



**Characteristics of Dissolved Organic Matter in Wastewater and Treated  
Wastewater from Para Rubber Industry**

**Nutthaporn Wanlaso**

**A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of  
Master of Science in Environmental Management**

**Prince of Songkla University**

**2012**

**Copyright of Prince of Songkla University**



**Characteristics of Dissolved Organic Matter in Wastewater and Treated  
Wastewater from Para Rubber Industry**

**Nutthaporn Wanlaso**

**A Thesis Submitted in Partial Fulfillment of the Requirements for the Degree of  
Master of Science in Environmental Management  
Prince of Songkla University**

**2012**

**Copyright of Prince of Songkla University**

**Thesis Title**                      Characteristics of Dissolved Organic Matter in Wastewater and Treated Wastewater from Para Rubber Industry

**Author**                                Ms.Nutthaporn Wanlaso

**Major Program**                    Environmental Management

---

**Major Advisor :**

.....  
(Asst. Prof. Dr. Charongpun Musikavong)

**Examining Committee:**

..... Chairperson  
(Dr. Oramas Suttinun)

**Co-advisors:**

.....  
(Asst. Prof. Dr. Thunwadee Suksaroj)

.....  
(Assoc. Prof. Dr. Suraphong Wattanachira)

.....  
(Asst. Prof. Dr. Chaisri Suksaroj)

.....  
(Assoc. Prof. Dr. Wilawan Mahabusarakam)

.....  
(Asst. Prof. Dr. Charongpun Musikavong)

.....  
(Asst. Prof. Dr. Thunwadee Suksaroj)

The Graduate School, Prince of Songkla University, has approved this thesis as partial fulfillment of the requirements for the Master of Science Degree in Environmental Management

.....  
(Prof. Dr. Amornrat Phongdara)

Dean of Graduate School

ชื่อวิทยานิพนธ์	ลักษณะสารอินทรีย์ละลายน้ำในน้ำเสียและน้ำทิ้งโรงงานอุตสาหกรรม ยางพารา
ผู้เขียน	นางสาวณัฐพร หวันท่าโธ๊ะ
สาขาวิชา	การจัดการสิ่งแวดล้อม
ปีการศึกษา	2555

### บทคัดย่อ

งานวิจัยนี้ได้ทำการเก็บน้ำเสียและน้ำทิ้งที่ผ่านการบำบัดของกระบวนการผลิตถุงมือยาง 3 โรงงานเพื่อวิเคราะห์การลดลงของค่า biological oxygen demand (BOD), chemical oxygen demand (COD), dissolved organic carbon (DOC), ultraviolet absorption at wavelength 254 nm (UV-254) และ trihalomethanes formation potential (THMFP) ตลอดจนศึกษาค่าศักยภาพการก่อตัวของ THMFP และลักษณะดัชนีตัวแทน THMFP ในน้ำเสียและน้ำทิ้งที่ผ่านการบำบัด บ่อแอนแอโรบิกและบ่อเติมอากาศของโรงงาน A ระบบ dissolved air flotation (DAF) และบ่อเติมอากาศของโรงงาน B และบ่อเติมอากาศของโรงงาน C ลดค่า BOD และ COD ได้ต่ำกว่ามาตรฐานน้ำทิ้งอุตสาหกรรม บ่อแอนแอโรบิกเป็นกระบวนการหลักที่ลดค่า DOC และ UV-254 ของโรงงาน A ระบบ DAF ของโรงงาน B เป็นกระบวนการหลักที่ลดค่า DOC และ UV-254 ค่า THMFP ของน้ำทิ้งที่ผ่านการบำบัดจากโรงงาน A B และ C มีค่าเท่ากับ 53 635 และ 207  $\mu\text{g/L}$  ตามลำดับ คลอโรฟอร์มเป็นองค์ประกอบหลักของ THMFP ที่เกิดจากน้ำเสียของทั้ง 3 โรงงาน ส่วนไดคลอโรโบรโมมีเทนเป็นองค์ประกอบหลักของ THMFP ที่เกิดจากน้ำทิ้งที่ผ่านการบำบัดจากโรงงาน A ในขณะที่คลอโรฟอร์มเป็นองค์ประกอบหลักของ THMFP ของน้ำทิ้งที่ผ่านการบำบัดจากโรงงาน B และโรงงาน C น้ำเสียที่เข้าสู่กระบวนการบำบัดและน้ำทิ้งที่ผ่านการบำบัดจากโรงงาน B และโรงงาน C มีศักยภาพสูงในการก่อให้เกิด THMFP ค่าดังกล่าวของน้ำเสียและน้ำทิ้งจากโรงงาน A มีค่าต่ำ สารกลุ่มทริปโตรฟานเป็นตัวแทนหลักของการเกิด THMFP ที่ถูกตรวจพบในน้ำเสียโรงงานผลิตถุงมือยาง บ่อแอนแอโรบิกและบ่อเติมอากาศของโรงงาน A ลดสารกลุ่มทริปโตรฟานได้ดีกว่า DOC และ UV-254 บ่อเติมอากาศที่ต่อจาก DAF ในโรงงาน B ลดสารกลุ่มทริปโตรฟานได้เพียงเล็กน้อย หมู่ฟังก์ชัน C=O ของหมู่เอไมด์ เกลือคาร์บอกซิลิกและ N-H สัญญาณการยึดของหมู่เอไมด์ (amide group-2) ตรวจพบในน้ำเสียและน้ำทิ้งที่ผ่านการบำบัดที่มีค่า THMFP/DOC สูง

**Thesis Title**            Characteristics of Dissolved Organic Matter in Wastewater and Treated  
Wastewater from Para Rubber Industry

**Author**                 Ms. Nutthaporn Wanlaso

**Major Program**        Environmental Management

**Academic Year**        2012

### ABSTRACT

The wastewater and treated wastewater from the three rubber glove manufacturing processes were collected for determining the reduction of biological oxygen demand (BOD), chemical oxygen demand (COD), dissolved organic carbon (DOC), ultraviolet absorption at wavelength 254 nm (UV-254), and trihalomethanes formation potential (THMFP). The ability of dissolved organic matter for creating THMFP and the nature of THMFP precursors in wastewater and treated wastewater were investigated. Anaerobic and aeration ponds of Plant A, dissolved air flotation (DAF) and aeration ponds of Plant B, and aeration ponds of Plant C can reduce BOD and COD of wastewater to be lower than industrial effluent standard. The anaerobic pond in Plant A was the main course of action that reduced DOC and UV-254. DAF in Plant B was the major process that reduced DOC and UV-254. The THMFP of treated wastewater from Plant A, B and C were 53, 637 and 207 µg/L, respectively. Chloroform was the major THMFP species in the wastewater from three plants. In treated wastewater from Plant A, the dichlorobromomethane was the major THMFP species, whereas the major THMFP species in the treated wastewater from Plant B and C was chloroform. Wastewater and treated wastewater from Plant B and C had a high reactivity to form THMFP whereas those of Plant A had a low reactivity. The tryptophan-like substance was the major THMFP precursors in the wastewater and treated wastewater of the rubber glove manufacturing process. The series of anaerobic and aeration ponds in Plant A can reduce tryptophan-like substances better than DOC and UV-254, whereas, aeration ponds after DAF in Plant B slightly reduced tryptophan-like substances. The C=O stretching of amide group, salts of carboxylic acids, N-H bending vibration of amide group were detected in the wastewater and treated wastewater which had the high THMFP/DOC value.

## ACKNOWLEDGEMENTS

This thesis could not have been finished without the help of my Professors, the staffs, my friends and my beloved parents. I would like to “thank you all for my success in this step”.

I would like to express my sincere gratitude to my thesis advisor, Assistant Professor Dr. Charongpun Musikavong, for his kindness, valuable suggestions, guidance and strong encouragement during the thesis work. Special respect and thanks are also extended to Assistant Professor Dr. Chaisri Suksaroj and Assistant Professor Dr. Thunwadee Suksaroj for their valuable suggestions and guidance as co-advisor. I am also thankful to Assoc. Prof. Dr. Suraphong Wattanachira, Assoc. Prof. Dr. Wilawan Mahabusarakam and Dr. Oramas Suttinun for their many helpful comments.

I would like to sincerely thank all of the students and staffs at the National Research Center for Environmental and Hazardous Waste Management (NRC-EHWM), Chiang Mai University for the use of their laboratory facilities and providing me with valuable information. Furthermore, I would like to express my sincere thanks to three rubber gloves manufacturing plants in Thailand for the permission to collect water samples and to the staffs for their kindly helps and supports during all sampling times.

Special thanks also go to all of the staff members of the Faculty of Environmental Management, Prince of Songkla University, Songkhal Province, Thailand for the supporting of the laboratory facilities and providing me with valuable information. I also wish to thank all friends at Faculty of Environmental Management and the Department of Environmental Engineering, Prince of Songkla University for their warm support and helps over the entire period of this research.

Finally I feel proud to dedicate this thesis with due respect to my beloved family for their wholehearted understanding, encouragement, and patient support throughout my entire study.

Nutthaporn Wanlaso

## CONTENTS

	<b>PAGE</b>
ABSTRACT (THAI)	iii
ABSTRACT (ENGLISH)	iv
ACKNOWLEDGEMENTS	v
CONTENT	vi
LISTS OF TABLES	ix
LISTS OF TABLES IN APPENDIX	xi
LISTS OF FIGURES	xii
LISTS OF FIGURES IN APPENDIX	xiv
ABBREVIATIONS AND SYMBOLS	xv
<b>CHAPTER I : INTRODUCTION</b>	<b>1</b>
1.1 Motivation	1
1.2 Objectives	3
1.3 Scopes of study	3
1.4 Benefit of this study	3
<b>CHAPTER II : BACKGROUND AND LITERATURE REVIEWS</b>	<b>5</b>
2.1 Dissolved Organic Matter	5
2.2 DOM Surrogate Paramters	6
2.2.1 UV absorbance at wavelength 254 nm. (UV-254)	7
2.2.2 Specific Ultraviolet Absorbance (SUVA)	7
2.2.3 Dissolved Organic Carbon (DOC)	8
2.3 Characterization of Dissolved Organic Matter (DOM)	9
2.3.1 Fluorescent Excitation-Emission Matrix (FEEM)	9
2.3.2 Fourier Transform Infrared (FTIR)	12
2.4 Disinfection by-Products	14
2.4.1 Trihalomethanes (THMs)	15

## CONTENTS (CONT.)

	<b>PAGE</b>
<b>CHAPTER III : METHODOLOGY</b>	<b>27</b>
3.1 Studied Site	27
3.1.1 The Selected Rubber Gloves Manufacturing Plants	27
3.1.2 The Natural Waterway	27
3.2 Sample Collection and Preservation	29
3.3 Experiment Procedure	29
3.4 Instruments and Analytical Methods	31
3.4.1 Instruments	31
3.4.2 Analytical Methods	33
<b>CHAPTER IV : DISSOLVED ORGANIC MATTER AND</b>	<b>39</b>
<b>TRIHALOMETHANNE FOR MATION POTENTIAL IN</b>	
<b>WASTEWATER OF RUBBER GLOVES MANUFACTURING</b>	
<b>PLANTS</b>	
4.1 Introduction and Objective	39
4.2 Material and Methods	40
4.2.1 Sample Collection and Experiment Procedure	40
4.3 Results and Discussions	40
4.3.1 Characteristics of Influent Wastewater	40
4.3.2 The Reduction of BOD and COD	42
4.3.3 The Reduction of DOC and UV-254	48
4.3.4 The Reduction of THMFP	56
4.4 Concluding Remarks	67



## CONTENTS (CONT.)

	<b>PAGE</b>
<b>CHAPTER V : CHARACTERIZATION OF TRIHALOMETHANE</b>	69
<b>PRECUSORS IN RUBBER GLOVE MANUFACRUTING</b>	
<b>PROCESSES BY FLUORESCENT EXCITAION-EMISION</b>	
<b>MATRIX AND FOURIER TRANSFORM INFRARED</b>	
<b>ANALYSIS</b>	
5.1 Introduction and Objective	69
5.2 Material and Methods	70
5.2.1 Sample Collection and Experiment Procedure	70
5.3 Results and Discussions	71
5.3.1 Reactivity of THMFP	71
5.3.2 Characterization of THMFP Precursors using FEEM	74
5.3.3 Characterization of THMFP Precursors using FTIR	82
5.4 Concluding Remarks	91
<b>REFERENCES</b>	93
<b>APPENDIX</b>	99
APPENDIX A: CALIBRATION DATA AND CURVES	101
APPENDIX B : EXPERIMENTAL DATA	104
<b>VITAE</b>	110

## LISTS OF TABLES

<b>TABLES</b>	<b>PAGE</b>
2.1 Basic chemical and physical characteristics of chloroform	17
2.2 Human uptakes of chloroform and trihalomethanes from drinking water, food and air.	20
2.3 The ratio of chemicals used for preparing the latex mixture	24
3.1 Analytical methods and instruments	33
3.2 Method condition of GC(HP6890) for analysis of THMFP	35
4.1 Basic water qualities of influent wastewater from three plants	40
4.2 Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant A on BOD and COD	44
4.3 Reduction efficiency and accumulated reduction efficiency of wastewater treatment system form Plant B on BOD and COD	46
4.4 Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant C on BOD and COD	48
4.5 Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant A on DOC, UV-254 and SUVA	51
4.6 Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant B on DOC, UV-254 and SUVA	52
4.7 Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant C on DOC, UV-254 and SUVA	56
4.8 Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant A on THMFP	59
4.9 Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant B on THMFP	62
4.10 Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant C on THMFP	65

