การกำจัดความขุ่นและการเกิดสารไตรฮาโลมีเทนในการโคแอกกูเลชั่นน้ำขุ่นผิวดินโดยใช้เฟอร์ริกจากเหล็กธรรมชาติในน้ำใต้ดินทำปฏิกิริยากับคลอรีน

นางสาวภควดี แสงจันทร์

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
สาขาวิชาการจัดการสิ่งแวดล้อม (สหสาขาวิชา)
บัณฑิตวิทยาลัย จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2552

TURBIDITY REMOVAL AND TRIHALOMETHANES (THMs) FORMATION IN TURBID SURFACE WATER COAGULATION USING FERRIC COAGULANT FROM NATURAL IRON IN GROUNDWATER REACTED WITH CHLORINE

Miss Pakawadee Sangchan

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Science Program in Environmental Management
(Interdisciplinary Program)
Graduate School
Chulalongkorn University
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Thesis Title	TURBIDITY REMOVAL AND TRIHALOMETHANES (THMs) FORMATION IN TURBID SURFACE WATER COAGULATION USING FERRIC COAGULANT FROM NATURAL IRON IN GROUNDWATER REACTED WITH CHLORINE
By	Miss Pakawadee Sangchan
Field of Study	Environmental Management
Thesis Advisor	Associate Professor Suraphong Wattanachira, D.Eng.

Accepted by the Graduate School, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

.... Dean of the Graduate School
(Associate Professor Pornpote Piumsomboon,Ph.D.)

THESIS COMMITTEE

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....Examiner
(Associate Professor Jin Anotai, Ph.D.)

....Examiner
(Pichet Chiwiwatworakul, Ph.D.)

....External Examiner
(Assistant Professor Bunyarit Panyapinyopol, Ph.D.)

ภควดี แสงจันทร์: การกำจัดความขุ่นและการเกิดสารไตรฮาโลมีเทนในการโคแอกกูเลชั่นน้ำขุ่นผิวดินโดยใช้เฟอร์ริกจากเหล็กธรรมชาติในน้ำใต้ดินทำปฏิกิริยากับคลอรีน (TURBIDITY REMOVAL AND TRIHALOMETHANES (THMs) FORMATION IN TURBID SURFACE WATER COAGULATION USING FERRIC COAGULANT FROM NATURAL IRON IN GROUNDWATER REACTED WITH CHLORINE) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : รศ.ดร. สุรพงษ์ วัฒนะจีระ, 107หน้า.

งานวิจัยนี้มีจุดมุ่งหมายเพื่อศึกษาความเป็นไปได้ในการใช้เฟอร์ริกโคแอกกูแลนท์ซึ่งถูกผลิตขึ้นจากเหล็กธรรมชาติที่มีอยู่ในน้ำใต้ดินทำปฏิกิริยากับคลอรีนเพื่อจำกัดความขุ่นในน้ำผิวดิน น้ำแม่ปิงเป็นแหล่งน้ำหลักที่ใช้อยู่ทั่วไปในปัจจุบัน ซึ่งนำมาใช้เป็นน้ำดิบสำหรับการผลิตน้ำประปาในเมืองเชียงใหม่ ได้ถูกเลือกเป็นน้ำขุ่นผิวดินสำหรับการทดลอง และน้ำใต้ดินที่ถูกเลือกมาในการศึกษาครั้งนี้มาจากบ่อน้ำตื้นบริเวณใกล้เคียงกับจุดเก็บตัวอย่างน้ำแม่ปิง โดยมีปริมาณเหล็กธรรมชาติประมาณ 21 มิลลิกรัม/ลิตร ของเหล็กรวม การโคแอกกูเลชั่นถูกทดลองด้วยเครื่องทดสอบการตกตะกอนน้ำ (จาร์เทส) โดยใช้สารละลายโซเดียมไฮโปคลอไรท์ที่ความเข้มข้นต่างกันในรูปของคลอรีนเติมลงไปในสัดส่วนของน้ำใต้ดินต่อน้ำผิวดินที่แตกต่างกัน ผลจากการทดลองพบว่าที่ความเข้มข้น 30 มิลลิกรัมของคลอรีนต่อน้ำใต้ดินหนึ่งลิตร คือปริมาณคลอรีนที่เหมาะสมสำหรับผลิตเฟอร์ริกโคแอกกูแลนท์ได้สูงสุด 21 มิลลิกรัม/ลิตร (ของเหล็กรวม) อัตราส่วนของน้ำใต้ดินต่อน้ำผิวดินที่ 35:65 ภายใต้การเติมปริมาณคลอรีนที่เหมาะสมตามที่ได้กล่าวไว้ข้างต้น พบว่าเป็นเงื่อนไขของการโคแอกกูเลชั่นที่เหมาะสมสำหรับการกำจัดความขุ่น โดยสามารถลดความขุ่นในน้ำผิวดินได้ต่ำกว่า 10 NTU ยิ่งไปกว่านั้น จากการปฏิบัติการโคแอกกูเลชั่นโดยการเติมคลอรีนลงไปในของผสมระหว่างน้ำใต้ดินและน้ำผิวดิน (หรือเรียกว่าวิธีการเติมคลอรีนแบบก่อน) ให้ประสิทธิภาพในการกำจัดความขุ่นได้ดีกว่า การเติมคลอรีนลงไปในน้ำใต้ดินก่อนที่จะผสมกับน้ำผิวดิน (หรือเรียกว่าวีธีการเติมคลอรีนแบบหลัง) อีกทั้งในการศึกษาครั้งนี้ยังได้สนใจในเรื่องการเกิดสารไตรฮาโลมีเทน ในน้ำที่ผ่านจากกระบวนการโคแอกกูเลชั่น ภายใต้เงื่อนไขทั้งหลายตามที่ได้กล่าวไว้แล้วข้างต้น จากผลการทดลองพบว่าปริมาณสารไตรฮาโลมีเทนทั้งหมด ที่อัตราส่วนของน้ำใต้ดินต่อน้ำผิวดินที่ 35:65 และ 50:50 ในน้ำดิบมีค่า 2.98 และ 2.67 ไมโครกรัม/ลิตร ตามลำดับ ในขณะที่น้ำที่ผ่านจากกระบวนการโคแอกกูเลชั่นที่อัตราส่วนเหล่านั้น มีค่าเพิ่มขึ้นถึง 51.17 และ 51.47 ไมโครกรัม/ลิตร ตามลำดับ ซึ่งมีค่าสูงเกินกว่าระดับการปนเปื้อนสูงสุดของสารไตรฮาโลมีเทนในระดับที่ 2 ที่ 40 ไมโครกรัม/ลิตร แต่ยังคงมีค่าไม่สูงเกินกว่าในระดับที่ 1 ที่ 80 ไมโครกรัม/ลิตร ตามมาตราฐานน้ำดื่ม ที่เสนอโดยองค์กรปกป้องสิ่งแวดล้อม U.S. Environmental Protection Agency (USEPA, 1998) นอกจากนี้แล้ว ค่าใช้จ่ายสารเคมีของสารสะลายโซเดียมไฮโปคลอไรท์ที่ถูกใช้ในกระบวนการโคแอกกูเลชั่นตามที่เสนอไว้ในการศึกษาครั้งนี้ และค่าใช้จ่ายสารเคมีในการโคแอกกูเลชั่นโดยใช้เฟอร์ริกคลอไรด์สำเร็จรูป ได้ถูกนำมาเปรียบเทียบ และกล่าวได้ว่าการโคแอกกูเลชั่นโดยการใช้โซเดียมไฮโปคลอไรท์เติมลงไปในของผสมระหว่างน้ำใต้ดินและน้ำผิวดินเพื่อผลิตเฟอร์ริกโคแอกกูแลนท์นั้น มีค่าใช้จ่ายสารเคมีถูกกว่าการใช้เฟอร์ริกคลอไรด์สำเร็จรูป

สาขาวิชา การจัดการสิ่งแวดล้อม ลายมือชื่อนิสิต

ปีการศึกษา 2552 ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก

5187554220: MAJOR ENVIRONMENTAL MANAGEMENT
KEYWORDS: COAGULATION/ GROUNDWATER/ TURBID SURFACE WATER/ NATURAL IRON/ TRIHALOMETHANE (THMs)

PAKAWADEE SANGCHAN: TURBIDITY REMOVAL AND TRIHALOMETHANES (THMs) FORMATION IN TURBID SURFACE WATER COAGULATION USING FERRIC COAGULANT FROM NATURAL IRON IN GROUNDWATER REACTED WITH CHLORINE. THESIS ADVISOR: ASSOC. PROF. SURAPHONG WATTANACHIRA, D. Eng., 107pp.

This research aimed at studying the possibility of using ferric coagulant which was produced from natural iron in groundwater reacted with chlorine for removing turbidity from surface water. Ping River water, which is currently the main water source utilized to produce water supply for Chiang Mai city, was selected as turbid surface water for the experiments. A selected groundwater in this study was from the shallow well near Ping River sampling point that naturally contains more or less 21 mg/L of total iron. Coagulations were experimented in Jar-test unit by using various sodium hypochlorite concentrations as chlorine sources added into different ratios of groundwater and surface water. The results shows that chlorine dosage of 30 mg as Cl_2 per one liter of groundwater was the optimal chlorine dosage for producing maximum ferric coagulant of about 21 mg/L(as total iron). The ratio of groundwater to surface water of 35:65 under the previous optimal chlorine dosage were found to be the most appropriate coagulation condition for turbidity removal which could reduced turbidity in surface water to be below 10 NTU. In addition, it was observed that coagulation operated by dosing chlorine into a mixture of groundwater and surface water (called as post-chlorine adding method) gave more efficient turbidity removal than that of dosing chlorine into groundwater before mixing with surface water (called as pre-chlorine adding method). This study was also interested on trihalomethanes (THMs) formation in the coagulated water under the above-mentioned operational conditions. The results shows that total THMs concentrations at ratios of groundwater to surface water of 35:65 and 50:50 in raw water were 2.98 μg/L and 2.67 μg/L, respectively, whereas those in coagulated waters were increased to be 51.17 μg/L and 51.47 μg/L, respectively, which were higher than the Maximum Contaminant Level (MCL) for THMs of 40μg/L for stage 2 but were lower than that of 80μg/L for stage 1 of drinking water standard issued by U.S. Environmental Protection Agency (USEPA, 1998). Furthermore, chemical cost of sodium hypochlorite used in the coagulation process proposed by this study and chemical cost of the coagulation by commercial ferric chloride were compared, it could be stated that coagulation by using sodium hypochlorite added into a mixture of groundwater and surface water to produce ferric coagulant was cheaper than that of utilizing commercial ferric chloride.

Field of Study : Environmental Management
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Student's Signature :
Advisor's Signature: Suraphong

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LIST OF ABBREVIATIONS

AMW	Apparent Molecular Weight
AWWA	American Water Works Association
$CaCO_3$	Calcium Carbonate
$CHBr_3$	Bromoform
$CHCl_2Br$	Bromodichloromethane
$CHCl_3$	Chloroform
$CHClBr_2$	Dibromochloromethane
Cl	Chlorine
cm	Centimeter
°C	Degree Celsius
DBPs	Disinfection by Products
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DPD	*N*, *N*-diethyl-*p*-phenylenediamine
ECD	Electron Capture Detector
EDTA	Disodiumethylenediamine Tetraacetate Dehydrate
EPA	Environmental Protection Agency
Fe^{2+}	Ferrous ion
Fe^{3+}	Ferric ion
g/cm^3	Gram per Cubic Centimeter
g/L	Gram per Liter
g/mol	Gram per Molar
GC	Gas Chromatograph
hr	Hour
KHP	Potassium Hydrogen Phthalate
KI	Potassium Iodide
L/mg-m	Liter per milligram-meter
MF	Microfiltration
MCL	Maximum Contaminant Level
mg/l	Milligram per Liter

MWCO	Molecular Weight Cut Off
NOM	Natural Organic Matter
NTU	Nepheo Turbidity Unit
PACl	Polyaluminium Chloride
s	Second
SUVA	Specific Ultraviolet Absorption
THMFP	Trihalomethanes Formation Potential
THMs	Trihalomethanes
TOC	Total Organic Carbon
USEPA	United States Environmental Protection Agency
UV-254	Ultraviolet absorbtion at wave length 254 nanometer
UV	Ultraviolet Absorbtion

CHAPTER I

INTRODUCTION

1.1 Motivation

In Thailand, surface water is one of the main water resources for water supply. Turbidity is a common parameter used for identification of surface water quality in water treatment process. Generally, turbidity of surface water is increased after rainfall and flooding due to run-off and soil erosion. Suspended sediments presented in turbid water can also absorb and transport nutrients, organic matter, heavy metals, and other chemicals. The utilization of turbid water is a problematic issue of water treatment plant as the operation cost will be raised and the health effects may be subsequently created.

In water treatment process, several technologies have been employed for turbidity removal such as filtration and coagulation. Coagulation is a common process in Thailand due to low cost construction and equipment, no need expert operator, and less maintenance. Conventional coagulation including coagulation/flocculation process and sedimentation process, are the regular systems installed in water supply plants and wastewater treatment plants (Volk *et al*., 2000). The most widely used coagulants are aluminum, iron salts and synthetic polymers (Gao *et al*., 2002).

Iron salt coagulant is one of the high effective coagulants for particle and turbidity removals as it is not only operated in wide pH range but also formed dense and rapid settling flocs (Reynolds and Richards, 1996). However, iron salts coagulant is not commonly used for water treatment due to its high cost. Natural iron (Fe^{2+} and Fe^{3+}) contained in groundwater is a common problematic element for groundwater utilization and it is subjected to be primarily removed. In contrast, the natural iron could be valuable and profitable since it can be utilized to produce ferric coagulant. From this concept, not only the operation cost of using iron salts coagulant such as ferric chloride ($FeCl_3$) was reduced but also the high treatment efficiency by coagulation was achieved. Based on this concept, turbidity removal of high turbid surface water might be achieved by adding groundwater containing high iron together with chlorine to form ferric coagulant. However, chlorination is of particularly concern since added chlorine could potentially react with dissolved organic matter (DOM) in such water and form carcinogenic disinfection by products (DBPs) e.g. trihalomethanes (THMs). The U.S. Environmental Protection Agency (USEPA) has set the maximum contaminant level (MCL) of 100μg/L for total trihalomethanes and has set a new MCL of 80μg/L for stage 1 of the disinfection by product rule (D/DBP Rule; USEPA 1998). In stage 2, the D/DBP Rule may lower the MCL for THMs to 40μg/L.

In this work, coagulation of high turbid surface water using ferric coagulant from natural iron in groundwater reacted with chlorine for removing turbidity was studied and trihalomethanes (THMs) formed from the coagulation process was also investigated. Furthermore, a comparison of chemical costs between commercial ferric chloride and ferric coagulant from natural iron in groundwater reacted with chlorine was evaluated.

1.2 Objectives

- To utilize groundwater containing high natural iron to produce ferric coagulant by adding chlorine in coagulation process for high turbid surface water treatment.

- To investigate trihalomethanes (THMs) in raw water and ferric coagulated water.

- To characterize dissolved organic matters (DOMs) in raw water, ferric coagulated water, and their fractionated waters.

- To introduce a fluorescence excitation-emission matrix (FEEM) technique for DOM characterization in raw water, ferric coagulated water.

1.3 Hypotheses

- Ferrous and ferric irons in natural water can be effective producing ferric coagulant by adding chlorine during coagulation process.

- Ferric coagulation can enhance the removal of turbidity and dissolved organic matter (DOM) in natural water.

- Trihalomethanes (THMs) formation may occurred by adding chlorine for ferric coagulant production in coagulation process.

1.4 Scopes of work

- Ping River water which was considered as high turbid surface water at Sanphisua, Chiang Mai, Thailand (henceforward called surface water), as well as groundwater from shallow-well groundwater near Ping River sampling point was considered as containing high irons (henceforward called groundwater) were selected.

- The optimal chlorine dosage, chlorine dosing methods, and the appropriate ratio of groundwater to surface water were determined.

- DOM surrogates (DOC, UV-254, and SUVA) were analyzed to determine water quality.

- Fluorescent excitation-emission matrix (FEEM) was utilized to characterize the fluorescent organic matter of the DOM.

- Characterization of DOM fractions for the appropriate ratio of groundwater to surface water with optimal conditions by using resin fractionation method was examined.

- The formation of trihalomethanes (THMs) during chlorination process was evaluated.

CHAPTER II

BACKGROUND AND LITERATURE REVIEWS

2.1 Trihalomethanes (THMs)

In 1974, researchers reported that trihalomethanes (THMs) were formed when chlorine reacted with naturally occurring humic substances in water treatment plants and water distribution systems (Rook, 1974). The first identification of chloro- and bromo-trihalomethanes (THMs) was done by Johannes Rook in 1974. The first class of halogenated disinfection by- products (DBPs) discovered in chlorinated drinking water. Since that time, the reduction of THMs has been the subject of intensive investigation in the water treatment field. Symon *et al*., 1975 described a survey of halogented organic compounds from 80 water supply plants. THMs have been found to be the most widespread organic contaminants in drinking water, and occured at higher concentrations than other disinfection by-products. The four THMs (chloroform, bromodichloromethane, dibromochloromethane and bromoform) are formed when chlorine-based disinfectants are added to source water with fairly high organic content, such as surface water. THMs are included among the 25 volatile organic compounds regulated under the Safe Drinking Water Act (SDWA) of 1987. These compounds are persistent and mobile, and pose a cancer risk to humans (Pereira, M.A. 1983; Munro, N.B. and Travis, C.C. 1986). Chloroform ($CHCl_3$), the most common THMs, is a proven animal carcinogen and a suspected human carcinogen.

THMs can be taken in by drinking the water and breathing its vaporous (for example when showering). They Most THMs are metabolized into a less-toxic form, but some are transformed into more reactive substances, especially at high concentrations. THMs are absorbed, metabolized and eliminated rapidly by mammals after oral or inhalation exposure. Following absorption, the highest tissue concentrations are attained in the fat, liver and kidneys. THMs induce cytotoxicity in the liver and kidneys of rodents exposed to doses of about 0.5 mmol/kg of body weight. The maximum contaminant level (MCL) of 100µg/L for total trihalomethanes (TTHMs) in finished drinking water was established by the US Environmental Protection Agency (USEPA) in the National Interim Primary Drinking Water Regulations in 1979. The USEPA has set a new MCL of 80µg/L for stage 1 of the disinfection by product rule (D/DBP Rule; USEPA 1998). In stage 2, the D/DBP Rule may lower the MCL for THMs to 40µg/L.

2.1.1 Chemistry of Trihalomethanes (THMs)

Trihalomethanes (THMs) is one of a family of organic compounds named as derivative of methane. Trihalomethanes are an important and predominant group of chlorinated drinking water byproducts that can occur as a result of the reaction between natural organic matter in the water and chlorine added as a disinfectant. Classes of organic compounds, based on the methane molecule (CH_4), where the hydrogen atoms normally present are replaced by three halogen atoms that may be chlorine, bromine, fluorine or iodine. The term 'Total Trihalomethanes' (TTHMs) describes four disinfection-by-products, chloroform, bromodichloromethane, dibromochloromethane, and bromoform that may be sampled in a water sample. The highest concentration among THMs is chloroform, followed by dibromochloromethane. The primary biochemical ancestors of THMs identified by many researchers were humic substances including humic acid and fulvic acid (Rook, 1976; Trussell and Umphes, 1978; Oliver and Lawrence, 1979). These materials also contributed to the natural color of the water (Amy *et al.*, 1983).

Four THMs species actually occurred in water supplies including chloroform, bromodichloromethane, dibromochloroform and bromoform are shown in Table 2.1.

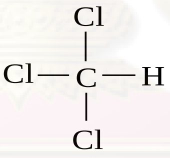
Table 2.1 Classes of currently known DBPs

DBP Class	Individual DBPs	Chemical Formular
Trihalomethanes ; THMs	Chloroform	$CHCl_3$
	Bromodichloromethane	$CHCl_2Br$
	Dibromochloroform	$CHClBr_2$
	Bromoform	$CHBr_3$

(Addaped from Krasner, 1999)

2.1.1.1 Chloroform

Chloroform is largely presented in drinking water. It is colorless and has a pleasant, nonirritating odor with a slightly sweet taste. It evaporates easily into the air and dissolves easily in water. The chemical structure of chloroform or trichloromethane ($CHCl_3$) is depicted as Figure 2.1.

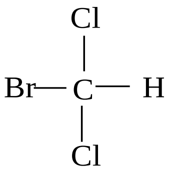


$$\mathrm{Cl-\overset{\displaystyle Cl\atop |}{\underset{\displaystyle |\atop Cl}{C}}-H}$$

Figure 2.1 Chloroform

2.1.1.2 Bromodichloromethane

The chemical structure of dichlorbromethane or bromodichloromethane ($CHCl_2Br$) is depicted as Figure 2.2.

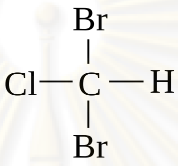


$$\mathrm{Br-\overset{\displaystyle Cl\atop |}{\underset{\displaystyle |\atop Cl}{C}}-H}$$

Figure 2.2 Bromodichloromethane

2.1.1.3 Dibromochloromethane

Dibromochloromethane is an organic compound of the trihalomethane group. It is a colorless to yellow heavy, nonflammable, liquid with a sweet odor. It is slightly soluble in water and readily evaporates to air. The chemical structure of dibromochloromethane or chlorodibromomethane ($CHClBr_2$) chemical structure is depicted as Figure 2.3.

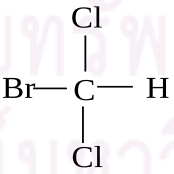


$$\begin{array}{c} \mathrm{Br} \\ | \\ \mathrm{Cl}-\mathrm{C}-\mathrm{H} \\ | \\ \mathrm{Br} \end{array}$$

Figure 2.3 Dibromochloromethane

2.1.1.4 Bromoform

Bromoform is a colorless heavy liquid that smell and taste like chloroform. It is slightly soluble in water. The chemical structure of bromoform or tribromomethane or methyl tribromide ($CHBr_3$) is depicted as Figure 2.4.



$$\begin{array}{c} \mathrm{Cl} \\ | \\ \mathrm{Br}-\mathrm{C}-\mathrm{H} \\ | \\ \mathrm{Cl} \end{array}$$

Figure 2.4 Bromoform

Table 2.2 demonstrate the chemical and physical properties of THMs including chloroform, bromodichloro methane, dibromochloromethane and bromoform.

