HPON) were in a range of 9% - 15%. While the hydrophilic base (HPIB) and hydrophobic base (HPOB) were found at very low percent distribution (4% - 6%). The results indicated that the HPIA and HPOA fractions were the two main fractions in this water source. Whereas, the HPIB and HPOB fractions were found at low percent distribution in this water source.

The ability of each DOM fraction to form THMs was studied by conducted the THMFP test in each DOM fraction. The results of THMFP concentration in each fraction are shown in Table 5.4. While percent distribution of THMFP in each fraction were summarized and are illustrated in Figure 5.8.



Rainy season

Dry season

Figure 5.8 Percent THMFP distribution in DOM fractions of raw surface water in rainy and dry season

From the Figure 5.8, the percent distribution of THMFP in each DOM fraction of raw surface water in rainy season from high to low were; HPOA, HPIA, HPOB, HPIB, HPIN, and HPON fractions, respectively. While, those in dry season were; HPOA, HPIA, HPOB, HPIB, HPIN, and HPON fractions, respectively. The two main precursors of THMs were found to be the HPOA and HPIA fractions. Both the HPOA and HPIA fractions were the two main sources of THMs among hydrophobic and hydrophilic species. These results agree with the results of Chang *et al*. (2001), which demonstrated that the HPOA fraction was the greatest contributor of precursors of THMs. The high percent distribution of THMFP in both two fractions was related to the high percent DOC distribution of these two fractions. It can be stated that the formation of THMFP was depended on the concentration of precursors (DOC concentration). However, the percent distribution of THMFP of HPOB and HPIB fractions were high in the range of 17% - 19% even though their percent DOC distribution was lower at 4% - 6% (mass DOC about 0.3 mg). From the results, it can be stated that the formation of THMs of each DOM fraction does not only depend on the concentration of a precursor (DOC concentration) but also the characteristics of DOM fraction.

5.3.2.2 Reduction of DOM fractions and their THMFP by in-line coagulation with ceramic membrane filtration

For investigating the efficiency of in-line coagulation with ceramic membrane filtration to reduce DOM fractions and their THMFP, the filtrated water at PACl dosage 40 mg/L was collected and fractionated into six DOM fractions. The results of DOM fractionation of filtrated water are shown in Table 5.6.

The results in Table 5.5 showed that percent different between water samples before fraction and total of fractionated water were ±9.4%, and ±8.9% in rainy, and dry season, respectively. This weight surplus may have come from resin bleeding during the elution process (Leenheer, 1981). From the review of literature, the percent different obtained from this results was acceptable. Day et al. (1991) and Marhaba and Pipada (2000) stated that the level of inaccuracy in the range of 10-15% was acceptable for the fractionation technique. The percent different were reported at 8% - 12% by Croue *et al*. (1993) and 9.7% by Janhom (2006).

Table 5.5 Characteristics of six DOM fractions of filtrated water in rainy and dry season

Season	Parameter	Fractionated water						Total	Unfractionated water	%Diff
		HPIA	HPIN	HPIB	HPOA	HPON	HPOB			
Rainy	DOC (mg/L)	0.45	0.23	0.08	0.22	0.18	0.05	1.26	1.10	±9.4
	Mass DOC (mg)	1.36	0.69	0.25	0.65	0.53	0.16	3.65	3.31	
	% Mass DOC	37	19	7	18	15	4	100		
	THMFP (mg/L)	51	41	51	40	21	36	240	104	
	% THMFP	21	17	21	17	9	15			
Dry	DOC (mg/L)	0.54	0.21	0.10	0.21	0.19	0.08	1.33	1.21	±8.9
	Mass DOC (mg)	1.61	0.63	0.29	0.7	0.56	0.25	4.04		
	% Mass DOC	40	16	7	17	14	6	100		
	THMFP (mg/L)	60	43	63	47	31	56	299	123	
	% THMFP	20	14	21	16	10	19			

The results in Table 5.5 showed the DOC and THMFP concentration of each DOM fraction of filtrated water. However, the fractionation was commonly reported in term of percent mass DOC distribution. Thus, the percent mass DOC distribution of each fraction of filtrated water in rainy and dry season were determined and illustrated in Figure 5.9.

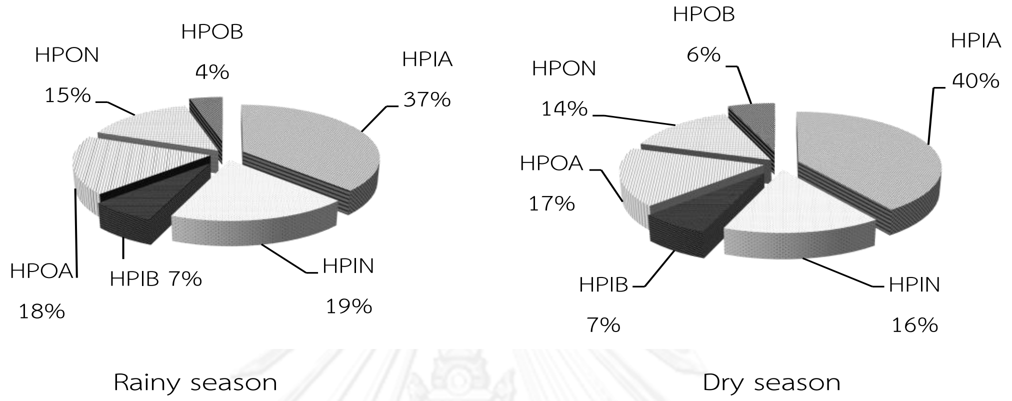


Figure 5.9 Percent DOC distribution of each DOM fraction of filtrated water at PACl dosage 40 mg/L in rainy and dry season

From the Figure 5.9, percent mass DOC distribution of each DOM fraction of filtrated water in rainy season from high to low were; HPIA, HPIN, HPOA, HPON, HPIB and HPOB fractions, respectively. While, those in dry season were; HPIA, HPOA, HPIN, HPON, HPOB and HPIB fractions, respectively. The total of HPI fractions (HPIA + HPIB + HPIN) in rainy and dry season were 63%. Whereas, the total of HPO fractions (HPOA + HPOB + HPON) in rainy and dry season were 37%. It can be indicated that DOM in filtrated water had more HPI fraction than HPO fraction. When compared the percent DOC distribution of filtrated water with those in raw water, it was found that the percent DOC distribution in HPI of filtrated water was higher than those in raw surface water. So, it can be indicated that HPO fraction was highly reduced by in-line coagulation with ceramic membrane filtration.

The hydrophilic acid (HPIA) was found at high percent distribution (37% and 40% in rainy and dry season). The results indicated that the HPIA fraction was the main fraction in filtrated water. While, the HPOA fraction, which found in high percent DOC distribution in raw surface water (29% and 24%), was found in the lower percent distribution at 18% and 17% in rainy and dry season, respectively. This indicates that in-line coagulation with ceramic membrane filtration can reduce DOM mostly in term of HPOA fraction. The percent distribution of hydrophilic neutral (HPIN) and hydrophobic neutral (HPON) were in a range of 14% - 19%. The hydrophilic base (HPIB) and hydrophobic base (HPOB) were lower percent distribution (4% - 7%).

The ability of each DOM fraction to form THMs was investigated by measuring THMFP of each DOM fraction. The results of THMFP concentration of each DOM fraction are reported in Table 5.5. While percent THMFP distribution in DOM fraction of filtrated water at PACl dosage 40 mg/L are shown in Figure 5.10

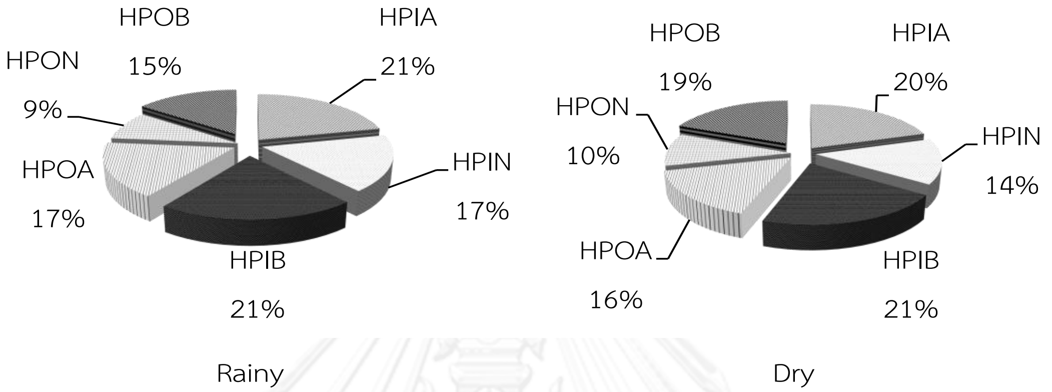


Figure 5.10 Percent THMFP distribution of DOM fractions of filtrated water at PACL dosage 40 mg/L in rainy and dry season

From the Figure 5.10, percent distribution of THMFP of DOM fraction of filtrated water in rainy season from high to low were; HPIA, HPOA, HPIN, HPON, HPOB, and HPIB fractions, respectively. While, those in dry season were; HPIA, HPOA, HPIN, HPON, HPOB, and HPIB fractions, respectively. The main precursor for THMs in filtrated water was HPIA and HPOA fractions both in rainy and dry season. The HPIA and HPOA fraction were the two main precursors of THMs among hydrophobic and hydrophilic species in filtrated water. While the HPOB and HPIB fractions were lower THMFP distribution at (4% - 6%). This indicates that the formation potential of THMs from HPOB and HPIB fraction was highly reduced by in-line coagulation with ceramic membrane filtration.

The reduction efficiency of in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L on each DOM fraction was investigated from the reduction of DOC concentration and THMFP. Table 5.6 and 5.7 summarized the mass DOC and THMFP concentration of each DOM fraction of raw surface water and filtrated water in rainy and dry season.

Table 5.6 The mass DOC and THMFP concentration of raw surface water and filtrated water in rainy season

Water samples	Parameter	Before fraction	Fractionated water							%Diff
			HPOA	HPON	HPOB	HPIA	HPIN	HPIB	Total	
Raw water	Mass DOC (mg)	6.4	2.1	0.6	0.3	2.7	1.1	0.3	7.1	±9.8
	THMFP (ug/L)	325	89	25	69	82	56	66	387	
Filtered water	Mass DOC (mg)	3.3	0.6	0.5	0.2	1.4	0.7	0.3	3.7	±9.4
	THMFP (ug/L)	104	40	21	36	51	41	51	240	

Table 5.7 The mass DOC and THMFP concentration of raw surface water and filtrated water in dry season

Water samples	Parameter	Before fraction	Fractionated water							%Diff
			HPOA	HPON	HPOB	HPIA	HPIN	HPIB	Total	
Raw water	Mass DOC (mg)	6.1	1.6	0.7	0.4	2.7	1.0	0.4	6.8	±9.3
	THMFP (ug/L)	275	76	34	73	83	52	75	394	
Filtered water	Mass DOC (mg)	3.6	0.7	0.6	0.3	1.6	0.2	0.1	3.5	±8.9
	THMFP (ug/L)	123	47	31	56	60	43	63	299	

The results from Table 5.6 and 5.7 showed that the in-line coagulation can reduce mass DOC from 6.4 and 6.1 mg/L of raw surface water to 3.3 and 3.6 mg/L in rainy and dry season, respectively. While THMFP in filtrated water was reduced from 325 and 275 μg/L in raw surface water to 104 and 123 μg/L in rainy and dry season, respectively. For each DOM fraction, the results showed that mass DOC and THMFP in each DOM fraction of filtrated water were lower than those of raw surface water. This indicates that in-line coagulation with ceramic membrane filtration can reduced DOM in all fraction. The reduction efficiency of each DOM fractions and their THMFP by in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L was determined and the results are illustrated in Figure 5.11.

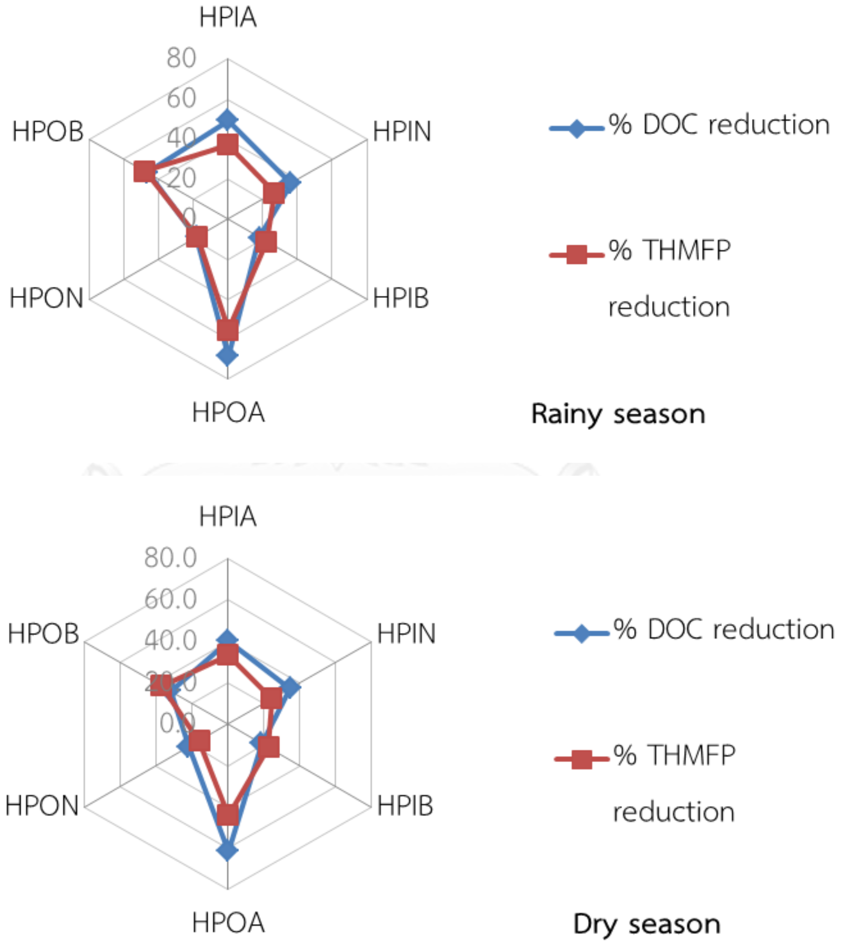


Figure 5.11 Percent reduction of DOC and THMFP in DOM fraction by in-line coagulation with ceramic membrane filtration at PACL dosage 40 mg/L in rainy and dry season

As seen in Figure. 5.11, the rank order of the percent DOC reduction of the six DOM fractions in rainy season, from high to low, was HPOA, HPIA, HPOB, HPIN, HPIB, and HPON. While, those in dry season was HPOA, HPIA, HPIN, HPOB, HPON, and HPIB. The HPOA fraction was the fraction that was highly reduced (68.5% in rainy and 61.3% in dry season) by in-line coagulation with ceramic membrane filtration. This indicates that the in-line coagulation with ceramic membrane filtration can reduce DOM, primarily its HPOA fraction. The high HPOA reduction led to a 55.1% and 44.1% THMFP reduction of this fraction in rainy and dry season, which was the highest among all fractions. The HPIA fraction was the fraction that was reduced most among the hydrophilic species (49.3% in rainy season and 40.4% in dry season). Marhaba and Van (1999) revealed that the HPIA fraction was one of the most difficult to remove by coagulation. Thus, it can be stated that in-line coagulation with ceramic membrane filtration can be used to enhance the reduction of the HPIA fraction in water. The THMFP reduction of this fraction was 37.2% and 33.4% in rainy and dry season, respectively, which was the highest among the hydrophilic species.

For the HPOB and HPIB fractions, DOC concentration were reduced by 46.5% and 18.3%, respectively in rainy season, and 32.0% and 18.8%, respectively, in dry season by in-line coagulation with ceramic membrane filtration. Marhaba and Van (2000) reported that coagulation could not effectively remove these two fractions from raw water. The use of alum coagulation can reduce HPOB and HPIB fractions from reservoir water by 10.2% and 10.7%, respectively (Janhom, 2006). The results for the HPIB fraction seem to corroborate their statement; however, the high DOC reduction results for the HPOB fraction appear to contradict it. Thus, it can be stated that the combination of in-line coagulation with ceramic membrane filtration can enhance the reduction of the HPOB fraction in water. The THMFP reduction of HPOB and HPIB fractions in rainy season was high at 48.0% and 22.3%, respectively, even though their DOC reductions were lower.

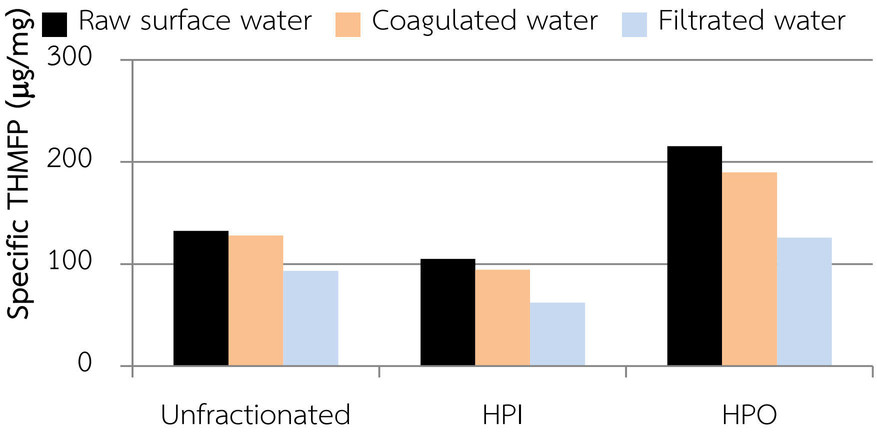
The HPON and HPIN fractions were of least concern as they were present in small quantities in this water source and were relatively inactive with chlorine. These two fractions tend to exhibit low specific THMFP values in comparison to other organic fractions (Marhaba and Van, 2000; Chang et al., 2001; Marhaba and Van, 1999). In-line coagulation with ceramic membrane filtration was able to reduce HPIN and HPON fractions in rainy season by 36.2% and 18.1%, respectively, which led to 26.6% and 17.5% THMFP reduction. Whereas, that in dry season were reduced by 35.0% and 22.0%, respectively, this led to 24.6% and 16.1% THMFP reduction.