4.11	THMFP in the treated effluent of this study compared with the values from raw water supply sources in southern of Thailand	65
4.12	Correlation coefficient between THMFP and DOC, and THMFP and UV-254	67
5.1	General assignment of FTIR spectra of tryptophan, humic acid and Suwannee River NOM	84
5.2	Functional group of DOM in the influent wastewater and treated wastewater of rubber glove manufacturing Plant A	85
5.3	Functional group of DOM in the influent wastewater and treated wastewater of rubber glove manufacturing Plant B	87
5.4	Functional group of DOM in the influent wastewater and treated wastewater of rubber glove manufacturing Plant C	89

## LISTS OF TABLES IN APPENDIX

<b>TABLES</b>	<b>PAGE</b>
A.1 Calibration data of UV-254 nm	100
A.2 Calibration curve of DOC	100
B.1 DOC of Plant A	103
B.2 BOD of Plant A	103
B.3 UV-254 of Plant A	103
B.4 COD of Plant A	103
B.5 THMFP of Plant A	104
B.6 DOC of Plant B	104
B.7 BOD of Plant B	105
B.8 UV-254 of Plant B	105
B.9 COD of Plant B	105
B.10 THMFP of Plant B	106
B.11 DOC of Plant C	106
B.12 BOD of Plant C	106
B.13 UV-254 of Plant C	107
B.14 COD of Plant C	107
B.15 THMFP of Plant C	107

## LISTS OF FIGURES

FIGURES	PAGE
2.1 Structure of tyrosine and tryptophan	12
2.2 Definition used in the formation potential test of a sample without free chlorine at the time of sampling	22
2.3 Definition used in the formation potential test of a sample with free chlorine at the time of sampling	22
2.4 The processing flow molded rubber (Dipping Process)	25
3.1 Schematic diagram of wastewater treatment system for plant A	28
3.2 Schematic diagram of wastewater treatment system for plant B	28
3.3 Schematic diagram of wastewater treatment system for plant C	29
3.4 Schematic diagram of experimental procedure	30
3.5 Instruments used during the experiment	31
3.6 Sample of the Fluorescent Excitation-Emission Matrix (FEEM)	38
4.1 BOD and COD of influent and effluent water of each wastewater treatment systems of plant A	43
4.2 BOD and COD of the water sample in the wastewater treatment plant of Plant B	45
4.3 BOD and COD of the water sample in the wastewater treatment plant of Plant C	47
4.4 DOC and UV-254 of the water sample in the wastewater treatment plant of Plant A	49
4.5 DOC and UV-254 of the water sample in the wastewater treatment plant of Plant B	53
4.6 DOC and UV-254 of the water sample in the wastewater treatment plant of Plant C	55
4.7 THMFP and THMFP species of the water sample from the wastewater treatment plant of Plant A	58

## LISTS OF FIGURES (CONT.)

FIGURES	PAGE
4.8 THMFP and THMFP species of the water sample from the wastewater treatment plant of Plant B	50
4.9 THMFP and THMFP species of the water sample in the wastewater treatment plant of Plant C	64
5.1 THMFP/DOC of wastewater and treated wastewater from the rubber glove manufacturing process Plant A	72
5.2 THMFP/DOC of wastewater and treated wastewater from the rubber glove manufacturing process Plant B	72
5.3 THMFP/DOC of wastewater and treated wastewater from the rubber glove manufacturing process Plant C	73
5.4 Sample of FEEM of influent wastewater from Plant A	75
5.5 Fluorescent intensity of influent wastewater and effluent water from Plant A	76
5.6 Sample of FEEM of influent wastewater from Plant B	77
5.7 Fluorescent intensity of influent wastewater and effluent water from Plant B	78
5.8 Sample of FEEM of wastewater from Plant C	80
5.9 Fluorescent intensity of influent wastewater and effluent water from Plant C	81

## LISTS OF FIGURES IN APPENDIX

<b>FIGURES</b>	<b>PAGE</b>
A.1 HP 6890 GC method	101

# CHAPTER I

## INTRODUCTION

### 1.1 Motivations

In southern part of Thailand, the rubber glove industry is one of the major industries in this region. A rubber glove manufacturing process consumes large amount of water, especially in washing process. Therefore, wastewater treatment plant operated hardly capable of treating this wastewater. For the wastewater treatment practice, it mainly focuses on the reduction of organic matter in terms of biochemical oxygen demand (BOD) and chemical oxygen demand (COD). This has been done because, BOD and COD are regulated in industrial effluent standard and have simple analysis procedure. Regard to the development of the dissolved organic matter (DOM) analysis, it was found that the organic matter in water or treated wastewater, even presented in small level, could potentially react with chlorine during the disinfection process to form carcinogenic disinfection by-products (DBPs), e.g. trihalomethanes (THMs), haloacetic acids (HAAs), and haloacetonitriles (HANs) (Rook, 1974; Krasner, 1989 and Marhaba and Washington, 1998). The treated wastewater from domestic and industry activities can be discharged to natural water sources. Unfortunately, if these water sources are used as indirect raw water supply the discharge DOM can react with chlorine to form DBPs.

Trihalomethanes (THMs) are primarily formed in raw or treated water through the reaction of chlorine or bromine with humic acids associated with decaying vegetation. Surveys have illustrated that THMs are ubiquitous in chlorinated drinking water supplies (Hubel and Edzwald, 1987). They are all considered to be possible carcinogens and therefore, human exposure to such compounds should be minimized (Norin and Renberg, 1980). The most well known health hazard is that THMs cause not only a depression of the central nervous system but also hepatotoxicity, nephrotoxicity, teratogenicity, and carcinogenicity. An important factor that significantly affects the formation of carcinogenic DBPs is the structure of the DOM. The DOM compositions present in treated wastewater vary according to the industry and the performance of a plant's treatment system (Charongpun Musikavong and Suraphong Wattanachira, 2007).



Therefore it is of imperative importance that the through investigation of the formation of DBPs should be conducted for each type of industrial wastewater.

DOM in wastewater consists of various compounds from simple structure to very complex polymers (Henze, 1992). Several parameters have been used to analyze these various complex compositions of DOM quantitatively and qualitatively. BOD, COD, dissolved organic carbon (DOC), ultraviolet absorbance at wavelength of 254 nm (UV-254) (USEPA, 1999) have typically been employed for quantitative analysis particularly to indicate wastewater quality. However, these parameters do not provide information on the composition of the DOM. Moreover complicated techniques have been utilized to qualify DOM in terms of their physical and chemical natures such as fourier transform infrared (FTIR) spectroscopy and Three-dimensional fluorescent spectroscopy technique, fluorescent excitation-emission matrix (FEEM). FEEM, is one potential method that provides information on DOM composition in water. The FEEM provides information on the putative origin of fluorescent organic matters in water as two distinct classes of fluorophores which are generally discussed, the humic-like fluorophores and the protein-like fluorophores (Chen *et al.*, 2003; Leenheer and Croue, 2003 and Sierra *et al.*, 2005). The application of FEEM is becoming increasingly widespread for river or fresh water (Coble, 1996; Croue *et al.*, 2000 and Nakajima *et al.*, 2002) and marine water (Coble *et al.*, 1990, Coble 1996) as this method does not only characterize the nature and source of DOM in water but also fingerprints organic pollutants in water according to its simplicity and its minimal sample amount and pretreatment (Nakajima *et al.*, 2002). Recently, the FEEM technique has also been successfully utilized to characterize and monitor DOM in wastewater, treated wastewater and leachate (Baker 2001, 2002; Baker and Curry 2004; Musikavong *et al.*, 2006 and Saadi *et al.*, 2006).

On this basis, it is important to understand the level and nature of DOM as well as its reactivity to form DBPs. The level and nature of DOM in treated wastewater are depend on wastewater characteristic and the performance of wastewater treatment plant. Therefore, it is inevitability to study the wastewater characteristic and capability of wastewater treatment plant for reducing DOM and DBPs. As mentioned previously, the rubber glove industry is the major

industry in the southern part of Thailand and it consumes large amount of water. Therefore, it was selected to be the studied site in this work.

The approaches here in were to characterize DOM in influent and effluent water from different processes of wastewater treatment of the rubber glove manufacturing process. FEEM was utilized to fingerprint DOM in influent and effluent water from each treatment step. Furthermore, FTIR analysis was used for identifying functional groups of DOM. This was done to identify and confirm the fluorescent organic compounds. The reduction of DOM during the treatment course was also appraised.

## **1.2 Objectives**

- 1.2.1 To characterize DOM in influent wastewater and effluent water from wastewater treatment systems of the rubber glove manufacturing plants.
- 1.2.2 To measure THMFP in influent wastewater and effluent water from treatment systems of the rubber glove manufacturing plants.
- 1.2.3 To evaluate the performance of wastewater treatment systems of the rubber glove manufacturing plant in reducing DOM and THMFP.

## **1.3 Scope of Study**

- 1.3.1 Influent wastewater and effluent water from each treatment step of the wastewater treatment system of three rubber glove manufacturing plants were considered as water sample.
- 1.3.2 All water samples were analyzed through DOM surrogate parameters including DOC, UV254, and THMFP.
- 1.3.3 FEEM was utilized to characterize the fluorescent organic matter of DOM.
- 1.3.4 FTIR analysis was employed to identify functional groups of DOM.

#### **1.4 Benefit of this study**

To know the characteristic of DOM in the wastewater and treated wastewater of rubber glove manufacturing plants and to use results obtained as a guideline for prevention and mitigation the formation of THMs.

## CHAPTER II

### BACKGROUND AND LITERATURE REVIEW

#### 2.1 Dissolved Organic Matter

Dissolved organic matter (DOM) is defined as a mixture of amide, carboxyl, hydroxyl, ketone, and various minor functional groups (Leenheer and Croue., 2003). DOM is typically dominated by humic substances generated by biological activity both in a watershed surrounding a water source (allochthonous DOM) and within the water source itself (autochthonous DOM) (Croue *et al.*, 2000). Humic substances include humic and fulvic acids, while non-humic substances include hydrophilic acids, proteins, carbohydrates, carboxylic acids, amino acids, and hydrocarbons. Humic and non-humic substances are the major component of DOM in water (Thurman, 1985; and Amy, 1994).

Organic matter in surface water is mainly comprised of humic substances 50-65% (Collin *et al.*, 1986; Leenheer and Croue, 2003) and non-humic substances. Humic or hydrophobic substances that precipitated at pH 1, was defined by Thurman and Malcolm in 1981 as polar, straw-colored, organic acids derived from soil humus and terrestrial/aquatic plants, which contributed from about 50% to more than 90% of organics in natural waters. Humic substances can be further categorized into humic acids, fulvic acids, and humic.

- Humic acids are not soluble in water with pH less than two. They can be extracted from soil by various reagents. They are dark brown to black in color. Humic acids are composed of complex aromatic macromolecules, such as amino sugars (Coelho *et al.*, 1997).
- Fulvic acids, light yellow to yellow-brown in color, are the fraction of humic substances that is soluble under all pH range. Fulvic acids are the remaining part in the solution after the removal of humic acids by acidification. They contain mostly acidic functional groups such as COOH (Leenheer *et al.*, 1995; and Chen *et al.*, 2002).
- Humic, black color, is a non-soluble part in any condition in the fraction of humic substances (Shih and Wu, 2002).

Non-humic substances mainly contain carboxylic acids, carbohydrates, amino acids, amino sugars, proteins, and nutrients (Marhaba and Van, 1999). Moreover, non humic substance (hydrophilic fractions) were also discovered to have higher COOH, phenolic-OH, and organic –N content compared to humic substance (the hydrophobic fractions). The presence of phenolic-OH could lead to trihalomethanes (THMs), the most well-known disinfection by-products (DBPs), due to the existence of an electron-donating substitute, i.e. -OH group. The –OH activates the ring that favors reaction with chlorine resulting in the formation of THMs and other chlorinated by-products (Rockwell and Larson, 1978). Also, hydrophilic organics can be separated into three fractions, hydrophilic acid, -base, and -neutral.

Wastewater and treated wastewater are the major allochthonous DOM in natural water sources. Sirivedkhin and Gray (2005) presented that effluent-derived organic matter (EfOM) was found to be dominated by more aliphatic compounds and had higher organic nitrogen and halogen content when compared with organic material derived from natural sources. Conclusive results from past research show that EfOM contained substantially higher nitrogen (Peschel and Wildt, 1988; and Debroux, 1998), halogens (Gray *et al.*, 1996), and sulfurs (Poerschmann *et al.*, 1998) when compared with natural organic matter (NOM). Nevertheless, the determination of aromaticity of EfOM was inconclusive since some researchers found EfOM to be aromatic-dominated (Dignac *et al.*, 2000), whereas others found it to be aliphatic-dominated (Peschel and Wildt, 1988; Gray 1966; and Debroux, 1998).

## 2.2 DOM Surrogate Parameters

DOMs are analyzed by combining nonspecific or surrogate parameters because no single analytical technique is capable of measuring the wide characteristics of DOMs. DOM surrogates include ultraviolet absorbance at wavelength of 254 nm (UV-254), specific ultraviolet absorbance (SUVA) and dissolved organic carbon (DOC).

### 2.2.1 UV absorbance at wavelength 254 nm (UV-254)

UV-254 is used to indicate 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 UV 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 NOM or precursor of THMs because humic substrates strongly absorb UV radiation (Eaton, 1995).