Table 2.2 Basic chemical and physical characteristics of Chloroform, Bromodichloro methane, Dibromochloromethane and Bromoform

Empirical Formula	**Molecular weight (g/mol)**	**Specific gravity (g/cm^3)**	**Boiling point (°C)**	**Melting point (°C)**	**Solubility in water (g/L)**
$CHCl_3$	119.37	1.472	61	-63	8.1
$CHCl_2Br$	163.82	1.472	90.1	-57.1	Insoluble
$CHClBr_2$	208.29	2.38	120	-63	4.75
$CHBr_3$	257.73	2.894	150	8.3	Insoluble

(Source: Ghazali, 1989)

2.1.2 Factors influencing THMs formation

The extensive literature regarding to THMs levels in disinfected source waters and control of THMs by various treatment processes testifies to the wide variety of factors influencing THMs formation the complex interrelationships between these factors. Variation of pH, the concentration and characteristics of precursor, chlorine concentration, temperature and contact time play a role in THMs formation reactions.

2.1.2.1 pH

The impact of pH on THMs concentrations has been reported by a number of researchers (Stevens *et al*., 1976; Lange & Kawczynski, 1978; Trussell & Umphres, 1978). In general, increasing pH has been associated with increasing concentrations of THMs. The rate of THM formation increased with the pH (Stevens *et al.*, 1976; Kavanaugh *et al.*, 1980) and reported a 3-fold increase in the reaction rate per unit pH.

Rook (1976) suggested that THMs formation increased significantly at pH values of 8 to 10, whereas in the range pH 1 to 7, pH has less of an influence on

THM formation. Trussell (1978) demonstrated that THMs can form in none existing of chlorine residual once the pH is raised. The chlorinated intermediates form at low pH and hydrolyze to form THMs once the pH is raised. Carlson & Hardy (1998) reported that at pH levels greater than 9.0, THMs formation decreased with increasing pH. It is possible that the shift in chlorine species from hypochlorous acid to hypochlorite affects THMs formation during short reaction times. AWWARF (1991) observed no relationship between pH and the concentrations of THMs at eight utilities over time, suggesting that although THMs concentrations for particular water are known to be pH dependent, factors other than pH influence THMs concentrations over a variety of source waters.

2.1.2.2 Precursor concentration and characteristics

THMs formation is a result of a reaction between chlorine and THMs precursors. It is obvious that the precursor concentrations would influence THMs concentrations. Rook (1976) studies varied concentrations of organic precursors, which are called total organic carbon (TOC) should be reduced before chlorination. In this regard, it was found that chloroform production from organic matter is linear in concentration up to 250 mg/l TOC.

Young and Singer (1979) showed that quantity of chloroform produced is depended upon TOC concentration in raw water. Chloroform formation increased as non-volatile TOC increased. The removal of TOC is a conservative indicator of the removal of the precursors of THMs (Milter *et al.*, 1994).

THMs formation was found to be directly related with the dissolved organic carbon (DOC) content. However, when different source waters were compared, poor relationships between DOC and THMs formation have been observed (EPA, 1981). This suggests that factors such as chemical functional groups in the DOC play an important role in the formation of THMs.

2.1.2.3 Chlorine concentration

Chlorine concentration is a factor affecting the type and concentration of DBPs formed. The THMs level rose with an increasing of chlorine dose (Kavanaugh *et al.,* 1980). However, there is some disagreement regarding the quantitative relations between chlorine concentration and THMs levels (or the rate of THMs production). Most investigators found a linear relationship between chlorine consumption and THMs production, with an order of reaction greater than or equal to unity (Trussell & Umphres, 1978; Kavanaugh *et al.*, 1980). However, it is also possible that the order of reaction changes during the course of the reaction.

Trussell and Umphres (1978) conducted a laboratory test with synthetic water prepared by adding 10 mg/L of humic acid, 1 mg/L of NH_3Cl (as NH_3) and 10 mg/L of standard pH 7 buffers to demineralized water (TOC 0.2 mg/L). Different amounts of chlorine were added to various portions. After 2 hours of contact time, the results show that higher THMs concentration occurred within a certain range of chlorine precursor to form THMs as chlorine has been used up to react with ammonia, bacterial disinfecting, etc. Muttamara *et al.*, 1995 showed the relationship between THMs concentrations and chlorine dosages. THMs concentrations increased as the chlorine dosages increased. At dosages of 7 and 10 mg/L chlorine, the total THMs concentrations at the end of the test run were found to be 124.5 μg/L and 158.3 μg/L, respectively. The level of THMs concentration increased with respect to the level of THMs precursors.

2.1.2.4 Temperature

On a conceptual basis, it may be that rapidly forming compounds are more reactive and form DBPs regardless of temperature. On the other hand, slowly forming compounds require higher activation energy, and an increase in the temperature supplies the energy. In addition to reaction kinetics, the temperature of source water can also affect disinfection efficiency. The formation rates of THMs have been shown to increase with temperature (AWWARF, 1991; Siddiqui and Amy, 1993). In studies on the effect of temperature on THMs,(Peters *et al*., 1980) found an Arrhenius dependency between the rate constant and temperature with activation energy of 10-20 kJ/mol. The impact of temperature on THMs was strongest at longer contact times (Carlson and Hardy, 1998).

The effect of temperature on the rate of THMs formation was investigated by Stevens *et al.*, 1976 using the Ohio River water collected from the winter to the summer. The results showed that the temperature differentials could easily account for most of the winter to summer in THMs concentration variations. The concentrations of THMs were higher during the summer and autumn than in the winter and spring.

2.1.2.5 Contact time

After chlorine addition, there is a period of rapid THMs formation for the initial few hours (e.g., 4 h), followed by a decline in the rate of THMs formation, suggesting fast and slow DOM reactive sites. Recknow and Singer (1984) ran a few sets of experiments. One of these experiments studied the formation of these chlorinated products as a function of the reaction time. They found that by varying the chlorine contact time, chloroform and total THMs increases rapidly in the first few hours and then slows to a generally steady rate of increase. Many authors have indicated that the concentration of chloroform appears to increase slowly even after 96 hr, suggesting that as long as low concentrations of free chlorine are present, chloroform continues to form. Bromochlorinated THMs species have been found to form more rapidly than chloroform. Further data from many sources indicate that bromoform formation slows at approximately 7-8 hr and levels off almost completely after 20 hr (AWWARF, 1991; Koch *et al*., 1991).

2.2 Disinfection by-Products

Disinfection by-products (DBPs) such as trihalomethans (THMs), which has been classified as potentially carcinogenic substances, in produced water are generated from the reaction between DOM and chlorine (Rook, 1974; Bellar *et al*., 1974). Rook (1974) was the pioneer researcher who discovered the DBPs in chlorinated drinking water. Since then there have been several studies that have led to a better understanding of DBPs, their precursors, the kinetic yield of DBPs forming reactions, and the active chemical classes for forming DBPs. (Kavanaugh *et al.*, 1980; Christman *et al.*, 1989; Miller and Uden, 1983; Steven, 1982; and White *et al*., 2003). The reaction of DOM with chlorine produces the major DBPs; they include THMs, haloacetic acids (HAAs), haloacetronitriles (HANs), haloketones (HKs), chloral hydrate (CH) and chloripicrin (CP). The general reaction of DOM with chlorine is as follows (Marhaba and Washington, 1998):

$$\text{DOM} + \text{free chlorine} \rightarrow \text{THMs} + \text{HAAs} + \text{HANs} + \text{other DBPs}$$

Factors influencing DBPs formation are the contact time of chlorine with DOM, chlorine or disinfectant dosage, turbidity, water temperature, pH, presence of other ions such as bromide, DOM concentration, and complex compositions of DOM. Among these factors, the complex composition of DOM is one of the important parameters. Harrington *et al.*, 1996 and White *et al.*, 2003 proposed that pyrolysis fragments of phenol classes were the best indicator of chlorine reactivity. Phenol correlated well with chloroform formations (Harrington *et al.*, 1996). The THMs and total organic halides (TOX) formation were observed to be related to the organic nitrogen content that expressed the presence of proteins and/or elevated algal content (Scully *et al*., 1988; Reckhow *et al.*, 1990; Gehr *et al.*, 1993; Young and Uden, 1994). Sirivedhin and Gray (2005) found that the combination of aromatic and aliphatic structures including some substituted with nitrogen and chlorine had a linear relationship with disinfection by product formation potential (DBPFP).

2.3 Dissolved Organic Matter (DOM)

Dissolved organic matter (DOM), defined as the complex matrix of organic material present in natural waters, affects significantly many aspects of water treatment. DOM even though present in a tiny quantity, can react with chlorine during chlorination to form halogenated disinfection by-products (DBPs) which are all classified as carcinogenic substances. DOM consists of humic substances, amino acids, sugars aliphatic acids, and a large number of organic molecules (Malcolm Pirnie Inc., 1993). Humic substances include humic and fulvic acids; while non-humic substances include hydrophilic acids, proteins, carbohydrates, carboxylic acids, amino acids, and hydrocarbons (Thurman, 1985; Amy, 1993). DOM can be separate into humic and non-humic fraction. The humic fraction has a more hydrophobic character than the non-humic fraction. The humic fraction consists of humic and fuvic acids. The non-humic consists of hydrophilic acids, proteins, amino acids and carbohydrate. However, in terms of their chemical properties and implication for water treatment, the humic substance is the most important (Owen, 1995). DOM which consists of humic and fuvic acid (aquatic humic), cause natural color, is the most important (Edzwald, 1993).

DOM plays a role in many aspects of water treatment. DOM is capable of forming complexes with metals such as iron. It can serve as a substrate for microbial growth and can exert significant oxidant demand, thereby interfering with both oxidation and disinfection during drinking water treatment. Depending on the concentration and type of DOM, the acidity of water can also be affected. DOM serves as the organic precursor. DBPs formation is influenced by water quality (e.g., TOC, pH, temperature) and treatment conditions (e.g., disinfectant dose, contact time, removal of DOM before the point of disinfectant application, prior addition of disinfectant).

Non-humic substances, such as algae and their extracellular products, have been shown to be precursors to THMs (Morris and Baum, 1978; Oliver and Shindler, 1980). Oliver and Shindler (1980) observed faster reaction kinetics between chlorine and algae than between chlorine and aquatic humic materials. Their results suggest that algae in surface waters may be a major contributor to THMs production. Humic acids have generally been found to be more reactive with chlorine than fulvic acids. There is also evidence that the humic fraction produces greater concentrations of HAAs and THMs than the non-humic fraction.

Marhaba and Washington (1998) reported that DOM contains precursors for disinfection by-product formation during water treatment disinfection operation. Furthermore, humic substances were characterized by non specific parameters, which are based on their organic carbon content (i.e., TOC), their ability to absorb UV light at 254 nm (i.e., UV-254), and their potential to form trihalomethanes (i.e., THMFP) have become a useful technique to characterize DOM.

Normally, DOM is characterized by nonspecific or Surrogate parameters. The surrogate parameters must be used to describe DOM because no single analytical technique is capable of measuring the widely varied characteristics of DOM. Commonly used DOM surrogates include total organic carbon (TOC), dissolved organic carbon (DOC), ultraviolet absorbance at wavelength of 254 nm (UV- 254) and THMFP. Moreover, THMFP removal is also presented to highlight any difference between TOC and THMFP removal (USEPA, 1999). DOM surrogate parameters are described below.

2.3.1 Total Organic Carbon (TOC)

TOC is defined as all carbon atom covalence bonded in organic molecules. TOC represents the total amount of organic carbon in water samples. The organic carbon in water and wastewater consists of a variety of organic compounds in various oxidation states. TOC is independent of the oxidation state of organic matter and does not measure other organically bound elements such as hydrogen and nitrogen (APHA, AWWA, and WEF, 1995).

Young and Singer (1979) showed that quantity of chloroform produced was depended upon TOC concentration in raw water. Chloroform formation increased as non-volatile TOC increased. The removal of TOC was a conservative indicator of the removal of the precursors of THMs (Milter *et al.*, 1994). Therefore, the percent removal of TOC was correlation to the percent removal of DBPs. The USEPA proposed the percentage removal TOC required for enhanced coagulation and softening. It depended upon the TOC and alkaline concentration in raw water. The details are shown in Table 2.3 (USEPA, 1999).

Table 2.3 Percent removal of TOC requirements for enhanced coagulation and softening

Source Water TOC (mg/L)	**Source Water Alkalinity (mg/L as $CaCO_3$)**		
	0 - 60	>60 - 120	>120
2.0 - 4.0	35%	25%	15%
4.0 - 8.0	45%	35%	25%
>8.0	50%	40%	30%

(Source: USEPA, 1999)

Kavanaugh (1978) demonstrated range of TOC for a variety of natural water, shown in Figure 2.5

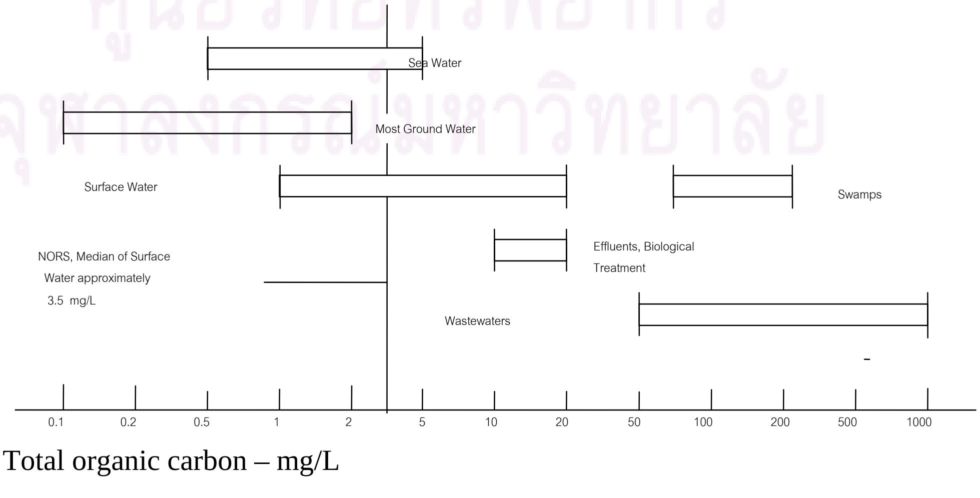


Figure 2.5 Range of TOC reported for a variety of natural water

2.3.2 Dissolve Organic Carbon (DOC)

Dissolved organic carbons are defined as the fraction of TOC that passes through a 0.7 μm GF/F filter paper. DOC is the independent of the oxidation state of the organic matter. Organic carbon in natural water can be composed in two fractions, particulate organic carbon (POC) and dissolve organic carbon (DOC). In surface water, between 50 and 60 % of humic substances is DOC (Thurman, 1985).

2.3.3 UV Absorbance at wavelength 254 nm (UV- 254)

UV-254 measurement is surrogate parameters to estimate the extent of DBP formation. Ultra-violet (UV) absorption at a wavelength of 253.7 nm 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). As noted by Edzwald *et al.*, 1985, humic aromatic compounds and molecules with conjugated double bonds absorb UV light, whereas simple aliphatic acids, alcohol, and sugars do not absorb UV light.

Organic compounds that are aromatic or that have conjugated double bonds absorb light in the ultraviolet wavelength region. Therefore, UV absorbance is a well-known technique for measuring the presence of naturally occurring organic matter such as humic substances. UV analysis is also affected by pH and turbidity (Edzwald, *et al.,* 1985). UV absorption is a useful surrogate measure for DOM or precursor of THMs because humic substrates strongly absorb ultraviolet radiation (Eaton, 1995)

2.3.4 Specific Ultraviolet Absorbance (SUVA)

The ratio between UV absorbance to DOC, referred to as specific absorbance (SUVA) ($cm^{-1}mg^{-1}$ L) demonstrates a relative index of humic content (Edzwald, 1993 and Owen *et al.,* 1993). Specific absorbance could suggest the nature of DOM and its consequent THMs formation (Krasner *et al.,* 1996). Higher specific absorbance values tend to indicate higher humic content. Specific absorbance of a humic sample depends upon the molecular weight of the substances. (Petterson *et al.*, 1995)

SUVA can be used as an indicator of its coagulation (or softening) ability to remove THM precursors. Water having a high SUVA (SUVA > 3 L/mg-m) have been found to contain organic matter that is more humic-like in character, higher in apparent molecular weight (AMW), and more readily removed by coagulation (Edzwald, 1993) whereas lower SUVA values (< 3L/mg-m) indicate the presence of organic matter of lower AMW that is more fulvic-like in character and more difficult to remove.

2.4 Conventional Coagulation/Flocculation Process

Coagulation/flocculation is a process used to remove turbidity, color, and some bacteria from water**.** The term “Coagulation” is the addition and rapid mixing of coagulants to destabilize the colloidal and fine suspended solids. Initial aggregation of the destabilized particles occurs in this process. Flocculation is the slow stirring or gentle agitation to aggregate the destabilized particles and form a rapid settling floc. It is commonly used in water treatment plants for settling of coagulated and flocculated waters to rapid sand filtration. (Reynolds and Richards., 1996)

The process is typically used for treating potable water. There are a variety of primary coagulants which can be used in a water treatment plant including metal-salts coagulants such as alum, ferric chloride and ferrous sulfate, polymerized metal-salt coagulants such as polyaluminium chloride (PACl), and organic polymers that may be cationic, anionic and noionic. This coagulation not only destabilizes particles, but also removes a fraction of natural organic matter present in natural water.

2.4.1 Ferric chloride

The simplified reaction of ferric chloride with natural bicarbonate alkalinity to form ferric hydroxide is

$$2FeCl_3 + 3Ca(HCO_3)_2 \longrightarrow \underline{2Fe(OH)_3}\downarrow + 3CaSO_4 + 6CO_2$$

If the natural alkalinity is insufficient for the reaction, slaked lime may be added to form the hydroxide, as given by the equation.

$$2FeCl_3 + 3Ca(OH)_2 \longrightarrow \underline{2Fe(OH)_3}\downarrow + 3CaCl_2$$

The optimum pH range for ferric chloride is from about 4 to 12. The floc formed is generally a dense, rapid settling floc. Ferric chloride is available in dry or liquid form. The dry chemical may be in powder or lump form, lump form being more common. The lump, which is 59 to 61% ferric chloride, contains six waters of crystallization and weight from 60 to 61 lb/ft (960 to 1026 kg/m^3). The powdered or anhydrous form is 98% ferric chloride, contains no water of crystallization, and weight from 85 to 90 lb/ft^3(1360 to1440 kg/m^3). The liquid form is 37 to 47% ferric chloride. (Reynolds and Richards., 1996)

2.4.2 Ferric coagulant

Based on the introduction as mention before, ferric coagulant was produced from natural iron in groundwater reacted with chlorine. Sodium Hypochlorite as chlorine sources are very strong oxidizing agents, which used to oxidizing ferrous ion (Fe^{2+}) to be ferric ion (Fe^{3+}) as follows:

$$2Fe^{2+} + OCl^- + H_2O \longrightarrow 2Fe^{3+} + Cl^- + 2OH^-$$

2.4.3 The ability of coagulants used to remove THMs precursor

Ferric chloride is also very effective for NOM removal. Dryfuse *et al.*, (1995) optimized TOC removal using bench-scale $FeCl_3$ coagulation for three different source waters. The percentage DOC removal ranged from 46 to 71 percent, and the removal of THMFP and HAAFP was slightly greater, ranging from 59 to 90 percent. Ferric chloride coagulation was found to preferentially remove the high molecular weight, humic fraction of organics; non-humics were also removed by $FeCl_3$ coagulation, but to a lesser extent. The differences between iron and aluminum-salt coagulants include the optimum pH values for organics removal, solubility, surface areas, and surface charge. A number of studies comparing alum to iron-based coagulants have found that iron achieved greater precursor removal than alum (e.g. Vilage *et al.*, 1997; Shorney *et al.*, 1998)

Chadik and Amy (1983) For Mississipi River Water, the untreated THMFP of 313µg/L were reduced to 141µg/L by ferric chloride coagulation. The indicated coagulant dosage was 20 mg Fe/L.

Crozes, White and Marshall (1995) studied TOC removal by alum, ferric chloride and a cationic synthetic polymer. Ferric chloride dosage between 40 and 60 mg/l and pH value between 5.5 and 6 were the optimum condition for TOC removal.

Musikavong (2004) reported that ferric chloride coagulation was slightly better than alum coagulation for removing surrogate parameter of NOM prior to reduce THMFP, while the maximum reduction of THMFP approximately 27 percent occurred at ferric chloride dosage 80 mg/L.

2.5 Resin Fractionation

Goslan (2004) fractionated raw water from a reservoir in the United Kingdom (UK) by the resin adsorptions technique into its hydrophobic fraction and hydrophilic fraction. The hydrophobic fraction was further separate into a humic acid fraction and a fulvic acid fraction by precipitation of the humic fraction at pH 1. The non-adsorbed material was designated the name hydrophilic non acid fraction.

Leenheer (1981) proposed the comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural water. He showed that DOM in a water sample can be fractionated by resin adsorption into six fractions including hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral and hydrophilic base with a recovery of greater than 90 %.

Marhaba and Pu (2000) Marhaba *et al*., (2003) utilized resin adsorption to isolate and fractionate dissolve organic matter (DOM) into six different fractions, which are operationally categorized as hydrophobic acid, hydrophobic neutral, hydrophobic base, hydrophilic acid, hydrophilic neutral and hydrophilic base

Leenheer and Croué (2003) demonstrated the relationships between organic compounds and the DOM fractions that are as follows; a hydrophobic neutral fraction (HPON) comprises hydrocarbons/tannins, a hydrophobic base fraction (HPOB) comprises aromatic amines, a hydrophobic acid fraction (HPOA) comprises fulvic acid, a hydrophilic neutral fraction (HPIN) comprises sugars, a hydrophilic base fraction (HPIB) comprises peptides/ amino and a hydrophilic acid fraction (HPIA) comprises polyuronic acids.

2.6 Three-Dimensional Fluorescence Spectroscopy (FEEM)

Marhaba and Pu (2000) reported that the fluorescence spectrometry (FEEM) is the total sum of emission spectra of a sample at different excitation wavelengths, recorded as a matrix of fluorescent intensity in coordinates of excitation (EX) and emission (EM) wavelengths, in a definite spectral window.

Coble (1996) said that fluorescence spectrometry has been widely used due to its simplicity and its requirement of minimal sample amounts and pretreatment. A three-dimensional excitation-emission matrix (FEEM) obtained by fluorescent spectrometry scanning the wavelengths of both excitation and emission can be used to distinguish DOMs in natural water.

Coble *et al.*, (1990) said that once the FEEM has been fully corrected for instrumental configuration. Data can be analyzed as excitation spectra, emission spectra or synchronous scan spectra, even though originally collected as emission scans.

Croue *et al.*, (2000) has recently summarized the methods used to characterize DOMs e.g., the use of chemical components such as amino acids and carbohydrates, molecular weight/size distribution, pyro-chromatogram and fluorescence spectrum.

Musikavong *et al.*, (2004) showed that major organic fractions could be characterized by the FEEM spectrum; the peak positions on the FEEM of these major organic fractions were similar to the peak positions on the FEEM of raw water from the wastewater treatment facility at the Industrial Estate in Lumphun.