Based on these results, the use of in-line coagulation with ceramic membrane filtration can reduce DOM fractions in rainy season as follows: HPOA (68.5%), HPIA (49.3%), HPOB (46.5%), HPIN (36.2%), HPIB (18.3%), and HPON (18.1%). While those in dry season as follows: HPOA (61.3%), HPIA (40.4%), HPIN (35.0%), HPOB (32.0%), HPON (22.0%), and HPIB (18.8%). This indicates that in-line coagulation with ceramic membrane filtration can reduce DOM, primarily its HPOA fraction, which thus reduces the THMFP of this fraction as well. In addition, it was able to effectively reduce the HPOB and HPIB fractions, which are difficult to reduce by conventional coagulation.

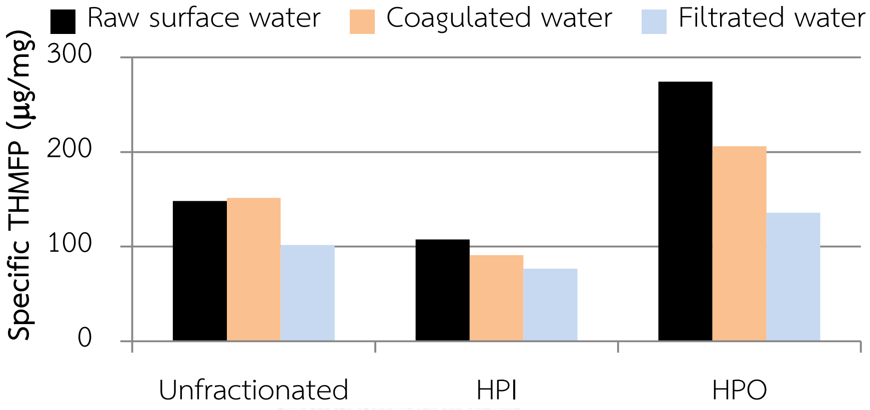
5.3.3 Specific THMFP

Specific THMFP is the ratio between the THMFP of each fraction and its DOC, which was used to determine the reactivity of the organic matter with chlorine to form THMs. Specific THMFP of DOM fraction in all water samples were investigated. Figure 5.12 showed the specific THMFP of unfractionated water, HPI fraction and HPO fraction of raw surface water, coagulated water from conventional coagulation at PACl dosage 40 mg/L and filtrated water from in-line coagulation with ceramic membrane at PACl dosage 40 mg/L for all season.

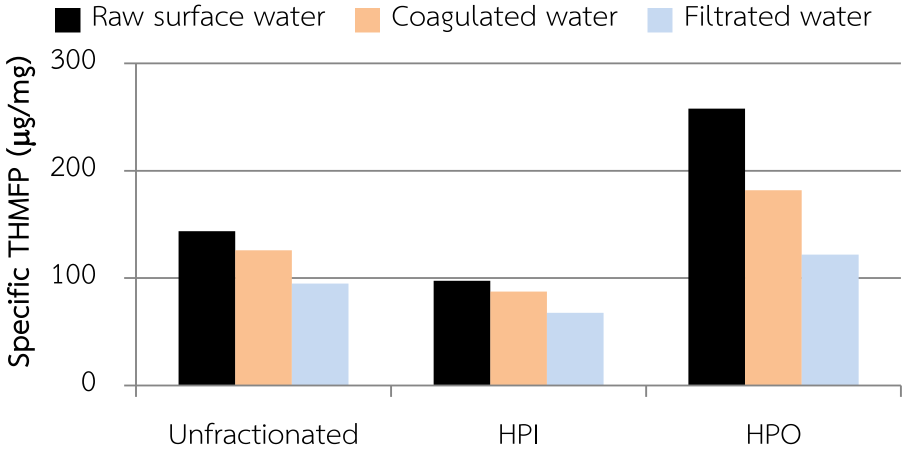
The results in Figure 5.12 showed that specific THMFP of HPO fraction was higher than those of HPI fraction and unfractionated water. This indicated that HPO fraction was the active source and had a high ability to form THMs in this water source. After raw surface water was coagulated and filtrated, specific THMFP of HPO fraction was still higher than those of HPI fraction and unfractionated water of coagulated and filtrated water. This indicated that the HPO fraction was still the active source for the formation of THMs in coagulated and filtrated water. However, specific THMFP of HPO and HPI fractions in coagulated and filtrated water were found to lower than those of raw surface water. This related to the decreasing of THMFP in coagulated and filtrated water. When comparing the decreasing of specific THMFP of HPI and HPO fractions in coagulated and filtrated water, it was found that specific THMFP of HPO fraction was higher decreased than those of HPI fraction. This result supported the results of DOM reduction by coagulation and in-line coagulation with ceramic membrane which found that DOM in term of HPO fraction was highly reduced by these two processes.



(a) Winter season



(b) Rainy season

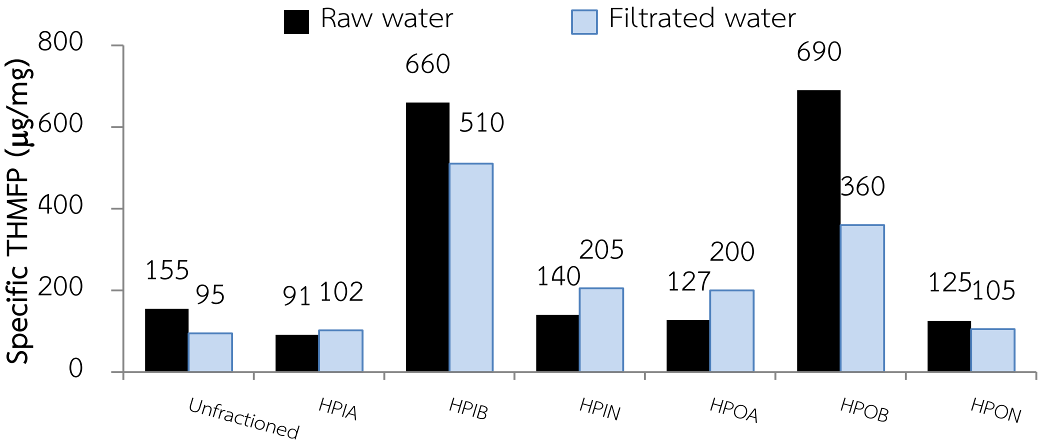


(c) Summer season

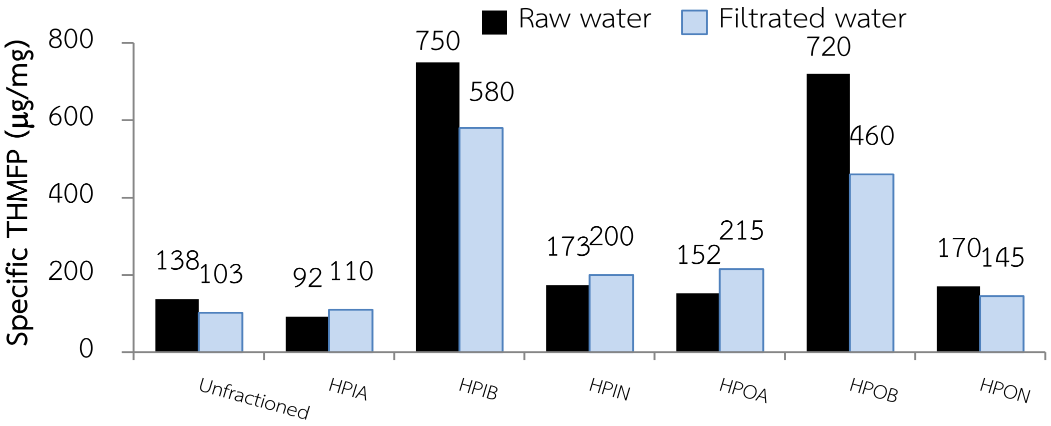
Figure 5.12 Specific THMFP of unfractionated water, HPI fraction and HPO fraction of raw surface water, coagulated water and filtrated water in (a) winter, (b) rainy, and (c) summer season

In addition, when comparing the specific THMFP in coagulated water and filtrated water, it was found that specific THMFP in filtrated water was lower than those in coagulated water. This can be indicated that the residual DOM in filtrated water had a lower ability to form THMs than those in coagulated water.

From the results in Figure 5.12, it was found that specific THMFP or the ability of DOM to form THMs were different. So, the specific THMFP of six DOM fractions was investigated for better understanding of the ability of DOM fraction to form THMs. Figure 5.13 showed the specific THMFP of six DOM fractions of raw surface water and filtrated water from in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L.



(a) Rainy season



(b) Dry season

Figure 5.13 Specific THMFP of DOM fractions of raw surface water and filtrated water in (a) rainy and (b) dry season

As can be seen in Figure 5.13, the specific THMFP of HPIB and HPOB fractions was the highest values among all fractions in both raw surface water and filtrated water. However, the specific THMFP of HPOB and HPIB fractions were decreased from 690 and 660 μg/mg of raw surface water to 360 and 510 μg/mg of filtrated water in rainy season, respectively. Whereas, those of dry season were decreased from 720 and 750 μg/mg of raw surface water to 460 and 580 μg/mg of filtrated water, respectively. This indicates that the in-line coagulation with ceramic membrane filtration can reduce the functional groups of DOM of HPOB and HPIB fractions that had high ability to form THMs. However, the HPOB and HPIB fractions were found to be the two main fractions for THMs formation in filtered water.

For the HPIA and HPOA fraction, the highest percent DOC distribution, the specific THMFP of these two fractions of raw surface water were 91 and 127 μg/mg, respectively, in rainy season. While those of in dry season were 92 and 152 μg/mg, respectively. The results indicated that the HPIA and HPOA fraction, which presence in a higher concentration in this water sources, had a low ability to form THMs. The high concentration of THMFP from these two fractions was caused by the high concentration of precursors. For the HPIN and HPON fraction, the specific THMFP were in the range of 105 - 205 μg/mg in rainy season and 145 - 200 μg/mg in dry season, respectively.

Interestingly, the specific THMFPs of HPIA, HPIN, and HPOA of filtered water were higher than those of raw surface water, even though their THMFP and DOC values in filtered water were lower than those of raw water. This can be explained by the fact that the formation of THMs in water was based on the level and characteristics of DOM. Some groups of DOM that are present in a tiny quantity may create a high level of THMs in water. In-line coagulation with ceramic membrane filtration was able to remove the functional groups of DOM of HPIA, HPIN, and HPOA that had a low ability to form THMs. Thus, the remaining ones had a high ability to form THMs.

Finally, considering the unfractionated water, the raw surface water before the in-line coagulation with ceramic membrane filtration process had a specific THMFP of 155 μg/mg, while that after treatment was decreased to 95 μg/mg in rainy season. While those in dry season were decreased from 138 μg/mg to 103 μg/mg. This result ensures that the in-line coagulation with ceramic membrane can be utilized for reducing the THMFP level of raw surface water.

5.3.4 THMs species

THMs are the disinfection by-products (DBPs) which occur during the chlorination process. During this process, chlorine can react with organic matter or humic substances to form THMs. In general, water supply production commonly used chlorination process for disinfection. Thus, THMs can be occurred in water supply during the disinfection process. Normally, THMs species that occur in water supply are including chloroform (CHCl3), bromodichloromethane (CHBrCl2), dibromochloroform (CHBr2Cl), and bromoform (CHBr3).

THMs species of each DOM fraction (HPI and HPO) for raw surface water, coagulated water at PACl dosage 40 mg/L, and filtrated water by in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L in winter, rainy, and summer season were investigated and illustrated in Figure 5.14 to 5.16, respectively.

The results illustrated that the most dominant THMs species in HPI and HPO fraction was chloroform (CHCl3). Percent distributions of chloroform (CHCl3) were found in the range of 82.6 - 91.1% and 80.6 - 91.8% in HPI and HPO fraction, respectively. The bromodichloromethane was found in the range of 8.9 - 17.4% and 7.5 - 17.8% in HPI and HPO fraction, respectively. For dibromochloroform, it was found only in HPO fraction with a low percent distribution (0.8 - 1.6%). The reduction efficiency of THMs species by coagulation process and in-line coagulation with ceramic membrane filtration was investigated. The results showed that coagulation process with PACl at 40 mg/L can highly reduce chloroform with 34.6% and 54.5% in HPI and HPO fraction, respectively. While, the reduction of bromodichloromethane was lower than 10% both in HPI and HPO fraction.

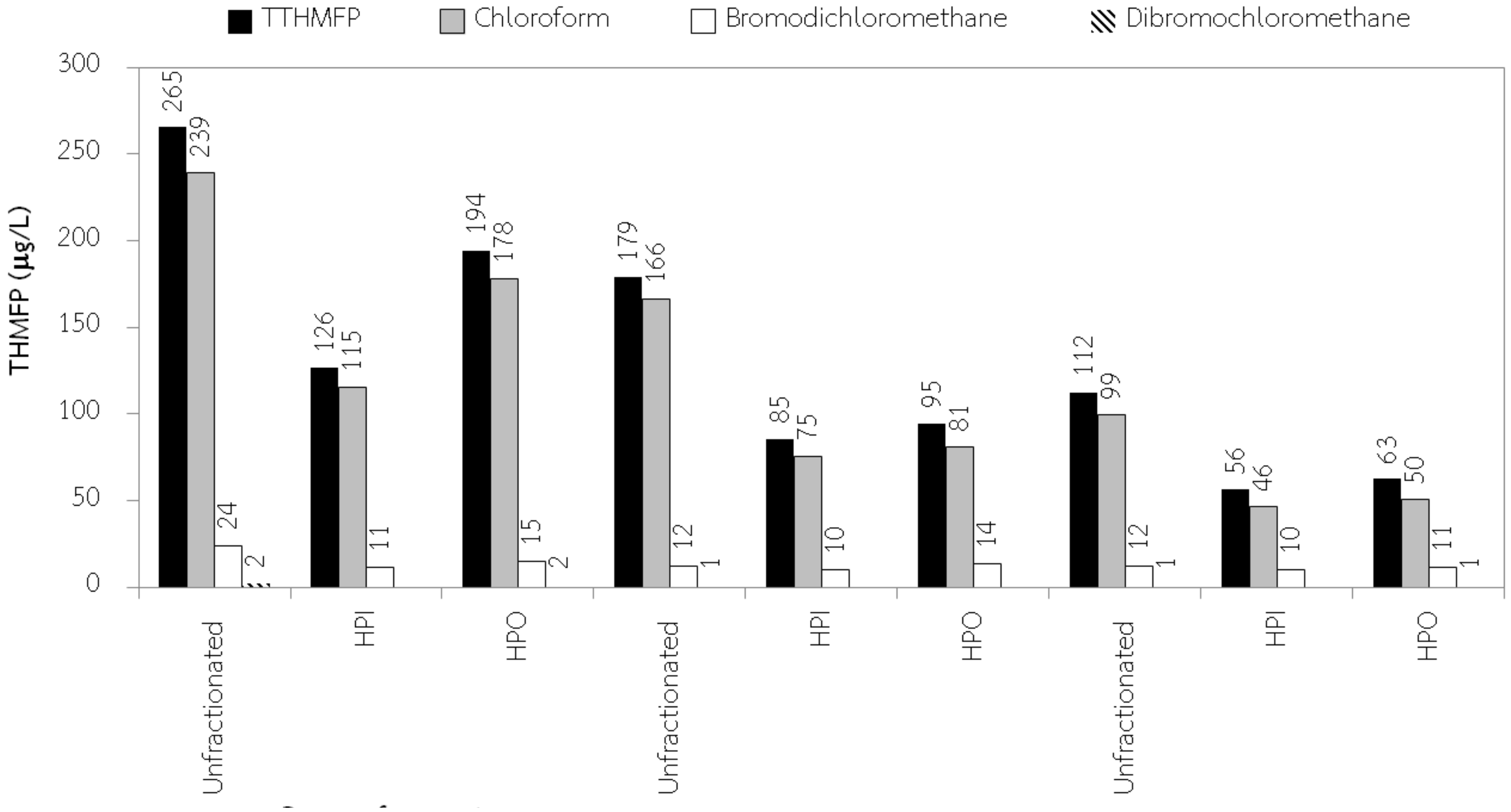


Figure 5.14 THMs species of DOM fractions of raw surface water, coagulated water and filtrated water in winter season