### 2.2.2 Specific Ultraviolet Absorbance (SUVA)

The ratio of UV absorbance to DOC, referred as specific absorbance (SUVA) ( $\text{cm}^{-1} \text{mg}^{-1} \text{L}$ ) 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 THM formation (Krasner *et al.*, 1996). Higher specific absorbance values tend to indicate higher humic content. Specific absorbance of a humic sample depends on the molecular weight of the substances (Pettersen *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 ( $\text{SUVA} > 3 \text{ L/mg-m}$ ) 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 ( $< 3 \text{ L/mg-m}$ ) indicate the presence of organic matter of lower AMW that is more fulvic-like in character and more difficult to remove.

SUVA applications to wastewater, Fukushima *et al.*, (1996) reported that the SUVA of total DOM increased as the lake water, influenced by pedogenic DOC, was allowed to further stabilize through biodegradation over a long period of time. Imai *et al.* (2002) reported

that since a biological treatment was employed in sewage treatment plants, it should produce effluent water with higher SUVA values than that of influent wastewater.

### **2.2.3 Dissolved Organic Carbon (DOC)**

Dissolve organic carbons are defined as the fraction of TOC that passes through a 0.45- $\mu\text{m}$ -pore-diam filter. (Standard method, 1995).

Organic carbon in natural water can be composed in two fraction, particulate organic carbon (POC) and dissolve organic carbon (DOC), Normally DOC is operationally defined as passing a 0.22  $\mu\text{m}$ . (J.K. Edzwarld, 1993). Since some types of 0.22  $\mu\text{m}$  filter paper are produced by the cellulose nitrite or cellulose acetate membrane, organic substances could be leached from these filter papers after filtration process. The GF/F filter paper with 0.7  $\mu\text{m}$  in diameter was therefore proposed to replace cellulose based membranes in DOC analysis (Musikavong, 2006).

Several parameters have typically been employed for this purpose, particularly for indicating wastewater quality (USEPA, 1999). However, these parameters do not provide information on the composition of the DOM, and in addition, the analysis of these parameters is rather tedious and time consuming and sometimes requires expensive analyzers and instruments. Other types of parameters have been proposed for the characterization of DOM, including resin fractionation,  $^{13}\text{C}$ - and  $^1\text{H}$ -nuclear magnetic resonance (NMR) spectroscopy, Fourier transform infrared (FTIR) spectroscopy, pyrolysis gas chromatography mass spectrometry (pyrolysis GC/MS), etc. Three-dimensional fluorescent spectroscopy technique – fluorescent excitation–emission matrix (FEEM) has recently been developed to describe the complex composition of DOM. In fact, the FEEM shows the fingerprint of the organic pollutants and therefore could be used to provide in-depth information on the putative origin of fluorescent organic matter in water. This technique was employed to identify matter such as tyrosine-like, tryptophan-like, humic and fulvic acid-like substances.

## 2.3 Characterization of Dissolved Organic Matter (DOM)

The DOM surrogates as explained in previous section are commonly used including DOC, UV254 and SUVA. Although such comprehensive indices are useful to evaluate the amount of organic matter and the potential of DOMs to form THMs in water, these parameters do not provide information on the composition of the DOMs.

Several techniques have been proposed for the characterization of DOMs, such as fourier transform infrared (FTIR) and three-dimensional fluorescent spectroscopy technique-fluorescent excitation-emission matrix (FEEM) etc. (Croue *et al.*, 2000 and Leenheer and Croue, 2003). These techniques could provide the specific organic composition of DOMs, however, some of them are rather complicated and sometimes requiring expensive analyzers and instruments.

### 2.3.1 Fluorescent Excitation-Emission Matrix (FEEM)

FEEM is the technique that produces information on the dynamics and chemical nature of bulk DOM as a function of its fluorescence intensity and fluorescent functional groups. FEEM could help to provide a better understanding of the complex composition of DOM in water as the FEEM shows the fingerprint of the organic pollutants and therefore could be used to provide in-dept information on the putative origin of fluorescent organic matter in water. This technique was employed to identify the matter such as tyrosine-like, tryptophan-like, humic and fulvic acid-like substances as described in Coble (1996), Nakajima *et al.* (2002), Chen *et al.* (2003), and Sierra *et al.* (2005).

Coble *et al.* (1993) proposed that the fluorescent peak of humic-like and protein-like substances were at  $230\text{nm}_{\text{Ex}}/420\text{-}450\text{nm}_{\text{Em}}$  and  $340\text{nm}_{\text{Ex}}/420\text{-}450\text{nm}_{\text{Em}}$ , and  $220\text{nm}_{\text{Ex}}/300\text{-}340\text{nm}_{\text{Em}}$  and  $275\text{nm}_{\text{Ex}}/300\text{-}340\text{nm}_{\text{Em}}$ , respectively. Coble (1996) utilized high-resolution fluorescent spectroscopy to characterize the DOM in water samples from a wide variety of freshwater, coastal and marine environments. The fluorescent signals of humic-like, tyrosine-like, and tryptophan-like were observed. The fluorescent peak positions of the major fluorescent component in bulk seawater were as follows: tyrosine-like and protein-like ( $275\text{nm}_{\text{Ex}}/310\text{nm}_{\text{Em}}$ ), tryptophan-like and protein-like ( $275\text{nm}_{\text{Ex}}/340\text{nm}_{\text{Em}}$ ), humic-like ( $260\text{nm}_{\text{Ex}}/380\text{-}460\text{nm}_{\text{Em}}$ ), marine humic-like ( $312\text{nm}_{\text{Ex}}/380\text{-}420\text{nm}_{\text{Em}}$ ) and humic-like ( $250\text{nm}_{\text{Ex}}/420\text{-}480\text{nm}_{\text{Em}}$ ).



Nakajima *et al.* (2002) applied three-dimensional fluorescent spectroscopy to investigate the water quality in the Tama River, Japan. It was found that FEEM of the water downstream of a lake exhibited a small but strong fluorescent peak at 225nm<sub>Ex</sub>/295nm<sub>Em</sub> and a weak fluorescent peak at 270nm<sub>Ex</sub>/295nm<sub>Em</sub>. These peaks were largely derived from algae. The FEEM of the water receiving treated sewage exhibited two distinctive peaks at around 345nm<sub>Ex</sub>/430nm<sub>Em</sub> and 240nm<sub>Ex</sub>/330-430nm<sub>Em</sub>. When compared with the fluorescent peaks of human urine, humic acid and a laundry detergent with fluorescent whitening agents, the fluorescent peak of the water receiving treated sewage at 345nm<sub>Ex</sub>/430nm<sub>Em</sub> was also detected in the FEEM of a laundry detergent.

Chen *et al.* (2003) divided excitation and emission boundaries into five regions based largely upon supporting literature. Fluorescent peaks have been associated with humic-like, tyrosine-like, tryptophan-like, and phenol-like organic compounds. In general, fluorescent 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). Fluorescent peaks at intermediate excitation wavelengths (250-280 nm) and shorter emission wavelengths (<380 nm) are related to soluble microbial byproduct-like material (Region IV). Fluorescent 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, fluorescent peaks with minimum excitation wavelengths of 250 nm indicated shoulders of fluorescent peaks located at shorter excitation wavelengths. Therefore, fluorescent peaks at shorter excitation wavelengths (<250 nm) and longer emission wavelengths (>350 nm) are related to fulvic acid-like materials (Region III).

Leenheer and Croue (2003) presented the major fluorescent components in a FEEM. Humic-like substances exhibited fluorescent peaks at 330-350nm<sub>Ex</sub>/420-480nm<sub>Em</sub> and 250-260nm<sub>Ex</sub>/380-480nm<sub>Em</sub>, whereas the fluorescent peak of marine humic-like substances was found at 310-320nm<sub>Ex</sub>/380-420nm<sub>Em</sub>. Protein-like and tyrosine-like substances exhibited a fluorescent peak at 270-280nm<sub>Ex</sub>/300-320nm<sub>Em</sub>, while tryptophan-like substances exhibited a fluorescent peak at 270-280nm<sub>Ex</sub>/320-350nm<sub>Em</sub>.

Yamashita and Tanoue (2003) reported that the fluorescent peak of tyrosine-like and protein-like substances was found at 270-275nm<sub>Ex</sub>/300-302nm<sub>Em</sub> whereas that of tryptophan-like and protein-like substances was found at 280nm<sub>Ex</sub>/342-346nm<sub>Em</sub>. In addition, fulvic acid-like substances and humic acid-like substances exhibited fluorescent peaks at 215nm<sub>Ex</sub>/437-441nm<sub>Em</sub> and 350-365nm<sub>Ex</sub>/446-465nm<sub>Em</sub>, respectively.

Janhom (2004) characterized the fluorescent organic matter in reservoir water of the Northern-Region Industrial Estate, Lumphun province, Thailand. A fluorescent peak at 275nm<sub>Ex</sub>/410nm<sub>Em</sub> representing humic-like substances was detected.

Phumpaisanchai (2005) used the FEEM to characterize the fluorescent organic matter in water from the Mae-Hia reservoir, Chiang Mai province and Bhumibol Dam reservoir in Tak province, Thailand. Fluorescent peaks at 260nm<sub>Ex</sub>/420nm<sub>Em</sub> and 330nm<sub>Ex</sub>/400nm<sub>Em</sub> were detected in the water from the Mae-Hia reservoir, whereas fluorescent peaks at 260nm<sub>Ex</sub>/420nm<sub>Em</sub> and 330nm<sub>Ex</sub>/410nm<sub>Em</sub> were found in the water from the Bhumibol Dam reservoir. These observations lead to the conclusion that, humic acid-like and fulvic acid-like substances were the major fluorescent organic matter in both the Mae-Hia reservoir and Bhumibol Dam reservoir.

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.

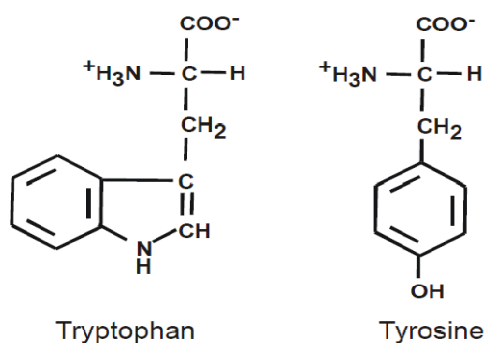
There are some studies that developed the relationship between the fluorescent intensity of outstanding peaks and DOM surrogates parameters such as DOC and THMFP. Marhaba and Kootchars (2000) used the fluorescent intensity to predict the disinfection by-product formation potential. The results show that the total THMs, total HAN and HAA6 (total of monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, dibromoacetic acid and tribromoacetic acid) for the river humic acid and fulvic acid correlated with the fluorescent intensity at 250nm<sub>Ex</sub>/450nm<sub>Em</sub>. Nakajima *et al.* (2002) found that the fluorescent intensity correlated well with total THMFP for a wide range of excitation/emission

wavelengths. The fluorescent intensity at  $255\text{-}295\text{nm}_{\text{Ex}}/245\text{-}385\text{nm}_{\text{Em}}$  correlated with total THMFP better than UV-260. The maximum value of the determination correlation coefficient ( $R^2$ ) of 0.90 at  $260\text{nm}_{\text{Ex}}/355\text{nm}_{\text{Em}}$  was determined. Lee and Ahn (2004) proposed that the fluorescent peak of protein-like substances at  $270\text{nm}_{\text{Ex}}/350\text{nm}_{\text{Em}}$  showed the best correlation with the Chemical COD values obtained by wet oxidation methods.

### 2.3.1.1 Structure of Tyrosine and Tryptophan

Tyrosine is one of the 22 amino acids that are used by cells to synthesize proteins. It is a non-essential amino acid with a polar side group. Aside from being a proteinogenic amino acid, tyrosine has a special role by virtue of the phenol functionality. It occurs in proteins that are part of signal transduction processes. It functions as a receiver of phosphate groups that are transferred by way of protein kinases (so-called receptor tyrosine kinases). Phosphorylation of the hydroxyl group changes the activity of the target protein.

Tryptophan is an essential amino acid. This means that it cannot be synthesized by the organism and therefore must be part of its diet. Amino acids, including tryptophan, act as building blocks in protein biosynthesis. The structure of tyrosine and Tryptophan are shown in Figure 2.1



**Figure 2.1 Structure of tyrosine and Tryptophan**

### 2.3.2 Fourier Transform Infrared (FTIR)

The FTIR spectroscopy is analysis technique that provides information about the chemical bonding or molecular structure of materials, whether organic or inorganic.

The technique works on the fact that bonds and groups of bonds vibrate at characteristic frequencies. A molecule that is exposed to infrared rays absorbs infrared energy at frequencies which are characteristic to that molecule. During FTIR analysis, a spot on the specimen is subjected to a modulated IR beam. The specimen's transmittance and reflectance of the infrared rays at different frequencies is translated into an IR absorption plot consisting of reverse peaks. The resulting FTIR spectral pattern is then analyzed and matched with known signatures of identified materials in the FTIR library.

FTIR has been widely used for the structural investigation of humic substances. Samples exposed to infrared light absorb energy corresponding to the vibrational energy of atomic bonds. The resulting absorption spectrum is a unique fingerprint of compound. FTIR analysis allowed the identification of inorganic and organic functional groups as well as elemental composition.