Musikavong *et al.*, (2005) demonstrated correlations of THMFP and fluorescent intensity of the influent wastewater and water samples from each pond at the wastewater treatment plant of the Northern Region Industrial Estate, Lamphun, Thailand. Their reported results showed that FEEM could be used to quantify the THMFP in the water source.

Chen *et al.*, (2003) defined excitation and emission boundaries into five regions based largely upon supporting literature. FEEM peaks have been associated with humic-like, tyrosine-like, tryptophan-like, or phenol-like organic compounds. In general, peaks at shorter excitation wavelengths (<250 nm) and shorter emission wavelengths (<350 nm) are related to simple aromatic proteins such as tyrosine (Regions I and II). Peaks at intermediate excitation wavelengths (250- ¢ 280 nm) and shorter emission wavelengths (<380 nm) are related to soluble microbial byproduct-like material (Region IV). Peaks at longer excitation wavelengths (>280 nm) and longer emission wavelengths (>380 nm) are related to humic acid-like organics (Region V). For fulvic acids, FEEMs with minimum excitation wavelengths of 250 nm indicated shoulders of FEEM peaks located at shorter excitation wavelengths. Therefore, peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) are related to fulvic acid-like materials (Region III).

CHAPTER III

METHODOLOGY

The study of turbidity removal and trihalomethanes (THMs) formation in turbid surface water coagulation using ferric coagulant from natural iron in groundwater reacted with chlorine was conducted by using the selected water sample sources of high turbid surface water and high iron groundwater in the area of Chiang Mai, Thailand. All experiments and analyses were done at the Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University during the period of June 2008 and January 2009.

3.1 Water samples

3.1.1 High turbid surface water

Ping River water at Sanphisua educational center in Chiang Mai Province, Thailand situated at N 18^{o}51’7”and E 98^{o}58’57.9” as shown in Figure 3.1 was selected as high turbid surface water sample in this study. This sampling point is located approximately 10 kilometers upstream of the center of Chiang Mai city (henceforward called surface water). Ping River water is currently the main water source utilized to producing water supply for Chiang Mai city. In general, turbidity of Ping River varies due to season changes. However, it typically contains high concentration of suspended solid measured in term of “Turbidity value” between 50 and 220 NTU. Water samples from Ping River used in this study were pumped from the depth of about 30 centimeters below water surface at the sampling point.

Figure 3.1 Sampling Point of Ping River at Sanphisua, Chiang Mai Province, Thailand

3.1.2 High natural iron groundwater

For ease of conducting the experiments, shallow well groundwater near Ping River sampling point as mentioned in 3.1.1 at Sanphisua educational center in Chiang Mai was considered as a groundwater source of this study. The 12 meter-depth shallow well as illustrated in Figure 3.2 which is located approximately 15 meters away from Ping River bank were selected and groundwater were sampled by pump. Typically groundwater from this shallow well contains total iron as high as about 20 mg/L (henceforward called groundwater).

All water samples in this study were collected and transported in polyethylene tanks and stored at 4^{o}C before analysis within 24 hours.

Figure 3.2 Sampling Point of shallow well at Sanphisua, Chiang Mai Province, Thailand

3.2 The experiments

3.2.1 Coagulation experiment

Most coagulation processes in water treatment in Thailand generally use alum as coagulant in order to mainly remove turbidity in water. Moreover, iron salts coagulant is one of the high effective coagulants for particle and turbidity removals as it is not only operated in wide pH range but also formed dense and rapid settling flocs (Reynolds and Richards, 1996). However, iron salts coagulant has not been commonly used for water treatment due to its cost. This research was investigated to utilization natural iron (Fe^{2+} and Fe^{3+}) high contained in groundwater to be ferric coagulant by adding chlorine for removing turbidity of high turbid surface. The appropriate ratio of groundwater to surface water and the optimal chlorine dosage with additional chlorination method were determined**.**

In this study the jar-test apparatus was conducted to these experiments to determine the optimal condition of coagulant doses and types. Jar-tests were performed using a programmable jar-test apparatus (PHIPPS&BIRD Jar-Tester, Model 7790-902) as shown in Figure 3.3. One liter of water sample was transferred into a 1.4-l square beaker for each batch of experiment with a rapid mixing at 150 rpm (G = 320 s^{-1}) for 60 seconds followed by a slow mixing at 30 rpm (G = 30s^{-1}) for 20 minutes and quiescent settling for 20 minutes. Thereafter, the supernatant was collected for further analyses.

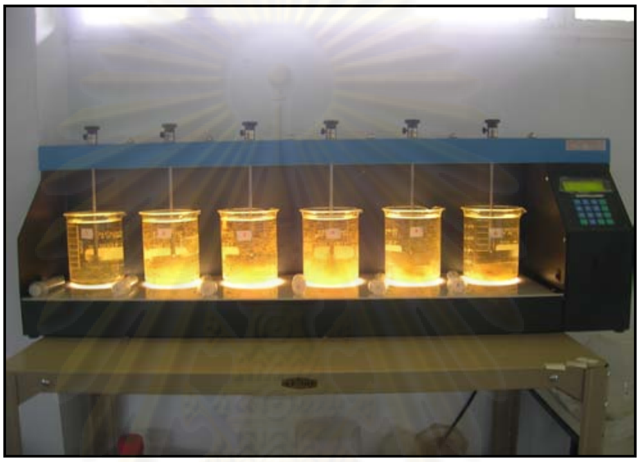


Figure 3.3 Jar-Test apparatus (PHIPPS&BIRD Jar-Tester, Model 7790-902)

3.2.1.1 Experiment no.1: Chlorine dosage for producing maximum ferric coagulant from natural iron in groundwater

Determination of the optimal chlorine dosage for producing the maximum ferric coagulant from natural iron in groundwater was examined. The maximum production of ferric coagulant was considered as the maximum total iron reduction in groundwater before and after adding chlorine in coagulation. The experimental conditions are depicted in Figure 3.4.

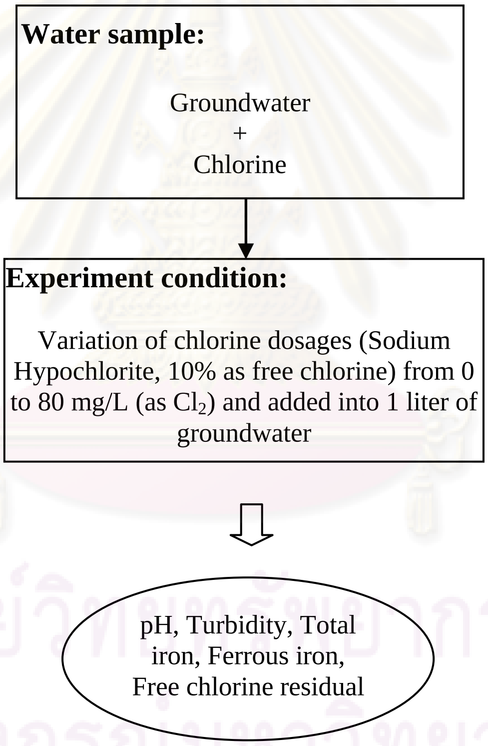


Figure 3.4 Water sample, experimental conditions and analytical parameters of the experiment no1: Chlorine dosage for producing maximum ferric coagulant from natural in groundwater

3.2.1.2 Experiment no.2: Appropriate ratio of groundwater (containing high iron) to surface water by adding 30 mg as CL_2 per one liter of groundwater

Determination of the appropriate ratio of groundwater to surface water by adding the optimal chlorine dosage (resulting from section 3.2.1.1) was examined. In this section, groundwater was mixed with surface water before adding optimal chlorine dosage in coagulation. The experimental conditions are depicted in Figure 3.5.

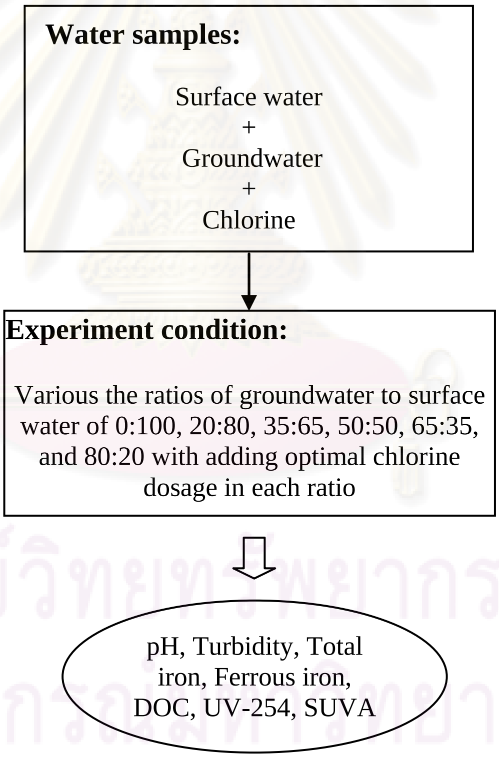


Figure 3.5 Water samples, experimental conditions and analytical parameters of the experiment no.2: Appropriate ratio of groundwater (containing high iron) to surface water by adding 30 mg as CL_2 per one liter of groundwater

3.2.1.3 Experiment no.3: Effects of different initial turbidity in the water of various ratios of groundwater to surface water on turbidity removal by using the optimal chlorine dosage of 30 mg as Cl_2 per one liter of groundwater

The effects of different initial turbidity in the water of various ratios of groundwater to surface water on turbidity removal by using the optimal chlorine dosage of 30 mg as Cl_2 per one liter of groundwater were determined. The experimental conditions are depicted in Figure 3.6.

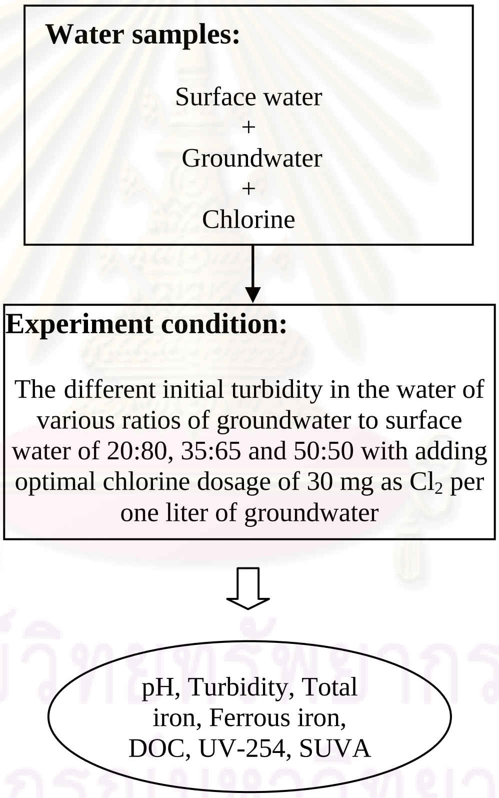


Figure 3.6 Water samples, experimental conditions and analytical parameters of the experiment no.3: Effects of different initial turbidity in the water of various ratios of groundwater to surface water on turbidity removal by using the optimal chlorine dosage of 30 mg as Cl_2 per one liter of groundwater

3.2.1.4. Experiment no.4: Effects of different chlorine dosing methods (pre-chlorine adding method and post-chlorine adding method)

Effects of different chlorine dosing with pre-chlorine adding method and post-chlorine adding method for producing ferric coagulant at the selected ratios of groundwater to surface water were demonstrated. The effect of pre-chlorine adding method was experimented by mixing the optimal amount of chlorine into groundwater before adding surface water, whereas, the effect of post-chlorination method was experimented by adding the optimal amount of chlorine into the mixtures of groundwater and surface water. The experimental conditions are depicted in Figure 3.7.

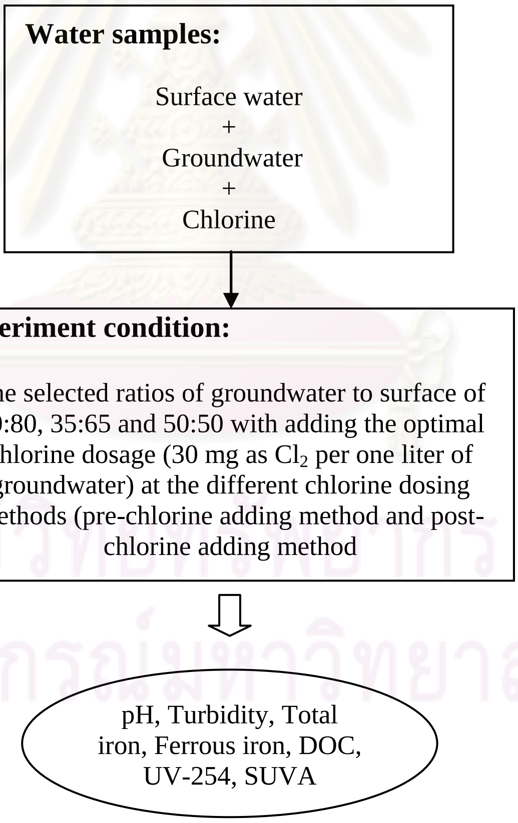


Figure 3.7 Water samples, experimental conditions and analytical parameters of the experiment no.4: Effects of different chlorine dosing methods (pre-chlorine adding method and post-chlorine adding method)

3.2.1.5. Experiment no.5: Turbidity removal by commercial ferric chloride coagulant

Determination of the turbidity removal efficiency of high turbid surface water (Ping River water) by commercial ferric chloride coagulant was demonstrated. Additionally, a commercial ferric chloride coagulant ($FeCl_3.6H_2O$) used in the experiment was an analytical grade. The experimental conditions are depicted in Figure 3.8.

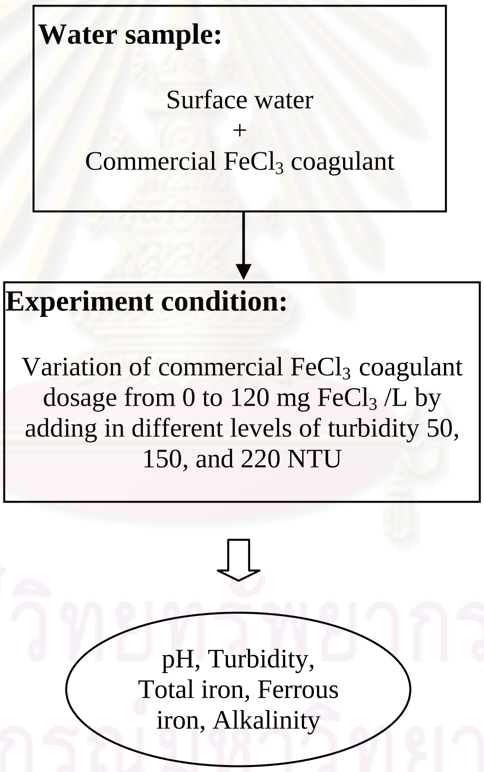


Figure 3.8 Water sample, experimental conditions and analytical parameters of the experiment no.5: Turbidity removal by commercial ferric chloride coagulant

3.2.2. Resin Fractionation procedure

The feasible appropriate ratios between groundwater and surface water from coagulation experiments were conducted to isolate DOM fractions by resin adsorption process. The raw water and coagulated water were filtered through 0.7 μm – GF/F filter paper and measured for UV-254, DOC, SUVA and FEEM.

Resin adsorption procedures were used to fractionate five liters of filtered water into 2 dissolved organic matter (DOM) fractions which consisting of hydrophobic (HPO) and hydrophilic (HPI) by using a series of DAX-8 resin (Leenheer, 1981). The diagram of the resin fractionation procedure is presented in Figure 3.9 and is described as follows:

3.2.2.1 Hydrophobic and Hydrophilic fractionation

- The water samples were filtered through 0.7 μm – GF/F filter paper and analyzed for DOC, UV-254, SUVA, FEEM and THMs.
- The remaining filtrates were acidified to pH 2 with 6 N HCl. Acidified water samples were fractionated into hydrophobic (humics) and hydrophilic (nonhumics) substances using the DAX-8.
- The organic substances that passed through the column were operationally defined as hydrophilic DOC while those that were adsorbed on the resin were defined as hydrophobic DOC. Adsorbed organic substances were eluted with 0.10 N NaOH (0.25bed volume) and 0.01 N NaOH (1.25 bed volumes), respectively.
- The pH of both fractions was adjusted to 7 prior to further analyses. The neutralized fractions were analyzed for DOC, UV-254, SUVA, FEEM, and THMs.

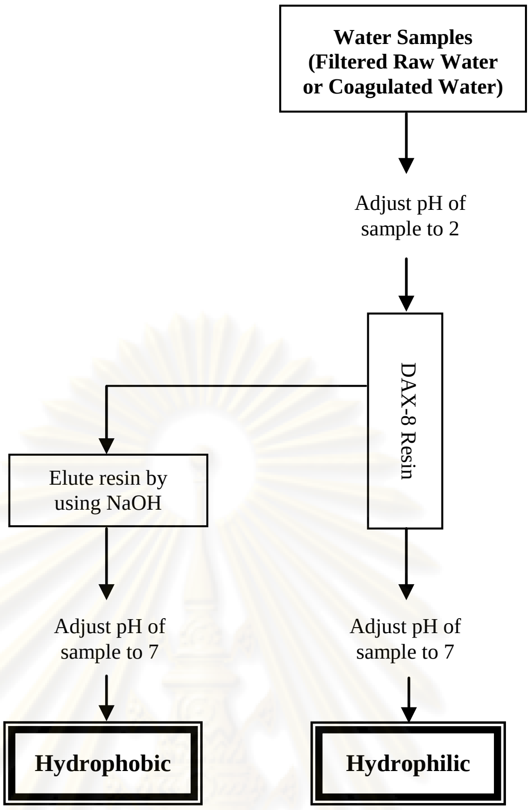


Figure 3.9 Diagram of resin fractionation procedure

Figure 3.10 Resin fractionation apparatus

3.2.2.2 Prepare DAX-8 resin

- The amount of DAX-8 resin was determined according to Leenheer (1981) with a capacity factor of 50 (K'=50) and a porosity of 0.60.
- DAX-8 resin was intensively refined with 0.1N NaOH for 24 hours and sequentially extraction with Acetone and Hexane for another 24 hours in a set of Soxhlet extraction apparatus.
- The refined DAX-8 resin was transferred into columns (2.5cm × 120cm) in slurry of Methanol.
- The packed resin was rinsed with two times 2.5 bed volumes of 0.1 N each NaOH first, then 0.1N HCl, and finished with Mill-Q water until the conductivity and DOC of the effluents were below 10 µs/cm and 0.2 mg/L, respectively.

Figure 3.11 Soxhlet extraction apparatus

3.3 Analytical methods

3.3.1 Physico-chemical parameters

The water samples were analyzed for pH, turbidity, total iron, ferrous iron, free chlorine residual, alkalinity, conductivity, TOC, UV-254, DOC, SUVA, FEEM, and THMs. The summary of analytical methods and standards used for analyzing the mentioned parameters demonstrated in Table 3.2 These parameters are described below.

The analyzed parameters were done by duplicate samples. The results of these analyses should be within ±5%, or corrective action is necessary

3.3.1.1 pH

pH was directly measured by a Model D-54 Horibra pH/Cond. Meter with an accuracy of ± 0.01 pH unit. The unit was daily calibrated with buffer solutions at pH 2.00 and 7.00 .

3.3.1.2 Temperature

Temperature was directly measured by Horiba Thermometer, Model D-13E.

3.3.1.3 Turbidity

WTW series Turb 430T, turbidity meter was used to measure turbidity.

3.3.1.4 Alkalinity

Alkalinity was measured in accordance with Standard Method 2320 B.

3.3.1.5 Electro conductivity

Electro conductivity was directly measured by WTW Conductivity meter, Model cond.330i

3.3.1.6 Total iron, Ferrous iron and Free chlorine residual

Total Iron, ferrous iron and free chlorine residual was directly measured by HACH Colorimeter, Model DR/890.

3.3.2 DOM Parameters

3.3.2.1 Dissolve Organic Carbon: DOC

DOC will be analyzed in accordance with Standard Method 5310D (Standard Method, 1995) using a TOC analyzer (O.I. analytical, USA). Milli-Q water (ELGA, UK) was used on every sample to clean the system. At least two replications of each measurement of the DOC analysis were performed.

3.3.2.2 Ultraviolet absorbance at wavelength 254 nm: UV-254

UV-254 was analyzed in accordance with Standard Method 5910B (Standard Methods, 1995) using a UV/VIS spectrometer: a Jasco V-350 spectrophotometer (Jasco Corporation, Japan) at 253.7 nm with matched quartz cells that provided a path length of 10 mm. At least two replications of each measurement of the UV-254 analysis were performed.

3.3.2.3 Three-Dimensional Fluorescence Spectroscopy: FEEM

Three-dimensional fluorescence spectroscopy (Fluorescent Excitation - Emission Matrixes: FEEM) is the total sum of emission spectra of a sample at different excitation wavelengths, recorded as a matrix of fluorescent intensity in coordinates of Excitation (Ex) and Emission (Em) wavelengths, in a definite spectral window. FEEM represent in physical signatures by JASCO FP-6200 Spectrofluorometer.

Quinine sulfate standard

The quinine sulfate [$(C_{20}H_{24}N_2O_2)_2H_2SO_42H_2O$] solution was used to check the stability of spectrofluorometry. The calibration curve was regularly established using 5 points of quinine sulfate in 0.1 M H_2SO_4. 10 quinine sulfate units (QSU) are equivalent to the fluorescent spectra of 10 μg/L of quinine sulfate solution at 450 nm with an excitation wavelength of 345 nm (Kasuga *et al*. 2003).