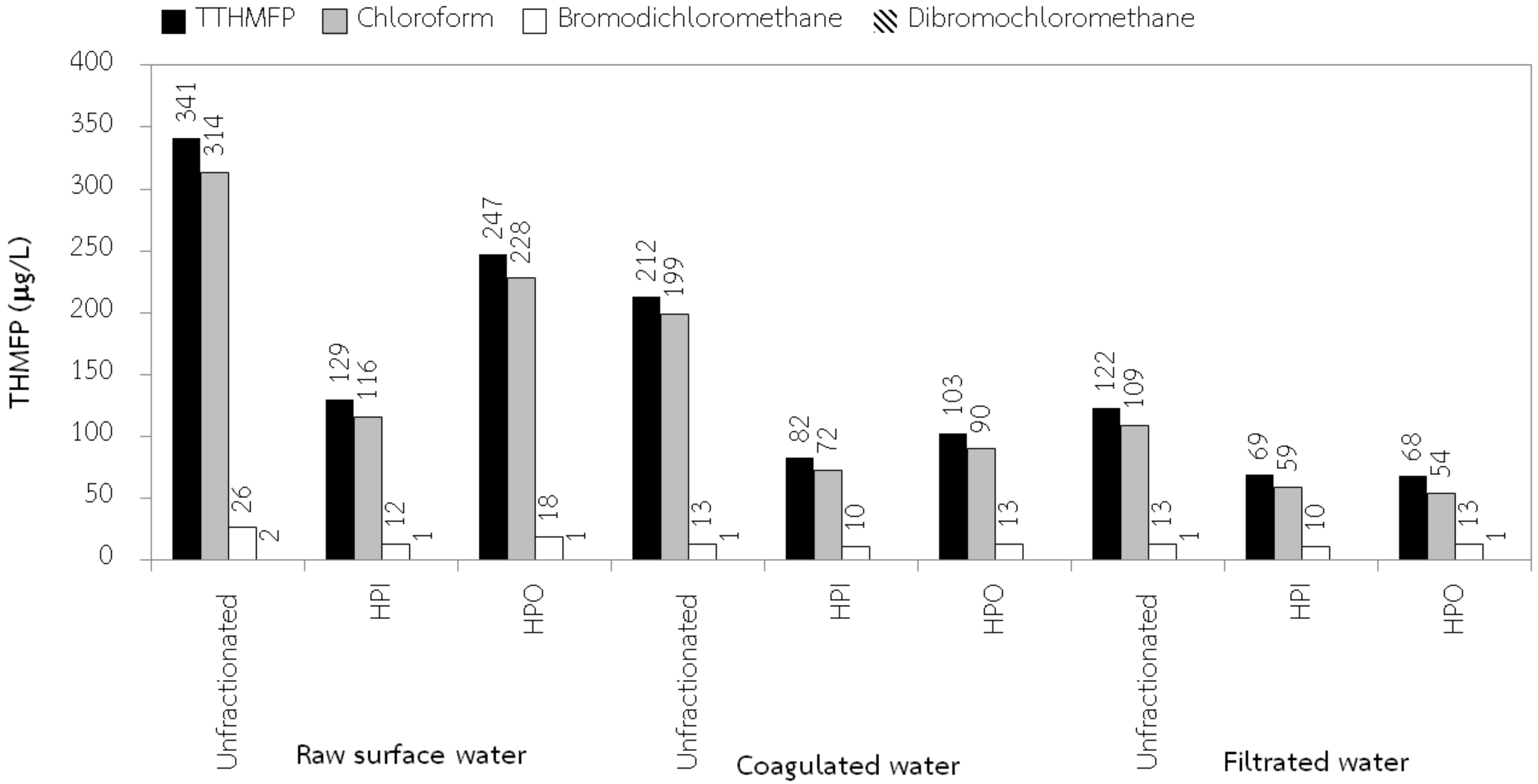


Figure 5.15 THMs species of DOM fractions of raw surface water, coagulated water and filtrated water in rainy season

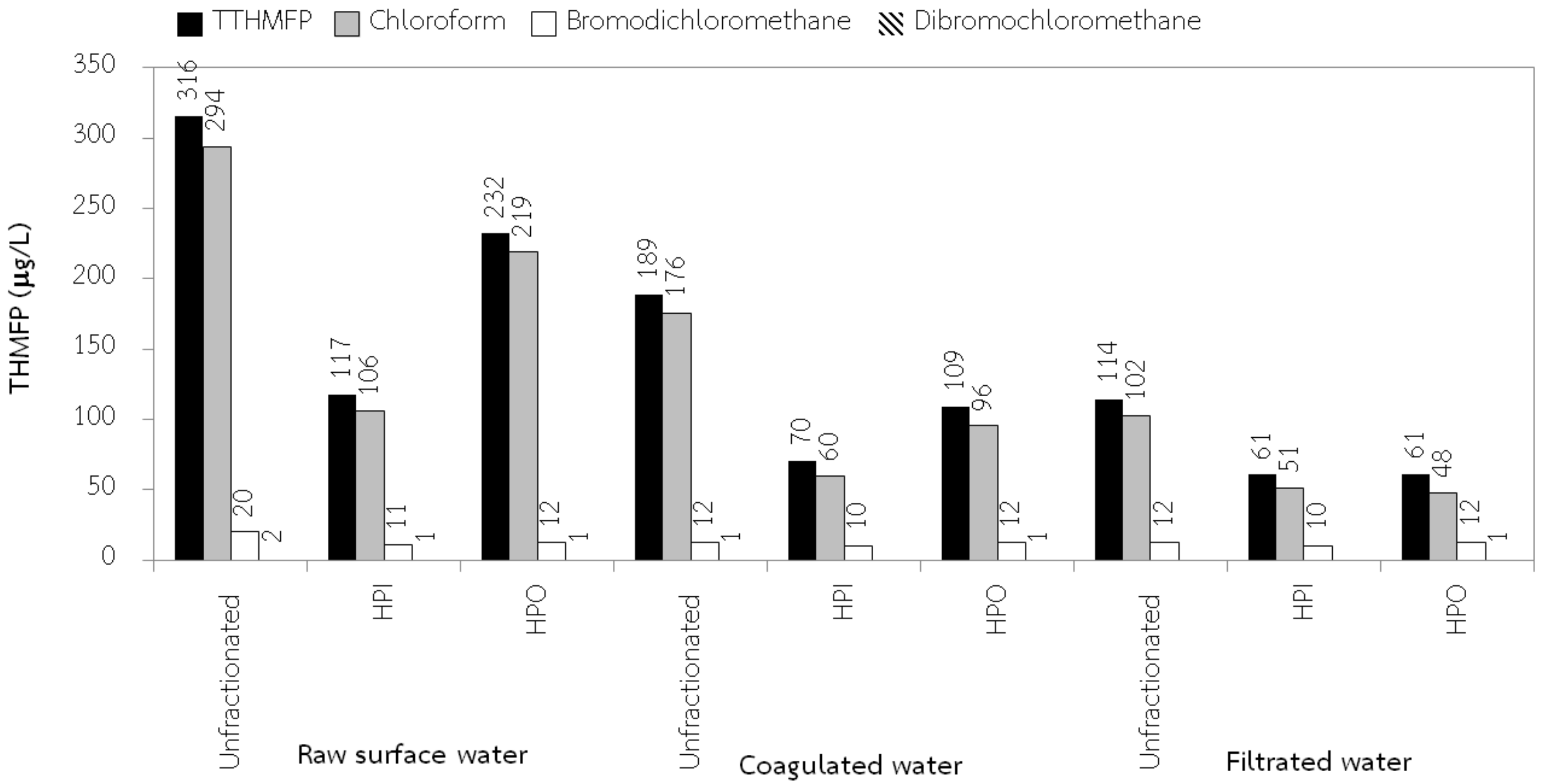


Figure 5.16 THMs species of DOM fractions of raw surface water, coagulated water and filtrated water in summer season

For the reduction efficiency of THMs species by in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L, the results showed that the percent reduction of chloroform was found to high at 59.8% and 71.7% in HPI and HPO fraction. While, those in bromodichloromethane was 12.5% and 23.4%, respectively. From the results, it can be stated that the in-line coagulation with ceramic membrane filtration provided the higher percent reduction of THMs species than conventional coagulation process.

Furthermore, the THMs species of six DOM fractions of raw surface water and filtrated water from in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L was investigated. The THMs species of DOM fraction of raw surface water and filtrated water in rainy and dry season are illustrated in Figure.5.17. and 5.18.

From the results, it was found that TTHMFP of raw surface water in rainy season was 325 μg/L which form $CHCl_3$ 299 μg/L, $CHCl_2Br$ 25 μg/L, and $CHBr_2Cl$ 2 μg/L. After filtrated with in-line coagulation with ceramic membrane filtration, TTHMFP was reduced to 104 μg/L which form $CHCl_3$ 93 μg/L, $CHCl_2Br$ 11 μg/L, and $CHBr_2Cl$ 1 μg/L. For dry season, TTHMFP of raw surface water was 275 μg/L which form $CHCl_3$ 250 μg/L, $CHCl_2Br$ 24 μg/L, and $CHBr_2Cl$ 2 μg/L. After filtrated with in-line coagulation with ceramic membrane filtration, TTHMFP was reduced to 123 μg/L which form $CHCl_3$ 110 μg/L, $CHCl_2Br$ 11 μg/L, and $CHBr_2Cl$ 1 μg/L.

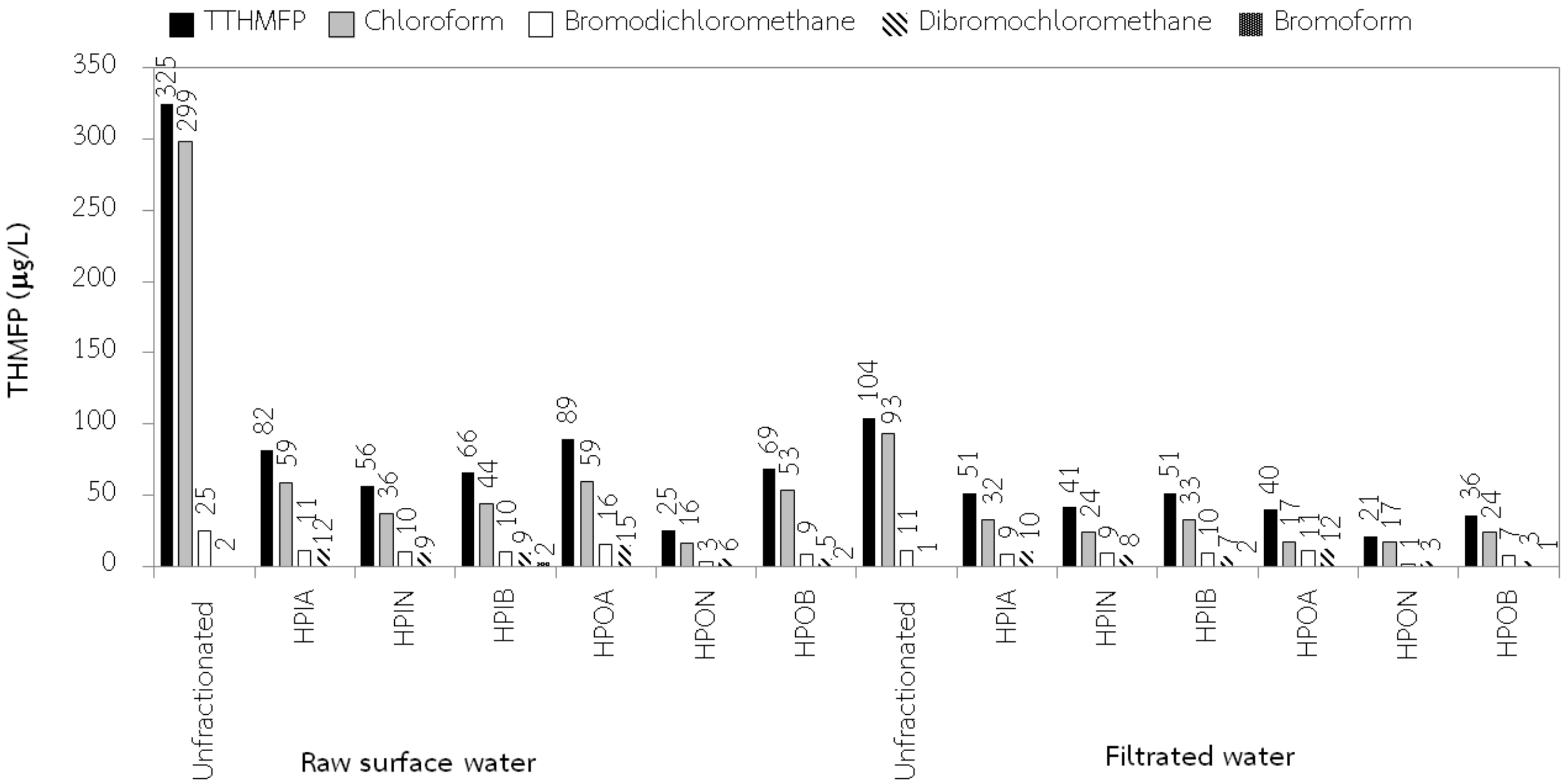


Figure 5. 17 THMs species of DOM fractions of raw surface water and filtrated water in rainy season

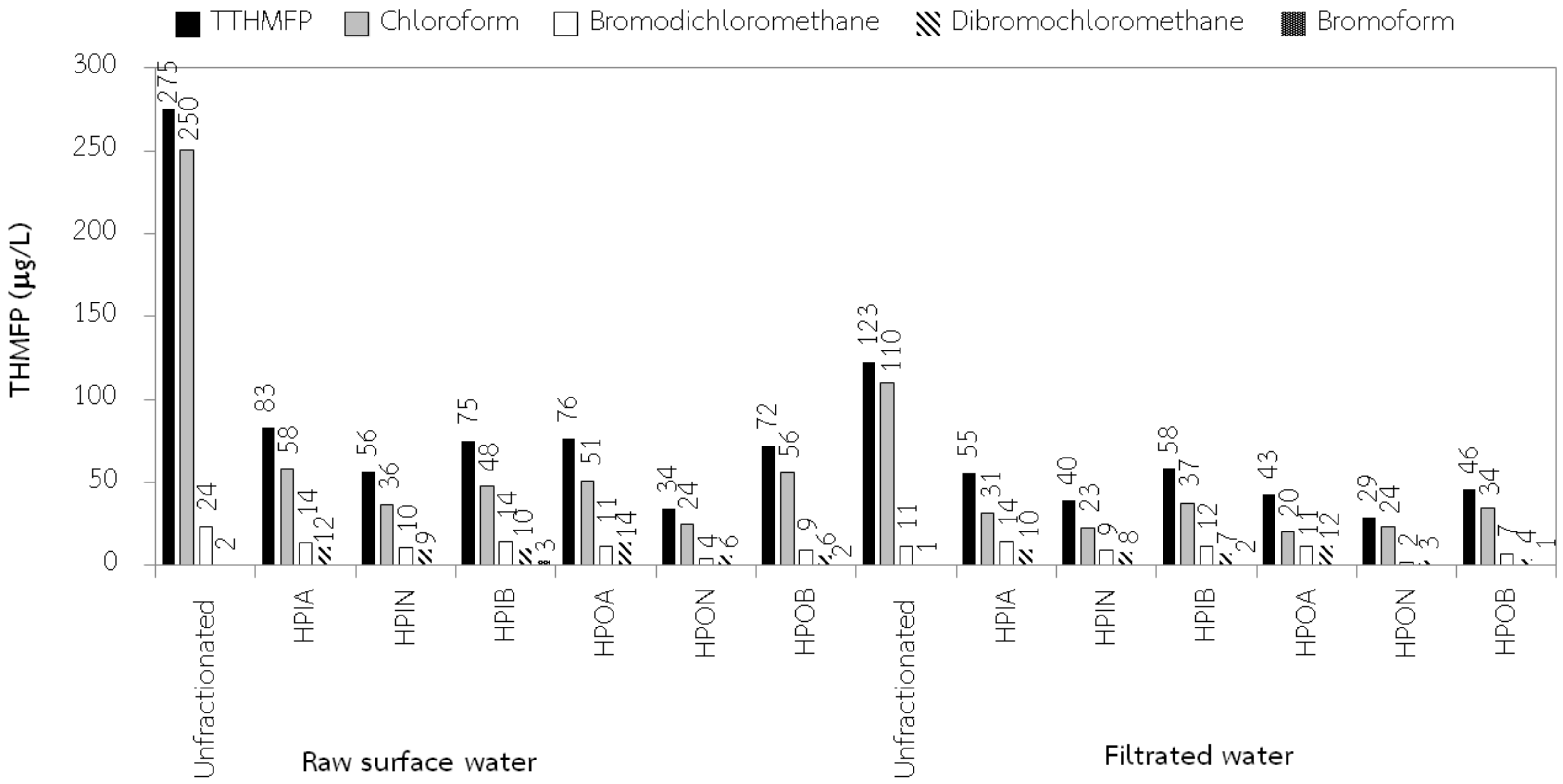


Figure 5. 18 THMs species of DOM fractions of raw surface water and filtrated water in dry season

The results of THMs species in six DOM fraction showed that the dominant THMs species in all fraction was chloroform. Percent distribution of chloroform in each DOM fraction of raw surface water was found in the range of 63.6 - 77.3%. While the other species as bromodichloromethane and dibromochloroform were found in lower percent distribution in the range of 12.0 - 18.8% and 8.0 - 18.7%, respectively. In case of bromoform, it was found in very low percent distribution only in HPOB and HPIB fractions. For filtrated water, chloroform was found to be the major THMs species in all fractions with percent distribution 47.1 - 82.2%. While those of bromodichloromethane and dibromochloroform were found in the range of 7.0 - 25.8% and 8.7 - 27.2%, respectively. In case of bromoform, it was found in very low percent distribuiton only in HPIB and HPOB fraction.

5.4 Concluding remarks

The resin fractionation technique was utilized to characterize DOM into DOM fraction including two fractions (HPI and HPO fractions) and six fractions (HPIA, HPIB, HPIN, HPOA, HPOB and HPON). The results of DOM fractionation of raw surface water showed that the HPI fraction was the major fraction in this water source at all season. Percent DOC distribution of HPI was in the range of 55 - 57% while that of HPO was 43 - 45%. However, the results of THMFP showed that the HPO fraction was the major source of THMFP. From the obtained results, it can be stated that HPO fraction was higher ability to form THMs than HPI fraction and should be concerned in water supply process.