FTIR spectra were used to measure the DOM present in the secondary effluent from the Wanchang Wastewater Treatment Plant (Harbin, China), by the Xue *et al.* (2008). The organic fractions HPO-A, HPO-N, TPI-A, and TPI-N were characterized by aliphatic C-H (2950-2850  $\text{cm}^{-1}$ , 1450  $\text{cm}^{-1}$  and 1390  $\text{cm}^{-1}$ ), aromatic C=C (1600  $\text{cm}^{-1}$ ), C=O (1640-1585  $\text{cm}^{-1}$ ), and C-O (1280-1137  $\text{cm}^{-1}$  and 1090-1040  $\text{cm}^{-1}$ ) peaks. The aliphatic C-H band was more pronounced for HPO-N and TPI-N than HPO-A and TPI-A. The aromatic C=C peaks were more prominent in HPO-A than in the others, which showed the highest adsorption intensity in the FTIR spectra of HPO-A. This observation corresponded well with the studies of Benoit *et al.*, (2008) that was found C=O stretching of amide groups (1670-1650  $\text{cm}^{-1}$ ), N-H bending vibration of amide groups (1570-1550  $\text{cm}^{-1}$ ), carboxylic C=O (2850-2500  $\text{cm}^{-1}$  and 1700  $\text{cm}^{-1}$ ) and alcohol C-O (1090-1040  $\text{cm}^{-1}$ ).

Xue *et al.* (2008) investigated the behavior and characteristics of dissolved organic matter (DOM) during soil aquifer treatment (SAT). The functional groups found C=O peak at 1730-1710  $\text{cm}^{-1}$ , O-H peak at about 1400  $\text{cm}^{-1}$ , C-O peak at 1250-1150  $\text{cm}^{-1}$ , aliphatic (C-H), C-H<sub>2</sub>, C-H<sub>3</sub> stretching peak at 2950-2850  $\text{cm}^{-1}$  and C=O stretching of amide groups peaks at

1660-1666  $\text{cm}^{-1}$ . Shirra *et al.* (2008) identified functional groups on granular activated carbon (GAC) as pretreatment to reverse osmosis (RO) of membrane bioreactor (MBR). The peaks at wavenumbers 3360  $\text{cm}^{-1}$  (N-H stretch) and 1610  $\text{cm}^{-1}$  (N-H bend and N-C=O stretch) are of primary amine and N-acetyl amino sugars, respectively, and the peak at 1410  $\text{cm}^{-1}$  (C-N stretch) is of secondary and tertiary amines, representing proteins. The peaks at wavenumber 1050  $\text{cm}^{-1}$  (C-O-C stretch) and 1160  $\text{cm}^{-1}$  (COH stretch) indicated carbohydrates (representing polysaccharides). Fulvic and humic acids spectra indicated bands at about 1720, 1650, 1500, 1210, 1160, 1100  $\text{cm}^{-1}$ . A fairly broad at 1700  $\text{cm}^{-1}$  was due to a carbonyl stretch in carboxylic acids and a small band at 1650  $\text{cm}^{-1}$  implies the presence of benzophenones. The benzene ring in aromatic compounds, normally, absorbs (stretching) at 1630-1430  $\text{cm}^{-1}$ . The band at 1200  $\text{cm}^{-1}$  and 1100  $\text{cm}^{-1}$  indicated C-O stretching and the presence of secondary alcohol (Samios *et al.*, 2005).

#### 2.4 Disinfection by-Products

The chlorination process has also produced disinfection by-products which are formed when chlorine used in water treatment plants reacts with bromide and natural organic matters (e.g. decaying vegetation) in the source water. The major DBPs include trihalomethans (THMs), haloacetic acids (HAAs), haloacetonitriles (HANs), haloketones (HKs), chloral hydrate (CH) and chloropicrin (CP). The general reaction of DOM with chlorine is as follows (Marhaba and Washington, 1998);



The concentrations of DBPs in the finished water are correlated to the DOM concentrations in the raw water as DOM is often a major component that reacts with chlorine to form DBPs. The DBPs precursors are generated via several sources. For instance, water treatment chemicals were shown to be a source of organic matter that led to the formation of DBPs (Feige *et al.*, 1980). The release of industrial chemicals and minerals is also largely an unknown contributor to DBP formation. In this case, the type of DBPs is highly site-specific. Furthermore, foodstuffs, occasionally, can also potentially be DBP precursors (Raymer *et al.*, 1999).

## 2.4.1 Trihalomethanes (THMs)

### 2.4.1.1 Background

THMs were formed when chlorine reacted with naturally occurring humic substances in water treatment plants and water distribution systems. 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 halogenated organic compounds from 80 water supply plants. THMs have been found to be the most widespread organic contaminants in drinking water, and occur at higher concentrations than other disinfection by-products. The four THMs (chloroform, bromodichloroform, dibromochloroform 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, 1983; Munro *et al.*, 1986). Chloroform ( $\text{CHCl}_3$ ), the most common THM, is a proven animal carcinogen and a suspected human carcinogen.

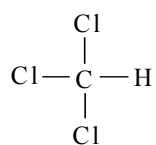
### 2.4.1.2 Chemistry of Trihalomethanes (THMs)

THMs are halogen-substituted single-carbon compounds with a general formula of  $\text{CHX}_3$ , where X may be fluorine, chlorine, bromine or iodine, or combinations thereof. THMs are a group of organic chemicals formed in water when chlorine reacts with natural organic matters (such as humic acids from decaying vegetation). The primary biochemical ancestors of THM identified by many researchers are humic substances including humic acid and fulvic acid (Rook, 1976; Trussell and Umphes, 1978 and Oliver and Lawrence, 1979). These materials also contribute to the natural color of the water (Amy *et al.*, 1983). Bromine was also identified as a precursor in the natural water, since its presence in chlorinated water may be oxidized by chlorine to form hypobromous acid (HOBr), which led to the formation of brominated THM species. Gould *et al.*, (1983) also observed iodine, to a lesser extent.

Four THM species that actually occur in water supplies are Chloroform ( $\text{CHCl}_3$ ), Bromo dichloromethane ( $\text{CHBrCl}_2$ ), Dibromochloroform ( $\text{CHBr}_2\text{Cl}$ ) and Bromoform ( $\text{CHBr}_3$ ).

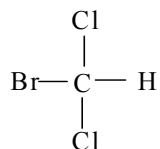
#### - Chloroform

Chloroform is largely present 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 basic chemical and physical characteristics of chloroform or trichloromethane ( $\text{CHCl}_3$ ) are shown in Table 2.1.



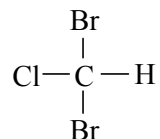
#### - Bromodichloromethane

The basic chemical and physical characteristics of dichlorobromomethane or Bromodichloromethane ( $\text{CHCl}_2\text{Br}$ ) are shown in Table 2.1.



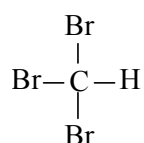
#### - Dibromochloromethane

The basic chemical and physical characteristics of dibromochloromethane or chlorodibromomethane ( $\text{CHClBr}_2$ ) are shown in Table 2.1.



### - Bromoform

The basic chemical and physical characteristics of bromoform or tribromomethane or methyl tribromide ( $\text{CHBr}_3$ ) are shown in Table 2.1.



**Table 2.1** Basic chemical and physical characteristics of Chloroform

<b>Empirical Formula</b>	<b>Molecular weight (g/mol)</b>	<b>Specific gravity (g/cm<sup>3</sup>)</b>	<b>Boiling point (°C)</b>	<b>Melting point (°C)</b>	<b>Solubility in water (g/L)</b>
<b>CHCl<sub>3</sub></b>	119.37	1.472	61	-63	8.1
<b>CHCl<sub>2</sub>Br</b>	163.82	1.472	90.1	-57.1	Insoluble
<b>CHClBr<sub>2</sub></b>	208.29	2.38	120	-63	4.75
<b>CHBr<sub>3</sub></b>	257.73	257.73	150	8.3	Insoluble

**Source:** Ghazali, 1989.

#### 2.4.1.3 Factors Influencing THMs Formation

Many studies have concluded that THM formation in drinking water such as pH, turbidity, concentration of precursors, chlorine dosages, temperature, and reaction time are presented as follow:

##### - pH

From the previous research works, It may lead one to the conclusion that THMs formation levels increase with pH. This supports the hypothesis that THM formation via the haloform reaction is basic-catalyzed. The other factors that influence the formation of THMs are function of precursor concentration, contact time, chlorine dose, bromide concentration and temperature (El-Shahat *et al.*, 2001).



### **- Turbidity**

Turbidity, or the cloudiness of the water, is caused by multiple factors such as clay, silt, fine organic and inorganic matter, soluble colored organic compounds, plankton, and other microscopic organisms. The Department of Environmental and Labor (2000) illustrated that chlorine efficiency increased as turbidity is decreased. This was attributed to the fact that turbidity interfered with the interaction between chlorine and substances in water.

### **- Precursor Concentration**

Since THM formation is a result of a reaction between chlorine and THM precursors, it is obvious that the precursor concentrations would influence THM concentrations. Rook (1976) studied varied concentrations of organic precursors, which were called total organic carbon (TOC) could be reduced before chlorinating. In this regard, it was found that Chloroform production from organic matter is linear in concentration up to 250 mg/l TOC.

In general, THM 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 THM formation were often observed (EPA, 1981). This suggests that factors such as chemical functional groups in the DOC played an important role in the formation of THMs.

### **- Chlorine Dosages**

R. Rhodes Trussell (1978) reported effected of chlorine dose on THM formation. Different concentration of chlorine between 1 and 80 mg/ L was added into synthetic water, with TOC of approximately 0.2 mg/L. In the region of small concentration of chlorine, THMs were inefficiently formed. After the region of small concentration, THMs rapidly developed. After a dose of about 20 mg/L, a substantial  $\text{Cl}_2$  residual developed, however THMs development were curtailed.

### - Temperature

The effect of temperature on the rate of THM formation was investigated by Stevens *et al.* (1976) using the Ohio River collected from winter to summer where concentrations of THMs were higher during summer and autumn than in winter and spring. 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 stronger at longer contact times (Carlson and Hardy, 1998).

### - Reaction Time

Many authors indicated that the concentration of chloroform appeared to increase slowly even after 96 h, suggesting that as long as low concentrations of free chlorine were present, chloroform continued to form. bromochlorinated THM species have been found to form more rapidly than chloroform. Results from many sources indicated that bromoform formation was quite slow, but proceeded for approximately 7-8 h before leveling off almost completely after 20 h (AWWARF, 1991; Koch *et al.*, 1991).

#### 2.4.1.4 Toxicity of THMs

THMs can be taken into body by drinking the water and breathing its vapors (for example when showering). They are then metabolized and eliminated induce cytotoxicity in the liver and kidneys of rodents rapidly. Most THMs are metabolized into a less-toxic form, but some are transformed into more reactive substances, especially at high concentrations. Following the uptake of THMs, they are attained in the fat, liver and kidneys. THMs exposed to doses of about 0.5 mmol/kg of body weight. A maximum contaminant level (MCL) of 100 µg/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 80 µg/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 40 µg/L. In Thailand, the standard level concerning THM has not been established yet.

Chloroform is the most common THMs found in chlorinated water and can be rapidly adsorbed on oral and intraperitoneal administration and subsequently metabolized into

carbon dioxide chloride ion, phosgene and other unidentified metabolites in test animals. The most toxic substance in the metabolism of chloroform seems to be phosgene (Cotruvo, 1981). Cotruvo also stated in the same year that in his a study, which measured chloroform levels in blood among groups of individuals drinking chlorinated water and non-chlorinated water, the group consuming chlorinated water showed significantly higher chloroform. And the human health effect observed in accidental, habitual and occupational exposures to chloroform are similar to those found in the experimental animals. These include effects on the central nervous system, liver and kidneys.

Cotruvo noted that it has been reported since 1945 that chloroform induced carcinogenicity. Hepatomas were produced in female Strain A mice given a repeated dose of 0.145-2.32 mg for a four month period. In the same year Cotruvo also reported that in a bioassay performed by NCI, rat and mice of both sexes were fed chloroform 90-200 mg/kg-d (rats) and 138-147 mg/kg-d (mice), five days a week for 72 weeks. Hepatocellular carcinomas were observed in male and female mice at both the high and low doses at a statistically significant level (Cotruvo, 1981).

The EPA computed U.S. human uptakes levels of THMs in milligrams per year from air, food and drinking water employing as number of assumption as shown in the Table 2.2.

**Table 2.2** Human uptakes of chloroform and trihalomethanes from drinking water, food and air

Chemical	Exposure level mg/l, mean and (range)		
	Drinking Water	Food	Air
Chloroform	64 (0.73-343)	9 (2-15.97)	20 (0.41-204)
Trihalomethanes	85 (0.73-572)	-	-

#### 2.4.1.5 Trihalomethanes Formation Potential (THMFP)

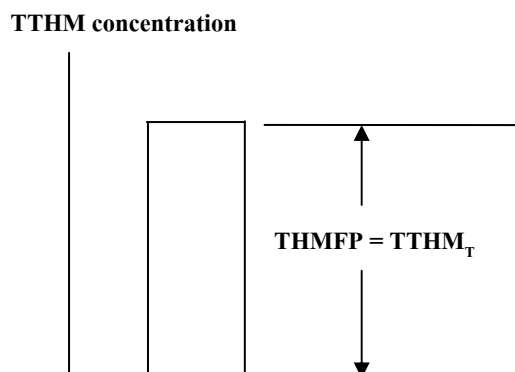
THMFP determines the potential of DOM to form THMs under relatively extreme chlorination conditions. THMFP is defined as the difference between the concentration of THMs after the collected sample was subjected to chlorination and the concentration of THMs at the time of sampling. The recommended (Standard Methods, 1995) chlorination conditions for THMFP tests include an incubation time of seven days with a free chlorine residual of 3 to 5 mg/L at the end of the incubation period. The recommended incubation temperature is  $25 \pm 2^\circ\text{C}$  and the recommended pH is  $7.0 \pm 0.2$  with phosphate buffer. The definition terms of THMFP are described as follows:

Total trihalomethanes (TTHMs) are the sum of all four compounds which include chloroform, bromoform, dichlorobromomethane and dibromochloromethane.