Spectrofluorometor operating conditions

The operating conditions used to measure the FEEM of all water samples in this study are following:

Measurement Mode: Emission
Band with excitation: 5 nm
Band with emission: 5 nm
Response: Medium
Sensitivity: High
Scanning speed: 2000 nm/min
Excitation wavelength: Start at 220 nm, end at 730 nm
Emission wavelength: Start at 220 nm, end at 730 nm
Excitation wavelength interval: 5 nm
Emission wavelength interval: 1 nm

FEEM measurement procedure

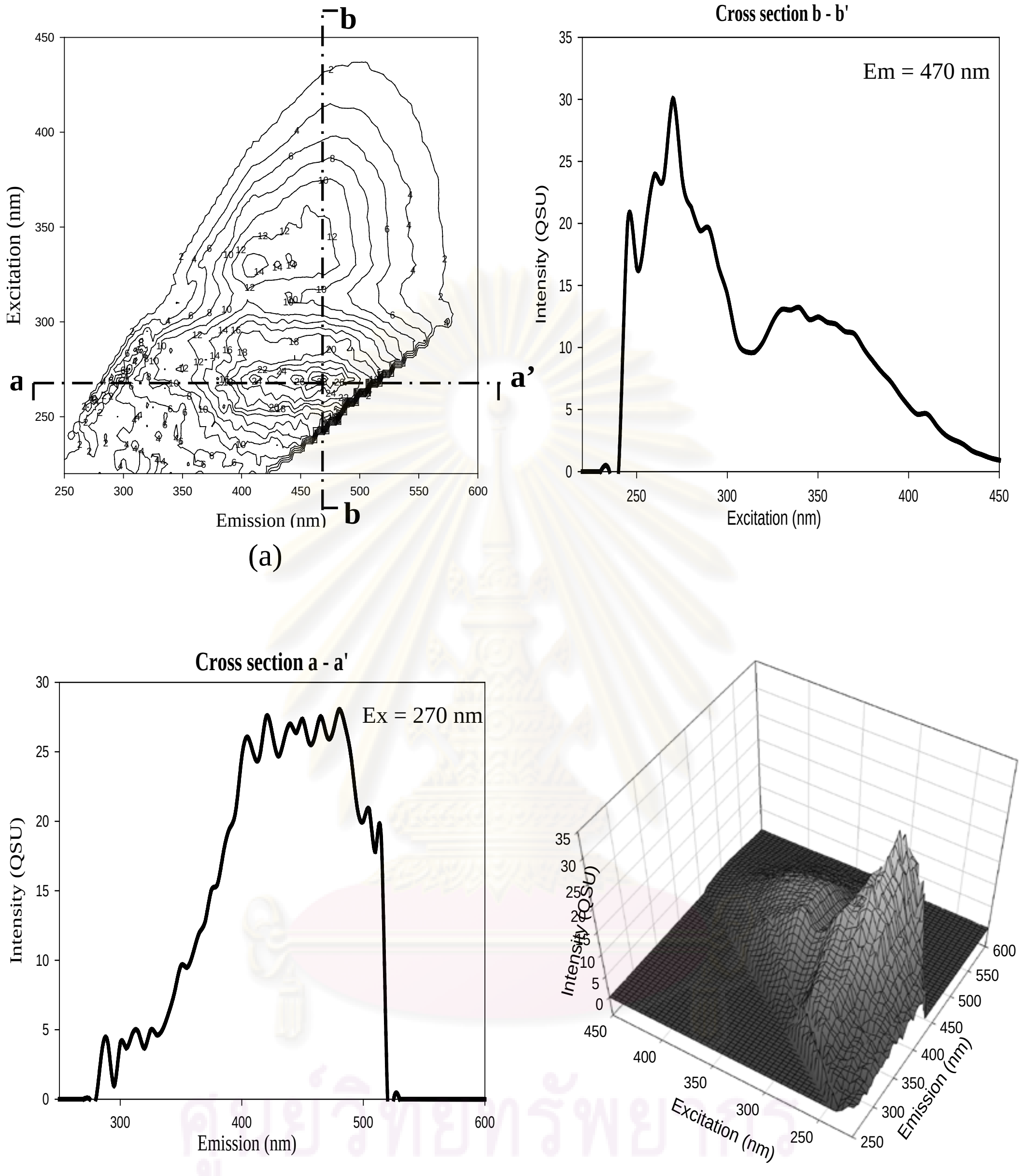
- Check the Raman Test Photometric Stability. The value should be less than ±1%/ hour**.**
- Measure the fluorescent intensity of the quinine sulfate solution of 10 QSU at 450 nm with an excitation wavelength of 345 nm.
- Measure the FEEM of the Milli-Q water.

- Measure the FEEM of the water samples
- Subtract the FEEM of the water samples with the FEEM of the Milli-Q water.
- Convert the fluorescent intensity of the subtracted FEEM of the water samples into QSU unit.
- Eliminate the influence of the primary and secondary scatter fluorescence and highlight the target peak by discarding the FEEM data when the excitation wavelength (Ex) ≥ emission wavelength (Em) or Ex X 2 ≤ Em (Komatsu *et al.* 2005)
- Remove the Rayleight and Raman scattering peaks at Em ± 10-15nm of each Ex (Zepp *et al.* 2004)

FEEM interpretation

FEEM can provide information on the putative origin of fluorescent organic matter of DOM in water.

Moreover, fluorescent excitation-emission wavelengths that exhibited fluorescent emission intensities were classified as fluorescent peaks as illustrated in Figure 3.12. In this study, the use of FEEM fluorescent emission intensities at peak position was utilized to evaluate the reduction of fluorescent organic matter of DOM after treatment process.



(a)

(b)

Figure 3.12 Sample of the three-dimensional view (a) and contour view (contour interval of 2 QSU) with fluorescent peaks and its sections (b) of a FEEM

3.3.3 Trihalomethanes (THMs)

THMs were measured in accordance with standard method 5710, formation of Trihalomethanes and other disinfection by-products. Gas Chromatography was used (Agilent 6890 Series Gas Chromatographic with ECD detector) under the following conditions:

Inlet Condition

Mode: Split, Initial temp: 225°C., Pressure: 31.33 psi, Split ratio: 10:1 Split flow 15.9 mL/min, Gas Type: Helium and Total flow: 20.5 mL/min

Oven Condition

The temperature programs of oven adjusted for analyzing THMs are shown in Table 3.1.

Table 3.1 Temperature programs for analyzing THMs

Ramp	Rate (°C/min)	Final temperature (°C)	Holding time of final temperature (min)
1	15	180	1.00[*]
2	15	130	1.00
3	15	180	1.00

[*] Initial temperature: 75°C, Initial temperature holding time: 1.00 min

Detector Condition

Temperature: 300 °C, Mode: Constant make up flow, Makeup flow: 60 mL/min, Makeup Gas Type: Nitrogen

3.3.3.1 Liquid-Liquid extraction

Water samples were extracted in accordance with standard method 6232 B Liquid-Liquid Extraction Gas Chromatography Method.

A summary of the analytical methods and instruments used in this study is illustrated in Table 3.2

Table 3.2 Analytical methods and instruments

Parameters	Analytical methods	Standards	Analytical instruments
pH	Direct measurement	-	Horiba pH/Cond. Meter model D-54
Turbidity	Direct measurement	-	WTW series Turb 430T, turbidity meter
Total iron	Direct measurement	USEPA	HACH colorimeter model DR/890.
Ferrous iron	Direct measurement	USEPA	HACH colorimeter model DR/890.
Free chlorine Residual	Direct measurement	USEPA	HACH colorimeter model DR/890.
Alkalinity	Titration Method	Standard method 2320B*	-
UV-254	Ultraviolet Absorption Method	Standard method 5910B*	Jasco, Model UV-530, UV-spectrometer
DOC	Wet Oxidation Method	Standard method 5310C*	O.I. analytical 1010 TOC Analyzer
FEEM analysis	-	-	JASCO FP-6200 spectrofluorometer
THMs	Liquid-Liquid Extraction Gas and Chromatography Method	Standard method 5710 and 6232 B	Gas Chromatography with electron capture detector (GC/ECD)

(*Standard Methods, 1995)

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characteristics of Ping River water and shallow-well groundwater

The summary of the characteristics of raw waters from Ping River and Shallow-well groundwater during the entire period of study are presented in Table 4.1.

Table 4.1 Raw water characteristics of Ping River and Shallow-well groundwater sources

Parameter	Raw water Source					
	Ping River			Shallow-well Groundwater		
	Range	Mean value	n	Range	Mean value	n
pH	7.15-7.86	7.48	5	6.48-7.04	6.65	5
Temperature (C^o)	24.0-26.5	25.3	5	23.0-24.7	23.6	5
Conductivity (µS/cm)	214-243.7	225.1	5	300.1-328.2	317.1	5
Turbidity (NTU)	50-220	102	8	0.9-2.3	1.2	5
Alkalinity(mg/LCaCO$_3$)	85.6-90.3	86.8	7	134.8-142.5	138.8	4
DOC (mg/L)	2.31-3.58	2.84	5	1.33-1.96	1.72	5
UV-254 (cm^{-1})	0.063-0.136	0.098	5	0.201-0.349	0.259	5
SUVA (L/mg-m)	2.68-4.03	3.42	5	11.27-18.09	15.03	5

Remark: n = number of observations

4.1.1 Physical and chemical characteristics

As data shown in Table 4.1, the average pH values of Ping River water and shallow-well groundwater were 7.48 and 6.65, respectively. It can be noticed that pH of two raw water sources was nearly neutral. However, the alkalinity should be analyzed because the coagulation process that utilizes ferric as coagulant was generally required the additional alkalinity in case of low alkalinity raw water.

Average alkalinity values of Ping River water and shallow-well groundwater were 86.8 and 138.8 mg/l as$CaCO_3$, respectively. For a brief calculation of the alkalinity consuming during coagulation process in this study, it is indicated that raw water not to required additional alkalinity to prevent pH drop.

Turbidity is basic parameter that generally used to represent the visible impurities presented in contaminated water because of its easy analysis. Turbidity, or the cloudiness of water, is caused by multiple numbers of factors such as clay, silt, fine organic and inorganic matter, and microorganisms. Interestingly, Ping River water has a wide range of turbidity 50-220 NTU or average value about 102 NTU that depends upon seasons. The period of this study was in between rainy season and dry season, therefore, the turbidity value observed in this study was very high in rainy season because of solid transportation, while it was lowed in dry season because of the sedimentation.

4.1.2 Dissolved organic matter (DOM) surrogate parameters

4.1.2.1 Dissolved organic carbon (DOC)

DOC is main surrogate parameter which represented DOM that generally found in natural water. As can be seen from Table 4.1, the average DOC values of Ping River water and groundwater were 2.84 and 1.72 mg/L, respectively. The values of DOC can indicate the concentration of NOM contained in natural water, which is originated from a result of decomposition processes from higher organic matter such as plants. When water gets in touch with high organic soils, a certain amount of these components can be drained into rivers as DOC.

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

UV-254 is another important DOM surrogate parameter because it 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). Although, DOM from different origins may have different elemental compositions and other chemical properties, their spectra are similar. In general, light absorbance of humic substances in the water will increase with the degree of aromatic rings in the humic substances, the ratio of carbon in aromatic nuclei to carbon in aliphatic or alicyclic side chains, the total carbon contents in the water, and the molecular weight of the humic acids. However, the value of UV-254 strongly depends on the concentrations of humic acids in water. As can be seen in Table 4.1, Average UV-254 values of the Ping River water and groundwater were 0.098 and 0.259 cm^{-1}, respectively. It can be indicated that a high UV-254 values observed from groundwater might be originated from the humic substances leached from the soil.

4.1.2.3 Specific ultraviolet absorbance (SUVA)

Recently, the specific UV-254 (defined as UV-254 per milligram of organic carbon, also known as SUVA) has also been used as another surrogate for DOM and the disinfection by-product (DBPs) precursors. SUVA is defined as a surrogate parameter used to estimate hydrophobic DOM; a higher SUVA means that the water is enriched in hydrophobic such as humic substance. Humic molecules contain aromatic, barboxyl, caobonyl, methoxyl and aliphatic units (Stevenson, 1982 and Christman *et al.*, 1983). In drinking water treatments, SUVA can be utilized to predict the reactivity of humic acids with coagulants and disinfectants (Edzwald, 1993). From the obtained data in Table 4.1, it can be seen that the average SUVA values of Ping River water were 3.42 L/mg-m and groundwater were 15.03 L/mg-m. Literatures reported that the groundwater may comprise of a high humic content and also have the ability for using coagulation process. Correspondingly, it was established by many researchers that water having high SUVA values (≥ 2.0 L/mg-m) enhanced coagulation is able to remove organic matter from the water (Edzwald and Benschoten, 1990). Water having a high SUVA value (SUVA > 3.0 L/mg-m) has been found to contain organic matter that is more humic-like in character, higher in AMW, and more readily removed by coagulation (Edzwald, 1993) whereas lower SUVA values (< 3.0 L/mg-m) indicate the presence of organic matter of lower AMW that is more fulvic-like in character and more difficult to remove. As the results obtained, SUVA value of Ping River water was more than 3.0 L/mg-m, therefore, it might be predicted that Ping River water treatment would be achievable by coagulation process.

4.2 The optimization of turbidity removal in high turbid surface water by using ferric coagulant

This section was aimed at investigate turbidity removal in high turbid surface water by using ferric coagulant produced from natural iron in groundwater reacted with chlorine. The appropriate ratio of groundwater to surface water and the optimal chlorine dosage were determined. The coagulation/flocculation process was conducted by jar-test experiments.

4.2.1 Chlorine dosage for producing maximum ferric coagulant from natural iron in groundwater

In order to determine the maximum ferric coagulant produced from natural iron in groundwater at different chlorine dosage, the experiments were conducted by using Jar test unit with chlorine dosages varied from 0 to 80 mg (as Cl_2) mixed into 1 litter of groundwater which contains natural total iron of approximately 21 mg/L. The maximum total iron reduction in groundwater before and after adding chlorine was considered to be the maximum production of ferric coagulant. This is based on the assumption that ferric coagulant was formed and then precipitated ferric salts were taken place. As a consequence, the reduction of total iron in groundwater after dosing chlorine was observed. As can be seen in Table 4.2 and Figure 4.1, total iron reduction increased rapidly at chlorine dosages from 0 to 20 $mgCl_2$ /L and then became steady when chlorine dosages of more than 30 $mgCl_2$ /L. In addition, it could be remarked that maximum ferric coagulant (maximum reduction of total iron) of about 21 mg/L (as total iron) could be produced by adding chlorine of 30 $mgCl_2$ /L into groundwater.

Table 4.2 pH and total iron in groundwater before and after dosing chlorine

Chlorine dosage ($mgCl_2$ /L)	Groundwater before dosing chlorine		Groundwater after dosing chlorine		Total iron reduction (mg/L)
	pH	Total iron (mg/L)	pH	Total iron (mg/L)	
0	6.71	21.1	6.74	19.7	1.4
10	6.71	21.1	6.70	1.76	19.3
20	6.71	21.1	6.62	1.27	19.8
30	6.71	21.1	6.82	0.38	20.7
50	6.71	21.1	6.94	0.48	20.6
80	6.71	21.1	7.23	0.46	20.6

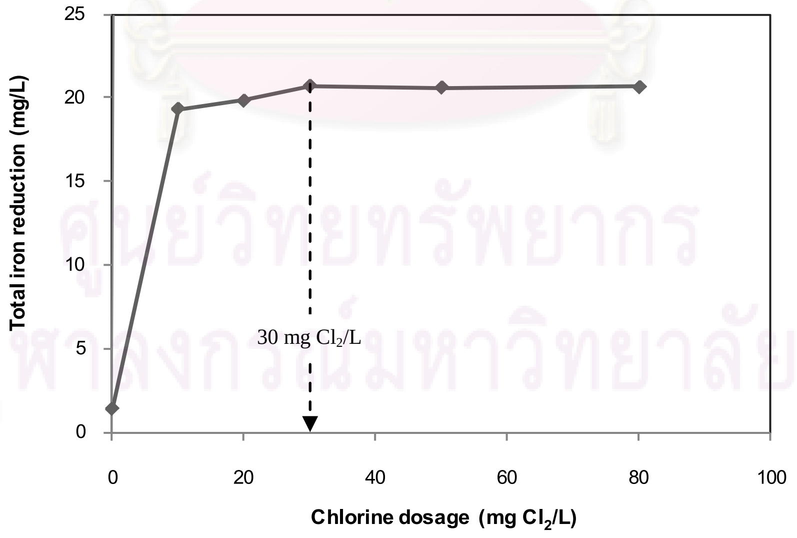
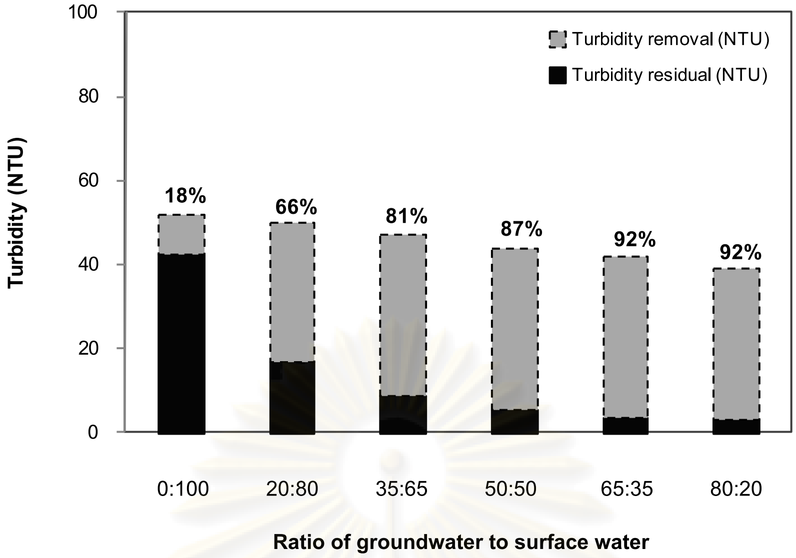


Figure 4.1 Total iron reduction at various chlorine dosages

4.2.2 Appropriate ratio of groundwater (containing high iron) to surface water by adding 30mg as Cl_2 per one liter of groundwater

The mixtures of groundwater and surface water were done under the different ratios of groundwater to surface water of 0:100, 20:80, 35:65, 50:50, 65:35 and 80:20 and then 30 mg as Cl_2 per one liter of groundwater were dosed into each mixture. This is due to the result of chlorine concentration of 30 mg as Cl_2 per one liter of groundwater that could be recommended to be the dosage for producing maximum ferric coagulant as mentioned in the previous section 4.2.1. The turbidity in the waters of all ratios before and after dosing chlorine by using Jar test unit was measured. Figure 4.2 shows the residual turbidity and percent turbidity removal obtained from all experimental conditions. It was found that the turbidity removals of 18, 66, 81, 87, 92 and 92 %, were observed from the ratios of groundwater to surface water 0:100, 20:80, 35:65, 50:50, 65:35 and 80:20, respectively.

Regarding to the appropriate ratio of groundwater to surface water, the ratios of groundwater to surface water of 35:65 and 50:50 were suitably applicable because of its residual turbidity and turbidity removal efficiency were good enough and acceptable. Although at the ratios of groundwater to surface water of 65:35 and 80:20 were also able to give a good quality of water, a high volume of groundwater using to blend with surface water was not applicable and practical according to economic point of view.

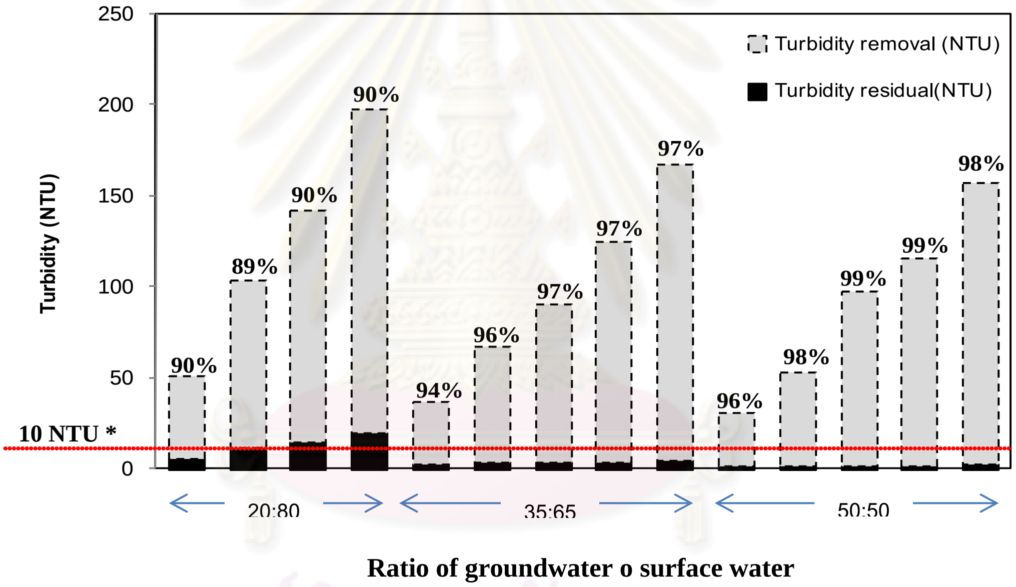


Remark : (%) = Percentage of turbidity removal

Figure 4.2 Residual turbidity and percent turbidity removal of different ratios of groundwater to surface water (at the optimal chlorine dosage of 30 mg as Cl_2 per one liter of groundwater)

4.2.2.1 Effects of different initial turbidity in the water of various ratios of groundwater to surface water on turbidity removal by using the optimal chlorine dosage of 30 mg as Cl_2 per one liter of groundwater

Based on the results obtained from section 4.2.2, the optimal chlorine dosage of 30 mg as Cl_2 per one liter of groundwater adding into the various ratios of groundwater to surface water of 20:80, 35:65 and 50:50 were experimented in order to study the effects of different turbidity in various ratios of groundwater to surface water on turbidity removal. The experiments under the conditions of different turbidity of surface water varied from 50-200 NTU, 40-160 NTU, and 30-160 NTU were performed at the ratios of groundwater to surface water of 20:80, 35:65 and 50:50, respectively. As illustrated in Figure 4.3, the results shown that the residual turbidity obtained in experiment at various initial turbidity and the ratio of groundwater to surface water of 20:80 were sometimes over 10 NTU which did not meet the turbidity standard of water supply set by Dept. of Health, Thailand. On the other hand, it was found that residual turbidity obtained at the ratios of groundwater to surface water of 35:65 and 50:50 with different initial turbidity were entirely lower than 10 NTU. Based on these results, it can be concluded that the variation of turbidity in surface water mixed with groundwater at different ratios would not significantly affect the performance of turbidity removal when 30 mg as Cl_2 per one liter of groundwater was applied. In addition, the ratio of groundwater to surface water of 35:65 dosing with 30 mg as Cl_2 per one liter of groundwater was the most suitable condition for practical implementation.