The using conventional coagulation and in-line coagulation with ceramic membrane filtration was effectively reduced DOM mostly of HPO fraction. Hence, THMFP from HPO fraction was found to higher reduce by both processes than those in HPI fraction. When compared the DOM fraction reduction efficiency between both processes, the results showed that the using of in-line coagulation with ceramic membrane filtration provided higher percent reduction than conventional coagulation both in HPI and HPO fractions.

For the six DOM fractionation, the results showed that HPIA and HPOA fractions were the major fraction of hydrophilic and hydrophobic group. Consequently, the HPIA and HPOA fractions were the two main precursors of THMs. Interestingly, the formation of THMs from HPOB and HPIB fraction was high even though their DOC concentration was low. This result was confirmed by the highest specific THMFP of these two fractions. These results indicated that the HPIB and

HPOB fraction had a high ability to form THMs when contact with chlorine. From the results, it can be stated that the formation of THMs was depended on the quantity and characteristics of DOM.

The reduction efficiency of DOM fraction by in-line coagulation with ceramic membrane filtration was investigated. The results showed that HPOA fraction was highly reduced by in-line coagulation with ceramic membrane filtration followed by HPIA fraction. Thus, the reduction of THMFP of these two fractions was found at the highest percent reduction. Furthermore, the combination process of in-line coagulation and ceramic membrane filtration can enhance the reduction efficiency of HPOB and HPIB fraction which difficult to remove by conventional coagulation. Interestingly, the results of specific THMFP of HPIA, HPIN and HPOA of filtrated water were higher than those of raw surface water. This indicates that in-line coagulation with ceramic membrane filtration can remove DOM in HPIA, HPIN and HPOA fraction that had a low ability to form THMs.

CHAPTER VI

CHEMICAL CLASSES OF UNFRACTIONATED AND FRACTIONATION DOM IN RAW SURFACE WATER, COAGULATED WATER AND FILTRATED WATER

6.1 Introduction and Objective

Dissolved organic matter is the complex mixture which difficult to identify. The quantity of DOM can be determined by using the surrogate parameters such as DOC, UV-254 and THMFP. However, the quality or characteristics of DOM are not provided. The characteristics of DOM are very important in the field of water treatment or potable water production. The different of DOM characteristics are resulted in the different of THMs formation. Understanding of relationship between characteristics of DOM and THMFP could help to improve the removal and control THMs (Musikavong, 2006). The major DOM fraction, major THMFP precursors and specific THMFP of DOM fractions were investigated and the results were presented in Chapter V. From the results of specific THMFP of each fraction, it was found that the HPIB and HPOB fractions which lower DOC concentration had the higher specific THMFP than the HPOA and HPIA fractions which defined as major DOM fraction. The obtained results indicate that the ability of DOM to form THMs was depended on quantity and characteristics of DOM. The different characteristics of DOM led to the different ability to form THMs. Thus, the characteristics or chemical classes of DOM fraction should be investigated. The chemical classes of DOM can be identified by using a gas chromatography (GC) and mass spectrometry (MS) technique coupling with pyrolyzer (pyrolysis GC/MS technique). This technique is useful to identify the chemical classes of DOM based on the obtained chemical fingerprint (fragment) of DOM. Many researcher were utilized the pyrolysis GC/MS to characterize the chemical classes in river water (Bruchet *et al*., 1990, Cunha *et al*., 2000, and White *et al*., 2003), reservoir and canal water (Page *et al*., 2003 and Musikavong and Wattanachira, 2013) and coagulated water (Page *et al*., 2003).

The objective of this chapter was aimed at investigating the characteristics of DOM fraction of raw surface water and filtrated water by using pyrolysis GC/MS technique. The common fragments, major fragments and prominent major fragments of DOM fractions were identified. The relationship between DOM characteristics and THMs formation were discussed. Furthermore, the reduction of chemical classes by in-line coagulation with ceramic membrane filtration was studied.

6.2 Material and Methods

6.2.1 Sample collection and GC/MS analysis

Raw surface water was collected two times in July 2012 and December 2012 to represent the nature of DOM in rainy and dry season, respectively. Raw surface water was separated into two portions. First portion was used for coagulation with PACl at dosage 40mg/L. Second portion was used for in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L. In addition, raw surface water and filtrated water in rainy season were fractionated into six DOM fractions. After that the fractionated water were collected. Raw surface water and coagulated water were filtrated through a pre-combusted (550°C) Whatman GF/F 0.7 μm filter before analyzed pyrolysis GC/MS. All water samples were identified the pyrolysis fragments and chemical classes of DOM by using GC/MS pyrolysis technique. (The detail of method and condition for GC/MS pyrolysis technique was illustrated in Chapter 3, section 3.4.6). Table 6.1 showed all water samples that used for pyrolysis GC/MS analysis.

Table 6.1 All water samples for pyrolysis GC/MS analysis

Water samples	Rainy season	Dry season
Raw surface water	/	/
Coagulated water (coagulation process at PACl dosage 40 mg/L)	/	/
Filtrated water (in-line coagulation with ceramic membrane filtration, PACl dosage 40 mg/L)	/	/
Fractionated water of raw surface water and filtrated water (HPOA, HPOB, HPON, HPIA, HPIB and HPIN fraction)	/	-

6.2.2 Interpretation of pyrolysis GC/MS data

The pyrolysis GC/MS technique was provided the pyrochromatograms which represented each pyrolysis fragment of DOM in water samples. First of all, the pyrolysis fragments were identified by comparing with the mass spectral libraries of the National Institute of Standard and Technology, USA. Based on the matching percentage, the pyrolysis fragments were categorized into three classes including the unknown fragment, the acceptable match fragment, and the satisfactory match fragment. The unknown fragment was defined when the matching percentage was lower than 85%. For the matching percentage between 85 - 90%, the pyrolysis fragments were defined to be the acceptable match fragment. In case of matching percentage were higher than 90%, the pyrolysis fragments were defined as the satisfactory match fragment (Musikavong and wattanachira 2013).

Page *et al*. 2002 stated that the quantification of pyrolysis products is very difficult due to the vast quantity. Thus, the relative ratio of area between fragments and one normalizing fragment is utilized to quantify the pyrolysis products from each pyrolysis fragment. The relative ratio of each pyrolysis fragment was determined by using the following equation:

$$\text{Relative ratio} = \frac{\text{Area of pyrolysis fragment}}{\text{Area of a normalizing pyrolysis fragment}}$$

From the results of pyrolysis fragment in this study, Octadecane was found in all water samples and had the highest matching percent (>90%). So, Octadecane was used as normalizing fragment. The limit of fragment identification was set at average relative ratio of 0.10. The fragment which have average relative lower than 0.10 were neglected. While, the average relative ratio at 0.20 was used as the limit of major fragment. The fragment which have relative ratio higher than 0.20 were defined as the major fragment. Furthermore, the major fragments that have average relative ratio more than 1 were defined as prominent major fragment (Musikavong, 2006).

After the pyrolysis fragment were obtained, all pyrolysis fragment were group together based on their chemical characteristics. The pyrolysis fragment were categorized into one of six chemical classes including aliphatic hydrocarbon (AL), organic nitrogen (ON), alcohol (AC), carboxylic acids (CA), ketones (KT) and other chemical class (OT).

6.3 Results and discussions

6.3.1 Chemical classes of raw surface water, coagulated water and filtrated water

The chemical classes of DOM of raw surface water, coagulated water and filtrated water of rainy season were investigated from pyrolysis fragments. The results showed that the common pyrolysis fragment of aliphatic hydrocarbon of raw surface water, coagulated water and filtrated water of rainy season were 1-tetradecane, eicosane, octacosane and octadecane. While hexadecanenitrille was recognized as common pyrolysis fragment of organic nitrogen.

The average relative ratio of each fragment of raw surface water, coagulated water and filtrated water was determined. The fragment that have average relative ratio higher than 1 were define as prominent major fragment. The results showed that the prominent major fragment of aliphatic hydrocarbon of raw surface water was 1-decane. While n-hexadecanoic acid and trichloroacetic acid were defined as prominent major fragments of carboxylic acids. For the other chemical class and organic nitrogen, 2-trideanone and heptadecanenitrille were defined as prominent major fragments, respectively. For coagulated water, the prominent major fragment was found only in aliphatic hydrocarbon (1-hexadecane). While pentadecane was the prominent major fragment of aliphatic hydrocarbon in filtrated water. The pylosysis fragments that have average relative ratio between 0.2 to 1 were defined as major fragment of DOM. The results of major fragment of raw surface water, coagulated water and filtrated water in each chemical classes of rainy season are shown in Table 6.2.

Table 6.2 The major fragments of raw surface water, coagulated water and filtrated water of rainy season

Chemical Classes	Major fragment (Average relative ratio from high to low)		
	Raw surface water	Coagulated water	Filtrated water
AC[1]	-2-Hexyl-1-octanol - 1-Dodecanol	-	-
AL[2]	- 1-tetradecane - 1-Undecane - 1-Pentadecane - 1-Hexadecane - Heneicosane - Octacosane - Eicosane	- Heneicosane - Octacosane - Tetracosane - Eicosane - Tetratriacontane	- Tetracosane - Tetratriacontane - Octacosane
CA[3]	-Tetradecanoic acid -Pentadecanoic acid	- n-Hexadecanoic acid -Pentafluoropropionic acid - Pentadecanoic acid	-Pentafluoropropionic acid
OT[4]	- 2-Nonadecanone -2-Pentadecanone	-	-
ON[5]	- Dodecanenitrille -Hexadecanenitrile - Tridecanenitrille	-	-

Remarks: 1= alcohol, 2= aliphatic hydrocarbon, 3= carboxylic acids 4= other chemical class, 5= organic nitrogen

As for dry season, the results showed that the common pyrolysis fragment of aliphatic hydrocarbon of raw surface water, coagulated water and filtrated water were eicosane, octacosane and octadecane. While hexadecanenitrile was recognized as common fragment of organic nitrogen. Based on the average relative ratio, the major fragment of raw surface water, coagulated water and filtrated water in each chemical classes were determined and illustrated in Table 6.3.

Table 6.3 The major fragments of raw surface water, coagulated water and filtrated water of dry season

Chemical Classes	Major fragment (Average relative ratio from high to low)		
	Raw surface water	Coagulated water	Filtrated water
AC[1]	- 2-Hexyl-1-octanol	-	-
AL[2]	- Heneicosane - Octacosane - Eicosane - Heptadecane - Hexadecane - Tetratetracontane - Nonadecane	- Pentadecane - Tetracosane - Octacosane - Eicosane	- Tetratriacontane - Octacosane
CA[3]	-Pentadecanoic acid -Tetradecanoic acid -Trichloroacetic acid	- n-Hexadecanoic acid -Pentafluoropropionic acid - Pentadecanoic acid	-
ON[4]	- Hexadecanenitrile - Tridecanenitrille	- Tetradecanenitrille	- Hexadecanenitrile
OT[5]	- Cyclotrisiloxane		

Remarks: 1= alcohol, 2= aliphatic hydrocarbon, 3= carboxylic acids 4= organic nitrogen, 5=other chemical class

The prominent major fragments of raw surface water, coagulated water and filtrated water were determined. The results showed that the prominent major fragment of aliphatic hydrocarbon of raw surface water was cyclopentadecane. While n-hexadecanoic acid was defined as prominent major fragment of carboxylic acids. For the ketones and organic nitrogen, the prominent major fragment was not found. For coagulated water, the prominent major fragment was found only in aliphatic hydrocarbon (1-hexadecane). While pentadecane was the prominent major fragment of aliphatic hydrocarbon in filtrated water.

The distribution of DOM chemical classes in water samples was determined by summarizing the average relative ratio of pyrolysis fragment in each chemical classes. The distribution of DOM chemical classes of raw surface water, coagulated water and filtrated water in rainy and dry season are illustrated in Table 6.4 and 6.5.

Table 6.4 Percent distribution of DOM chemical classes of water samples in rainy season

Chemical classes	Water samples		
	Raw surface water	Coagulated water	Filtrate water
Aliphatic hydrocarbon	39	78	89
Alcohol	8	-	-
Carboxylic acids	28	18	8
Organic nitrogen	13	4	4
Other	12	-	-

Table 6.5 Percent distribution of DOM chemical classes of water samples in dry season

Chemical classes	Water samples		
	Raw surface water	Coagulated water	Filtrate water
Aliphatic hydrocarbon	49	80	92
Alcohol	2	-	-
Carboxylic acids	42	16	8
Organic nitrogen	6	4	8
Other	2	-	-

From the results in Table 6.4, it was found that chemical classes in raw surface water were aliphatic hydrocarbon, alcohol, carboxylic acids, ketones and organic nitrogen. The highest percent distribution of chemical classes was found at aliphatic hydrocarbon (39%), followed by carboxylic acids (28%). While the percent distribution of ketones and organic nitrogen was 12% and 13%. The lowest percent distribution of chemical classes in raw surface water was alcohol (8%). For coagulated water, aliphatic hydrocarbon was found to have the highest percent distribution (78%). While, the percent distribution of carboxylic acids and organic nitrogen were 18% and 4%, respectively. For filtrated water, three chemical classes of DOM including aliphatic hydrocarbon, carboxylic acids and organic nitrogen were found. Aliphatic hydrocarbon was found to have the highest percent distribution (89%) followed by carboxylic acids (8%) and organic nitrogen (4%).

As for the distribution of DOM chemical classes of dry season as shown in Table 6.5, it was found that the chemical classes of raw surface water were aliphatic hydrocarbon, alcohol, carboxylic acids, organic nitrogen and other chemical class. The highest percent distribution of chemical classes was aliphatic hydrocarbon (49%), followed by carboxylic acids (42%). While the percent distribution of organic nitrogen, alcohol and other chemical class was found at 6%, 2% and 2%, respectively. For coagulated water, aliphatic hydrocarbon was found to have a highest percent distribution (80%) followed by carboxylic acids (16%) and organic nitrogen (4%). While, the results of percent distribution of chemical classes of filtrated water showed that the highest percent distribution of chemical classes was aliphatic hydrocarbon (92%) followed by organic nitrogen (8%).

From the results of percent distribution of chemical classes in raw surface water, it was found that aliphatic hydrocarbon was the major chemical classes of DOM in raw surface water both in rainy and dry season. This results was well corresponded with the results of Musikavong and Suraphong (2013) which reported that the major chemical classes of reservoir and canal were aliphatic hydrocarbon with percent distribution in the range of 30 - 55%. While the carboxylic acids was found to be the second predominant of chemical classes in raw surface water. Musikavong and Suraphong (2013) reported that the major chemical classes of humic acids were aromatic hydrocarbon (38%), aliphatic hydrocarbon (27%) and phenolic compound (19%). While the chemical classes of Suwanee River natural organic matter (SR-NOM) were aromatic hydrocarbon (27%), phenolic compounds (20%) and aldehyde and ketones (19%). From the results, it can be indicated that major DOM in raw surface water were humic acid-like and SR-NOM-like.

After raw surface water was coagulated by PACl coagulation, three chemical classes including aliphatic hydrocarbon, carboxylic acids and organic nitrogen were found in coagulated water. Alcohol and ketones were not found in coagulated water. Aliphatic hydrocarbon was found to be the major chemical classes of DOM in coagulated water. While the chemical classes in filtrated water were aliphatic hydrocarbon, carboxylic acids and organic nitrogen. Alcohol and ketones were not found in filtrated water. The major chemical classes of DOM in filtrated water was aliphatic hydrocarbon. From the results, it can be indicated that alcohol and ketones might be removed during coagulation and filtration process.

6.3.2 Chemical classes of DOM fractions of raw surface water and filtrated water from in-line coagulation with ceramic membrane filtration

After DOM in water samples were fractionated into six DOM fractions. The fractionated water of raw surface water and filtrated water from in-line coagulation with ceramic membrane filtration were collected and analyzed for their DOM chemical classes. The results of chemical classes of DOM were showed separately in each fraction.

6.3.2.1 Chemical classes of HPIA

From the results of chemical classes of HPIA fractions, it was found that the chemical classes of DOM of HPIA fraction in raw surface water and filtrated water were aliphatic hydrocarbon, carboxylic acids and organic nitrogen. The prominent major fragment of aliphatic hydrocarbon of HPIA fraction in raw surface water and filtrated water was 1-Hexadecane. While, the major fragments of HPIA fraction of raw surface water and filtrated water in each chemical classes are shown in Table 6.6.

The results in Table 6.6 showed that most of the major fragment was found in aliphatic hydrocarbon both in raw surface water and filtrated water. Six major fragments including heneicosane, octacosane, tetracosane, tetratriacontane, eicosane and 1-tetradecane were found in raw surface water. While only five major fragments (pentadecane, octacosane, tetracosane, tetratriacontane, eicosane) were found in filtrated water. However, the major fragments of carboxylic acids (n-hexadecanoic acid, pentafluoropropionic acid and pentadecanoic acid) were found only in raw surface water.

Table 6.6 The major fragments of HPIA fragment of raw surface water and filtrated water

Chemical Classes	Major fragment (Average relative ratio from high to low)	
	Raw surface water	Filtrated water
AL[1]	- Heneicosane - Octacosane - Tetracosane - Tetratriacontane - Eicosane - 1-tetradecane	- Pentadecane - Octacosane - Tetracosane - Tetratriacontane - Eicosane
CA[2]	- n-Hexadecanoic acid - Pentafluoropropionic acid - Pentadecanoic acid	-

Remarks: 1= aliphatic hydrocarbon and 2= carboxylic acids

Percent distribution of DOM chemical classes in HPIA fraction of raw surface water and filtrated water was obtained by summarizing the pyrolysis fragment of HPIA fraction. The results of percent chemical classes distribution of HPIA fraction of raw surface water and filtrated water are shown in Table 6.7.