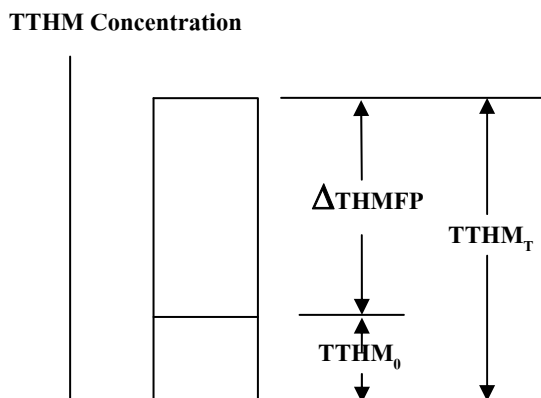
$\text{THM}_0$  is the total THMs concentration at the time of the sampling. It can range from non-detectable to several hundred micrograms per liter if the sample has been chlorinated.

$\text{TTHM}_7$  is the total concentration of all four THMs compounds that are formed when the sample is incubated at  $25 \pm 2^\circ\text{C}$  in the presence of excess free chlorine over a 7-day reaction time under the recommended chlorination conditions for THMFP (Standard Methods, 1995).

THMFP or  $\Delta\text{THMFP}$  is the difference between the final TTHMP concentration and the initial  $\text{TTHM}_0$  concentration as shown in Figures 2.2 and 2.3, respectively. THMFP determinations provide a worst-case scenario of the concentration of THMs that may be formed.



**Figure 2.2** Definition used in the formation potential test of a sample without free chlorine at the time of sampling



**Figure 2.3** Definition used in the formation potential test of a sample with free chlorine at the time of sampling

El-Shahat, Abdel-Halim and Hassan (1998) evaluated trihalomethnes in water treatment plants output in Cairo, at three sampling locations, Mostord, Tebbin and Rod El-Frag. Mean values of THMs in the water treatment plants outputs (Sept. 1991-Dec. 1991) ranged from

31.70 to 61.41  $\mu\text{g/L}$ . Moreover, mean values of THMs in water treatment plant outputs (Jan. 1992 - August 1992) ranged from 19.19 to 42.30  $\mu\text{g/L}$ .

El-Shahat, Abdel-Halim and Hassan (2001) investigated THMs in various stages of the water treatment process at the Tebbin, Rod El-Farag and Mostorod water treatment plants during summer and water seasons. Stages of the water treatment process that were investigated consist of raw water, clarifier and filter effluent and finished water. The results showed that the highest THMs concentration occurred in finish water and its range was between 41.70 and 54.50  $\mu\text{g/L}$  in the summer, and 29.00 and 34.90  $\mu\text{g/L}$  in the winter. Moreover, THMs concentration in filter effluent is higher than that of clarifier and THMs concentrations in clarifier is higher than that of raw water.

## **2.5 Manufacturing process of latex gloves**

The production step of manufacturing process for production of latex gloves can be summarized as follows: (Boonprasert P., 2008)

### **1. To prepare the chemicals used in the production of content latex**

Diammonium hydrogen phosphate: DAP, ( $\text{NH}_3$ ), (Tetra Methyl Thiuram Disulphide:TMTD), (ZnO) are the major chemical used in the production of the content latex.

### **2. To prepare the raw material used in the production of medical gloves**

- 1) Coagulant
- 2) Natural rubber latex
- 3) Polychloroprene rubber latex
- 4) Blends
- 5) Nitrile coating latex
- 6) Slurry powder

### 3. To prepare latex compound used as an intermediate layer

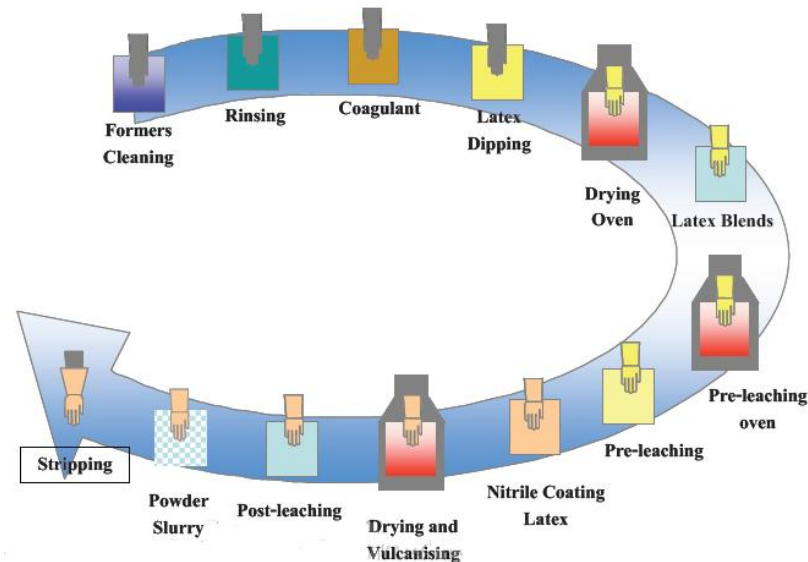
Preparation of latex compounds is for using as an intermediate layer and for the adhesion of layer in nitrile latex which is a coating of the glove. Table 2.3 shows the ratio of chemicals used for preparing the latex mixture.

**Table 2.3** The ratio of chemicals used for preparing the latex mixture

Chemicals	Quantity (phr)
Soft water	-
100% Igepal CO-630	0.5
100% Darvan WAQ	0.20
54% Maturated NR latex compound	0, 25, 50, 75, 90
54% Maturated CR latex compound	0, 5, 10, 15, 20
45% NBR TYLAC 6874-01 latex	0, 25, 50, 75, 90

Preparation of rubber compound can be developed by filling the tank with soft water. Igepal CO-630 was stirred with hot water until they are mixed. Fill the solution into a tank. The solution was mixed slowly for at least 15 minutes with Darvan WAQ. Then, they were mixed for 15 minutes, the concentrated natural rubber compound weighed and filled, as shown in the Table. 2.3. Stir quickly at least 20 minutes, weigh and fill tires chloroprene rubber latex by volume, as shown in Table 2.3. Stir quickly for at least 20 minutes, weigh and fill latex nitrile concentration by volume, as shown in Table 2.3. Stir quickly for at least 30 min and analyzed for percent solids (% TSC) and the pH was then recorded.

#### 4. The Processing of medical gloves latex.



**Figure 2.4** The processing flow molded rubber (Dipping Process)

(Boonprasert P., 2008)

##### 4.1 Dipping Process

The dipping process consist of 13 subprocess as shown in the Figure. 2.4. It start with the formers cleaning of the glove formers with citric acid. After that the glove former is cleaned by water. Then, the glove formers are dipped into a calcium nitrate is used as coagulant to help the latex mixture adhere to the formers. Next, the glove formers are dipped into a latex compound tank then it is baked in a drying oven at 175 °C. After that the glove formers are dipped into a latex blend tank. The latex coating on the glove former is treated as strength when wetting gel in pre-leaching oven at 175 °C. Then the film latex is rolled at rim and then the glove formers are pre-leached by water. After that the glove former is dipped into a nitrile latex tank. When the film latex is passed the leaching process, it is baked by the oven at 100-300°C. After that latex glove is leached by water and powder slurry for clean up chemicals and protect the adhesion of the glove. Next step, the gloves are dried and take off from the glove formers.

The finally process, the gloves will be spin with tumbler at 80 °C for 25 minutes and was cooled at temperatures below 42 °C for 12 minutes with a spinning speed of the machine



of 43 rpm. After the completion of this process, the gloves will be washed with a chlorine solution in the next process.

#### **4.2 The chlorination process**

The chlorination process is used in the production of gloves latex powder free. The powdered latex gloves will be turned inside out which is a coated with the nitrile latex before it is put into the chlorinator at approximately 900 ppm. It is washed with clean water again before being coated with a lubricant. When gloves are coated with lubricant. Gloves will be dried approximately at 60 °C with cyclone dryer. Then turn that side out and bake it again. The finally process the gloves will be cooled by blowing cold air in the dryer to cool.

## **CHAPTER 3**

### **METHODOLOGY**

#### **3.1 Studied Site**

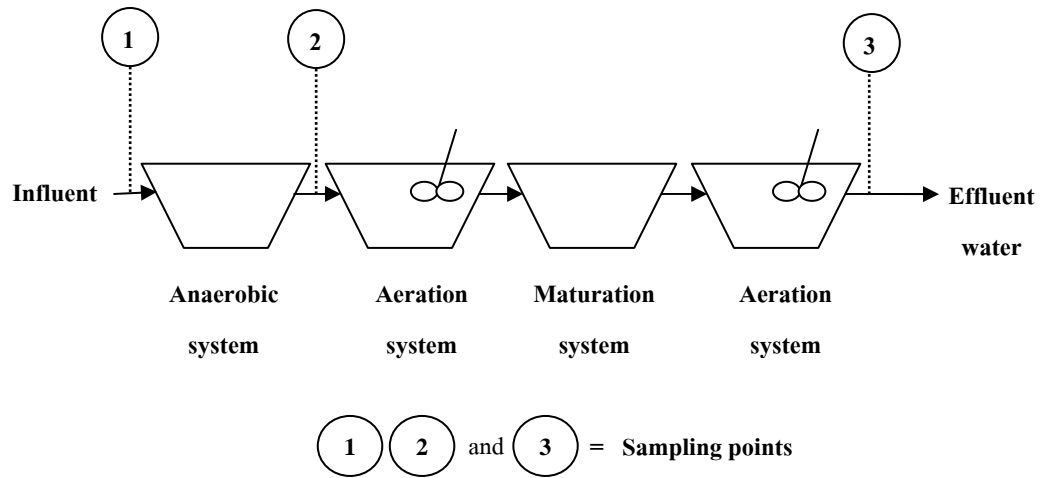
##### **3.1.1 The Selected Rubber Glove Manufacturing Plants**

Three rubber gloves manufacturing plants in Thailand (namely Plant A, B and C) were selected as the studied site this study. These three plants were selected because they have generated wastewater more than 5,000 m<sup>3</sup>/d. All plants are located in the southern of Thailand. In production process, the water is used in washing activities and the resulting wastewater is treated before being discharged to natural waterways. The natural waterway in this study is located near to all plants. Besides, it is also the raw water for water supply production in urban and local area.

##### **3.1.2 Wastewater Treatment Plant and Sample Collections.**

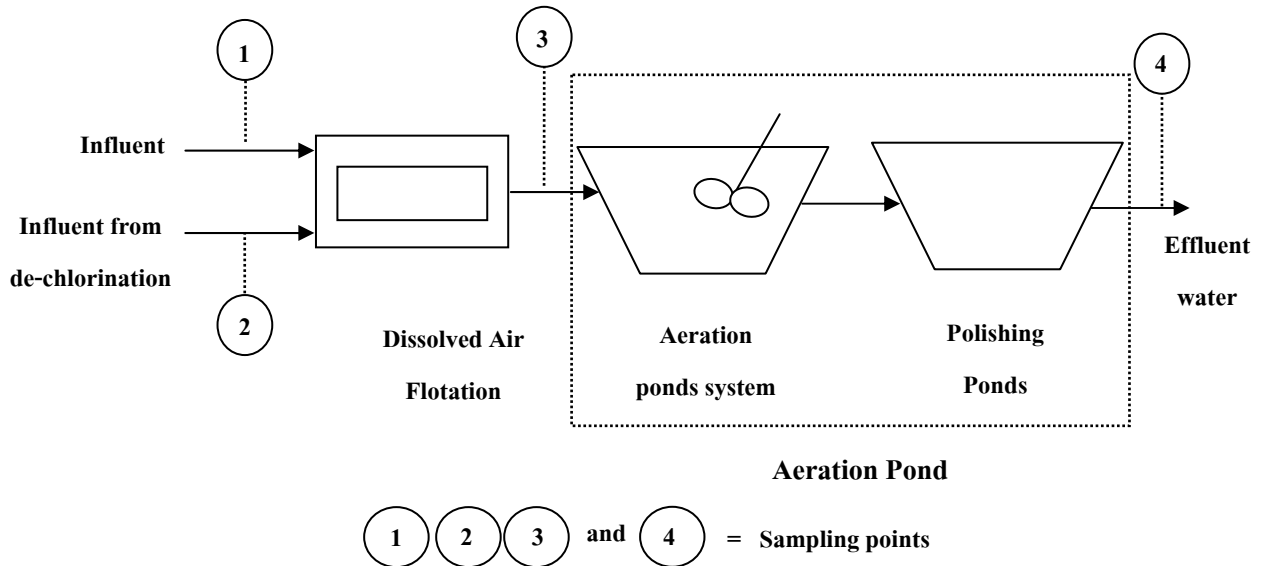
The wastewater treatment system of Plant A consists of anaerobic ponds and aeration ponds connected in series. Plant B consists of dissolved air floatation (DAF) and aeration ponds. Plant C utilized aeration ponds system to treat wastewater. The schematic diagram of wastewater treatment system of Plant A, B and C is presented in Figure 3.1, 3.2 and 3.3, respectively. The DAF system in Plant B is designed to remove suspended solids (SS) such as particles and other. The removal is achieved by dissolving air in the water or wastewater under pressure and then releasing the air at atmospheric pressure in a flotation tank or basin. The released air forms tiny bubbles which adhere to the suspended matter causing the suspended matter to float to the surface of the water where it may then be removed by a skimming device.