Remarks: * = Turbidity standard of water supply set by Dept. of Health, Thailand (10 NTU)
(%) = Percentage of turbidity removal

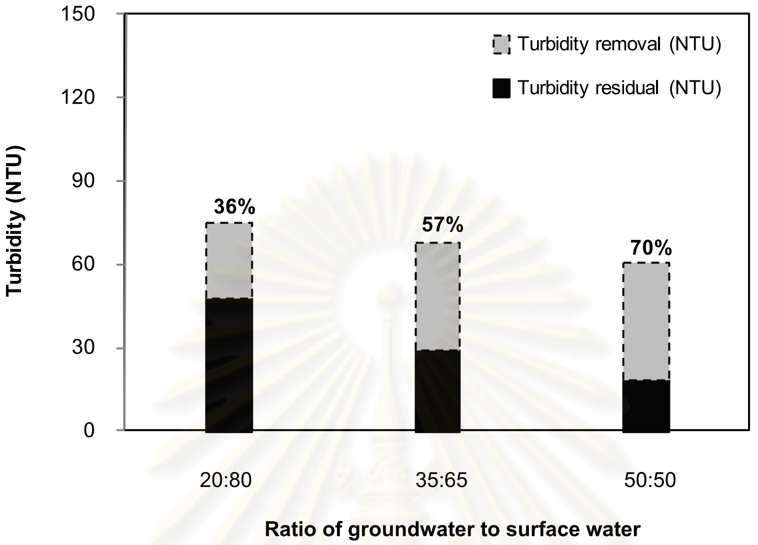
Figure 4.3 Residual turbidity and percentages of turbidity removal of the different ratios of groundwater to surface water of 20:80, 35:65 and 50:50 (at the optimal chlorine dosage of 30 mg as Cl_2 per one liter of groundwater and initial turbidity varied from approximately 50-200 NTU)

4.2.2.2 Effects of different chlorine dosing methods (pre-chlorine adding method and post-chlorine adding method)

With regard to the coagulation of selected ratios of groundwater to surface water (20:80, 35:65 and 50:50), the different results of water quality gained from the effects of using different methods of chlorine dosing for producing ferric coagulant namely pre-chlorine adding method and post-chlorine adding method were investigated. In case of pre-chlorine adding method, the optimal amount of chlorine (at 30 mg as Cl_2 per one liter of groundwater) was dosing into groundwater prior to mixing with surface water. Figure 4.4 illustrates the residual turbidity and percent turbidity removal obtained by using pre-chlorine adding method. The results indicated that the turbidity removal efficiency of 36, 57 and 70%, were obtained in the ratios of groundwater to surface water of 20:80, 35:65 and 50:50, respectively. For post-chlorine adding method, the optimal amount of chlorine (at 30 mg as Cl_2 per one liter of groundwater) was dosing into the mixtures of groundwater and surface water. The residual turbidity and percentage of turbidity removal by using post-chlorine adding method is depicted in Figure 4.5. It was found that the efficiency of turbidity removal of 81, 93 and 96% were achieved at the respective ratios of groundwater to surface water of 20:80, 35:65 and 50:50.

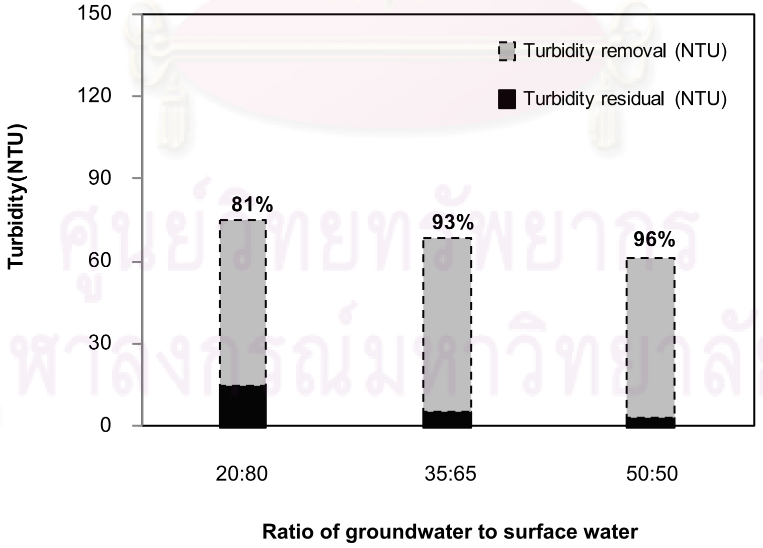
According to the results, it was found that the efficiencies of turbidity removal of all experiments obtained from post-chlorine adding method were higher than that of obtained from pre-chlorine adding method. This may be attributed to the reason that in the post-chlorine adding method, turbidity in surface water has already well mixed with high iron groundwater before ferric coagulant formed. Therefore, efficiency of turbidity entrapment by $Fe(OH)_3$ floc formed in the mixtures of waters in post-chlorine adding method were better than that of occurred in pre-chlorine adding method.

From the combined results of this section and the section 4.2.1 and 4.2.2, it can be additionally concluded that the most appropriate condition of this study was the ratio of groundwater to surface water of 35:65 with chlorine dosage of 30 mg as Cl_2 per one liter of groundwater under post-chlorine adding method.



Remark : (%) = Percentage of turbidity removal

Figure 4.4 Residual turbidity and percent turbidity removal by using pre-chlorine adding method at different groundwater to surface water ratios



Remark : (%) = Percentage of turbidity removal

Figure 4.5 Residual turbidity and percent turbidity removal by using post-chlorine adding method at different groundwater to surface water ratios

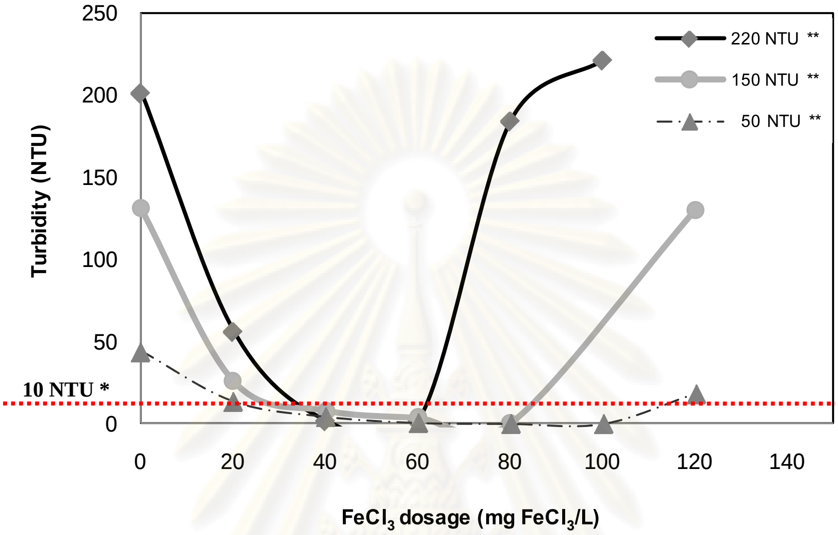
4.2.3 Turbidity removal by using commercial ferric chloride coagulant

This section demonstrated the turbidity removal efficiency of high turbid surface water by using commercial ferric chloride coagulant. A commercial ferric chloride coagulant ($FeCl_3.6H_2O$) used in the experiment was an analytical grade. The commercial ferric chlorides concentration in between 0-120 mg $FeCl_3$ /L were varied and added in different levels of turbidity 50, 150, and 220 NTU.

The factors that influence the quantity of inorganic coagulant (ferric chloride) needed to achieve destabilization of the particulate are including pH, ionic species, temperature, type and concentration of particulates, concentration of the coagulant, and the mixing condition at the point of coagulant condition. Of these solution parameters affecting coagulant-particulate interactions, the solution pH plays a dominant role. Therefore, the results examined in this topic were focused on pH value and the concentration of ferric chloride coagulant added.

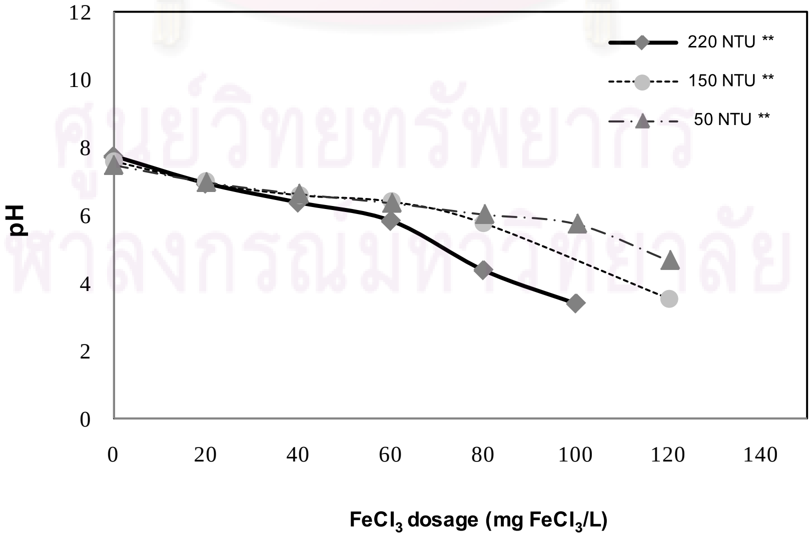
The results of turbidity and pH of the experiments were illustrated in Figure 4.6 and Figure 4.7, respectively. It was found that at 0-20 mg $FeCl_3$ /L of commercial ferric chloride added, the different levels of all turbidities (50 ,150 and 200 NTU) were rapidly decreasing while pH were more than 4. Correspondingly, the previous study has reported that at pH more than 4, the formation of ferric iron on precipitate occur causing entrapment of the particulates which is called “sweep floc”. This sweep floc mechanism usually requires a greater quantity of coagulant than charge neutralization, resulting in the formation of larger quantities of sludge (Jame M. Montgomery). Therefore, the turbidity removals by coagulation-flocculation process at 0-20 mg $FeCl_3$ /L of commercial ferric chloride added in this study are almost from the mechanism called “sweep flocculation”.

Additionally, it was found that 40 mg $FeCl_3$ /L dosage of commercial ferric chloride added in different levels of turbidity in surface water are optimum for turbidity removal so as to achieve the turbidity standard of 10 NTU of water supply set by Dept. of Health, Thailand. However, the increment of turbidity in coagulated water was observed in all experiments at the commercial $FeCl_3$ dosages were higher than 40 mg/L (optimal dosage). This is corresponding to the theoretical phenomenon generated by using an overdose of the coagulant in water coagulation process.



Remark: * = Turbidity standard of water supply by Dept. of Health, Thailand. 10 NTU)
** = Turbidity of surface water

Figure 4.6 Turbidity of coagulated water at different commercial $FeCl_3$ dosages



Remark: ** = Turbidity of surface water

Figure 4.7 pH of coagulated water at different commercial $FeCl_3$ dosages

4.3 Chemical cost of coagulation process by using commercial ferric chloride coagulant and ferric coagulant produced from natural iron in ground water reacted with chlorine

In this section was comparing the chemical costs for coagulation process by using commercial ferric chloride coagulant and ferric coagulant produced from natural iron in groundwater reacted with chlorine.

Iron (III) Chloride Hexahydrate ($FeCl_3.6H_2O$) is the one of iron salts coagulant term or so called ferric chloride ($FeCl_3$). In general, the price of ferric chloride solution in commercial grade as 40% of ferric Chloride is 30 Bath per liter. Based on the results as section 4.2 before, in terms of using analytical ferric chloride coagulant in coagulation found that at 40 mg $FeCl_3$ /L in turbid surface water was the optimal dosage which achieved to remove turbidity lower than 10 NTU. According to the calculation cost, the possible cost of ferric chloride ($FeCl_3$) used to treat one cubic meter of surface water is 3.00 Baht.

For using ferric coagulant produced from natural iron in groundwater reacted wuth chlorine, sodium hypochlorite solution (NaOCl) containing 10% as free chlorine (Cl_2) was introduced to use as strong oxidizing agent for reacting with natural iron in groundwater and then ferric coagulant could be formed. At the present, the price of NaOCl solution in commercial grade observed in Thailand is about 8 Bath per liter. Based on the results obtained from section 4.2, the appropriate ratio of groundwater to surface water was 35% and the optimal chlorine dosage was 30 mg as Cl_2 per one liter of groundwater to achieve turbidity removal lower than 10 NTU. According to the calculation cost, the possible cost of sodium hypochlorite (NaOCl) used to treat one cubic meter of surface water is 1.28 Baht.

Thus, the utilization of ferric coagulant produced from natural iron in groundwater reacted with chlorine was achieved to reduce the expenses according to economy concept.

4.4 DOM fractionation of raw water and coagulated water

Resin fractionation has been employed by many researchers to fractionate DOM in groundwater (Swietlik *et al.,* 2004), reservoir water (Imai *et al.*, 2001 and 2002, Goslan *et al.* 2004; and Janhom 2004) and river water (Marhaba and Van 1999, Imai *et al.*, 2001; and Kimura *et al.,* 2004) in order to provide a better understanding of the characteristics of the DOM in the water. For instance, resin fractionation can separate the DOM into specific organic groups based on their physical and chemical properties. DOM in water samples can be fractionated into two categories using DAX-8 resins: the hydrophobic organic fraction and hydrophilic organic fraction. Thruman (1985) expands on the characteristics of each fraction. The hydrophobic fractions, which are more aromatic carbon than the hydrophilic products and are low organically bound nutrients, contained the acidic products. Hydrophilic fractions mainly consist of proteins, carbohydrates, carboxylic acids, amino acids and amino sugar (Marhaba and Van, 2000). The variation of hydrophobic and hydrophilic materials in different water may diverge depending on the source of materials, geology, biological process etc.

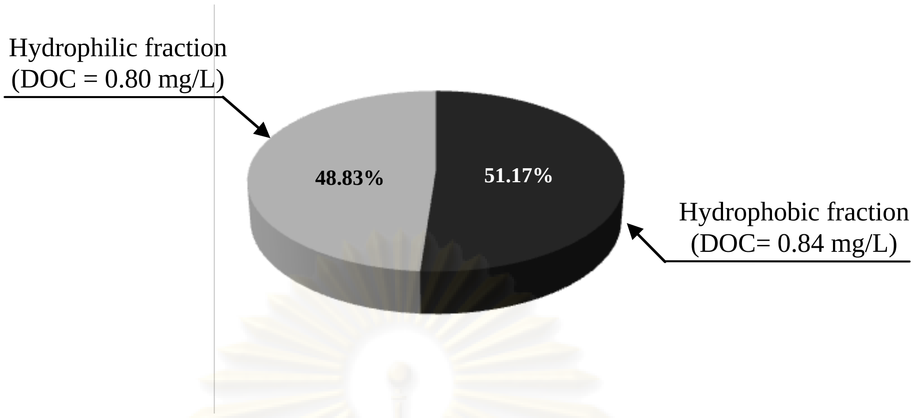
In order to characterize DOM fractions in raw water and coagulated water, resin fractionation was introduced to this section. Raw water and coagulated water were filtrated through 0.75 µm glass fiber filter before fractionated into hydrophobic organic fraction and hydrophilic organic fraction that was followed fractionation method created by Leenheer (1981). Raw water means the mixtures of groundwater and surface water at ratios of groundwater to surface water of 35:65 and 50:50, while coagulated water means the mixtures of groundwater and surface water at ratios of groundwater to surface water of 35:65 and 50:50 after coagulation process by using ferric coagulant produced from natural iron in groundwater reacted chlorine (at 30 mg as Cl_2 per one liter of groundwater under post-chlorine adding method). DOM mass distributions of two fractions were calculated based on DOC mass. The summation of the hydrophobic DOC and hydrophilic DOC was compared with the values of the respective bulk samples to check possible losses in the organic material during fractionation procedures.

4.4.1 DOM fractions in raw water

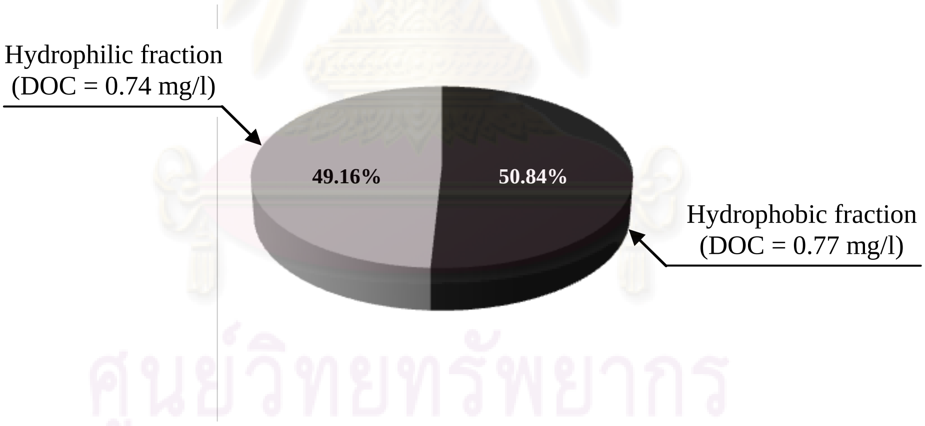
As percent distribution of DOC concentrations of DOM fractions depicted in Figure 4.8, it was observed that hydrophobic fraction and hydrophilic fraction of raw water at ratio of groundwater to surface water of 35:65 were 0.84 and 0.80 mg/L of DOC, respectively, or accounted for 51.17 and 48.83% of total DOC, respectively, and that at ratio of groundwater to surface water of 50:50 were 0.77 and 0.74 mg/L of DOC, respectively, or accounted for 50.84 and 49.16%, respectively. On the other hand, it could be stated that the ratio of hydrophobic fraction to hydrophilic fraction (HPO:HPI) at ratios of groundwater to surface water of 35:65 and 50:50 were 1:0.95 and 1:0.96, respectively.

Considering in term of the distribution of organic fractions in raw water, the hydrophobic fraction was comparable with hydrophilic fraction at both of ratios of ground water to surface water 35:65 and 50:50. However, the hydrophobic fraction and hydrophilic fraction were found to be the major DOM fractions in raw water at both ratios of groundwater to surface water. This result was consistent with the previous study of Musikavong (2006), the relationship between hydrophilic and hydrophobic in river water is demonstrated. In the case of low DOC concentrations (1.1-2.8 mg/L of DOC), either hydrophobic or hydrophilic could be the dominant DOM fraction. Whilst, in the case of high DOC concentrations (3.8-8.4 mg/L of DOC), hydrophilic becomes frequently the dominant DOM fraction in river water. Thruman (1985), reported that humic species (hydrophobic fraction) typically dominant in NOM contributing from 50 to 90% of the DOC in most natural waters. The hydrophobic fraction was slightly more abundant in reservoir water (51 to 62%) than in the river water (41 to 50%), Martin-Mousset *et al.*, 1997. Tadanier *et al.*, (1999) analyzed the source water from Drummond Lake and Chickahominy River (Virginia), and reported that the hydrophobic acid dissolved material matrix (DMM) fraction dominated the dissolved organic matter (DOM) distributions, followed by the hydrophilic neutral fraction. In Taiwan, Huang and Yeh (1997) reported that hydrophobic organics from the Feng-San Stream yielded a higher halogenated organics formation potential because of its higher aromatic content, phenolic acidity, and ultraviolet absorbance. On the other hand, Marhaba and Van (2000) found that hydrophilic acid was a dominant fraction in the water treatment plant in Northern New Jersey, USA. Owen *et al.,* (1995) also found that hydrophilic fraction accounted for about half of the DOC (44 to 58%) meanwhile, 42% to 56% of hydrophobic. Unfortunately, no one has been reported the distribution of organic fractions case of a mixtures between river water and surface water.

According to the results obtained in Figure 4.9, the summation of DOC mass of two DOM fractions in raw water was lower than the DOC mass of unfractionated raw water. The percent differences were about 18.26% for raw water (at ratio of groundwater to surface water of 35:65) and 19.17% for raw water (at ratio of groundwater to surface water of 50:50). The percent differences between the summations of the DOC mass of the two DOM fractions and the DOC mass of unfractionated water were determined in order to confirm the effectiveness of the resin fractionation method. The weight surplus may have come from resin bleeding during the elution process (Leenheer, 1981). Day *et al.,* (1991) and Marhaba and Pipada (2000) reported tolerance of percent differences of DOC from the resin fractionation process as much as 10-15%. Croue *et al.,* (1993) also reported in wastewater a variation of 8-12% of percent differences of DOC. The loss of DOC weight after the resin fractionation process may be due to the effectiveness of the elution process since some DOM is still absorbed in the resins. In accordance with the high level of percent differences of DOC, it can be deducted that raw water used in the current study was slight DOC concentration, thus, the possibility of an error occurred during fractionation procedure are often presented as shown in a high percent DOC differences more than 15%. The characteristics of DOM fractions in filtered raw water of raw water at ratios of groundwater to surface water of 35:50 and 50:65 are depicted in appendix A (Table A-6a and A-6b).

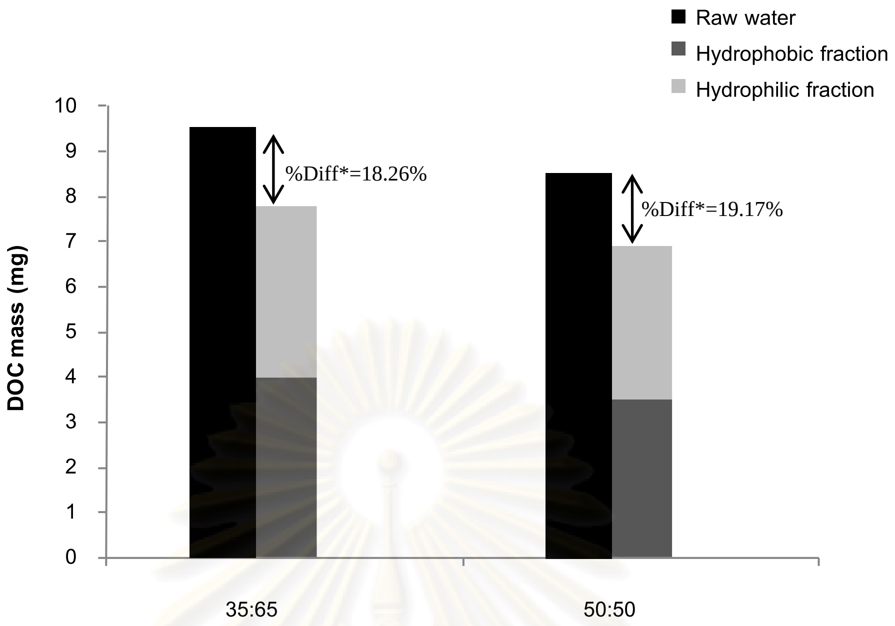


Raw water at ratio of groundwater to surface water of 35:65



Raw water at ratio of groundwater to surface water of 50:50

Figure 4.8 Percent DOC distribution and DOC concentrations of DOM fractions in raw water at ratios of groundwater to surface water of 35:65 and 50:50



Ratio of groundwater to surface water

%Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

Figure 4.9 DOC mass of DOM fractions in raw water at ratios of groundwater to surface water of 35:65 and 50:50

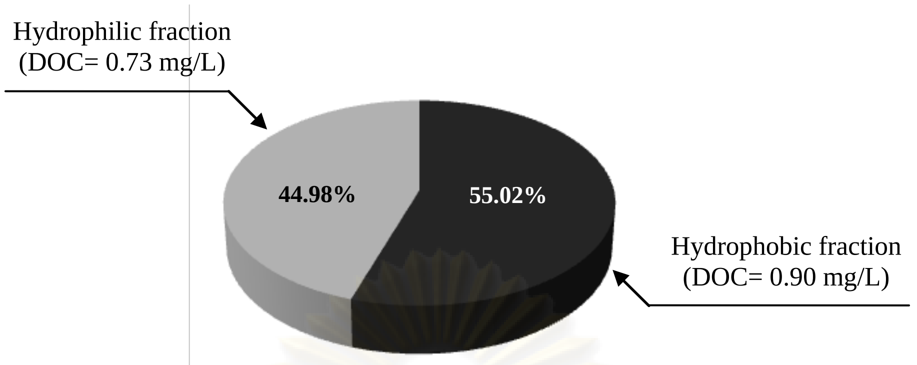
4.4.2 DOM fractions in coagulated water

The percent distribution of DOM fractions from coagulated water by using ferric coagulant produced from natural iron in groundwater reacted with chlorine (at 30 mg as Cl_2 per one liter of groundwater under post-chlorine adding method) at the ratios of groundwater to surface water of 35:65 and 50:50 were exhibited in Figure 4.10.