Table 6.7 Percent distribution of chemical classes in HPIA fraction of raw surface water and filtrated water

Chemical classes	Water samples	
	Raw surface water	Filtrate water
Aliphatic hydrocarbon	81	97
Alcohol	2	-
Carboxylic acids	16	1
Organic nitrogen	2	2
Other	-	-

The results in Table 6.7 showed that aliphatic hydrocarbon was the highest percent distribution of chemical classes in raw surface water (81%) followed by carboxylic acids (16%). The others chemical classes including alcohol and organic nitrogen were found to have lowest percent distribution (2%). For filtrated water, aliphatic hydrocarbon was found to have the highest percent distribution (97%). While the organic nitrogen and carboxylic acids were found to have 2% and 1%, respectively.

6.3.2.2 Chemical classes in HPIB

The results of chemical classes in HPIB fraction in raw surface water showed that the chemical classes of HPIB fraction were aliphatic hydrocarbon, carboxylic acids and organic nitrogen. The prominent major fragment of HPIB fraction was found only in carboxylic acids (n-Hexadecanoic acid). While the prominent major fragment of other chemical classes did not found in raw surface water. For filtrated water, the chemical classes in HPIB fraction were aliphatic hydrocarbon and carboxylic acids. n-Hexadecanoic acid of carboxylic acids was found as the only one prominent major fragment of HPIB fraction in filtrated water. The major fragment of each chemical class of HPIB fraction in raw surface water and filtrated water were investigated and the results are shown in Table 6.8.

Table 6.8 The major fragments of HPIB fraction of raw surface water and filtrated water

Chemical Classes	Major fragment (Average relative ratio from high to low)	
	Raw surface water	Filtrated water
AL[1]	- Pentadecane - Octacosane - Eicosane - Tetracosane - Nonadecane	- Pentadecane - Octacosane - Eicosane
ON[2]	- Hexadecanenitrile - Tetradecanenitrille	-

Remarks: 1= aliphatic hydrocarbon and 2= organic nitrogen

The results in Table 6.8 showed that the major fragments of HPIB fraction of raw surface water were found in aliphatic hydrocarbon and organic nitrogen. While those in filtrated water were found only in aliphatic hydrocarbon. The major fragment of aliphatic hydrocarbon in raw surface water were pentadecane, octacosane, eicosane, tetracosane and nonadecane. Whereas, those in filtrated water were pentadecane, octacosane, and eicosane. For organic nitrogen, the major fragments of raw surface water were hexadecanenitrille and tetradecanenitrille.

The percent distribution of chemical classes of HPIB fraction was investigated by summarizing the pyrolysis fragment of HPIB fraction of raw surface water and filtrated water, respectively. The results of percent distribution of chemical classes of raw surface water and filtrated water are shown in Table 6.9.

Table 6.9 Percent distribution of chemical classes in HPIB fraction of raw surface water and filtrated water

Chemical classes	Water samples	
	Raw surface water	Filtrate water
Aliphatic hydrocarbon	67	83
Alcohol	-	-
Carboxylic acids	21	17
Organic nitrogen	12	-
Other	-	-

The results showed that the highest percent distribution of chemical classes of HPIB fraction of raw surface water was aliphatic hydrocarbon (67%) followed by carboxylic acids (21%) and organic nitrogen (12%). While in filtrated water, aliphatic hydrocarbon was the highest percent distribution (83%) followed by carboxylic acids (17%). Organic nitrogen did not detect in filtrated water. The results indicated that percent distribution of carboxylic acids was decreased from 21% in raw surface water to 17% in filtrated water. Whereas the organic nitrogen which found 12% distribution in raw surface water was not found in filtrated water.

6.3.2.3 Chemical classes in HPIN

The results of pyrolysis fragment of HPIN fraction showed that the chemical classes of HPIN fraction in raw surface water were aliphatic hydrocarbon, carboxylic acids, organic nitrogen and other chemical class. While those of filtrated water were aliphatic hydrocarbon and other chemical class. From the results, the prominent major fragment of HPIN fraction in raw surface water was not found in any chemical classes. While two prominent major fragments (pentadecane and tetracosane) of aliphatic hydrocarbon were found in HPIN fraction of filtrated water. The results of major fragments of raw surface water and filtrated water are shown in Table 6.10

Table 6.10 The major fragments of HPIN fraction of raw surface water and filtrated water

Chemical Classes	Major fragment (Average relative ratio from high to low)	
	Raw surface water	Filtrated water
AL[1]	- Heneicosane - Octacosane - Heptadecane - 1-Hexadecane - Eicosane - Tetratriacontane	- Tetratriacontane - Octacosane - Eicosane
CA[2]	- n-Hexadecanoic acid - Trichloroacetic acid	-
ON[3]	-	-
OT[4]	-	- Cyclotrisiloxane

Remarks: 1= aliphatic hydrocarbon, 2=carboxylic acids, 3= organic nitrogen and 4=other chemical classes

The results in Table 6.10 showed that the major fragments of HPIN fraction in raw surface water were found in aliphatic hydrocarbon and carboxylic acids. The major fragments of HPIN fraction of aliphatic hydrocarbon were heneicosane, octacosane, heptadecane, 1-Hexadecane, eicosane and tetratriacontane. For the carboxylic acids, the major fragment was n-Hexadecanoic acid and trichloroacetic acid. For the filtrated water, the major fragments were found only in aliphatic hydrocarbon and other chemical class. Three major fragment of aliphatic hydrocarbon were tetratriacontane, octacosane and eicosane. While cyclotrisiloxane was found to be the major fragment of other chemical class.

The percent distribution of chemical classes of HPIN fraction of raw surface water and filtrated water were investigated by summarizing the pyrolysis fragment of HPIN fraction. Percent distributions of chemical classes of HPIN fraction are shown in Table 6.11.

Table 6.11 Percent distribution of chemical classes of HPIN fraction in raw surface water and filtrated water

Chemical classes	Water samples	
	Raw surface water	Filtrate water
Aliphatic hydrocarbon	84	96
Alcohol	-	-
Carboxylic acids	11	-
Organic nitrogen	2	-
Other	3	4

The results from Table 6.11 showed that the highest percent distribution of chemical classes of HPIN fraction in raw surface water was aliphatic hydrocarbon (84%). The rest of chemical class was found at carboxylic acids (11%), organic nitrogen (2%) and other chemical class (3%).

For filtrated water, the aliphatic hydrocarbon was found to have the highest percent distribution (96%). While percent distribution of other chemical class was 4%. From the results, it can be indicated that the carboxylic acids and organic nitrogen was removed from raw surface water through in-line coagulation with ceramic membrane filtration.

6.3.2.3 Chemical classes in HPOA

The results of pyrolysis fragment of HPOA fraction in raw surface water showed that the chemical classes of DOM in HPOA fraction of raw surface water were aliphatic hydrocarbon, carboxylic acids, organic nitrogen, alcohol and other chemical classes. From the results, it was found that the prominent major fragments of raw surface water were n-Hexadecanoic acid and Tetradecanoic acid in carboxylic acids. For the filtrated water, three chemical classes including aliphatic hydrocarbon, carboxylic acids and alcohol was found in HPOA fraction of filtrated water. The prominent major fragment of HPOA fraction was not found in all chemical classes. The major fragment of HPOA fraction of raw surface water and filtrated water were investigated. The results of major fragment of HPOA fraction are shown in Table 6.12.

Table 6.12 The major fragments of HPOA fraction of raw surface water and filtrated water

Chemical Classes	Major fragment (Average relative ratio from high to low)	
	Raw surface water	Filtrated water
AC[1]	- 2-Hexyl-1-octanol	- 2-Hexyl-1-octanol
AL[2]	- Heneicosane - Octacosane - Eicosane - Heptadecane - Hexadecane - 1-Hexadecane - 1-tetradecane - Tetratetracontane - 1-Pentadecane - Nonadecane	- Heneicosane - Heptadecane - Octacosane - Eicosane - Tetratriacontane - Nonadecane - 1-Hexadecane
CA[3]	- Tetradecanoic acid - Trichloroacetic acid	- n-Hexadecanoic acid
ON[4]	- Hexadecanenitrile	-
OT[5]	- Cyclotrisiloxane	-

Remarks: 1= alcohol, 2=aliphatic hydrocarbon, 3=carboxylic acids, 4=organic nitrogen and 5=other chemical classes

From the results in Table 6.12, it was found that the major fragments of HPOA fraction of raw surface water were found in aliphatic hydrocarbon, carboxylic acids, organic nitrogen and other chemical class. The major fragments of HPOA fraction of aliphatic hydrocarbon were heneicosane, octacosane, eicosane, heptadecane, hexadecane, 1-hexadecane, 1-Tetradecane, tetratetracontane, 1-Pentadecane and nonadecane. For carboxylic acids, the major fragments were n-Hexadecanoic acid and tetradecanoic acid. While, the major fragments of organic nitrogen and other chemical class were hexadecanenitrille and cyclotrisiloxane, respectively.

For filtrated water, the major fragments of HPOA fraction were found in aliphatic hydrocarbon and carboxylic acids. The major fragments of HPOA fraction of aliphatic hydrocarbon were heneicosane, heptadecane, octacosane, eicosane, tetratriacontane, nonadecane and 1-Hexadecane whereas those of carboxylic acids were n-Hexadecanoic acid.

The chemical classes of HPOA fraction was investigated by summarizing the pyrolysis fragment of HPOA fraction. Percent distribution of chemical classes of HPOA fraction in raw surface water and filtrated water were determined and the results are shown in Table 6.13.

Table 6.13 Percent distribution of chemical classes of HPOA fraction in raw surface water and filtrated water

Chemical classes	Water samples	
	Raw surface water	Filtrate water
Aliphatic hydrocarbon	48	85
Alcohol	2	3
Carboxylic acids	40	12
Organic nitrogen	3	-
Other	7	-

From the results of percent distribution of chemical classes in raw surface water as shown in Table 6.13, it was found that the highest percent distribution of chemical classes was aliphatic hydrocarbon (48%) followed by carboxylic acids (40%). While the percent distribution of alcohol, organic nitrogen and other chemical class was 2%, 3% and 7%, respectively. For the filtrated water, the results showed that the highest percent distribution of chemical classes was aliphatic hydrocarbon (85%). While, the percent distribution of alcohol and carboxylic acids were 3% and 12%, respectively. From the results, it was indicated that the aliphatic hydrocarbon was the highest percent distribution both in raw surface water and filtrated water. The organic nitrogen and other chemical class which presence in raw surface water were not found in filtrated water.

6.3.2.5 Chemical classes in HPOB

The pyrolysis fragment of HPOB fraction of raw surface water and filtrated water were investigated. The results showed that the chemical classes in HPOB fraction of raw surface water were alcohol, aromatic hydrocarbon, aliphatic hydrocarbon, carboxylic acids, organic nitrogen and cyclotrisiloxane. While those in filtrated water were alcohol, aliphatic hydrocarbon and organic nitrogen. The prominent major fragment of HPOB fraction of raw surface water and filtrated water did not found in any chemical classes. However, the major fragment of HPOB fraction of raw surface water and filtrated water were detected as illustrated in Table 6.14.

The results showed that the major fragment of HPOB fraction in raw surface water were found in alcohol, aliphatic hydrocarbon, carboxylic acids, organic nitrogen and other chemical class. The major fragments of HPOB fraction of aliphatic hydrocarbon were heneicosane, octacosane, eicosane, heptadecane, nonadecane, 1-Hexadecane, 1-Pentadecane, tetratetracontane and 1-Tetradecane. For the carboxylic acids, the major fragment was n-Hexadecanoic acid. While the major fragments of alcohol, organic nitrogen and other chemical class were 2-Hexyl-1-octanol, hexadecanenitrille and cyclotrisiloxane, respectively.

For the major fragment of filtrated water, it was found in alcohol, aliphatic hydrocarbon and organic nitrogen. Seven major fragment including heneicosane, heptadecane, octacosane, tetratriacontane, eicosane, nonadecane, and 1-Hexadecane were found in aliphatic hydrocarbon. For the organic nitrogen, one major fragment (hexadecanenitrile) was found.

Table 6.14 The major fragments of HPOB fraction of raw surface water and filtrated water

Chemical Classes	Major fragment (Average relative ratio from high to low)	
	Raw surface water	Filtrated water
AC[1]	- 2-Hexyl-1-octanol	-
AL[2]	- Heneicosane	- Heneicosane
	- Octacosane	- Heptadecane
	- Eicosane	- Octacosane
	- Heptadecane	- Tetratriacontane
	- Nonadecane	- Eicosane
	- 1-Hexadecane	- Nonadecane
	- 1-Pentadecane	- 1-Hexadecane
	- Tetratetracontane	
	- 1-tetradecane	
CA[3]	- n-Hexadecanoic acid	-
ON[4]	- Hexadecanenitrile	- Hexadecanenitrile
OT[5]	- Cyclotrisiloxane	-

Remarks: 1= alcohol, 2=aliphatic hydrocarbon, 3=carboxylic acids, 4=organic nitrogen and 5=other chemical classes

Percent distribution of chemical classes of HPOB fraction in raw surface water and filtrated water were investigated by summarizing pyrolysis fragment of HPOB fraction of raw surface water and filtrated water. The results of percent distribution of chemical classes of HPOB fraction are shown in Table 6.15.

Table 6.15 Percent distribution of chemical classes of HPOB fraction in raw surface water and filtrated water

Chemical classes	Water samples	
	Raw surface water	Filtrate water
Aliphatic hydrocarbon	71	93
Alcohol	3	3
Carboxylic acids	15	-
Organic nitrogen	3	4
Other	7	-

The results of percent distribution of chemical classes of raw surface water showed that the highest percent distribution of HPOB fraction of raw surface water was aliphatic hydrocarbon (71%). The second highest percent distribution was carboxylic acids (15%). The rest of chemical classes were found to have low percent distribution including alcohol (3%), aromatic hydrocarbon (3%), organic nitrogen (3%) and other chemical class (4%), respectively. For filtrated water, the highest percent distribution of chemical classes was aliphatic hydrocarbon (93%). While the percent distribution of alcohol and organic nitrogen were 3% and 4%, respectively. The results indicated that the carboxylic acids which found to have 15% in raw surface water were not detected in filtrated water.

6.3.2.6 Chemical classes in HPON

The pyrolysis fragment of HPON fraction in raw surface water and filtrated water were investigated. The results showed that the chemical classes of HPON fraction in raw surface water were aliphatic hydrocarbon, carboxylic acids, organic nitrogen and other chemical class. The prominent major fragment of HPON fraction of raw surface water was determined. The results showed that the prominent major fragments of HPON fraction in raw surface water were found in aliphatic hydrocarbon and carboxylic acids. In aliphatic hydrocarbon, the prominent major fragments were pentadecane and tetracosane whereas those of carboxylic acids was n-Hexadecanoic acid. For filtrated water, the chemical classes of HPON fraction were aliphatic hydrocarbon and carboxylic acids. The prominent major fragment of HPON fraction in filtrated water was only found in aliphatic hydrocarbon which was pentadecane and tetracosane. The major fragments of HPON fraction of raw surface water and filtrated water were investigated and the results are shown in Table 6.16.

Table 6.16 The major fragments of HPON fraction of raw surface water and filtrated water

Chemical Classes	Major fragment (Average relative ratio from high to low)	
	Raw surface water	Filtrated water
AL[1]	- Octacosane - Eicosane	- Octacosane - 1-tetradecane - 1-Hexadecane - Eicosane
CA[2]	-	-n-Hexadecanoic acid
ON[3]	-	-
OT[4]	- Cyclotrisiloxane	-

Remarks: 1=aliphatic hydrocarbon, 2=carboxylic acids, 3=organic nitrogen and 4=other chemical classes

The results of major fragment of HPON fraction showed that the major fragments of raw surface water were found in aliphatic hydrocarbon and other chemical classes. The major fragment of aliphatic hydrocarbon was octacosane and eicosane. While those of other chemical class was cyclotrisiloxane. For filtrated water, the major fragments were found in aliphatic hydrocarbon and carboxylic acids. The major fragment of aliphatic hydrocarbon were octacosane, 1-tetradecane, 1-hexadecane and eicosane whereas those of carboxylic acids was n-Hexadecanoic acid.

Percent distribution of chemical classes of HPON fraction of raw surface water and filtrated water was determined by summarizing pyrolysis fragment of HPON fraction of raw surface water and filtrated water. The results of percent distribution of chemical classes of HPON fraction are shown in Table 6.17.

Table 6.17 Percent distribution of HPON fraction of raw surface water and filtrated water

Chemical classes	Water samples	
	Raw surface water	Filtrate water
Aliphatic hydrocarbon	70	92
Alcohol	-	-
Carboxylic acids	19	8
Organic nitrogen	2	-
Other	8	-

The results from Table 6.17 showed that the highest percent distribution of chemical classes of HPON fraction of raw surface water was aliphatic hydrocarbon (70%) followed by carboxylic acids (19%). The rest of chemical class was found to have low percent distribution which organic nitrogen (2%) and other chemical class (8%). For filtrated water, the highest percent distribution of chemical classes of HPON fraction was aliphatic hydrocarbon (92%). While the lowest percent distribution of chemical classes of HPON fraction was carboxylic acids. From the results, it can be indicated that the aliphatic hydrocarbon was the highest percent distribution of chemical classes of HPON fraction both in raw surface water and filtrate water.

Furthermore, percent distribution of DOM chemical classes in six DOM fractions for raw surface water and filtrated water by in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L was investigated. Percent distribution of chemical classes of DOM fraction of raw surface water and filtrated water were summarized and illustrated in Table 6.18 and 6.19.