For the sample collections in Plant A, the influent wastewater, effluent water from anaerobic system, and effluent water from the wastewater treatment plant were collected as shown in Figure 3.1



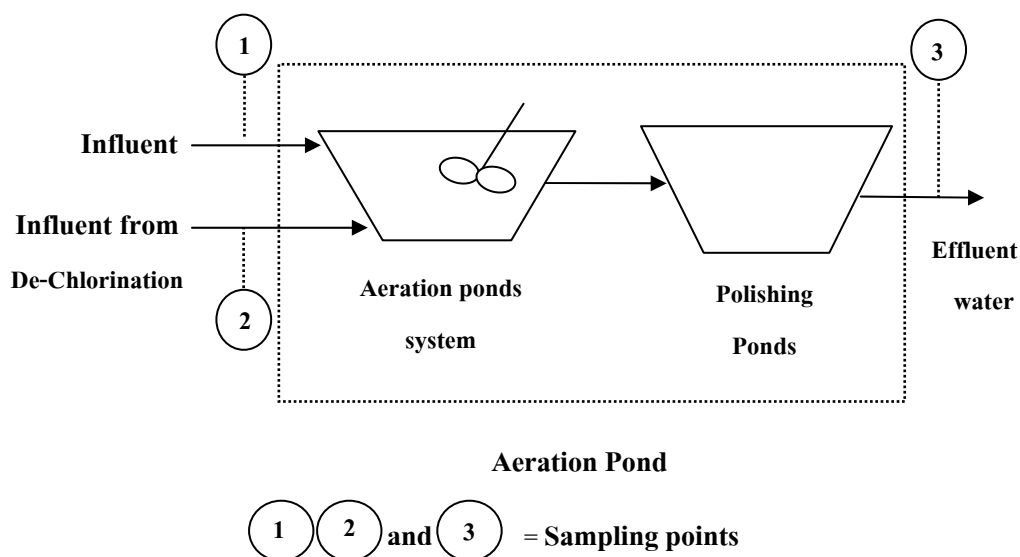
**Figure 3.1** Schematic diagram of wastewater treatment system of Plant A

For Plant B, the influent wastewater, influent from de-chlorination, effluent water from DAF system, and effluent water from the wastewater treatment plant were collected as shown in Figure 3.2.



**Figure 3.2** Schematic diagram of wastewater treatment system of Plant B

For Plant C, the influent wastewater, influent from de-chlorination, and effluent water from the wastewater treatment plant were collected as shown in Figure 3.3.



**Figure 3.3** Schematic diagram of wastewater treatment system of Plant C

### 3.2 Sample Collection and Preservation

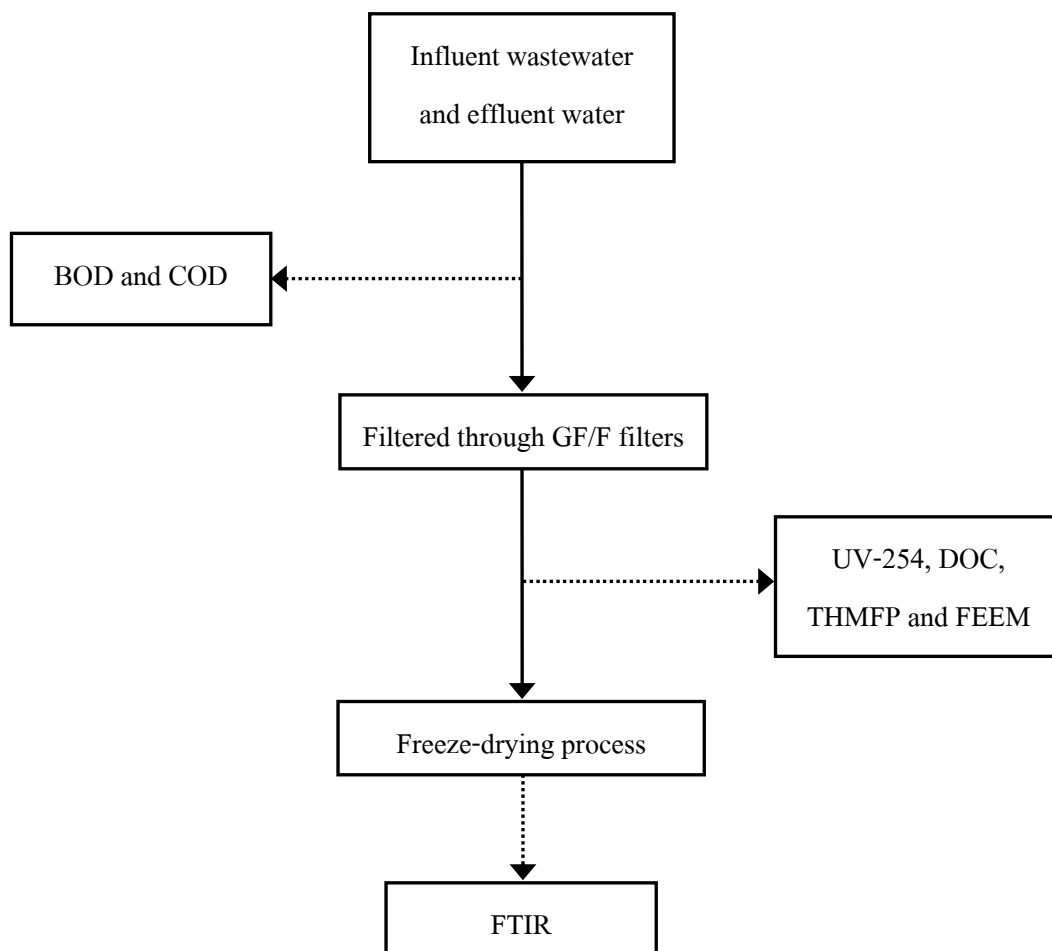
The wastewater samples were collected from each treatment step of the wastewater treatment system of three rubber gloves manufacturing plants as shown in Figure 3.1 - 3.3 for twice times in January 6 and April 9, 2010 for Plant A, March 2 and July 6, 2010 of Plant B and Plant C. The water samples collected were preserved at a temperature of 4°C until experiment.

### 3.3 Experimental Procedure

The experimental procedures are shown in the following steps and conclusively described of Figure 3.4.

All of wastewater samples were measured for their pH, total suspended solid (TSS), biochemical oxygen demand (BOD) and chemical oxygen demand (COD). For measurements of DOM surrogate parameters, wastewater samples were filtered through a pre combusted (550°C for 2 h) Whatman GF/F (nominal pore size 0.7 µm). Filtered wastewater samples were analyzed for ultraviolet absorbance at 254 nm (UV-254), dissolved organic carbon

(DOC), trihalomethane formation potential (THMFP) and fluorescent excitation-emission (FEEM). The freeze-dried samples were analyzed for flourier transform infrared (FTIR).



**Figure 3.4** Schematic diagram of experimental procedure

### 3.4 Instruments and Analytical Methods

#### 3.4.1 Instruments

The instruments utilized in this experiment are shown in Figure 3.5.

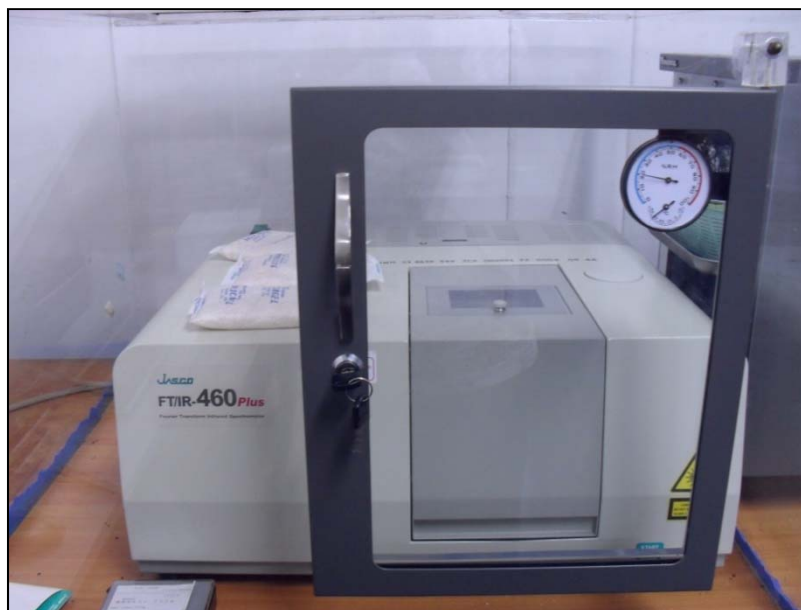


a. TOC Analyzer (O.I. Analytical 1010 TOC Analyzer)



b. Spectrofluorometer (FP-6200 spectrofluorometer from JASCO)

**Figure 3.5** Instruments used during the experiment



c. Fourier Transform Infrared Spectrometer  
(FTIR-460 plus spectrometer from JASCO)



d. Gas Chromatography with ECD detector control by computer  
(Agilent 6890 Series Gas Chromatography).

**Figure 3.5** Instruments used in the experiment (Cont.)

### 3.4.2 Analytical Methods

The wastewater samples were analyzed for BOD, COD, UV-254, DOC, FEEM, FTIR and THMFP.

The analytical methods and standards are tabulated in Table 3.1.

**Table 3.1** Analytical methods and instruments

Parameter	Analytical method	Instrument
1. DOC (mg/L)	5310 C*. Wet-Oxidation Method	O.I. analytical 1010 TOC analyzer
2. THMFP (mg/L)	5710 B*. Trihalomethane Formation Potential	Gas Chromatography with ECD detector
3. UV-254 (cm <sup>-1</sup> )	5910 B*. Ultraviolet Absorption Method	Spectrophotometer model UV-1601
4. COD	Close reflux, Titrimetric Method	-
5. BOD	5 Day BOD Test	-
6. FEEM	-	JASCO FP-6200 spectrofluorometer
7. FTIR	-	Jasco FTIR 460 plus

**Source:** Standard Methods, 1995.

The detail information of analytical procedure are described as follows:

#### - DOC (Dissolved Organic Carbon)

The samples were filtered through a combusted 0.7 µm GF/F filter paper prior to measurement by O.I. analytical 1010 TOC Analyzer. DOC of water samples were measured in accordance with standard method 5310 Total Organic Carbon (TOC); section 5310 C Wet Oxidation Method.



#### **- THMFP**

THMFP were measured in accordance with standard method 5710, The neutralized solution was buffered by a phosphate solution before incubation at  $25 \pm 2$  °C in amber bottles with PTFE liners. At the end of the 7-day reaction period, samples should have a remaining free chlorine residual of between 3 and 5 mg/L. The residual chlorine was measured according to the procedures mentioned in Standard Method 4500-Cl G, the *N,N*-dechloro-*p*-phenylenediamine colorimetric method. The level of chlorine was then represented by the light absorbance at 515 nm using a spectrophotometer spectronic unicam Genesys 10 UV with matched quartz cells that provided a path length of 10 mm. THMs were extracted with pentane in accordance with Standard Method 6232B. Agilent Gas Chromatography-6890 with an electron capture detector (ECD) (Agilent technologies Inc., Wilmington, Delaware, USA) and chromatographic column (J&W Science DB-624, DE, USA) with 0.2-mm X 25 m 1.12  $\mu$ m film was used to analyze THMs under the following operating conditions (Table 3.2).

#### **- BOD**

Biochemical oxygen demand was measured in accordance with 5 Day BOD Test. (Standard Method 5210B (5-day BOD Test))

#### **- COD**

Chemical Oxygen Demand was measured in accordance with Close reflux and titration method. (Standard Method 5220C)

#### **- UV-254**

UV-254 was analyzed in accordance with Standard Method 5910B using a spectrophotometer 10 UV at 254 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. All samples were adjusted to pH 7 by NaOH or H<sub>2</sub>SO<sub>4</sub> prior to the measurement. Potassium biphthalate (KHP) was used to check precision of spectrophotometer.

**Table 3.2** Method condition of GC(HP6890) for analysis of THMFP

<b>Manufacture name/model</b>	<b>HP 6890 GC</b>
<b>Inlet conditions</b>	Mode: Split Initial temp: 225 °C Pressure: 31.14 psi Split ration: 10:1 Split flow: 96.4 mL/min Total flow: 108.7 mL/min Gas type: Helium
<b>Column</b>	HP-5 5% phenyl Methyl Siloxane Length: 30 m Diameter: 320 um Film thickness: 0.25 um Mode: constant flow Initial flow: 9.6 mL/min Init pressure: 31.15 psi
<b>Detector</b>	ECD Temperature: 300 °C Mode: Constant make up flow Make up flow: 60.0 mL/min Make up Gas type: Nitrogen
<b>Injection temperature</b>	225 °C
<b>Initial temperature</b>	60 °C initial time 1.00 min
<b>Temperature program</b>	10 °C/minute to 100 °C 1 minute 10 °C/minute to 130 °C 1 minute 10 °C/minute to 180 °C 1 minute
<b>Final time duration</b>	16 minute

### **- FEEM**

FEEM is 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  $[(C_{20}H_{24}N_2O_2)_2H_2SO_4 \cdot 2H_2O]$  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  $\mu\text{g/L}$  of quinine sulfate solution at 450 nm with an excitation wavelength of 345 nm (Kasuga *et al.*, 2003).