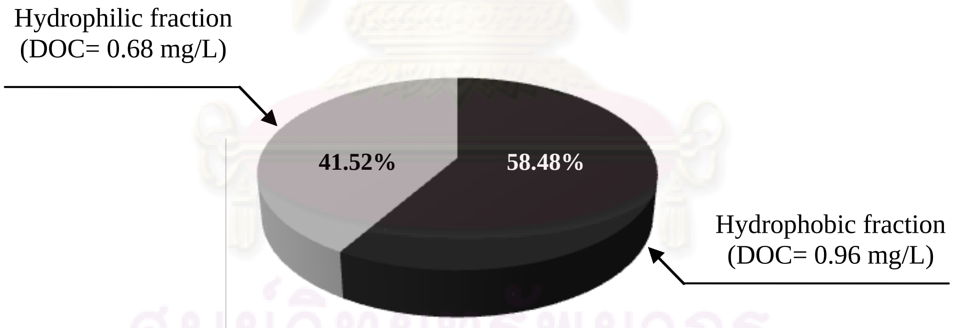
As the results exhibited in Figure 4.10, hydrophobic fraction and hydrophilic fraction of coagulated water at the ratio of groundwater to surface water of 35:65 were 0.90 and 0.73 mg/L of DOC, respectively, or accounted for 55.02 and 44.98% of total DOC, respectively, and that at ratio of groundwater to surface water of 50:50 were 0.96 and 0.68 mg/L of DOC, respectively, or accounted for 58.48 and 41.52%, respectively. It could be stated that the ratio of hydrophobic fraction to hydrophilic fraction (HPO: HPI) at ratios of groundwater to surface water of 35:65 and 50:50 were 1:0.81 and 1:0.71, respectively.

Considering in term of the distribution of organic fractions in coagulated water, the hydrophobic fraction was comparable with hydrophilic fraction. It was founded that after coagulated at both ratios of groundwater to surface water 35:65 and 50:50, the hydrophobic fraction was become to be the major DOM fraction while the hydrophilic fraction was demoted from major DOM fraction. Nevertheless, the DOC concentrations reduction of each DOM fractions is interesting in order to compare the DOC reduction efficiency with different condition and with the previous study (described in section 4.4.3).

Figure 4.11 depicted that the percent differences between the summations of the DOC mass of the two DOM fractions in coagulated water was lower than the DOC mass of unfractionated coagulated water. The percent differences were about 14.89% for coagulated water (at ratio of groundwater to surface water of 35:65) and 12.25% for coagulated water (at ratio of groundwater to surface water of 50:50). The characteristics of DOM fractions in filtered raw water of raw water at ratios of groundwater to surface water of 35:65 and 50:50 are depicted in appendix A (Table A-7a and A-7b).

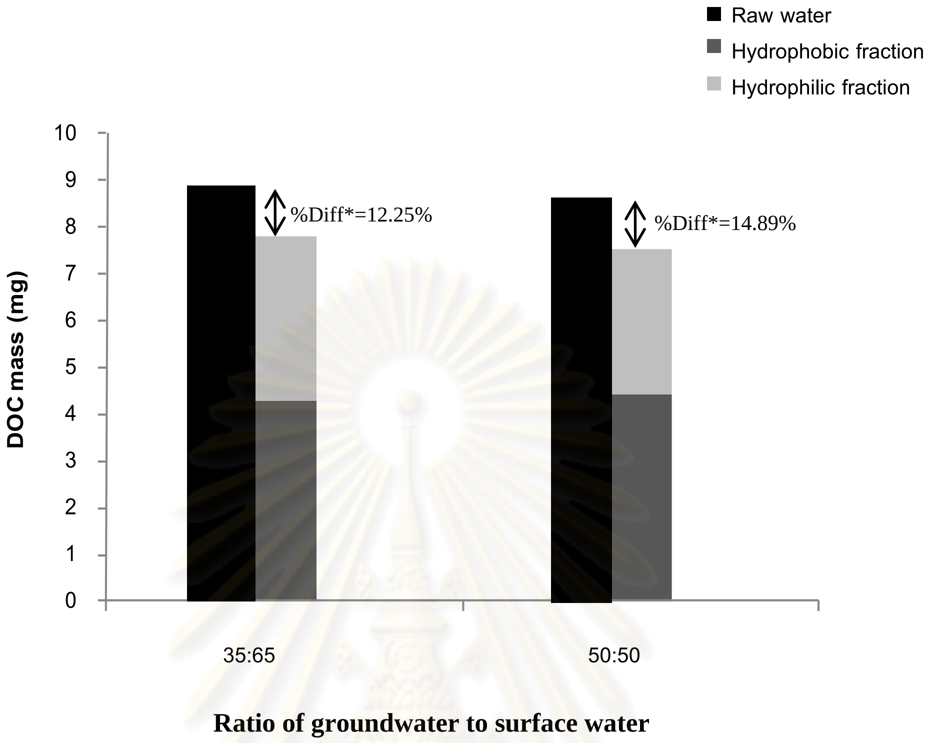


Coagulated water at ratio of groundwater to surface water of 35:65



Coagulated water at ratio of groundwater to surface water of 50:50

Figure 4.10 Percent DOC distribution and DOC concentrations of DOM fractions in coagulated water by using ferric coagulant produced from natural iron in groundwater reacted with chlorine (at 30mg as Cl_2 per one liter of groundwater under post-chlorine adding method) at ratios of groundwater to surface water of 35:65 and 50:50



%Diff* = (Unfractionated water –fractionated water) / Unfractionated water × 100

Figure 4.11 DOC mass of DOM fractions in coagulated water by using ferric coagulant produced from natural iron in groundwater reacted with chlorine (at 30mg as Cl_2 per one liter of groundwater under post-chlorine adding method) at ratios of groundwater to surface water of 35:65 and 50:50

4.4.3 DOC concentrations reduction of DOM fractions

The DOC concentrations reduction of DOM fraction by coagulation which using ferric coagulant produced from natural iron in groundwater reacted with chlorine (at 30mg as Cl_2 per one liter of groundwater under post-chlorine adding method) at ratios of groundwater to surface water of 35:65 and 50:50 were investigated and demonstrated in Figure 4.12 and Figure 4.13, respectively.

From the results shown in Figure 4.12, it was found that the coagulation process at ratio of groundwater to surface water of 35:65 can reduce 10.65% of bulk

DOC. After the coagulation process, the hydrophobic DOC concentration was increased while the hydrophilic DOC concentration was decreased. It can be stated that hydrophobic fraction, which mainly consist of humic and fulvic species (Reckhow *et al.,* 1992), cannot be reduced by coagulation process that using ferric coagulant produced by natural iron in groundwater reacted with chlorine. In contrast, hydrophilic fraction was removable by the coagulation process.

As shown in Figure 4.13, the DOC concentrations reduction of DOM fraction at ratio of groundwater to surface water of 50:50 were different from those at ratio of groundwater to surface water of 35:65. The hydrophilic fraction of coagulated water was also lowers than that of raw water (8.12% reduction). The coagulation cannot reduce hydrophobic fraction. In this case, the bulk DOC concentrations cannot be reduced after coagulation process. Contradictory with the several studies, the DOM fraction investigation in Mae Hea Reservoir and Bhumiphol Dam were indicated that the alum coagulation can reduce the hydrophobic fraction (51.2-59.7%) and hydrophilic fraction (27.4-43.6%) (Jiarsirikul V., 2003). Janhom T. (2005) investigate the DOM fractions reduction in the Northern Region Industrial Estate Reservoir, the results indicated that the alum coagulation can efficiently reduce the hydrophobic fraction and hydrophilic fraction of 44.6 and 54.9%, respectively.

According to the results obtained in this section, it could be concluded that the higher ratio of groundwater to surface water, the higher hydrophobic fraction formed after coagulation. Hydrophilic fraction was removable at both of two ratios (35:65 and 50:50). Furthermore, the DOM could be reduced inefficiently after coagulation process that using ferric coagulant produced from natural iron in groundwater reacted with chlorine.

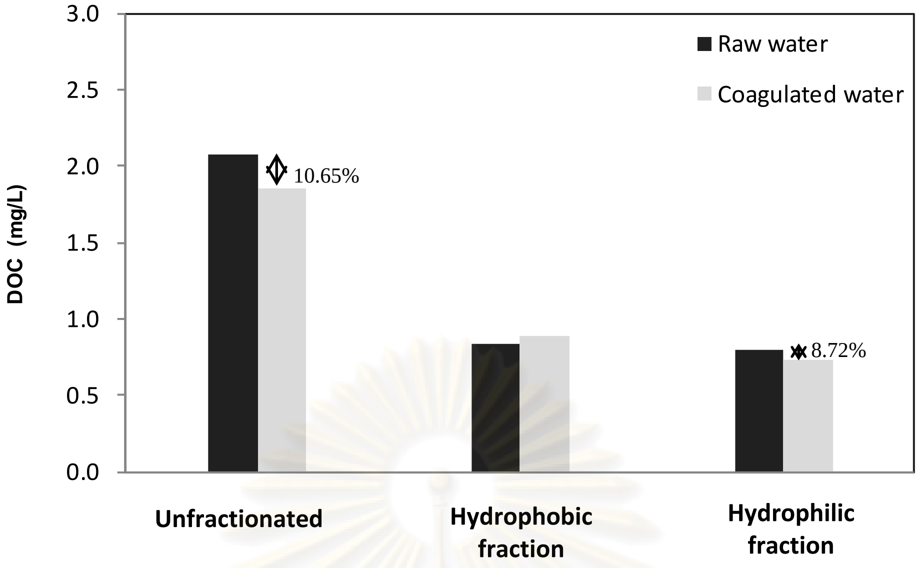


Figure4.12 DOC concentration reduction of DOM fraction of raw water and coagulated water by using ferric coagulant produced from natural iron in groundwater reacted with chlorine (at 30mg as Cl_2 per one liter of groundwater under post-chlorine adding method) at ratio of groundwater to surface water of 35:65

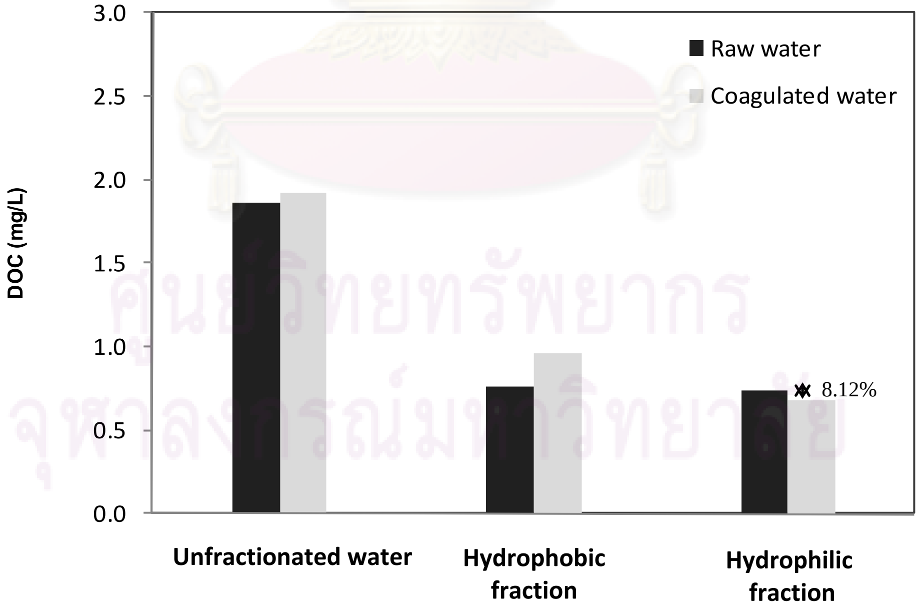


Figure 4.13 DOC concentration reduction of DOM fraction of raw water and coagulated water by using ferric coagulant produced from natural iron in groundwater reacted with chlorine (at 30mg as Cl_2 per one liter of groundwater under post-chlorine adding method) at ratio of groundwater to surface water of 50:50

4.5 Total trihalomethanes (THMs) formation

From the hypotheses mentioned in Chapter I, the disinfection by-products (DBPs) could be formed from the interaction between chlorine and organic substances in water. Total trihalomethanes (THMs), which is including four species (chloroform, bromodichloromethane, dibromochloromethane, and bromoform) has been investigated as a major DBPs that can be formed during disinfection process on natural water. This study was utilized ferric coagulant produced from natural iron in groundwater reacted with chlorine for turbidity removal in surface water. Therefore, there was a possibility of THMs forming during this coagulation process. Hence, the aim of this section was to investigate the formation of THMs during this process that utilizes ferric coagulant produced from natural iron in groundwater reacted with chlorine.

Raw water means the mixtures of groundwater and surface water at ratios of groundwater to surface water of 35:65 and 50:50, while the coagulated water was a mixtures of groundwater to surface water that collected from coagulation process where the ferric coagulant was produced from the natural iron in groundwater reacted with chlorine (at 30 mg as Cl_2 per one liter of groundwater under post-chlorine adding method) at ratios of groundwater to surface water of 35:65 and 50:50.

Based on the investigation of total trihalomethanes (THMs) formation as shown in Table 4.3, total THMs concentration was scarcely found in both raw groundwater and raw surface water. This may be due to the fact that raw groundwater and raw surface water may not contain chlorine and halogen compounds.

During the coagulation experiment with using ferric coagulant produced from natural iron in groundwater reacted with chlorine, the total trihalomethanes (THMs) concentration of both raw water and coagulated water were also investigated. Table 4.4 illustrates the total THMs concentration of raw water and coagulated water at ratios of groundwater to surface water of 35:65 and 50:50, the results present that the total concentration of THMs in raw water at ratios of groundwater to surface water of 35:65 and 50:50 were 2.98 and 2.67μg/L, respectively. While the total concentration of THMs in coagulated water at ratios of groundwater to surface water of 35:65 and 50:50 were 51.17 and 51.47 µg/l, respectively.

It can be conclusively stated that the coagulation process by using ferric coagulant produced from natural iron in groundwater reacted chlorine of 30 mg as Cl_2 per one liter of groundwater could cause trihalomethanes (THMs) formation. Since an increase in trihalomethanes (THMs) concentration after coagulation process from 2.98 to 51.17μg/L and from 2.67 to 51.47μg/L were observed for coagulation experiment at ratios of groundwater to surface water of 35:65 and 50:50, respectively, as depicted in Figure 4.14. According to these results, the trihalomethanes (THMs) concentrations in coagulated water at ratios of groundwater to surface water of 35:65 and 50:50 were slightly higher than the trihalomethanes (THMs) standard rule of stage two (maximum contaminant level for THMs > 40μg/L.), which proposed by US Environmental Protection Agency (USEPA) 1998, but lower than the standard rule of stage one (maximum contaminant level for THMs < 80μg/L.).

Based on this finding, it could be stated that the concept of using ferric coagulant produced from natural iron in groundwater reacted with chlorine may potentially be applied for high turbid surface water treatment.

Table4.3 Total THMs concentration of raw surface water and raw groundwater

Parameter	Raw water	
	Surface water	Groundwater
Total THMs concentration (µg/L)	2.48	1.07

Table4.4 Total THMs concentration of raw water and coagulated water at ratios of groundwater to surface water of 35:65 and 50:50

Parameter	Ratio of groundwater to surface water 35:65		Ratio of groundwater to surface water 50:50	
	Raw water	Coagulated water	Raw water	Coagulated water
Total THMs concentration (µg/L)	2.98	51.17	2.67	51.47

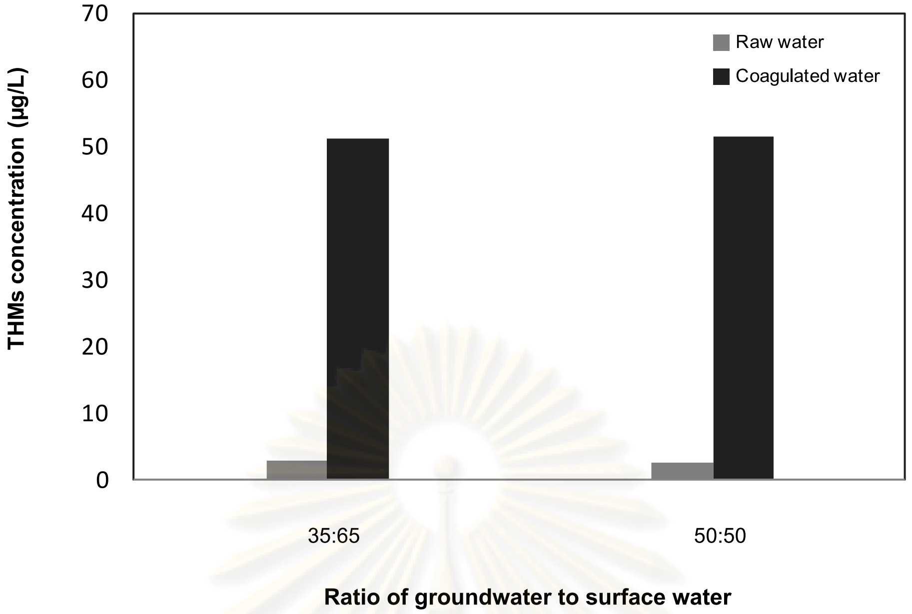


Figure 4.14 Increment of total THMs concentration at ratios of groundwater to surface water of 35:65 and 50:50 of raw water and coagulated water by using ferric coagulant produced from natural iron in groundwater reacted with chlorine (at 30mg as Cl_2 per one liter of groundwater under post-chlorine adding method)

4.6 FEEM signatures of DOMs

Three-dimensional fluorescence spectroscopy (Fluorescent Excitation - Emission Matrixes: FEEM) provides the total summary of the emission spectra of a sample at different excitation wavelengths, recorded as a matrix of fluorescent intensities in coordinates of excitation (EX) and emission (EM) wavelengths. Recently, FEEM was successfully employed to establish the fingerprint of organic compounds in water (Marhaba, Pu, and Bengraine, 2003; Nakajima, Hanabusa, and Furumai, 2002). The filtered raw water and coagulated water were adjusted to neutral pH before analyzing with a spectrofluorometer.

In order to characterize DOM in all waters, the FEEM of all waters were established. The peak position on the FEEM was the highest fluorescent intensity of each DOM signature that was exhibited in each region position and also reported in coordinates of “nm in excitation (ex) and nm emission (em)”. The FEEM of raw water and coagulated water (by using ferric coagulant produced from natural iron reacted with chlorine of 30mg as Cl_2 per one liter of groundwater under post-chlorine adding method) at ratio of groundwater to surface water of 35:65 were investigated. For removing the insoluble substances that could interfere FEEM results, all water samples were filtrated through 0.75 µm glass fiber filter before analyzing FEEM.

Using consistent excitation and emission wavelength boundaries for each FEEM, Chen *et al.,* (2003) operationally defined excitation and emission boundaries into five regions based largely upon supporting literature. FEEM peaks have been associated with humic-like, tyrosine-like, tryptophan-like, or phenol-like organic compounds. In general, peaks at shorter excitation wavelengths (<250 nm) and shorter emission wavelengths (<350 nm) are related to simple aromatic proteins such as tyrosine (Regions I and II). Peaks at intermediate excitation wavelengths (250 - 280 nm) and shorter emission wavelengths (<380 nm) are related to soluble microbial by-product-like material (Region IV). Peaks at longer excitation wavelengths (>280 nm) and longer emission wavelengths (>380 nm) are related to humic acid-like organics (Region V). For fulvic acids, FEEMs with minimum excitation wavelengths of 250 nm indicate shoulders of FEEM peaks located at shorter excitation wavelengths. Therefore, peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) are related to fulvic acid-like materials (Region III). All these five regions are separately demonstrated in Figure 4.15. These demonstrated the relationships between FEEM peak position and organic compounds that might be utilized to explain the characteristics of organic compounds in the studied waters. FEEM peaks of the major DOM fractions were compared with the location of FEEM peaks based on literature reports by Chen *et al.,* 2003.