Table 6.18 The chemical classes of DOM of raw surface water

Chemical classes	DOM fraction					
	HPIA	HPIN	HPIB	HPOA	HPON	HPOB
Aliphatic hydrocarbon	81	84	67	48	70	71
Alcohol	2	-	-	2	-	3
Carboxylic acids	16	11	21	40	19	15
Organic nitrogen	2	2	12	3	2	3
Other	-	3	-	7	8	4

Table 6.19 The chemical classes of DOM of filtrated water

Chemical classes	DOM fraction					
	HPIA	HPIN	HPIB	HPOA	HPON	HPOB
Aliphatic hydrocarbon	76	96	83	85	92	93
Alcohol	-	-	-	3	-	3
Carboxylic acids	1	-	17	12	8	-
Organic nitrogen	2	-	-	-	-	4
Other	-	4	-	-	-	-

The results in Table 6.18 showed that three chemical classes including aliphatic hydrocarbon, carboxylic acids and organic nitrogen were found in all DOM fraction of raw surface water. Aliphatic hydrocarbon was found at the highest percent distribution in all DOM fractions (48% - 84%). HPOA fraction was found to have the highest percent distribution of carboxylic acids (40%). For the organic nitrogen, it was found at the highest percent distribution in HPIB fraction (12%). While alcohol was found in HPIA, HPOA and HPOB fraction. For other chemical class, it was found in HPIN, HPOA, HPON and HPOB fraction.

From the results of percent distribution of chemical classes of DOM fraction in filtrated water (Table 6.19), it was found that aliphatic hydrocarbon was found in all DOM fractions and presented in the highest percent distribution (76% - 96%). For the carboxylic acids and organic nitrogen which found in all DOM fraction of raw surface water, the results showed that carboxylic acids was found only in HPIA, HPIB, HPOA and HPON fraction with the range of 1% - 17%. While organic nitrogen was found only in HPIA and HPOB fraction with low percent distribution (2% -4%). For alcohol, it was found in HPOA and HPOB fraction whereas other chemical class was found only in HPIN fraction.

The obtained results of chemical classes of DOM fraction in raw surface water indicate that aliphatic hydrocarbon, carboxylic acids and organic nitrogen were found in all DOM fractions of raw surface water. While aliphatic hydrocarbon was found in all DOM fractions of filtrated water. The results indicate that aliphatic hydrocarbon was commonly found both in raw surface water and filtrated water. However, the results of THMFP indicate that raw surface water and filtrated water had a different THMFP. Thus, the relationship of DOM chemical classes and specific THMFP was investigated and discuss in the section.

6.3.3 Reactivity of chemical classes in each DOM fraction to form THMs

The reactivity of chemical classes in each DOM fraction to form THMs was investigated. In order to discuss the ability of chemical classes, the DOC concentration, specific THMFP and percent distribution of chemical classes were consider. Figure 6.1 illustrated the DOC concentration, specific THMFP and chemical classes of each DOM fraction.

The specific THMFP of HPIA fraction (the highest DOC concentration) was very low. Thus, aliphatic hydrocarbon and carboxylic acids in HPIA fraction might be inactive with chlorine to form THMs. Based on the increasing of specific THMFP in filtrated water, it can be indicated that aliphatic hydrocarbon and carboxylic acids which reduced by in-line coagulation with ceramic membrane filtration was low ability to form THMs. For the HPIN fraction, the DOC concentration of this fraction was relatively high but the specific THMFP was moderately low. This indicated that aliphatic hydrocarbon in HPIN fraction might be inactive with chlorine to form THMs. The specific THMFP of HPIN fraction in filtrated water was higher than those in raw surface water. This indicates that the in-line coagulation with ceramic membrane filtration can reduced aliphatic hydrocarbon and carboxylic acids which had low ability to form THMs. Interestingly, HPIB fraction, which was found at very low DOC concentration, was very high specific THMFP. This indicates that aliphatic and carboxylic acids of HPIB fraction can easily to react with chlorine to form THMs. From the decreasing of specific THMFP in filtrated water, it can be stated that aliphatic hydrocarbon, carboxylic acids and organic nitrogen that were reduced by in-line coagulation with ceramic membrane filtration were high ability to form THMs.

For hydrophobic group, HPOA fraction (the highest DOC concentration) was very low specific THMFP. Aliphatic hydrocarbon and carboxylic acids of HPOA fraction might be inactive with chlorine to form THMs. When consider the specific THMFP of HPOA in raw surface water and filtrated water, it was found that the specific THMFP in filtrated water was higher than those in raw surface water. This indicates that in-line coagulation with ceramic membrane filtration can reduce aliphatic hydrocarbon and carboxylic acids which had low ability to form THMs. For HPON fraction, the DOC concentration was moderately high while the specific THMFP was relatively low. Aliphatic hydrocarbon of HPON fraction might be inactive with chlorine to form THMs. The decreasing of specific THMFP in filtrated water indicates that the in-line coagulation with ceramic membrane filtration can reduce aliphatic hydrocarbon which had high ability to form THMs. In case of HPOB fraction, which found at the lowest DOC concentration in the hydrophobic group, the specific THMFP was very high. Aliphatic hydrocarbon of HPOB fraction might be active with chlorine to form THMs. Considered to the specific THMFP of HPOB fraction of raw surface water and filtrated water, it can be indicated that aliphatic hydrocarbon and carboxylic acids that was reduced by in-line coagulation with ceramic membrane filtration had high ability to form THMs.

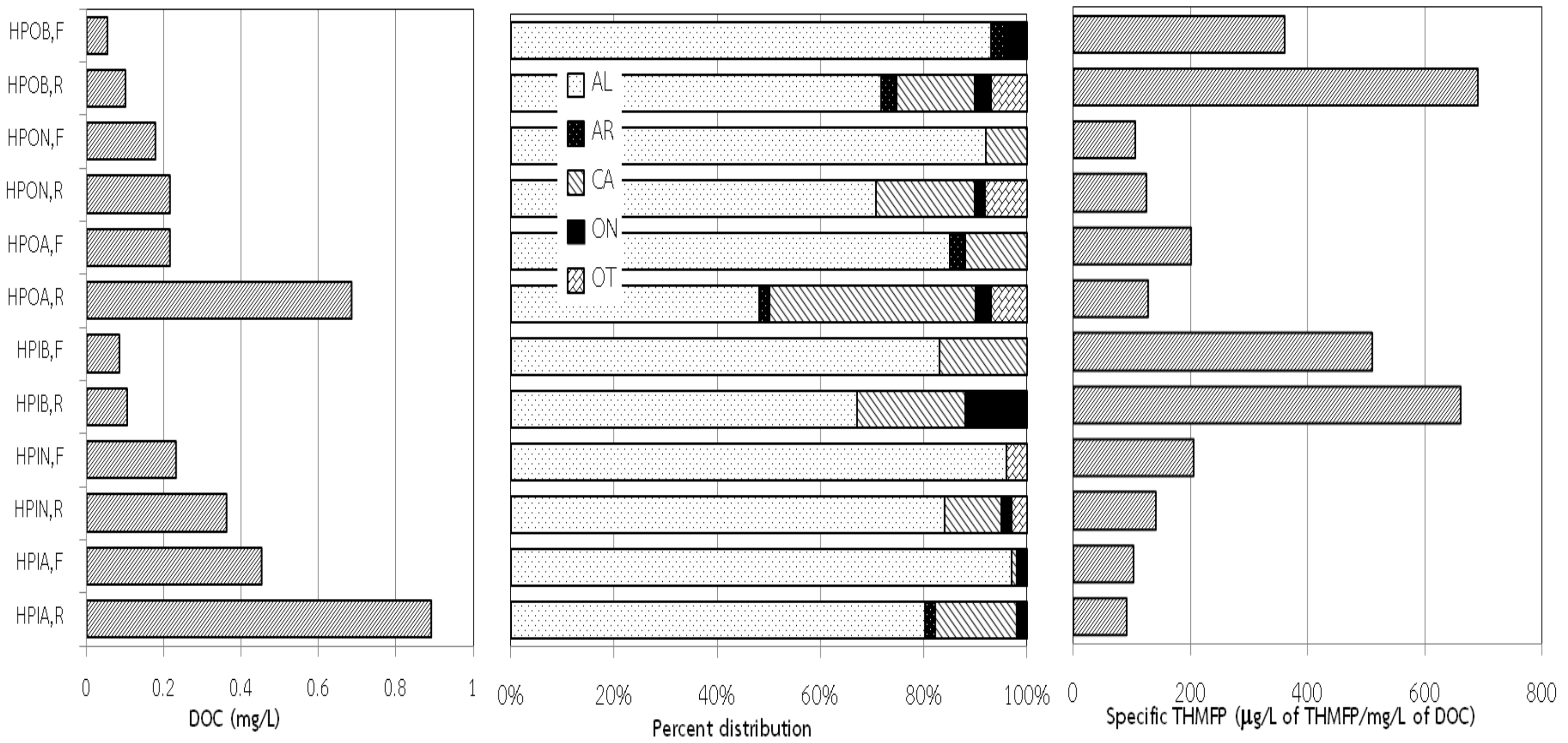


Figure 6.1 The DOC concentration, specific THMFP and chemical classes of DOM fraction in raw surface water and filtrated water

6.4 Concluding Remarks

From the investigation of chemical classes of DOM, it was found that five chemical classes of DOM including aliphatic hydrocarbon, alcohol, carboxylic acids, organic nitrogen and other chemical class were found in raw surface water. The major chemical classes of DOM in raw surface water was aliphatic hydrocarbon which found at the highest percent distribution (39% and 49% in rainy and dry season, respectively). For the coagulated water and filtrated water, the chemical classes of DOM were aliphatic hydrocarbon, carboxylic acids and organic nitrogen. The major chemical classes of DOM in coagulated water and filtrated water was aliphatic hydrocarbon which found in highest percent distribution (>78%). The other chemical classes of DOM such as alcohol and ketones did not found in coagulated and filtrated water, this can be indicated that these chemical classes of DOM might be removed through coagulation process and in-line coagulation with ceramic membrane filtration.

The chemical classes of DOM in each DOM fraction of raw surface water and filtrated water were investigated. The results showed that three chemical classes of DOM including aliphatic hydrocarbon, carboxylic acids and organic nitrogen were found in all DOM fractions of raw surface water. Aliphatic hydrocarbon was found at the highest percent distribution in all DOM fractions (48% - 84%) which indicates that aliphatic hydrocarbon was the main chemical classes of DOM in all DOM fractions of raw surface water. For carboxylic acids, it was found at the highest percent distribution (40%) in HPOA fraction. While the organic nitrogen, it was found at the highest percent distribution (12%) in HPIB fraction. For the chemical classes of DOM in DOM fraction of filtrated water, it was found that aliphatic hydrocarbon was found in all DOM fractions at the highest percent distribution (76% - 96%). It can be indicated that the major chemical classes of DOM in DOM fraction of filtrated water was aliphatic hydrocarbon. The carboxylic acids was found only in HPIA, HPIB, HPOA and HPON fraction with the low percent distribution while the organic nitrogen was found only in HPIA and HPOB fraction. The investigation of relationship between chemical classes and specific THMFP indicates that DOM chemical classes in each DOM fraction provided the different ability to form THMs. Aliphatic hydrocarbon in HPIA, HPIN, HPOA and HPON was found to have low ability to form THMs but those in HPIB and HPOB fraction was found to highly active with chlorine to form THMs. Furthermore, the ability of chemical classes of DOM in each DOM fraction that was reduced by in-line coagulation with ceramic membrane filtration to form THMs was investigated. The results showed that chemical classes of DOM in HPIB, HPOB and HPON fraction that was reduced by in-line coagulation with ceramic membrane filtration was highly active with chlorine to form THMs. While those in HPIA, HPIN and HPOA was low ability to form THMs.

CHAPTER VII

CONCLUSION AND RECOMMENDATION

7.1 Conclusion

1. The in-line coagulation with ceramic membrane filtration was the effectively technique that can utilize for DOM reduction in turbid water source. Percent reduction efficiency of DOC, UV-254 and THMFP by in-line coagulation with ceramic membrane filtration at optimal PACl dosage (40 mg/L) was found in the range of 40 - 48%, 67 – 75% and 58 – 68%, respectively.

2. The in-line coagulation with ceramic membrane filtration can be utilized to reduce DOM from high turbid water source without the significantly decreased of filtration flux and reduction efficiency during the experimental periods (30 days). However, the using of pre-chlorination for membrane fouling control not suitable because it can created high concentration of THMs in filtrated water.

3. HPIA and HPOA fraction were found as the major DOM fraction and the main precursors for THMs formation of this water source. However, the specific THMFP result indicates that the HPIB and HPOB fraction, lower mass DOC distribution, had a high specific THMFP values. This can be indicated that HPOB and HPIB fraction had a high ability to form THMs. The formation of THMs was depended on the quantity and characteristics of DOM.

4. HPOA fraction was highly reduced by in-line coagulation with ceramic membrane filtration with percent reduction higher than 60%. Consequently, the reduction of THMFP of this fraction was high. In addition, in-line coagulation with ceramic membrane filtration can reduced HPOB and HPIB fraction which difficult to remove by conventional coagulation. Furthermore, the results of specific THMFP in filtrated water showed that DOM in HPIA, HPIN and HPOA fraction which reduced by in-line coagulation with ceramic membrane filtration had a low ability to form THMs.

5. The major chemical classes of DOM in raw surface water, coagulated water and filtrated water were aliphatic hydrocarbon which found at the highest percent distribution. For the chemical classes of DOM in DOM fraction, aliphatic hydrocarbon was found at the highest percent distribution in all DOM fractions both in raw surface

water (48 - 84%) and filtrated water (76 – 96%). From the investigation of relationship of chemical classes and the formation of THMs, it was found that aliphatic hydrocarbon in each DOM fraction provided the different ability to form THMs.

7.2 Recommendation

1. The efficiency of in-line coagulation with ceramic membrane filtration for DOM and THMFP was successfully investigated in this study. However, the filtrated water quality in term of microbial reduction was not determined. Thus, the further work should be concern in the microbial aspects.

2. In this study, the characteristics of DOM was investigated by using resin fraction method and pyrolysis GC/MS technique. However, there are many techniques that can be utilized to characterize DOM. So, the DOM characterization by using other technique such as FEEM or FTIR was interested.

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APPENDIX

APPENDIX A

EXPERIMENTAL DATA

APPENDIX A-1

DOC, UV-254, SUVA, THMFP, TURBIDITY AND pH

Table A-1 DOC, UV-254, SUVA, THMFP, turbidity and pH of raw surface water and coagulated water at various PACl concentrations in rainy season

Parameters	Raw water	Rainy season					
		PACl concentration (mg/L)					
		0	10	20	30	40	50
Turbidity (NTU)	291	278	103	35.6	10.5	6.84	4.12
pH	7.6	7.6	7.4	7.3	7.2	7.1	7.0
DOC (mg/L)	2.3	2.3	2.2	1.9	1.6	1.4	1.3
UV-254 (cm^{-1})	0.076	0.076	0.074	0.059	0.030	0.025	0.022
SUVA (L/mg-m)	3.3	3.3	3.3	3.1	1.9	1.9	1.7
THMFP (ug/L)	330	302	265	231	211	189	176

Table A-2 DOC, UV-254, SUVA, THMFP, turbidity and pH of raw surface water and coagulated water at various PACl concentrations in winter season

Parameters	Raw water	Winter season					
		PACl concentration (mg/L)					
		0	10	20	30	40	50
Turbidity (NTU)	57.1	50.6	5.51	3.07	1.44	1.01	0.62
pH	7.7	7.6	7.5	7.3	7.2	7.1	7.0
DOC (mg/L)	2.0	1.9	1.8	1.7	1.5	1.3	1.3
UV-254 (cm^{-1})	0.086	0.081	0.077	0.066	0.056	0.037	0.028
SUVA (L/mg-m)	4.4	4.3	4.2	4.0	3.7	2.7	2.1
THMFP (ug/L)	258	227	202	195	182	165	163

Table A-3 DOC, UV-254, SUVA, THMFP, turbidity and pH of raw surface water and coagulated water at various PACl concentrations in summer season

Parameters	Raw water	Summer season					
		PACl concentration (mg/L)					
		0	10	20	30	40	50
Turbidity (NTU)	94	83	4.02	3.85	1.26	1.01	1.1
pH	7.8	7.7	7.6	7.4	7.3	7.2	7.1
DOC (mg/L)	2.2	2.1	2.0	1.8	1.7	1.5	1.4
UV-254 (cm^{-1})	0.066	0.060	0.057	0.034	0.029	0.019	0.017
SUVA (L/mg-m)	3.0	2.8	2.8	1.9	1.7	1.3	1.2
THMFP (ug/L)	302	285	254	234	212	188	167

Table A-4 DOC, UV-254, SUVA, THMFP, turbidity and pH of raw surface water and filtrated water at various PACl concentrations in rainy season

Parameters	Raw water	Rainy season			
		PACl concentration (mg/L)			
		0	20	30	40
Turbidity (NTU)	291	0.24	0.18	0.02	0.01
pH	7.6	7.6	7.4	7.3	7.2
DOC (mg/L)	2.3	2.0	1.7	1.3	1.2
UV254 (cm^{-1})	0.076	0.043	0.026	0.023	0.022
SUVA (L/mg-m)	3.3	2.2	1.6	1.7	1.8
THMFP (ug/L)	330	260	198	135	108

Table A-5 DOC, UV-254, SUVA, THMFP, turbidity and pH of raw surface water and filtrated water at various PACl concentrations in winter season

Parameters	Raw water	Winter season			
		PACl concentration (mg/L)			
		0	20	30	40
Turbidity (NTU)	57.1	0.16	0.19	0.01	0.02
pH	7.7	7.5	7.5	7.4	7.3
DOC (mg/L)	2.0	1.7	1.5	1.4	1.2
UV254 (cm-1)	0.086	0.035	0.027	0.024	0.021
SUVA (L/mg-m)	4.4	2.1	1.8	1.8	1.8
THMFP (ug/L)	258	191	174	142	107