#### ***Spectrofluorometer Operating Conditions***

A JASCO FP-6200 spectrofluorometer was used to measure the FEEM of all water samples in this study using the following operating conditions:

Measurement Mode: Emission

Band with excitation: 5 nm.

Band with emission: 5 nm.

Response: Medium

Sensitivity: Medium

Scanning speed: 2000 nm/min

Excitation wavelength: Start at 220 nm., end at 600 nm.

Emission wavelength: Start at 220 nm., end at 600 nm.

Excitation wavelength interval: 5 nm.

Emission wavelength interval: 1 nm.

### ***FEEM Measurement Procedure***

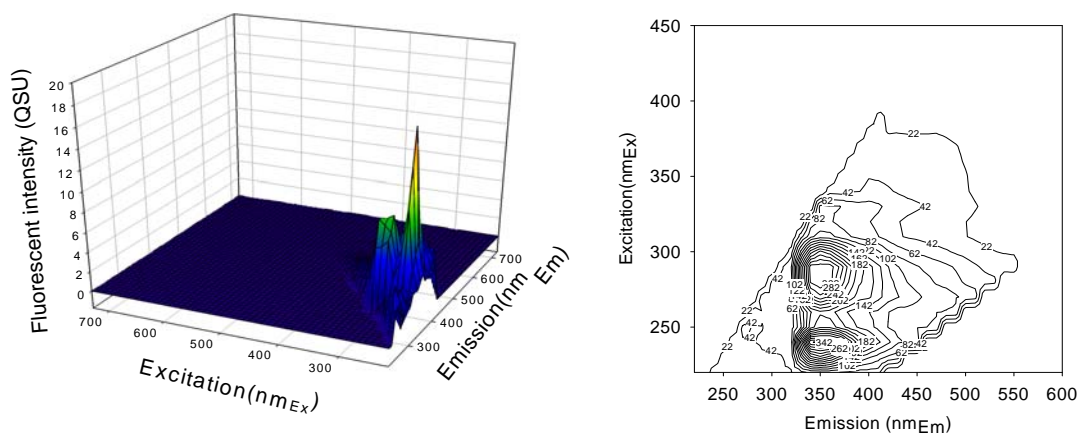
Check the Raman Test Photometric Stability. The value should be less than  $\pm 1\%$ /hour.

- 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 DI water.
- Measure the FEEM of the water samples.
- Subtract the FEEM of the water samples with the FEEM of the DI 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 ( $Ex$ )  $\geq$  emission wavelength ( $Em$ ) or  $Ex \times 2 \leq Em$  (Komatsu *et al.*, 2005).
- Remove the Rayleigh and Raman scattering peaks at  $Em \pm 10-15$  nm. 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 3.6. 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.



**Figure 3.6** Sample of the Fluorescent Excitation-Emission Matrix (FEEM) (a) the three-dimensional view and (b) contour view (contour interval of 2 QSU) with fluorescent peaks and its sections of a FEEM

- **FTIR** (Fourier Transform Infrared)

Filtered water samples were pre-freezed at  $-20\text{ }^{\circ}\text{C}$  for at least 12 hr. Then they were placed in freeze-drying unit at  $-57^{\circ}\text{C}$  and 0.004 bars until the uniform powder was obtained. For each water sample, this process was repeated several times to produce sufficient amount uniform powder for FTIR analysis. Pellets were made using 1-2 mg of powder combined with 150 mg of KBR. The FTIR spectra were analyzed on a Jasco FTIR-460 spectrometer at a resolution of  $4\text{ cm}^{-1}$  by collecting 16 scans per sample in a wave number range of  $4000\text{--}400\text{ cm}^{-1}$ .

**CHAPTER 4**

**REDUCTION OF DISSOLVED ORGANIC MATTER AND  
TRICHALOMETHANE FORMATION POTENTIAL IN WASTEWATER OF  
RUBBER GLOVES MANUFACTURING PLANTS**

**4.1 Introduction and Objective**

The rubber glove industry is one of the major industries in the southern part of Thailand. A rubber glove manufacturing process consumes large amount of water, especially in washing process. Therefore, wastewater treatment plant operated hardly capable of treating this wastewater. For the wastewater treatment practice, it mainly focuses on the reduction of organic matter in terms of biochemical oxygen demand (BOD) and chemical oxygen demand (COD).

When treated wastewater is discharged to the surface water and it can be used as indirect water supply reused. The remaining organic matter in treated wastewater, even presented in a small level, can be caused the serious concern. The organic matter especially dissolved organic matter (DOM) could potentially react with chlorine during the disinfection process of water supply plant to form carcinogenic disinfection by-products (DBPs), e.g. trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs) (Krasner, 1989) (Marhaba and Washington, 1998) and (Rook, 1974). The level of DOM in treated wastewater depends on the performance of the wastewater treatment plant. Presently the different wastewater treatment processes are used to treat the wastewater from the rubber glove process. The study of the level of DOM in wastewater and the performance capability of the rubber glove manufacturing processes for reducing the DOM are limited.

The objective of this work was to determine the level of DOM in the wastewater of the rubber glove manufacturing processes in terms of dissolved organic carbon (DOC), ultraviolet adsorption at wavelength 254 nm (UV-254) and trihalomethanes formation potential (THMFP). In addition, the performance capability of different wastewater treatment

process of the rubber glove manufacturing in the reduction of DOC, UV-254 and THMFP was evaluated.

## 4.2 Material and Methods

### 4.2.1 Sample Collection and Experimental Procedure

The wastewater samples were collected from each treatment process of the wastewater treatment system of three rubber glove manufacturing plants for twice times in January 6 and April 9, 2010 for Plant A, March 2 and July 6, 2010 for Plant B and Plant C. The wastewater treatment process and sampling points were presented already in Chapter 3. All of wastewater samples were measured for their pH, total suspended solid (TSS), biochemical oxygen demand (BOD) and chemical oxygen demand (COD). For measurements of DOM surrogate parameters, wastewater samples were filtered through a pre-combusted ( $550^{\circ}\text{C}$  for 2 h) Whatman GF/F (nominal pore size  $0.7\ \mu\text{m}$ ). Filtered wastewater samples were analyzed for ultraviolet absorbance at 254 nm (UV-254), dissolved organic carbon (DOC) and trihalomethane formation potential (THMFP).

## 4.3 Results and Discussions

### 4.3.1 Characteristics of Influent Wastewater

The basic water qualities of influent wastewater from three plants are presented in Table 4.1.

**Table 4.1** Basic water qualities of influent wastewater from three plants

Parameter	Plant A		Plant B				Plant C			
	1 <sup>st</sup>	2 <sup>st</sup>	1 <sup>st</sup> Sampling		2 <sup>nd</sup> Sampling		1 <sup>st</sup> Sampling		2 <sup>nd</sup> Sampling	
	Sampling	Sampling	Inf.1	Inf.2	Inf.1	Inf.2	Inf.1	Inf.2	Inf.1	Inf.2
<b>pH</b>	9.8	8.3	9.4	2.6	9.4	2.9	7.1	6.9	8	6.8
<b>TSS(mg/L)</b>	239	188	16	20	16	19	23	8	43	8
<b>BOD(mg/L)</b>	229	388	70	20	66	23	20	9	22	11
<b>COD(mg/L)</b>	1513	1697	1798	156	1751	146	95	29	101	34
<b>BOD/COD</b>	0.15	0.23	0.04	0.13	0.04	0.15	0.21	0.31	0.21	0.32

**Note:** Inf. 1 = Influent wastewater from the process

Inf.2 = Influent wastewater from the de-chlorination process.

For Plant B and C, the influent wastewater to the systems consisted of two sources; (1) influent wastewater; (2) influent de-chlorination. The calculation of concentration of contaminant to the system was done using the following equation;

$$A + (B)C + D \quad \text{Equation (1)}$$

A : Flow of influent wastewater, m<sup>3</sup>/d

B : Concentration of organic matter in influent wastewater, g/m<sup>3</sup>

C : Flow of influent de-chlorination, m<sup>3</sup>/d

D : Concentration of organic matter in influent de-chlorination, g/m<sup>3</sup>

As can be seen in Table 4.1, for Plant A, the pH was detected in the base range, the COD of 1,513 and 1,697 mg/L were found in the first and second samplings, respectively. The BOD of influent wastewater in the first and second samplings was 229 and 388 mg/L, respectively. The characteristics of the influent wastewater from the first and second sampling were considerably similar. In the case of Plant B, the nature of wastewater from the first and second samplings was considerably similar. Considering the influent wastewater from the process, the pH of the first and second samplings was as high as 9.4. BOD of 70 and 66 mg/L were detected in wastewater from the first and second sampling, respectively, whereas COD of the first and second samplings were 1,798 and 1,751 mg/L, respectively. Wastewater from de-chlorination had BOD of 20 mg/L and COD of 156 mg/L for the first sampling, while that of second sampling was 23 and 146 mg/L, respectively.

For Plant C, the characteristic of wastewater from the first and second sampling was considerably the same. For the process wastewater, the pH of the first and second sampling was close to neutral. BOD of 20 and 22 mg/L were detected in wastewater from the first and second sampling, respectively, whereas COD of the first and second samplings were 95 and 101 mg/L, respectively. Wastewater from de-chlorination had BOD of 9 mg/L and COD of 29 mg/L for the first sampling, while that of second sampling was 11 and 44 mg/L, respectively.



By using equation 1 for calculation BOD and COD,  $BOD_{\text{summation}}$  of influent wastewater of Plant B were 51 and 50 mg/L for the first sampling and second sampling.  $COD_{\text{summation}}$  of 1194 and 1160 mg/L were detected in wastewater from the first and second sampling, respectively.

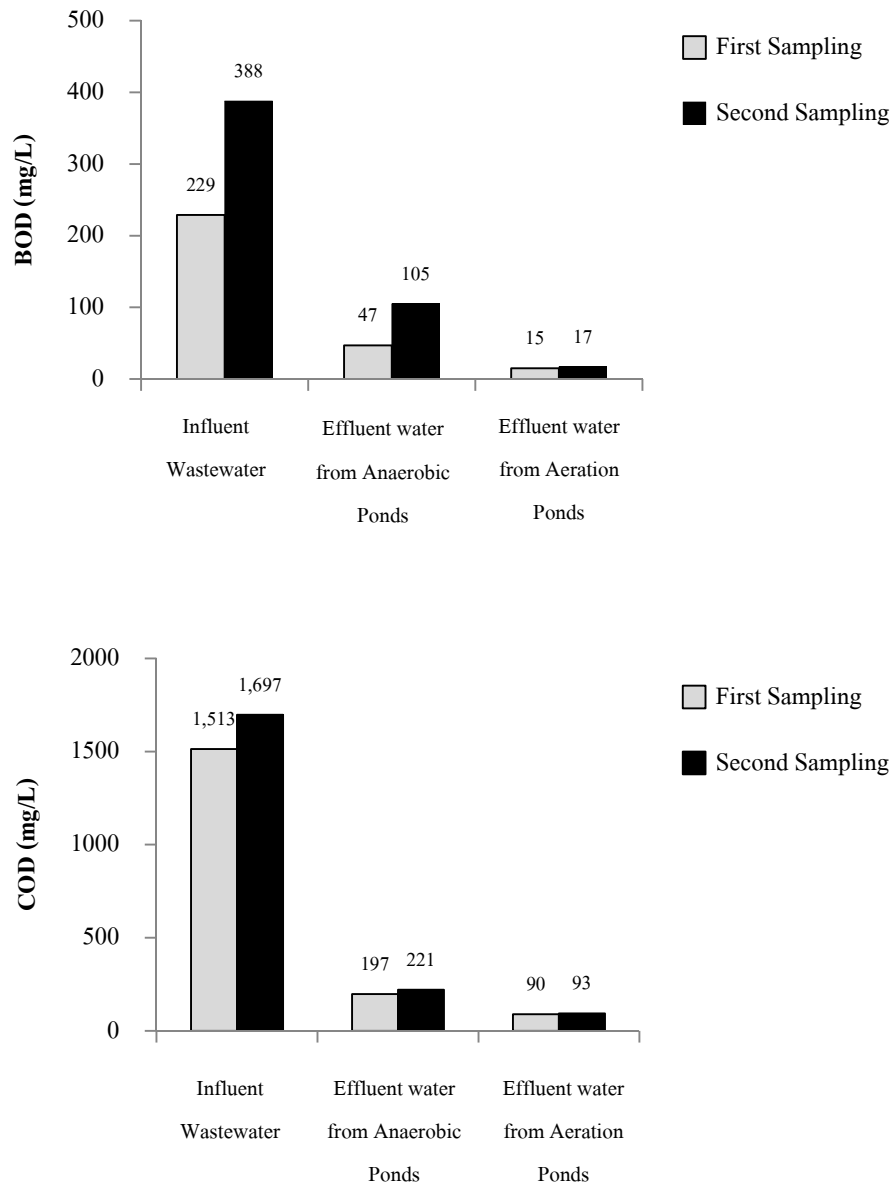
For Plant C, the  $BOD_{\text{summation}}$  of Influent wastewater were 16 and 18 mg/L for the first sampling and second sampling.  $COD_{\text{summation}}$  was 70 mg/L for the first sampling and 76 mg/L for second sampling.