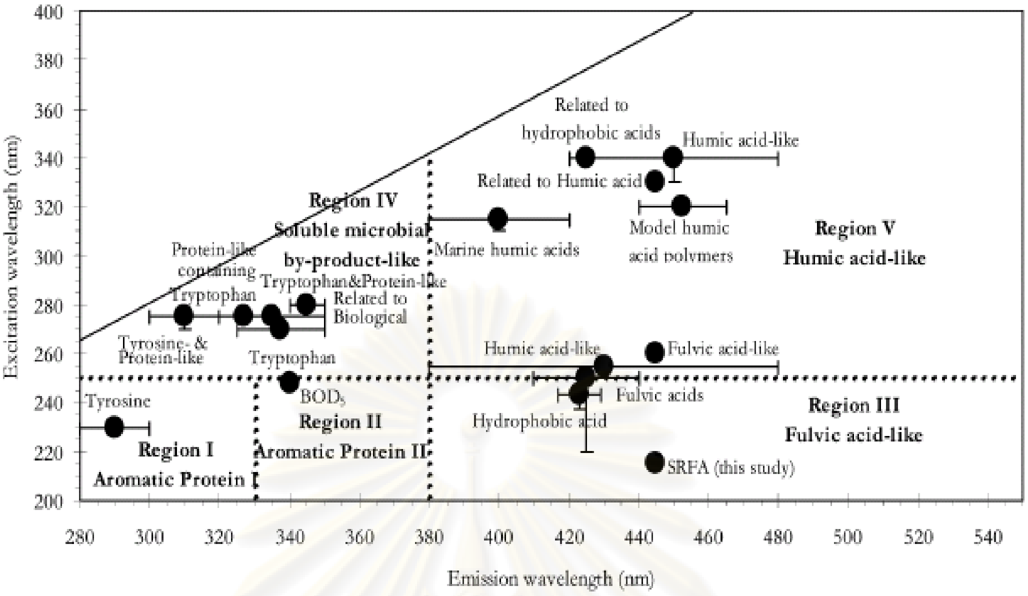
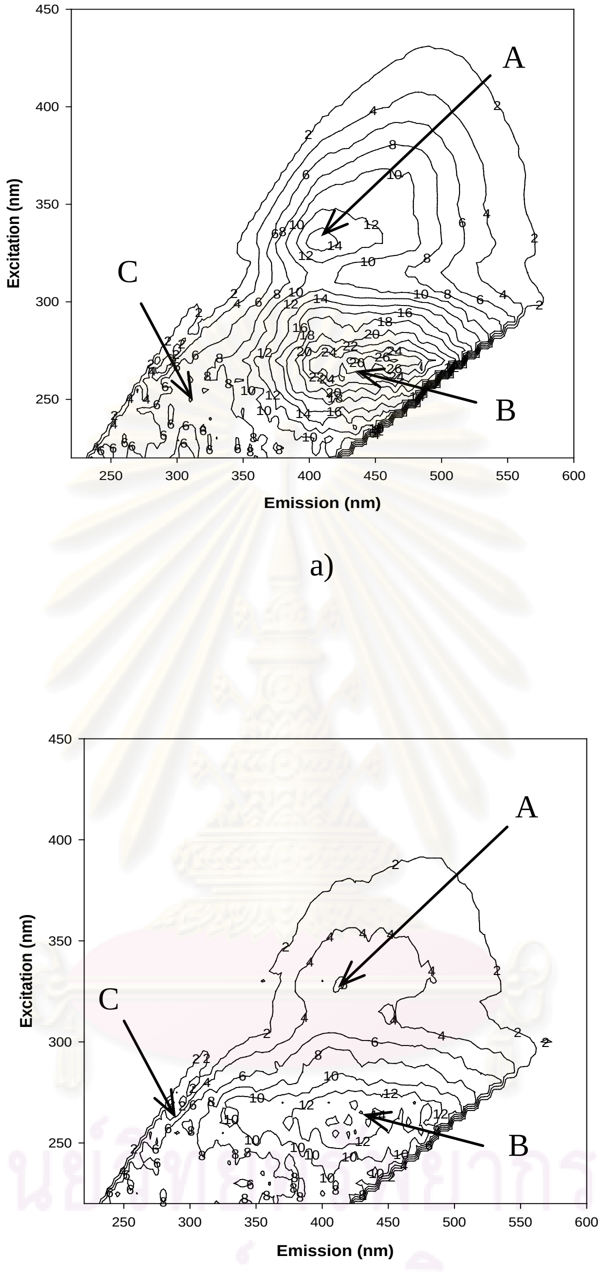


Figure 4.15 Location of FEEM peaks and excitation and emission wavelength boundaries for five FEEM regions based on literature reports by Chen *et al.*, 2003

The FEEM contours of raw water and coagulated water by using ferric coagulant produced from natural iron in groundwater reacted with chlorine of 30mg as Cl_2 per one liter of groundwater under post-chlorine adding method) at ratio of groundwater to surface water of 35:65 are presented in Figures 4.16

As FEEM contours shown in Figure 4.16, FEEM of raw water at ratio of groundwater to surface water of 35:65 established three peaks, firstly, a peak (A) located at regionV of 335nm/410 nm (excitation/emission), secondly, a peak (B) located at regionV of 265 nm/ 430nm, and thirdly, a peak(C) located at regionIV of 290 nm/ 320nm. FEEM of coagulated water (by using ferric coagulant produced from natural iron in groundwater reacted with chlorine of 30mg as Cl_2 per one liter of groundwater under post-chlorine adding method) at ratio of groundwater to surface water of 35:65 established three peaks, firstly, a peak (A) located at regionV of 330nm / 410nm, secondly, a peak (B) located at regionV of 280 nm/ 425nm, and thirdly, a peak(C) located at regionIV of 270 nm/ 295nm. The results of FEEM peak position were correspond to the FEEM peak positions from several water sources reported by previous study (Table4.5).



a)

b)

Figure 4.16 FEEM contours and peak position A, B, and C at ratio of groundwater to surface water of 35:65 of a) raw water and b) coagulated water by using ferric coagulant produced form natural iron in groundwater reacted with chlorine (at 30 mg as Cl_2 per one liter of groundwater under post-chlorine adding method) presented with contour intervals of 2 QSU

Table 4.5 Summary of the FEEM positions and fluorescent DOM substances from several water sources

Substances	Excitation(nm)/ Emission(nm)	Sources	References
Humic acid	250/450	Suwannee River, Peat and soil standards ,IHSS	Marhaba and Kochar (2000)
	235-255/453-465	Commercially available humic acid, Wako	Nakajima *et al.*, (2002)
	260/485, 330/470	Suwannee River Humic Acid (1S101H), IHSS	Sierre *et al.*, (2005)
	270/550, 360/560	Elliot Soil Humic acid (1S102H), IHSS	Sierre *et al.*, (2005)
	261/457, 325/452	Suwannee River humic acid (SRHA, with larger MW and high aromaticity)	Her *et al.*, (2003)
Fulvic acid and Humic acid-like proposed	235/435, 320/430 290-340/395-430	Lake water, Japan Groundwater, from Sutherland, Scotland; Derbyshire, England; Dordogne, France; Wiltshire, England	Komatsu *et al.*, (2005)
	230/440, 340/440	Hawaiian River water	Coble *et al.*, (1993)
	260/380-460, 350/420-480	Bulk seawater	Coble (1996)
	337/423	Natural water and Wastewater, USA	Her *et al.*, (2003)

(Source: Janhom *et al.*, 2009)

From the five boundaries reported by Chen *et al.*, (2003) as depicted in Figure 4.15, this might explain the organic compounds of DOM contained in water samples. According to the observed FEEM contour results, peak positions of raw water and coagulated water that located in regions V and IV are characterized into humic acid-like and soluble microbial by-product-like, respectively.

Considering in the peak intensities, the level of fluorescent intensities depends upon the level of organic substances in the water. Musikavong *et al.*, (2006) suggested that the fluorescent intensity in the QSU units of each fluorescent peak could be further utilized to determine the quantity of all fluorescent organic matters in water by adding the fluorescent intensities of all FEEM peaks.

The reduction in the fluorescent organic matters could therefore be reflected by the difference in the fluorescent intensities of the fluorescent organic matter by coagulation process. As the results shown in Table 4.6, fluorescent intensities at peak position A, B, and C of raw water were reduced by the coagulation process. It could be stated that humic acid-like and soluble microbial by-product-like (as located in regions V and IV, respectively) were reduced by the coagulation process. These results were corresponded to the results of DOC reduction (as shown in previous section) as the literature reported that in case of high organic content (high DOC) in water the high value of fluorescent intensities are observed, whereas in case of low organic content (low DOC), low values of fluorescent intensities are obtained (Homklin, 2004). As the results of FEEM intensity reductions in this study, it was also corresponded to the results of THMs formation by coagulation process. THMs were formed by the interaction between organic substances and chlorine during coagulation process that utilized ferric coagulant from natural iron in groundwater reacted with chlorine, therefore the FEEM intensities could be reduced due to the coagulation process.

Table4.6 Fluorescent intensities, FEEM peak region and FEEM peak position at ratio of groundwater to surface water of 35:65 of raw water and coagulated water by using ferric coagulant produced from natural iron in groundwater reacted with chlorine (at 30mg as Cl_2 per one liter of groundwater under post-chlorine adding method)

Sample water	Excitation wavelength (nm)	Emission wavelength (nm)	Fluorescent intensity	FEEM peaks region	FEEM peaks position
Raw water	335	410	55.24	V	A
	265	430	68.71	V	B
	290	320	43.69	IV	C
Coagulated water	330	410	13.52	V	A
	280	425	14.07	V	B
	270	295	48.81	IV	C

CHAPTER V

CONCLUSIONS

Based on the obtained results from the study of ferric coagulant produced from natural iron in groundwater reacted with chlorine for turbidity removal of turbid surface water (Ping River), the following conclusions could be drawn.

1. Chlorine dosage of 30 mg as Cl_2 per one liter of groundwater was the optimal chlorine dosage for producing maximum ferric coagulant of about 21 mg/L (as total iron).

2. The ratio of groundwater to surface water of 35:65 under the optimal chlorine dosage were found to be the most appropriate coagulation condition for turbidity removal which could reduced turbidity in surface water to be below 10 NTU.

3. Coagulation operated by dosing chlorine into a mixtures of groundwater and surface water (called as post-chlorine adding method) gave more efficient turbidity removal than that of dosing chlorine into groundwater before mixing with surface water (called as pre-chlorine adding method).

4. Total THMs concentrations in raw water at ratios of groundwater to surface water of 35:65 and 50:50 were 2.98 and 2.67μg/L, respectively, whereas those in coagulated waters at ratios of groundwater to surface water of 35:65 and 50:50 were increased to be 51.17 and 51.47μg/L, respectively, which were higher than the Maximum Contaminant Level (MCL) for THMs of 40 μg/L for stage 2 but were lower than that of 80 μg/L for stage 1 of drinking water standard issued by U.S. Environmental Protection Agency (USEPA, 1998).

5. Chemical cost of sodium hypochlorite used in the coagulation process proposed by this study and chemical cost of the coagulation by commercial ferric

chloride were compared, as a consequence, it could be stated that coagulation by using sodium hypochlorite added into a mixtures of groundwater and surface water to produce ferric coagulant was cheaper than that of utilizing commercial ferric chloride.

6. Hydrophobic and hydrophilic DOM fraction in raw water at ratio of groundwater to surface water of 35:65 were 51.17 and 48.83% of total DOC, respectively, and those water at ratio of groundwater to surface water of 50:50 are 50.84 and 49.16% of total DOC, respectively. Hydrophobic fraction and hydrophilic fraction of coagulated water at the ratio of groundwater to surface water of 35:65 are 55.02 and 44.98% of total DOC, respectively, and those water at ratio of groundwater to surface water of 50:50 are 58.48 and 41.52%, respectively.

7. By the Fluorescent Excitation-Emission Matrixes (FEEM) results obtained that, raw water and coagulated water (at ratio of groundwater to surface water of 35:50) are mainly consists of humic acids-like and soluble microbial by-product-like substance

CHAPTER VI

RECOMMENDATIONS FOR FUTURE WORK

The following statements are recommended for future studies.

1. Other widely used coagulants such as alum ($Al_2Cl(OH)_5$ and $Al_2(SO_4)_3$), synthetic polymers polyaluminumchloride (PACl), and other iron salts ($FeSO_4$ and $Fe_2(SO_4)_3$) should be recommended so as to make the comparison with the results obtained in this study.

2. Due to the formations of total trihalomethanes (THMs) were observed in the coagulated water without chlorine residual concentration data in this study. Chlorine demand, chlorine residual, Trihalomethane formation potential (THMFP), and details of THMFP species are recommended to be the significant parameter for consideration and discussion in the future works.

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APPENDICES

APPENDIX A

EXPERIMENTAL DATA

Table A-1 Chlorine demand for producing ferric coagulant and data of iron in raw groundwater and their coagulated water

Cl_2 dosage (mg/L)	Raw groundwater			Coagulated water			Free Cl_2 residual (mg/L)	Cl_2 demand (mg/L)
	T-iron(mg/L)	Fe^{2+}(mg/L)	Fe^{3+}(mg/L)	T-iron(mg/L)	Fe^{2+}(mg/L)	Fe^{3+}(mg/L)		
0	21.1	13.05	8.05	19.7	9.85	9.85	0.97	-0.97
10	21.1	13.05	8.05	1.76	0.1	1.66	0.46	9.54
20	21.1	13.05	8.05	1.27	0.08	1.19	7.6	12.4
30	21.1	13.05	8.05	0.38	0.08	0.3	19.3	10.7
50	21.1	13.05	8.05	0.48	0.07	0.41	39	11
80	21.1	13.05	8.05	0.46	0.07	0.39	-	-

Table A-2 Appropriate ratio of groundwater (containing high iron) to surface water by adding 30mg as Cl_2 per one liter of groundwater

Table A-2a Quality of raw groundwater and raw surface water

Water sample	Turb. (NTU)	T-iron (mg/L)	Fe^{2+} (mg/L)	Fe^{3+} (mg/L)	pH	Alkalinity (mg/l CaCO3)	DOC (mg/L)	UV-254 (cm^{-1})	SUVA (L/mg-m)
Groundwater	0.9	19.5	9.35	10.15	7.04	137.5	1.963	0.3491	17.7840
Surface water	52	4.52	0.91	3.61	7.86	87.85	3.580	0.1361	3.8017

Table A-2b Water quality of before and after coagulation at different ratio of groundwater to surface water

Ratio of groundwater to surface water	Cl^- dosage (mg/L)	Water quality before coagulation					Water quality after coagulation					% of Turb. removal
		Turb. (NTU)	pH	DOC (mg/l)	UV-254 (cm^{-1})	SUVA (L/mg-m)	Turb. (NTU)	pH	DOC (mg/l)	UV-254 (cm^{-1})	SUVA (L/mg-m)	
0:100	0	52	7.86	2.56	0.0932	3.6406	42.4	7.83	3.58	0.1320	3.6872	18.46
20:80	6	50	7.51	2.78	0.0819	2.9460	16.8	7.5	3.01	0.0945	3.1395	66.40
35:65	10.5	47	7.34	2.65	0.0711	2.6830	8.83	7.34	2.87	0.0586	2.0418	81.21
50:50	15	44	7.18	3.04	0.1210	3.9803	5.35	7.24	2.98	0.0621	2.0839	87.84
65:35	19.5	42	7.07	1.98	0.0436	2.2020	3.35	7.18	2.04	0.0512	2.5098	92.02
80:20	24	39	7.12	2.21	0.0555	2.5113	3.13	7.13	1.97	0.0471	2.3909	91.97

Table A-3 Effects of different initial turbidity in the water of various ratios of groundwater to surface water (20:80, 35:65 and 50:50) on turbidity removal by using the optimal chlorine dosage of 30 mg as Cl_2 per one liter of groundwater

Table A-3a Quality water of raw groundwater and raw surface water (of ratio of groundwater to surface water 20:80)

Water sample	**Turb. (NTU)**	**T-iron (mg/L)**	**Fe^{2+} (mg/L)**	**Fe^{3+} (mg/L)**	**pH**	**Alkalinity (mg/l CaCO3)**	**DOC (mg/L)**	**UV-254 (cm^{-1})**	**SUVA (L/mg-m)**
Groundwater	0.45	22.6	10.3	12.3	6.58	140.25	1.696	0.3068	18.0896
Surface water	100	4.15	1.35	2.8	7.52	89.25	2.688	0.1043	3.8802

Table A-3b Quality water of before and after coagulation at ratio of groundwater to surface water 20:80

Ratio of groundwater to surface water (%)	**Cl_2 dosage (mg/L)**	**Water quality before coagulation**					**Water quality after coagulation**					**% of Turb. removal**
		Turb. (NTU)	**pH**	**DOC (mg/l)**	**UV-254 (cm^{-1})**	**SUVA (L/mg-m)**	**Turb. (NTU)**	**pH**	**DOC (mg/l)**	**UV-254 (cm^{-1})**	**SUVA (L/mg-m)**	
20:80	6	0.34	6.59	2.215	0.0516	2.3296	2.13	7.34	2.319	0.0587	2.5313	-
20:80	6	51	7.05	1.716	0.0551	3.2110	5.25	7.45	2.817	0.0651	2.3110	89.71
20:80	6	103	7.06	2.041	0.0829	4.0617	11.1	7.51	2.569	0.0914	3.5578	89.22
20:80	6	141	7.15	1.978	0.0664	3.3569	14.2	7.54	3.255	0.0730	2.2427	89.93
20:80	6	197	7.07	1.767	0.0730	4.1313	18.9	7.48	3.321	0.0783	2.3577	90.41
20:80	6	248	7.08	2.171	0.0703	3.2381	29.5	7.47	3.010	0.0725	2.4086	88.10

Table A-3c Quality water of raw groundwater and raw surface water (of ratio of groundwater to surface water 35:65)

Water sample	Turb. (NTU)	T-iron (mg/L)	Fe^{2+} (mg/L)	Fe^{3+} (mg/L)	pH	Alkalinity (mg/l CaCO3)	DOC (mg/L)	UV-254 (cm^{-l})	SUVA (L/mg-m)
Groundwater	1.02	19.7	10.05	9.65	6.53	142.5	1.888	0.2451	12.9820
Surface water	90	3.55	1.27	2.28	7.15	90.25	2.590	0.1044	4.0309

Table A-3d Quality water of before and after coagulation at ratio of groundwater to surface water 35:65

Ratio of groundwater to surface water (%)	Cl_2 dosage (mg/L)	Water quality before coagulation					Water quality after coagulation					% of Turb. removal
		Turb. (NTU)	pH	DOC (mg/l)	UV-254 (cm^{-l})	SUVA (L/mg-m)	Turb. (NTU)	pH	DOC (mg/l)	UV-254 (cm^{-l})	SUVA (L/mg-m)	
35:65	10.5	0.64	6.74	2.321	0.0420	1.8096	1.54	6.89	2.154	0.0365	1.6945	-
35:65	10.5	36	6.77	2.448	0.0109	0.4453	2.16	7.02	2.097	0.0396	1.8884	94.00
35:65	10.5	67	6.79	2.541	0.0169	0.6651	2.84	7.03	2.161	0.0406	1.8788	95.76
35:65	10.5	90	6.81	2.335	0.0152	0.6510	3.09	7.02	2.324	0.0413	1.7771	96.57
35:65	10.5	124	6.82	2.460	0.0168	0.6829	3.35	7.01	2.308	0.0437	1.8934	97.30
35:65	10.5	167	6.85	2.423	0.0184	0.7594	4.53	7.05	2.397	0.0438	1.8273	97.29

Table A-3e Quality water of raw groundwater and raw surface water (of ratio of groundwater to surface water 50:50)

Water sample	Turb. (NTU)	T-iron (mg/L)	Fe^{2+} (mg/L)	Fe^{3+} (mg/L)	pH	Alkalinity (mg/l CaCO3)	DOC (mg/L)	UV-254 (cm^{-1})	SUVA (L/mg-m)
Groundwater	1.5	21.1	10.15	10.95	6.61	134.82	1.718	0.1937	11.2747
Surface water	75	3.36	0.98	2.38	7.48	85.58	3.018	0.0809	2.6806

Table A-3f Quality water of before and after coagulation at ratio of groundwater to surface water 50:50

Ratio of groundwater to surface water (%)	Cl_2 dosage (mg/L)	Water quality before coagulation					Water quality after coagulation					% of Turb. removal
		Turb. (NTU)	pH	DOC (mg/l)	UV-254 (cm^{-1})	SUVA (L/mg-m)	Turb. (NTU)	pH	DOC (mg/l)	UV-254 (cm^{-1})	SUVA (L/mg-m)	
50:50	15	0.98	6.96	2.742	0.0156	0.5689	0.6	6.91	3.393	0.0578	1.7035	38.78
50:50	15	30.1	6.9	2.489	0.0204	0.8196	1.08	6.98	3.076	0.0367	1.1931	96.41
50:50	15	52.7	6.86	2.287	0.0257	1.1237	1.29	6.98	2.862	0.0362	1.2648	97.55
50:50	15	96.5	6.58	2.286	0.0266	1.1636	1.18	6.98	2.934	0.0357	1.2168	98.78
50:50	15	115.1	6.91	2.311	0.0318	1.3760	1.27	6.98	2.884	0.0351	1.2171	98.90
50:50	15	156.3	6.9	2.620	0.0399	1.5229	2.56	7.00	2.783	0.0377	1.3547	98.36

Table A-4 Effects of different chlorine dosing methods (pre-chlorine adding method and post-chlorine adding method)

Table A-4a Quality of raw groundwater and raw surface water (of ratio of groundwater to surface water 20:80, 35:65 and 50:50)

Water sample	Turb. (NTU)	T-iron (mg/L)	Fe^{2+} (mg/L)	Fe^{3+} (mg/L)	pH	DOC (mg/L)	UV-254 (cm^{-1})	SUVA (L/mg-m)
Groundwater	2.33	19.7	12.6	7.1	6.48	1.332	0.2005	15.0526
Surface water	80	3.7	1.15	2.55	7.4	2.312	0.0629	2.7206

Table A-4b Quality water with pre-chlorine adding method at different groundwater to surface water ratio

% Groundwater to surface water	Cl_2 dosage (mg/L)	Water quality before coagulation		Water quality after coagulation		% of Turb. removal
		Turb. (NTU)	pH	Turb. (NTU)	pH	
20:80	10.5	75	6.48	48	7.82	36.00
35:65	10.5	68	6.48	29.3	7.39	56.91
50:50	10.5	61	6.48	18.5	7.08	69.67

Table A-4c Quality water with post-chlorine adding method at different groundwater to surface water ratio

% Groundwater to surface water	Cl_2 dosage (mg/L)	Water quality before coagulation		Water quality after coagulation		% of Turb. removal
		Turb. (NTU)	pH	Turb. (NTU)	pH	
20:80	10.5	75	7.24	14.4	7.68	80.80
35:65	10.5	68	7.01	4.87	7.35	92.84
50:50	10.5	61	6.94	2.64	7.10	95.67

Table A-5 Turbidity removal by using commercial $FeCl_3$ coagulant

Table A-5a Quality water of surface water at 50 NTU with before and after coagulation

$FeCl_3$ dosage (mg/L)	Raw water						Coagulated water					
	Turb. (NTU)	Alkalinity (mg/l CaCO3)	T-iron (mg/L)	Fe^{2+} (mg/L)	Fe^{3+} (mg/L)	pH	Turb. (NTU)	Alkalinity (mg/l CaCO3)	T-iron (mg/L)	Fe^{2+} (mg/L)	Fe^{3+} (mg/L)	pH
0	50	87.83	1.3	0.6	0.7	7.23	43.9	79.33	1.2	0.58	0.62	7.48
20							13.7	70.83	0.7	0.23	0.47	6.98
40							4.48	62.33	0.5	0.1	0.4	6.64
60							0.79	48.17	0.4	0	0.4	6.37
80							0.24	36.83	0.3	0	0.3	6.04
100							0.18	25.50	0.4	0.05	0.35	5.76
120							18.3	8.50	21.8	0.25	21.55	4.69
140							49.7	8.50	43.6	0.75	42.85	3.57
160							52.1	2.83	46.6	1.25	45.35	3.22

Table A-5b Quality water of surface water at 150 NTU with before and after coagulation

$FeCl_3$ dosage (mg/L)	Raw water						Coagulated water					
	Turb. (NTU)	**Alkalinity (mg/l CaCO3)**	**T-iron (mg/L)**	**Fe^{2+} (mg/L)**	**Fe^{3+} (mg/L)**	**pH**	**Turb. (NTU)**	**Alkalinity (mg/l CaCO3)**	**T-iron (mg/L)**	**Fe^{2+} (mg/L)**	**Fe^{3+} (mg/L)**	**pH**
0	150	86.67	4.87	2.52	2.35	7.43	131	85.71	3.54	2.33	1.21	7.63
10							58.6	85.00	2.38	2.21	0.17	7.27
20							26	77.50	1.6	1.46	0.14	6.99
30							32.5	65.00	1.38	1.33	0.05	6.79
40							7.92	60.00	0.71	0.53	0.18	6.63
50							2.27	50.00	0.35	0.34	0.01	6.54
60							3.45	40.00	0.33	0.05	0.28	6.44
80							0.22	25.00	0.38	0.15	0.23	5.80
120							130	22.50	40.4	2.65	37.75	3.58
160							128	-	52.8	2.63	50.17	3.05
200							131	-	65.6	2.95	62.65	2.81
250							135	-	73.1	3.25	69.85	2.67

Table A-5c Quality water of surface water at 220 NTU with before and after coagulation

$FeCl_3$ dosage (mg/L)	Raw water						Coagulated water					
	Turb. (NTU)	Alkalinity (mg/l CaCO3)	T-iron (mg/L)	Fe^{2+} (mg/L)	Fe^{3+} (mg/L)	pH	Turb. (NTU)	Alkalinity (mg/l CaCO3)	T-iron (mg/L)	Fe^{2+} (mg/L)	Fe^{3+} (mg/L)	pH
0	220	80	7.7	2.98	4.72	7.5	201	37.31	6.7	2.78	3.92	7.75
20							56	0.00	2.25	0.83	1.42	6.95
40							1.74	0.00	0.4	0.18	0.22	6.39
60							1.5	0.00	0.95	0.15	0.8	5.85
80							184	0.00	28.2	2.7	25.5	4.4
100							221	0.00	40.4	3.3	37.1	3.42

Calculation of sodium hypochlorite solution cost

Based on the results obtained from topic 4.2, the appropriate ratio of groundwater to surface water was 35:65 and the optimal chlorine dosage was 30 mg as Cl_2 per one liter of groundwater. The calculation list of chemical cost as follows:

<u>Given data</u>

- Chlorine dosage of one liter of commercial 10%NaOCl = 100,000 $mgCl_2$
  (10% as free chlorine, Cl_2)
- Chlorine dosage required for one liter of a mixture = 10.5 $mgCl_2$
  (350 ml of groundwater : 650 ml of surface)
- A price of one liter of NaOCl = 8 Baht.