Table A-6 DOC, UV-254, SUVA, THMFP, turbidity and pH of raw surface water and filtrated water at various PACl concentrations in summer season

Parameters	Raw water	Summer season			
		PACl concentration (mg/L)			
		0	20	30	40
Turbidity (NTU)	94	0.22	0.13	0.01	0.01
pH	7.8	7.7	7.4	7.3	7.2
DOC (mg/L)	2.2	1.9	1.5	1.3	1.2
UV254 (cm-1)	0.066	0.034	0.027	0.023	0.021
SUVA (L/mg-m)	3.0	1.8	1.8	1.7	1.8
THMFP (ug/L)	302	211	166	135	98

APPENDIX A-2

FLOW RATE AND FLUX OF CERAMIC MEMBRANE FILTRATION

Table A-7 Flux and flow rate of ceramic membrane filtration of raw surface water

Volume (L)	Avg.Time (sec)	Flow rate (L/s)	Flow rate (m^3/day)	Flux(m^3/m^2-day)
0.2	14.20	0.01408	1.21690	28.97
0.4	29.74	0.01287	1.11197	26.48
0.6	45.80	0.01245	1.07597	25.62
0.8	61.70	0.01258	1.08679	25.88
1.0	78.15	0.01216	1.05046	25.01
1.2	94.20	0.01246	1.07664	25.63
1.4	110.77	0.01207	1.04285	24.83
1.6	127.43	0.01200	1.03721	24.70
1.8	143.96	0.01210	1.04537	24.89
2.0	160.92	0.01179	1.01887	24.26
2.2	178.16	0.01160	1.00232	23.86
2.4	196.00	0.01121	0.96861	23.06
2.6	213.38	0.01151	0.99425	23.67
2.8	230.44	0.01172	1.01290	24.12
3.0	247.98	0.01140	0.98518	23.46
3.2	265.92	0.01115	0.96321	22.93
3.4	284.54	0.01074	0.92803	22.10
3.6	302.23	0.01131	0.97682	23.26
3.8	320.42	0.01100	0.94997	22.62
4.0	338.80	0.01088	0.94015	22.38

Table A-8 Flux and flow rate of ceramic membrane filtration of raw surface water with PACl 20 mg/L

Volume (L)	Avg.Time (sec)	Flow rate (L/s)	Flow rate (m^3/day)	Flux(m^3/m^2-day)
0.2	14.10	0.01418	1.22553	29.18
0.4	29.87	0.01268	1.09575	26.09
0.6	44.35	0.01381	1.19337	28.41
0.8	59.48	0.01322	1.14210	27.19
1.0	74.48	0.01333	1.15200	27.43
1.2	89.86	0.01300	1.12354	26.75
1.4	105.42	0.01285	1.11054	26.44
1.6	121.29	0.01260	1.08885	25.92
1.8	136.86	0.01285	1.10983	26.42
2.0	152.91	0.01246	1.07664	25.63
2.2	169.59	0.01199	1.03597	24.67
2.4	185.17	0.01284	1.10911	26.41
2.6	200.96	0.01267	1.09436	26.06
2.8	217.01	0.01246	1.07664	25.63
3.0	233.54	0.01210	1.04537	24.89
3.2	249.91	0.01222	1.05559	25.13
3.4	265.97	0.01245	1.07597	25.62
3.6	282.07	0.01242	1.07329	25.55
3.8	298.51	0.01217	1.05109	25.03
4.0	315.01	0.01212	1.04727	24.94

Table A-9 Flux and flow rate of ceramic membrane filtration of raw surface water with PACl 30 mg/L

Volume (L)	Avg.Time (sec)	Flow rate (L/s)	Flow rate (m^3/day)	Flux(m^3/m^2-day)
0.2	13.38	0.01495	1.29148	30.75
0.4	29.61	0.01232	1.06470	25.35
0.6	44.26	0.01365	1.17952	28.08
0.8	60.13	0.01260	1.08885	25.92
1.0	75.81	0.01276	1.10204	26.24
1.2	91.64	0.01263	1.09160	25.99
1.4	107.62	0.01252	1.08135	25.75
1.6	123.48	0.01261	1.08953	25.94
1.8	139.70	0.01233	1.06535	25.37
2.0	156.01	0.01226	1.05947	25.23
2.2	172.73	0.01196	1.03349	24.61
2.4	189.00	0.01229	1.06208	25.29
2.6	205.29	0.01228	1.06077	25.26
2.8	221.64	0.01223	1.05688	25.16
3.0	238.45	0.01190	1.02796	24.48
3.2	254.67	0.01233	1.06535	25.37
3.4	271.39	0.01196	1.03349	24.61
3.6	288.33	0.01181	1.02007	24.29
3.8	305.34	0.01176	1.01587	24.19
4.0	322.34	0.01176	1.01647	24.20

Table A-10 Flux and flow rate of ceramic membrane filtration of raw surface water with PACl 40 mg/L

Volume (L)	Avg.Time (sec)	Flow rate (L/s)	Flow rate (m^3/day)	Flux(m^3/m2-day)
0.2	11.11	0.01800	1.55536	37.03
0.4	23.11	0.01667	1.44000	34.29
0.6	35.13	0.01664	1.43760	34.23
0.8	47.54	0.01612	1.39243	33.15
1.0	60.04	0.01600	1.38240	32.91
1.2	73.17	0.01523	1.31607	31.34
1.4	86.00	0.01559	1.34684	32.07
1.6	99.36	0.01497	1.29341	30.80
1.8	112.77	0.01491	1.28859	30.68
2.0	126.51	0.01456	1.25764	29.94
2.2	140.56	0.01423	1.22989	29.28
2.4	154.36	0.01449	1.25217	29.81
2.6	168.39	0.01426	1.23165	29.32
2.8	182.68	0.01400	1.20924	28.79
3.0	197.03	0.01394	1.20418	28.67
3.2	211.02	0.01430	1.23517	29.41
3.4	225.67	0.01365	1.17952	28.08
3.6	240.16	0.01380	1.19255	28.39
3.8	255.30	0.01321	1.14135	27.17
4.0	270.41	0.01324	1.14361	27.23

APPENDIX B

EXPERIMENT DATA OF IN-LINE COAGULATION WITH CERAMIC MEMBRANE FILTRATION IN CONTINUOUS OPERATED

Table B-1 Turbidity of raw surface water and filtrated water during experimental periods

Rainy season			Winter season			Summer season		
Days	Turbidity (NTU)		Days	Turbidity (NTU)		Days	Turbidity (NTU)	
	Raw water	Filtrated water		Raw water	Filtrated water		Raw water	Filtrated water
1	416	0.10	1	38.1	0.10	1	53.0	0.14
2	384	0.14	2	28.2	0.10	2	54.8	0.12
3	350	0.12	3	42.0	0.11	3	52.0	0.11
4	302	0.10	5	34.1	0.13	4	58.8	0.10
5	326	0.10	6	27.5	0.10	5	52.9	0.10
6	291	0.10	7	30.3	0.10	7	35.6	0.10
7	242	0.16	8	33.6	0.12	8	41.9	0.15
8	208	0.15	9	36.2	0.14	9	42.4	0.12
9	224	0.15	10	35.6	0.11	10	39.1	0.10
11	184	0.10	12	31.4	0.11	11	47.6	0.13
12	254	0.10	13	35.8	0.10	12	53.4	0.13
13	313	0.10	14	39.9	0.10	14	69.7	0.16
15	249	0.12	15	38.6	0.10	15	55.6	0.10
16	167	0.11	16	38.8	0.14	16	89.5	0.12
17	194	0.11	17	43.3	0.12	17	76.1	0.11
18	301	0.10	19	51.2	0.10	18	89.5	0.10
19	410	0.14	20	59.3	0.10	19	54.0	0.10
20	265	0.10	21	46.9	0.10	21	40.3	0.10
22	256	0.15	22	53.1	0.10	22	40.6	0.11

Table B-1 Turbidity of raw surface water and filtrated water during experimental periods (continued)

Rainy season			Winter season			Summer season		
Days	Turbidity (NTU)		Days	Turbidity (NTU)		Days	Turbidity (NTU)	
	Raw water	Filtrated water		Raw water	Filtrated water		Raw water	Filtrated water
23	227	0.10	23	50.1	0.16	23	45.8	0.12
24	150	0.13	24	43.9	0.13	24	65.0	0.10
25	127	0.16	25	54.0	0.12	25	62.6	0.10
26	468	0.10	26	51.9	0.14	26	44.7	0.14
27	468	0.14	27	51.8	0.14	27	45.3	0.11
28	276	0.17	28	48.9	0.1	28	48.3	0.12
29	205	0.15	29	48.5	0.1	29	62.6	0.1
30	169	0.1	30	42.0	0.1	30	50.9	0.1
31	275.0	0.12				31	54.5	0.11

Table B-2 DOC concentration of raw surface water and filtrated water during experimental periods

Rainy season			Winter season			Summer season		
Days	DOC (mg/L)		Days	DOC (mg/L)		Days	DOC (mg/L)	
	Raw water	Filtrated water		Raw water	Filtrated water		Raw water	Filtrated water
2	3.0	2.6	2	1.8	1.4	2	2.6	2.3
5	2.7	2.4	6	1.7	1.5	7	3.0	2.6
8	2.6	2.4	9	1.5	1.3	11	2.8	2.4
11	2.7	2.4	13	1.6	1.4	14	2.2	2.0
16	3.0	2.7	16	1.6	1.4	18	2.4	2.2
22	2.7	2.5	22	1.7	1.5	23	2.5	2.2
26	2.9	2.7	26	1.7	1.5	28	2.5	2.2
30	2.7	2.5	29	1.7	1.5	31	2.3	2.1
Avg.	2.8	2.5	Avg.	1.7	1.4	Avg.	2.6	2.3

Table B-3 UV-254 absorbance of raw surface water and filtrated water during experimental periods

Rainy season			Winter season			Summer season		
Days	UV-254 (cm^{-1})		Days	UV-254 (cm^{-1})		Days	UV-254 (cm^{-1})	
	Raw water	Filtrated water		Raw water	Filtrated water		Raw water	Filtrated water
2	0.0608	0.0442	2	0.0198	0.0158	2	0.0352	0.0284
5	0.0607	0.0452	6	0.0212	0.0164	7	0.0313	0.0242
9	0.0503	0.0384	9	0.0202	0.0154	11	0.029	0.0213
11	0.0717	0.0375	13	0.0224	0.0178	14	0.0473	0.0359
16	0.0697	0.0472	16	0.0232	0.0168	18	0.0267	0.0209
22	0.0609	0.0455	22	0.0269	0.0201	23	0.0374	0.0264
26	0.0715	0.0539	26	0.0256	0.0194	28	0.0366	0.0282
31	0.0618	0.0429	29	0.0264	0.0216	31	0.0386	0.0305
Avg.	0.063	0.044	Avg.	0.023	0.018	Avg.	0.035	0.026

Table B-4 THMs of raw surface water and filtrated water during experimental periods

Rainy season			Winter season			Summer season		
Days	THMs (μg/L)		Days	THMs (μg/L)		Days	THMs (μg/L)	
	Raw water	Filtrated water		Raw water	Filtrated water		Raw water	Filtrated water
2	4.18	84.9	2	2.02	58.8	2	2.64	70.8
8	3.56	85.4	9	1.93	61.2	11	2.75	73.8
16	3.41	87.6	16	2.21	59.8	18	2.71	69.9
22	3.87	86.8	22	1.88	60.1	23	2.63	73.6
26	3.92	88.6	29	2.11	59.8	28	2.6	72.0
Avg.	3.79	86.6	Avg.	2.03	59.9	Avg.	2.67	72.0

Table B-5 Chlorine residual in filtrated water during experimental periods

Rainy season		Winter season		Summer season	
Days	Cl (mg/L)	Days	Cl (mg/L)	Days	Cl (mg/L)
	Filtrated water		Filtrated water		Filtrated water
2	0.06	2	0.07	2	0.03
8	0.08	9	0.01	11	0.04
16	0.06	16	0.06	18	0.04
22	0.05	22	0.05	23	0.05
26	0.04	29	0.04	28	0.04
Avg.	0.06	Avg.	0.05	Avg.	0.04

Table B-6 Flux of ceramic membrane during experimental periods

Days	Rainy season		Days	Winter season		Days	Summer season	
	Flow rate (m^3/day)	Flux (m^3/m^2-day)		Flow rate (m^3/day)	Flux (m^3/m^2-day)		Flow rate (m^3/day)	Flux (m^3/m^2-day)
1	42.4	101	1	60.7	144	1	60.8	145
2	42.3	101	2	60.6	144	2	60.6	144
3	42.3	101	3	60.6	144	3	60.7	144
4	42.2	100	5	60.6	144	4	60.7	144
5	42.1	100	6	60.7	145	5	60.6	144
8	42.1	100	7	60.6	144	7	60.9	145
9	41.9	100	8	60.6	144	8	60.7	145
10	41.5	99	9	60.6	144	9	60.7	144
11	41.5	99	10	60.5	144	10	60.6	144
12	40.9	97	12	60.5	144	11	60.5	144
13	41.0	98	13	60.6	144	12	60.6	144
15	41.1	98	14	60.6	144	14	60.7	144
16	41.1	98	15	60.6	144	15	60.8	145
17	41.3	98	16	60.6	144	16	60.8	145
18	41.3	98	17	56.8	135	17	60.6	144
19	41.1	98	19	56.8	135	18	60.8	145
20	40.9	97	20	57.5	137	19	60.6	144
22	40.9	97	21	58.1	138	21	60.8	145
23	40.8	97	22	58.1	138	22	60.6	144
24	40.3	96	23	58.2	139	23	59.9	143
25	41.0	98	24	58.0	138	24	60.8	145
26	41.1	98	26	58.2	139	25	60.7	144
27	39.7	95	27	57.8	138	26	60.6	144
29	40.0	95	28	57.7	137	28	60.7	144
30	39.7	94	29	57.9	138	29	60.6	144
31	39.8	95	30	58.8	140	30	60.6	144

APPENDIX C

RESIN FRACTIONATION DATA

Table C-1 Resin fractionation data of coagulation process at PACl dosage 10 mg/L in rainy season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	3.42	2.67	6.09	6.86	-12.8
%DOC mass	56	44	100	-	-
DOC (mg/L)	1.14	8.88	-	2.29	-
Cal Conc.	1.14	0.89	2.03	2.29	-

Table C-2 Resin fractionation data of coagulation process at PACl dosage 20 mg/L in rainy season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	3.22	2.35	5.57	6.14	-10.2
%DOC mass	58	42	100	-	-
DOC (mg/L)	1.07	7.83	-	2.05	-
Cal Conc.	1.07	0.78	1.86	2.05	-

Table C-3 Resin fractionation data of coagulation process at PACl dosage 30 mg/L in rainy season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	3.07	1.86	4.92	4.87	1.06
%DOC mass	62	38	100	-	-
DOC (mg/L)	1.02	6.18	-	1.62	-
Cal Conc.	1.02	0.62	1.64	1.62	-

Table C-4 Resin fractionation data of coagulation process at PACl dosage 40 mg/L in rainy season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.68	1.60	4.29	4.28	0.27
%DOC mass	63	37	100	-	-
DOC (mg/L)	0.89	5.35	-	1.43	-
Cal Conc.	0.89	0.53	1.43	1.43	-

Table C-5 Resin fractionation data of coagulation process at PACl dosage 50 mg/L in rainy season

Parameter	Fractionated water		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.57	1.52	4.10	4.21	-2.69
%DOC mass	63	37	100	-	-
DOC (mg/L)	0.86	5.08	-	1.40	-
Cal Conc.	0.86	0.51	1.37	1.40	-

Table C-6 Resin fractionation data of coagulation process at PACl dosage 10 mg/L in winter season

Parameter	Fractionated water		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	3.36	2.50	5.86	5.49	6.30
%DOC mass	57	43	100	-	-
DOC (mg/L)	1.12	8.34	-	1.83	-
Cal Conc.	1.12	0.83	1.95	1.83	-

Table C-7 Resin fractionation data of coagulation process at PACl dosage 20 mg/L in winter season

Parameter	Fractionated water		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	3.17	2.30	5.46	5.11	6.56
%DOC mass	58	42	100	-	-
DOC (mg/L)	1.06	7.65	-	1.70	-
Cal Conc.	1.06	0.76	1.82	1.70	-

Table C-8 Resin fractionation data of coagulation process at PACl dosage 30 mg/L in winter season

Parameter	Fractionated water		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.96	1.87	4.84	4.76	1.54
%DOC mass	61	39	100	-	-
DOC (mg/L)	0.99	6.24	-	1.59	-
Cal Conc.	0.94	0.62	1.61	1.59	-
Meas DOC	100	10	-	-	-

Table C-9 Resin fractionation data of coagulation process at PACl dosage 40 mg/L in winter season

Parameter	Fractionated water		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.66	1.55	4.21	4.31	-2.48
%DOC mass	63	37	100	-	-
DOC (mg/L)	0.89	5.18	-	1.44	-
Cal Conc.	0.89	0.52	1.40	1.44	-

Table C-10 Resin fractionation data of coagulation process at PACl dosage 50 mg/L in winter season

Parameter	Fractionated water		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.57	1.46	4.03	4.22	-4.65
%DOC mass	64	36	100	-	-
DOC (mg/L)	0.86	4.87	-	1.41	-
Cal Conc.	0.86	0.49	1.34	1.41	-

Table C-11 Resin fractionation data of coagulation process at PACl dosage 10 mg/L in summer season

Parameter	Fractionated water		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	3.20	2.63	5.82	6.16	-5.79
%DOC mass	55	45	100	-	-
DOC (mg/L)	1.06	8.77	-	2.05	-
Cal Conc.	1.06	0.88	1.94	2.05	-