<u>Calculation</u>

- Chlorine dosage required for one litter of surface water = (1,000ml/650ml)(10.5$mgCl_2$)
  = 16.15 $mgCl_2$
- One litter of surface required NaOCl = 16.15 $mgCl_2$/(100,000 $mgCl_2$/L)
  = 0.00016 L
- One cubic meter of surface water required NaOCl = 0.16 L
- NaOCl cost for one cubic meter of surface water = 8 x 0.16 L
  = 1.28 Baht.

Calculation of commercial ferric chloride cost

According to the result as 4.3 before, in terms of using commercial ferric chloride coagulant in coagulation found that at 40 mg $FeCl_3$/L as ferric chloride in turbid surface water was the optimal dosage which achieved to remove turbidity. The calculation list of chemical cost as follows:

Given data

- $FeCl_3$ dosage of one liter of commercial 40% $FeCl_3$ (40% as $FeCl_3$) = 400,000 mg $FeCl_3$
- $FeCl_3$ dosage required for one liter of surface water = 40.0 mg $FeCl_3$
- A price of one liter of 40% $FeCl_3$ = 8 Baht.

Calculation

- One litter of surface required $FeCl_3$ = 40 mg $FeCl_3$/ (100,000 $FeCl_3$/L)

= 0.0001 L

- One cubic meter of surface water required $FeCl_3$ = 0.1 L
- $FeCl_3$ cost for one cubic meter of surface water = 30 x 0.1L

= 3.00 Baht.

Table A-6 Characteristics of DOM fractions in raw water

Table A-6a Raw water at ratio of groundwater to surface water of 35:65

Parameter	Raw water 35% of groundwater to surface water						
	Unfractionated water	Fractionated water		Sum of fraction	%Fraction		%Diff*
	Filtered raw water	Hydrophobic (HPO)	Hydrophilic (HPI)		Hydrophobic (HPO)	Hydrophilic (HPI)	
DOC (mg)	9.55	3.99	3.81	7.80	51.17	48.83	18.26
DOC (mg/L)	2.08	0.84	0.80	1.64	51.17	48.83	-
UV-254 (cm^{-1})	0.036	0.028	0.029	-	-	-	-
SUVA (L/mg-m)	1.720	3.381	3.580	-	-	-	-
THMs (µg/L)	2.98	-	-	-	-	-	-

Table A-6b Raw water at ratio of groundwater to surface water of 50:50

Parameter	Raw water 50% of groundwater to surface water						
	Unfractionated water	Fractionated water		Sum of fraction	%Fraction		%Diff*
	Filtered raw water	Hydrophobic (HPO)	Hydrophilic (HPI)		Hydrophobic (HPO)	Hydrophilic (HPI)	
DOC (mg)	8.57	3.52	3.40	6.92	50.84	49.16	19.17
DOC (mg/L)	1.86	0.77	0.74	1.51	50.84	49.16	-
UV-254 (cm^{-1})	0.035	0.028	0.026	-	-	-	-
SUVA (L/mg-m)	1.861	3.594	3.520	-	-	-	-
THMs (µg/L)	2.67	-	-	-	-	-	-

Table A-7 Characteristics of DOM fractions in coagulated water

Table A-7a Coagulated water at ratio of groundwater to surface water of 35:65

Parameter	Coagulated water 35% of groundwater to surface water						
	Unfractionated water	Fractionated water		Sum of fraction	%Fraction		%Diff*
	Filtered Coagulated water	Hydrophobic (HPO)	Hydrophilic (HPI)		Hydrophobic (HPO)	Hydrophilic (HPI)	
DOC (mg)	8.90	4.30	3.51	7.81	55.02	44.98	12.25
DOC (mg/L)	1.85	0.90	0.73	1.63	55.02	44.98	-
UV-254 (cm^{-1})	0.025	0.022	0.018	-	-	-	-
SUVA (L/mg-m)	1.373	2.474	2.392	-	-	-	-
THMs (µg/L)	51.17	-	-	-	-	-	-

Table A-7b Coagulated water at ratio of groundwater to surface water of 50:50

Parameter	Coagulated water 50% of groundwater to surface water						
	Unfractionated water	Fractionated water		Sum of fraction	%Fraction		%Diff*
	Filtered Coagulated water	Hydrophobic (HPO)	Hydrophilic (HPI)		Hydrophobic (HPO)	Hydrophilic (HPI)	
DOC (mg)	8.86	4.41	3.13	7.54	58.48	41.52	14.89
DOC (mg/L)	1.93	0.96	0.68	1.64	58.48	41.52	-
UV-254 (cm^{-1})	0.029	0.027	0.015	-	-	-	
SUVA (L/mg-m)	1.506	2.787	2.250	-	-	-	
THMs (µg/L)	51.47	-	-	-	-	-	

APPENDIX B

CALIBRATION DATA AND CURVES

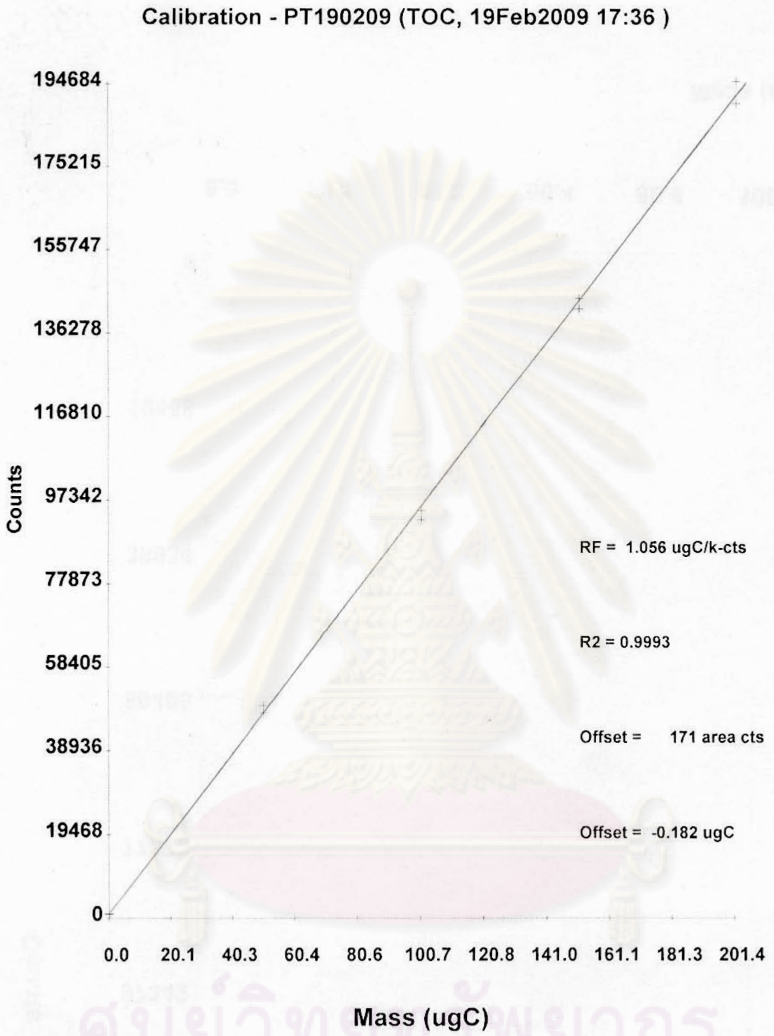
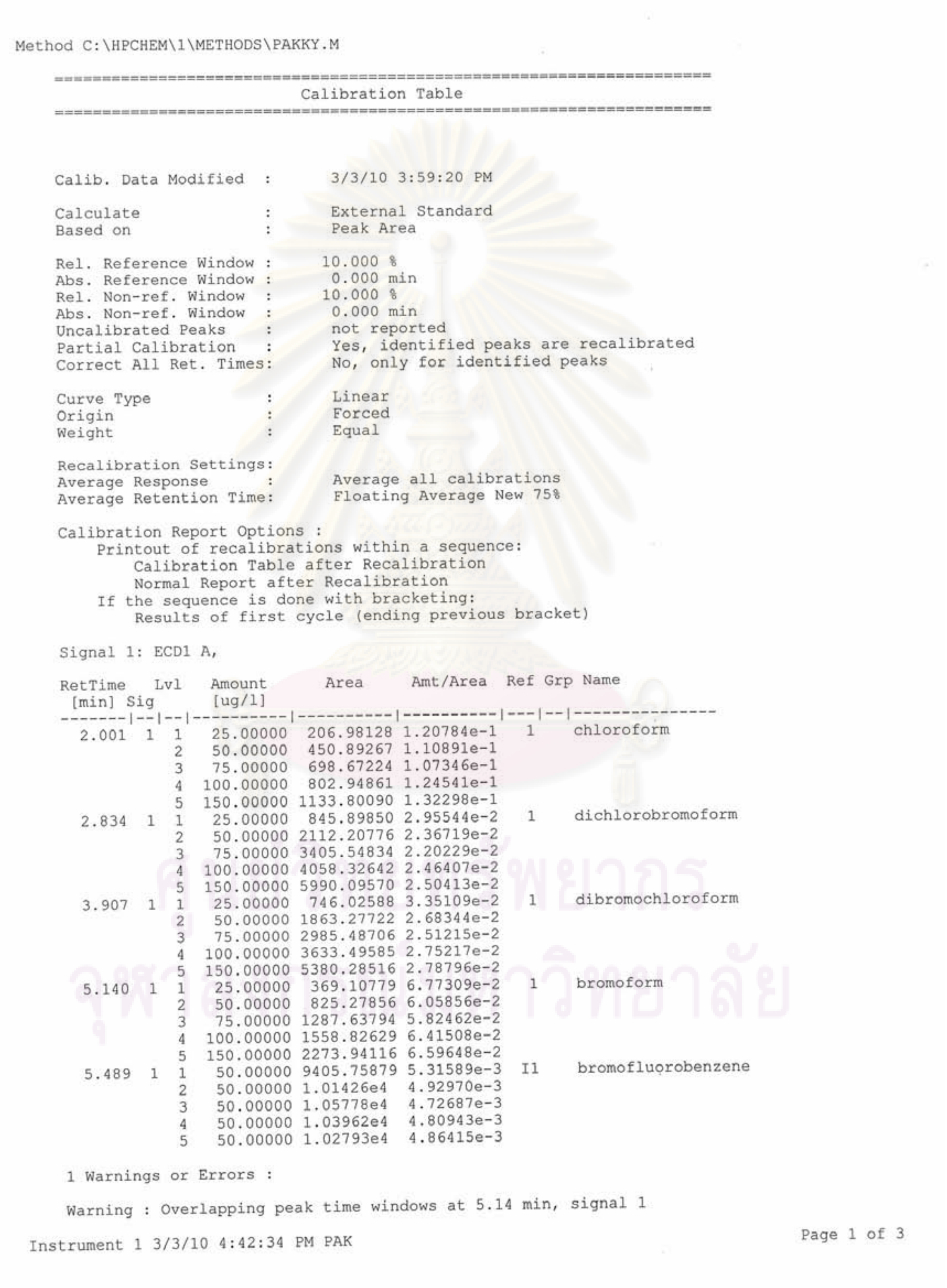
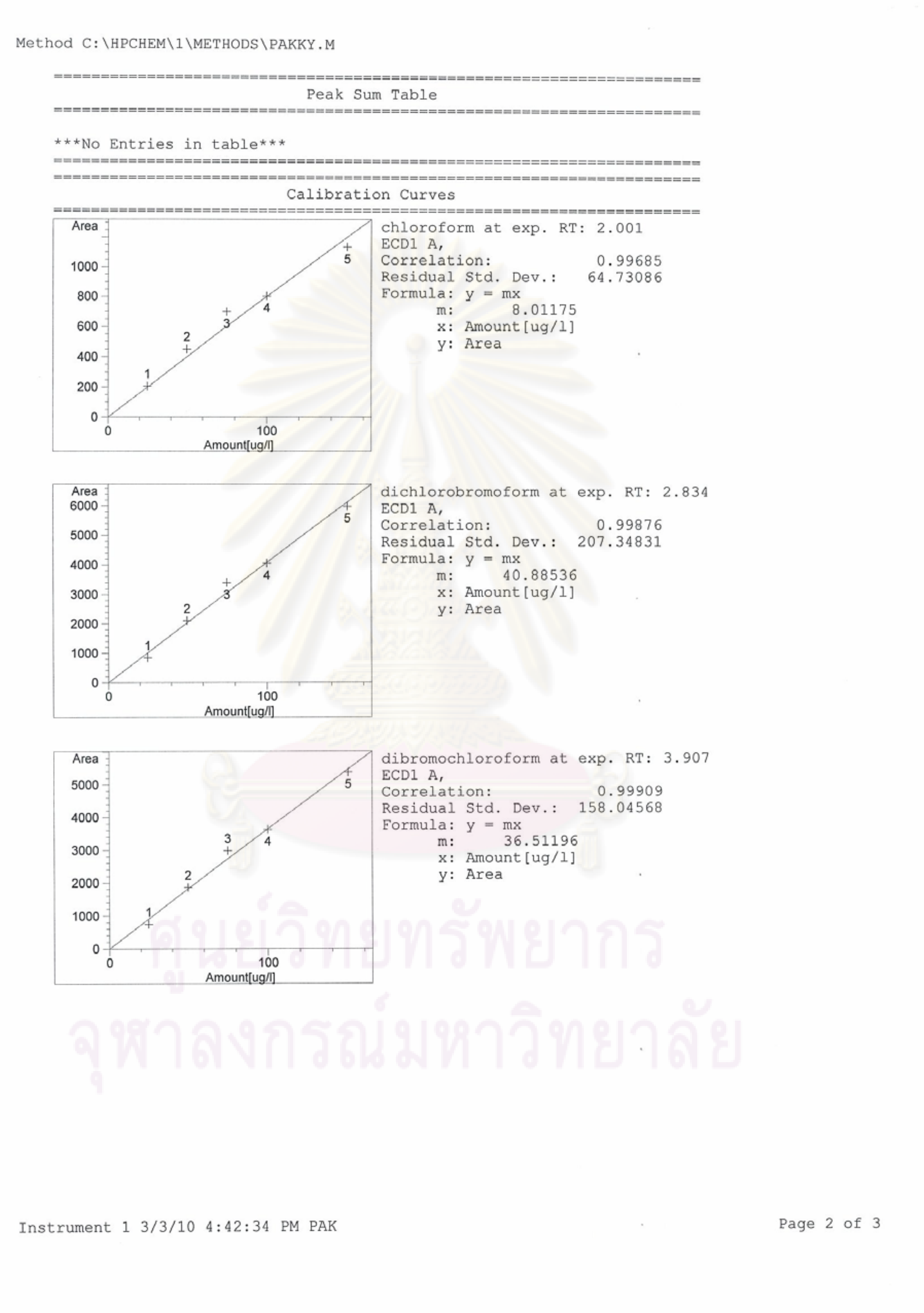


Figure B-1: Calibration curve of TOC

Table B-1: Calibration data of THMs



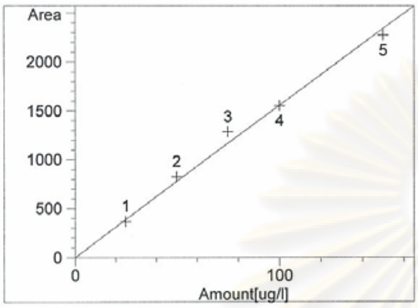
```
Method C:\HPCHEM\1\METHODS\PAKKY.M

    =====================================================================
                             Calibration Table
    =====================================================================



    Calib. Data Modified  :       3/3/10 3:59:20 PM

    Calculate             :       External Standard
    Based on              :       Peak Area

    Rel. Reference Window :      10.000 %
    Abs. Reference Window :       0.000 min
    Rel. Non-ref. Window  :      10.000 %
    Abs. Non-ref. Window  :       0.000 min
    Uncalibrated Peaks    :       not reported
    Partial Calibration   :       Yes, identified peaks are recalibrated
    Correct All Ret. Times:       No, only for identified peaks

    Curve Type            :       Linear
    Origin                :       Forced
    Weight                :       Equal

    Recalibration Settings:
    Average Response      :       Average all calibrations
    Average Retention Time:       Floating Average New 75%

    Calibration Report Options :
        Printout of recalibrations within a sequence:
            Calibration Table after Recalibration
            Normal Report after Recalibration
        If the sequence is done with bracketing:
            Results of first cycle (ending previous bracket)

    Signal 1: ECD1 A,

    RetTime   Lvl   Amount      Area     Amt/Area  Ref Grp Name
     [min] Sig      [ug/l]
    -------|--|--|----------|----------|----------|---|--|---------------
      2.001  1  1   25.00000  206.98128 1.20784e-1  1     chloroform
                2   50.00000  450.89267 1.10891e-1
                3   75.00000  698.67224 1.07346e-1
                4  100.00000  802.94861 1.24541e-1
                5  150.00000 1133.80090 1.32298e-1
      2.834  1  1   25.00000  845.89850 2.95544e-2  1     dichlorobromoform
                2   50.00000 2112.20776 2.36719e-2
                3   75.00000 3405.54834 2.20229e-2
                4  100.00000 4058.32642 2.46407e-2
                5  150.00000 5990.09570 2.50413e-2
      3.907  1  1   25.00000  746.02588 3.35109e-2  1     dibromochloroform
                2   50.00000 1863.27722 2.68344e-2
                3   75.00000 2985.48706 2.51215e-2
                4  100.00000 3633.49585 2.75217e-2
                5  150.00000 5380.28516 2.78796e-2
      5.140  1  1   25.00000  369.10779 6.77309e-2  1     bromoform
                2   50.00000  825.27856 6.05856e-2
                3   75.00000 1287.63794 5.82462e-2
                4  100.00000 1558.82629 6.41508e-2
                5  150.00000 2273.94116 6.59648e-2
      5.489  1  1   50.00000 9405.75879 5.31589e-3  I1    bromofluorobenzene
                2   50.00000 1.01426e4  4.92970e-3
                3   50.00000 1.05778e4  4.72687e-3
                4   50.00000 1.03962e4  4.80943e-3
                5   50.00000 1.02793e4  4.86415e-3

     1 Warnings or Errors :

     Warning : Overlapping peak time windows at 5.14 min, signal 1
```



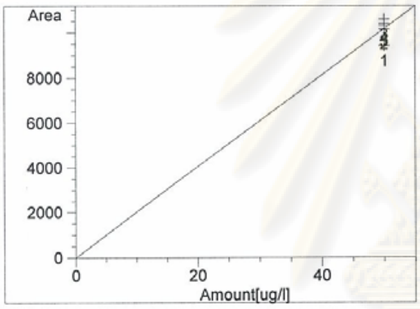
```
Method C:\HPCHEM\1\METHODS\PAKKY.M

     =====================================================================
                              Peak Sum Table
     =====================================================================

     ***No Entries in table***
     =====================================================================
     =====================================================================
                           Calibration Curves
     =====================================================================
                                 chloroform at exp. RT: 2.001
                                 ECD1 A,
                                 Correlation:             0.99685
                                 Residual Std. Dev.:    64.73086
                                 Formula: y = mx
                                       m:       8.01175
                                       x: Amount[ug/l]
                                       y: Area

                                 dichlorobromoform at exp. RT: 2.834
                                 ECD1 A,
                                 Correlation:             0.99876
                                 Residual Std. Dev.:   207.34831
                                 Formula: y = mx
                                       m:      40.88536
                                       x: Amount[ug/l]
                                       y: Area

                                 dibromochloroform at exp. RT: 3.907
                                 ECD1 A,
                                 Correlation:             0.99909
                                 Residual Std. Dev.:   158.04568
                                 Formula: y = mx
                                       m:      36.51196
                                       x: Amount[ug/l]
                                       y: Area

Instrument 1 3/3/10 4:42:34 PM PAK                                    Page 2 of 3
```

Figure B-2: Calibration data of THMs

```
Method C:\HPCHEM\1\METHODS\PAKKY.M
```



```
bromoform at exp. RT: 5.140
ECD1 A,
Correlation:             0.99897
Residual Std. Dev.:    71.90869
Formula: y = mx
      m:      15.61305
      x: Amount[ug/l]
      y: Area
```



```
bromofluorobenzene at exp. RT: 5.489
ECD1 A,
Correlation:             0.99921
Residual Std. Dev.:   451.05391
Formula: y = mx
      m:     203.20686
      x: Amount[ug/l]
      y: Area
```

```
=====================================================================
```

Figure B-2 cont.**:** Calibration data of THMs

BIOGRAPHY

Name	Pakawadee Sangchan
Date of Birth	January 31, 1986
Place of Birth	Bangkok, Thailand
Academic Background	Wattanothaipayap School, Chiang Mai, Thailand Certificate of Mathayomsuksa 6 Faculty of Engineering, Chiang Mai University, Chiang Mai Bachelor of Engineering (B. Eng.) in Environmental Engineering
Presentation:	Sangchan P., Wattanachira L., and Wattanachira S. “Coagulation of turbid surface water using ferric chloride produced from natural iron in groundwater reacted with chlorine”. Proceeding of International Conference on Green and Sustainable Innovation 2009, Chiang Rai, Thailand, December 2 – 4, 2009.