Table C-12 Resin fractionation data of coagulation process at PACl dosage 20 mg/L in summer season

Parameter	Fractionated water		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	3.07	2.29	5.36	5.55	-3.69
%DOC mass	57	43	100	-	-
DOC (mg/L)	1.02	7.62	-	1.85	-
Cal Conc.	1.02	0.76	1.79	1.85	-

Table C-13 Resin fractionation data of coagulation process at PACl dosage 30 mg/L in summer season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.96	1.87	4.83	5.06	-4.80
%DOC mass	61	39	100	-	-
DOC (mg/L)	0.99	6.24	-	1.69	-
Cal Conc.	0.99	0.62	1.61	1.69	-

Table C-14 Resin fractionation data of coagulation process at PACl dosage 40 mg/L in summer season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.47	1.65	4.12	4.53	-9.93
%DOC mass	60	40	100	-	-
DOC (mg/L)	0.82	5.50	-	1.51	-
Cal Conc.	0.82	0.55	1.37	1.51	-

Table C-15 Resin fractionation data of coagulation process at PACl dosage 50 mg/L in summer season

Parameter	Fractionated water		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.42	1.54	3.96	4.51	-13.89
%DOC mass	61	39	100	-	-
DOC (mg/L)	0.81	5.13	-	1.50	-
Cal Conc.	0.81	0.51	1.32	1.50	-

Table C-16 Resin fractionation data of in-line coagulation with ceramic membrane filtration at PACl dosage 20 mg/L in rainy season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	3.07	1.96	5.03	4.97	1.15
%DOC mass	61	39	100	-	-
DOC (mg/L)	1.02	6.53	-	1.66	-
Cal Conc.	1.02	0.65	1.68	1.66	-

Table C-17 Resin fractionation data of in-line coagulation with ceramic membrane filtration at PACl dosage 30 mg/L in rainy season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.74	1.54	4.27	4.04	5.61
%DOC mass	64	36	100	-	-
DOC (mg/L)	0.91	5.13	-	1.35	-
Cal Conc.	0.91	0.51	1.42	1.35	-

Table C-18 Resin fractionation data of in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L in rainy season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.39	1.30	3.68	3.63	1.32
%DOC mass	65	35	100	-	-
DOC (mg/L)	0.80	4.32	-	1.21	-
Cal Conc.	0.80	0.43	1.23	1.21	-

Table C-19 Resin fractionation data of in-line coagulation with ceramic membrane filtration at PACl dosage 20 mg/L in winter season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.99	1.96	4.96	4.57	7.78
%DOC mass	60	40	100	-	-
DOC (mg/L)	1.00	6.55	-	1.52	-
Cal Conc.	1.00	0.65	1.65	1.52	-

Table C-20 Resin fractionation data of in-line coagulation with ceramic membrane filtration at PACl dosage 30 mg/L in winter season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.67	1.54	4.20	4.10	2.57
%DOC mass	63	37	100	-	-
DOC (mg/L)	0.89	5.12	-	1.37	-
Cal Conc.	0.89	0.51	1.40	1.37	-

Table C-21 Resin fractionation data of in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L in winter season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.29	1.27	3.56	3.56	-0.11
%DOC mass	64	36	100	-	-
DOC (mg/L)	0.76	4.23	-	1.19	-
Cal Conc.	0.76	0.42	1.19	1.19	-

Table C-22 Resin fractionation data of in-line coagulation with ceramic membrane filtration at PACl dosage 20 mg/L in summer season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.93	2.04	4.96	4.49	9.40
%DOC mass	59	41	100	-	-
DOC (mg/L)	0.98	6.79	-	1.50	-
Cal Conc.	0.98	0.68	1.65	1.50	-

Table C-23 Resin fractionation data of in-line coagulation with ceramic membrane filtration at PACl dosage 30 mg/L in winter season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.66	1.56	4.22	4.04	4.47
%DOC mass	63	37	100	-	-
DOC (mg/L)	0.89	5.21	-	1.35	-
Cal Conc.	0.89	0.52	1.41	1.35	-

Table C-24 Resin fractionation data of in-line coagulation with ceramic membrane filtration at PACl dosage 40 mg/L in winter season

Parameter	Fractionated		HPI+HPO	Unfractionated water	% Diff
	HPI	HPO			
Mass DOC (mg)	2.24	1.30	3.53	3.49	1.29
%DOC mass	63	37	100	-	-
DOC (mg/L)	0.75	4.33	-	1.16	-
Cal Conc.	0.75	0.43	1.18	1.16	-

APPENDIX D

PYROLYSIS GC/MS DATA

Table D-1 Average relative ratio of the pyrolysis fragment in raw surface water, coagulated water and filtrated water in rainy season

Chemical classes	pyrolysis fragment	Average relative ratio		
		Raw water	Coagulated water	Filtrated water
AC[1]	1-Dodecanol	0.89		
AC	2-Hexyl-1-octanol	0.90		
AL[2]	1-Decane	1.09		
AL	1-Hexadecane	0.91	2.75	
AL	1-Pentadecane	0.91		
AL	1-tetradecane	1.00	0.16	0.15
AL	1-Undecane	0.98		
AL	Eicosane	0.71	0.33	0.12
AL	Heneicosane	0.87	0.9	
AL	Octacosane	0.81	0.79	0.4
AL	Octadecane	1.00	1	1
AL	Pentadecane			1.25
AL	Tetracosane		0.59	0.85
AL	Tetratriacontane		0.28	0.41
CA[3]	1,2-Benzenedicarboxylic acid		0.13	
CA	n-Hexadecanoic acid	3.60	0.78	
CA	Pentadecanoic acid	0.46	0.31	
CA	Pentafluoropropionic acid		0.36	0.36
CA	Tetradecanoic acid	0.85		

Table D-1 Average relative ratio of the pyrolysis fragment in raw surface water, coagulated water and filtrated water in rainy season (continued)

Chemical classes	pyrolysis fragment	Average relative ratio		
		Raw water	Coagulated water	Filtrated water
CA	Trichloroacetic acid	1.06		
OT[4]	2-Tridecanone	1.04		
OT	2-Pentadecanone	0.54		
OT	2-Nonadecanone	0.90		
ON[5]	Dodecanenitrille	0.78		
ON	Heptadecanenitrille	1.04		
ON	Hexadecanenitrile	0.49	0.16	0.17
ON	Tetradecanenitrille		0.18	
ON	Tridecanenitrille	0.46		
	Sum of relative ratio of AL	8.28	6.80	4.18
	Sum of relative ratio of AC	1.79	0.00	0.00
	Sum of relative ratio of CA	5.97	1.58	0.36
	Sum of relative ratio of OT	2.48	0.00	0.00
	Sum of relative ratio of ON	2.77	0.34	0.17
	Sum of relative ratio	21.29	8.72	4.71

Remark: 1=Alcohol, 2=Aliphatic hydrocarbon, 3=Carboxylic acids, 4=other chemical classes and 5=Organic nitrogen

Table D-2 Average relative ratio of the pyrolysis fragment in raw surface water, coagulated water and filtrated water in dry season

Chemical classes	pyrolysis fragment	Average relative ratio		
		Raw water	Coagulated water	Filtrated water
AC[1]	2-Hexyl-1-octanol	0.22		
AL[2]	1-Hexadecane		2.95	
AL	1-Pentadecane		0.11	
AL	1-tetradecane		0.12	
AL	Cyclopentadecane	2.36		
AL	Eicosane	0.72	0.21	0.09
AL	Heneicosane	0.87		
AL	Heptadecane	0.57		
AL	Hexadecane	0.34		0.08
AL	Nonadecane	0.23		
AL	Octacosane	0.75	0.57	0.39
AL	Octadecane	1.00	1	1
AL	Pentadecane		0.93	1.34
AL	Tetracosane		0.59	1.03
AL	Tetratetracontane	0.27		
AL	Tetratriacontane		0.19	0.41

Table D-2 Average relative ratio of the pyrolysis fragment in raw surface water, coagulated water and filtrated water in dry season (continued)

Chemical classes	pyrolysis fragment	Average relative ratio		
		Raw water	Coagulated water	Filtrated water
CA[3]	1,2-Benzenedicarboxylic acid		0.1	
CA	n-Hexadecanoic acid	4.18	0.64	
CA	Pentadecanoic acid	0.95	0.29	
CA	Pentafluoropropionic acid		0.3	
CA	Tetradecanoic acid	0.67		
CA	Trichloroacetic acid	0.23		
ON[4]	Hexadecanenitrile	0.63	0.08	0.38
ON	Tetradecanenitrille		0.22	
ON	Tridecanenitrille	0.18		
OT[5]	Cyclotrisiloxane	0.35		
	Sum of relative ratio of AL	7.11	6.67	4.34
	Sum of relative ratio of AC	0.22	0.00	0.00
	Sum of relative ratio of CA	6.03	1.33	0.00
	Sum of relative ratio of ON	0.81	0.30	0.38
	Sum of relative ratio of OT	0.35	0.00	0.00
	Sum of relative ratio	14.52	8.30	4.72

Remark: 1=Alcohol, 2=Aliphatic hydrocarbon, 3=Carboxylic acids, 4= Organic nitrogen and 5= other chemical classes

Table D-3 Average relative ratio of the pyrolysis fragment of HPIA fraction in raw surface water and filtrated water

Chemical classes	pyrolysis fragment	Average relative ratio	
		Raw water	Filtrated water
AC[1]	1-Dodecanol	0.14	
AL[2]	1-Hexadecane	3.48	3.14
AL	1-Pentadecane	0.15	
AL	1-tetradecane	0.2	
AL	Eicosane	0.24	0.21
AL	Heneicosane	0.89	
AL	Nonadecane		0.05
AL	Octacosane	0.67	0.67
AL	Octadecane	1	1
AL	Pentadecane		0.95
AL	Tetracosane	0.61	0.65
AL	Tetratriacontane	0.25	0.39
CA[3]	1,2-Benzenedicarboxylic acid	0.17	
CA	n-Hexadecanoic acid	0.58	
CA	Pentadecanoic acid	0.29	
CA	Pentafluoropropionic acid	0.41	0.06

Table D-3 Average relative ratio of the pyrolysis fragment of HPIA fraction in raw surface water and filtrated water (continued)

Chemical classes	pyrolysis fragment	Average relative ratio	
		Raw water	Filtrated water
ON[4]	Hexadecanenitrile		0.16
ON	Tetradecanenitrille	0.16	
	Sum of relative ratio of AL	7.49	7.06
	Sum of relative ratio of AC	0.14	0.00
	Sum of relative ratio of CA	1.45	0.06
	Sum of relative ratio of ON	0.16	0.16
	Sum of relative ratio	9.24	7.28

Remark: 1=Alcohol, 2=Aliphatic hydrocarbon, 3=Carboxylic acids and 4= Organic nitrogen

Table D-4 Average relative ratio of the pyrolysis fragment of HPIB fraction in raw surface water and filtrated water

Chemical classes	pyrolysis fragment	Average relative ratio	
		Raw water	Filtrated water
AL[1]	Eicosane	0.54	0.50
AL	Nonadecane	0.35	
AL	Octacosane	0.77	0.75
AL	Octadecane	1.00	1.00
AL	Pentadecane	0.90	0.87
AL	Tetracosane	0.51	
CA[2]	n-Hexadecanoic acid	1.31	0.66
ON[3]	Hexadecanenitrile	0.45	
ON	Tetradecanenitrille	0.27	
	Sum of relative ratio of AL	4.07	3.12
	Sum of relative ratio of CA	1.31	0.66
	Sum of relative ratio of ON	0.72	0.00
	Sum of relative ratio	6.10	3.78

Remark: 1=Aliphatic hydrocarbon, 2=Carboxylic acids and 3=Organic nitrogen

Table D-5 Average relative ratio of the pyrolysis fragment of HPIN fraction in raw surface water and filtrated water

Chemical classes	pyrolysis fragment	Average relative ratio	
		Raw water	Filtrated water
AL[1]	1-Hexadecane	0.68	
AL	Eicosane	0.34	0.33
AL	Heneicosane	0.95	
AL	Heptadecane	0.70	
AL	Nonadecane	0.15	0.18
AL	Octacosane	0.75	0.60
AL	Octadecane	1.00	1.00
AL	Pentadecane		1.49
AL	Tetracosane		1.36
AL	Tetratriacontane	0.27	0.66
CA[2]	n-Hexadecanoic acid	0.42	
CA	Trichloroacetic acid	0.20	
ON[3]	Hexadecanenitrile	0.13	
OT[4]	Cyclotrisiloxane	0.17	0.23
	Sum of relative ratio of AL	4.84	5.62
	Sum of relative ratio of CA	0.62	0.00
	Sum of relative ratio of ON	0.13	0.00
	Sum of relative ratio of OT	0.17	0.23
	Sum of relative ratio	5.76	5.85

Remark: 1=Aliphatic hydrocarbon, 2=Carboxylic acids, 3= Organic nitrogen and 4=other chemical classes

Table D-6 Average relative ratio of the pyrolysis fragment of HPOA fraction in raw surface water and filtrated water

Chemical classes	pyrolysis fragment	Average relative ratio	
		Raw water	Filtrated water
AC[1]	2-Hexyl-1-octanol	0.20	0.19
AL[2]	1-Hexadecane	0.31	0.22
AL	1-Pentadecane	0.28	0.16
AL	1-tetradecane	0.29	0.17
AL	9-Octadecane	0.19	
AL	Eicosane	0.64	0.53
AL	Heneicosane	0.84	0.94
AL	Heptadecane	0.57	0.82
AL	Hexadecane	0.32	
AL	Nonadecane	0.25	0.31
AL	Octacosane	0.79	0.78
AL	Octadecane	1.00	1.00
AL	Tetratetracontane	0.29	0.16
AL	Tetratriacontane		0.45
CA[3]	1,2-Benzenedicarboxylic acid		0.15
CA	3-Chloropropionic acid	0.19	
CA	Aminomethane sulfonic acid		11.10
CA	n-Hexadecanoic acid	3.07	0.50
CA	Tetradecanoic acid	1.30	
CA	Trichloroacetic acid	0.24	0.12

Table D-6 Average relative ratio of the pyrolysis fragment of HPOA fraction in raw surface water and filtrated water (continued)

Chemical classes	pyrolysis fragment	Average relative ratio	
		Raw water	Filtrated water
ON[4]	Hexadecanenitrile	0.31	
OT[5]	Cyclotrisiloxane	0.82	
	Sum of relative ratio of AL	5.77	5.54
	Sum of relative ratio of AC	0.20	0.19
	Sum of relative ratio of CA	4.80	0.77
	Sum of relative ratio of ON	0.31	0.00
	Sum of relative ratio of OT	0.82	0.00
	Sum of relative ratio	11.90	6.50

Remark: 1=Alcohol, 2=Aliphatic hydrocarbon, 3=Carboxylic acids, 4= Organic nitrogen and 5= other chemical classes

Table D-7 Average relative ratio of the pyrolysis fragment of HPOB fraction in raw surface water and filtrated water

Chemical classes	pyrolysis fragment	Average relative ratio	
		Raw water	Filtrated water
AC[1]	2-Hexyl-1-octanol	0.22	
AC	1-Decanol, 2-Hexyl		0.16
AL[2]	1-Hexadecane	0.33	0.21
AL	1-Pentadecane	0.28	
AL	1-tetradecane	0.23	
AL	Eicosane	0.53	0.50
AL	Heneicosane	0.92	0.91
AL	Heptadecane	0.51	0.86
AL	Nonadecane	0.33	0.30
AL	Octacosane	0.81	0.84
AL	Octadecane	1.00	1.00
AL	Tetratetracontane	0.24	0.15
AL	Tetratriacontane		0.55
CA[3]	n-Hexadecanoic acid	0.92	
CA	Trichloroacetic acid	0.18	

Table D-7 Average relative ratio of the pyrolysis fragment of HPOB fraction in raw surface water and filtrated water (continued)

Chemical classes	pyrolysis fragment	Average relative ratio	
		Raw water	Filtrated water
ON[4]	Hexadecanenitrile	0.23	0.22
OT[5]	Octadecanal	0.22	
OT	Cyclotrisiloxane	0.32	
	Sum of relative ratio of AL	5.18	5.32
	Sum of relative ratio of AC	0.22	0.16
	Sum of relative ratio of CA	1.10	0.00
	Sum of relative ratio of ON	0.23	0.22
	Sum of relative ratio of OT	0.54	0.00
	Sum of relative ratio	7.27	5.70

Remark: 1=Alcohol, 2=Aliphatic hydrocarbon, 3=Carboxylic acids, 4= Organic nitrogen and 5= other chemical classes

Table D-8 Average relative ratio of the pyrolysis fragment of HPON fraction in raw surface water and filtrated water

Chemical classes	pyrolysis fragment	Average relative ratio	
		Raw water	Filtrated water
AL[1]	1-Hexadecane		0.51
AL	1-tetradecane		0.52
AL	Eicosane	0.43	0.42
AL	Octacosane	0.63	0.61
AL	Octadecane	1	1
AL	Pentadecane	1.15	1.3
AL	Tetracosane	1.08	1.22
CA[2]	n-Hexadecanoic acid	1.18	0.48
ON[3]	Tetradecanenitrille	0.15	
OT[4]	Cyclotrisiloxane	0.5	
	Sum of relative ratio of AL	4.29	5.58
	Sum of relative ratio of CA	1.18	0.48
	Sum of relative ratio of ON	0.15	0.00
	Sum of relative ratio of OT	0.50	0.00
	Sum of relative ratio	6.12	6.06

Remark: 1=Aliphatic hydrocarbon, 2=Carboxylic acids, 3= Organic nitrogen and 4= other chemical classes

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