BOD of 20 mg/L and COD of 120 mg/L were set in the industrial effluent standard, Thailand. During the time of sampling, the BOD and COD in wastewater of plant C were lower than standard.

By considering the BOD/COD, all wastewater from three plants had the low BOD/COD values, especially for Plant A. When the low level of BOD/COD value was found in the wastewater, it is hardly to treat by the biological treatment.

#### **4.3.2 The Reduction of BOD and COD**

Figure 4.1 presents the BOD and COD of influent and effluent water of each treatment system of Plant A. For the first sampling, the anaerobic ponds could reduce BOD by 79 percent as show in Table 4.2. The value of BOD in the effluent water from the anaerobic pond was 47 mg /L. The aeration ponds were also able to reduce BOD by 68 percent. The BOD in the effluent water from the aerobic ponds was 15 mg/L. For second sampling, the BOD of the influent wastewater was 388 mg/L. The anaerobic ponds reduced BOD by 73 percent. The BOD in the effluent water from the anaerobic ponds was 105 mg/L. The aeration ponds reduced BOD by 84 percent; BOD in the effluent water from the aeration ponds was 17 mg/L.



**Figure 4.1** BOD and COD of influent and effluent water of each wastewater treatment systems of Plant A

**Table 4.2** Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant A on BOD and COD

Parameters	Reduction efficiency <sup>a</sup>				Accumulated reduction efficiency <sup>b</sup>			
	Anaerobic Ponds		Aeration Ponds		Anaerobic Ponds		Aeration Ponds	
	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling
BOD	79	73	68	84	79	73	93	96
COD	87	87	55	58	87	87	94	95

**Remark:** <sup>a</sup> BOD reduction efficiency = ((BOD influent water to pond – BOD effluent water from pond)/ BOD influent water to pond)\*100.

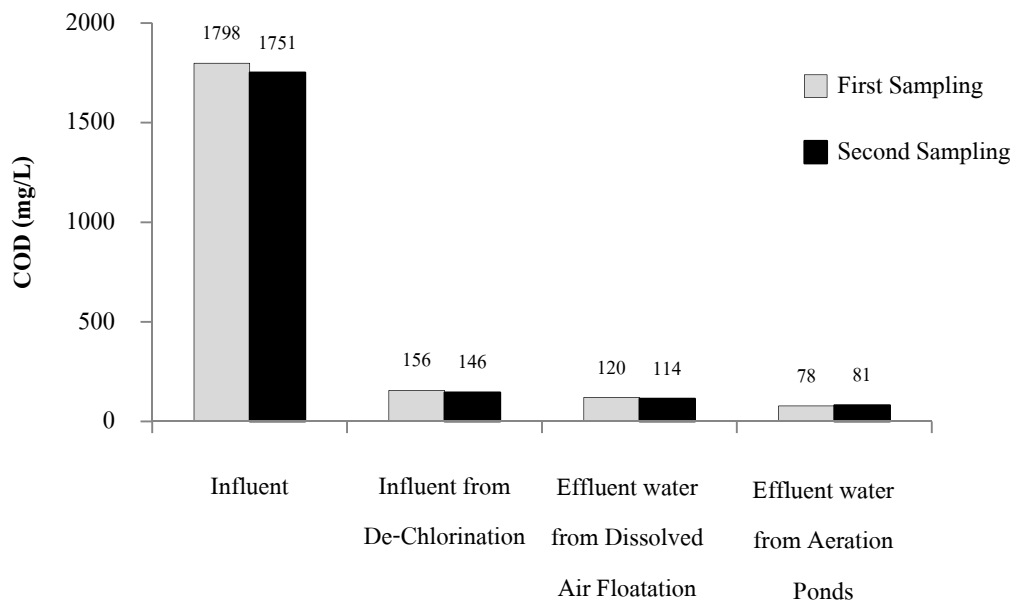
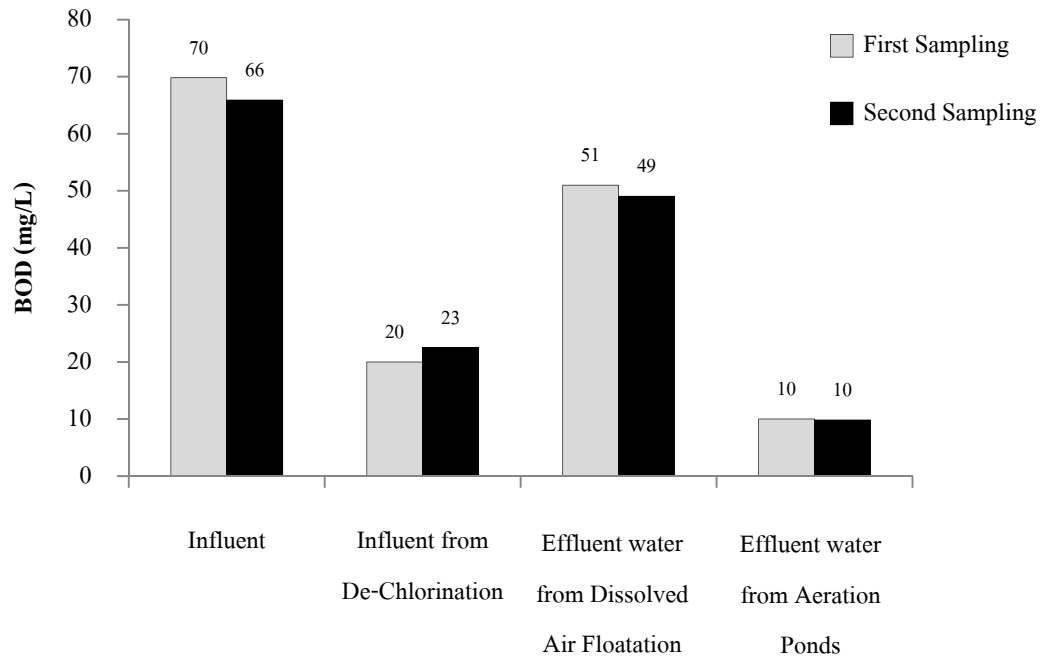
<sup>b</sup> Accumulated BOD reduction efficiency =((BOD influent wastewater – BOD effluent water from pond)/ BOD influent wastewater )\*100.

For COD reduction, the anaerobic ponds could reduce COD by 87 percent. The value of COD in the effluent water from the anaerobic pond was 197 mg/L. The aeration ponds were also able to reduction COD by 55 percent. The COD in the effluent water from the aerobic ponds was 90 mg/L. In the second sampling, the anaerobic ponds reduced COD by 87 percent. The COD in the effluent water after the anaerobic ponds was 221 mg/L. The aeration ponds reduced COD by 58 percent; COD in the effluent water from the aerobic ponds was 93 mg/L.

Given the total BOD and COD reduction; the wastewater treatment process of Plant A by anaerobic and aerobic ponds could reduce average BOD and COD by 95 and 94 percents, respectively. The anaerobic pond was the main course of action that reduced BOD and COD. The COD and BOD in treated wastewater from Plant A were lower than industrial effluent standards of Thailand.

In the case of Plant B (Figure 4.2), for the first sampling, DAF slightly reduced BOD. BOD of 51 mg/L was observed in the effluent water from DAF. The aeration ponds could reduction BODs by 80 percent as show in Table 4.3. The value of BOD in the effluent water from the aeration ponds was 10 mg/L. In the second sampling, BOD of wastewater and de-chlorination wastewater was 66 and 23 mg/L, respectively. The BOD of the effluent water from

DAF was 49 mg/L. The aeration ponds reduced BOD by 80 percent. The BOD in the effluent water from the aeration ponds was 10 mg/L.



**Figure 4.2** BOD and COD of influent and effluent water of each wastewater treatment systems of Plant B

**Table 4.3** Reduction efficiency and accumulated reduction efficiency of wastewater treatment system form Plant B on BOD and COD

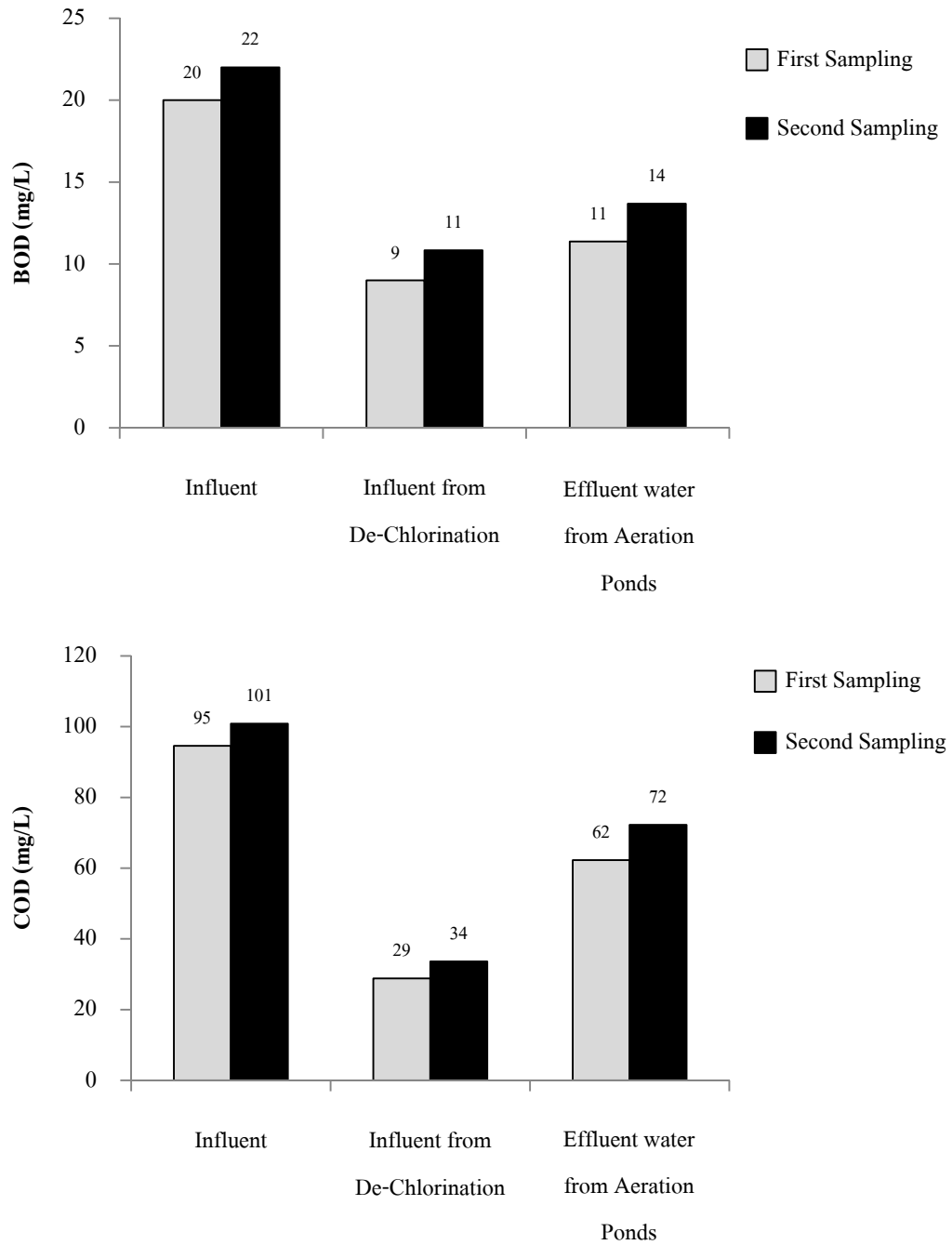
Parameters	Reduction efficiency				Accumulated reduction efficiency			
	DAF		Aeration Ponds		DAF		Aeration Ponds	
	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling
BOD	1	2	80	80	1	2	81	80
COD	90	90	36	29	90	90	94	93

DAF effectively reduced COD, it could reduce COD by 90 percent. The aeration ponds could reduction COD by 36 percent. The value of COD in the effluent water after the aeration ponds was 78 mg/L. In the second sampling, CODs of wastewater and de-chlorination wastewater were 1,751 and 146 mg/L, respectively. The COD of the effluent water from DAF was 114mg/L. The aeration ponds reduced COD by 29 percent. The COD in the effluent water after the aeration ponds was 81 mg/L.

Considering the total BOD and COD reduction, the wastewater treatment process of Plant B by DAF and aeration ponds could reduce BOD and COD in influent wastewater to lower than standard of BOD of 20 mg/L and COD of 120 mg/L. DAF was the main course of action on reducing COD while BOD was successfully removed by aeration ponds.

For Plant C (Figure 4.3), in the first sampling, BOD of 11 mg/L was observed in the effluent water from aeration ponds system. In the second sampling, The BOD of the effluent water from aeration ponds was 14mg/L. The aeration ponds could reduce BOD by 29 and 24 percent as show in Table 4.4, respectively. For the first sampling, COD of 62 mg/L was observed in the effluent water from aeration ponds system. In the second sampling, the COD of the effluent water from aeration ponds was 72 mg/L. The aeration ponds could reduce COD by 12 and 5 percent, respectively. Considering the total BOD and COD reduction, the wastewater

treatment process of Plant C by aeration ponds could reduce BOD and COD in wastewater to lower than standard value.



**Figure 4.3** BOD and COD of influent and effluent water of each wastewater treatment systems of Plant C

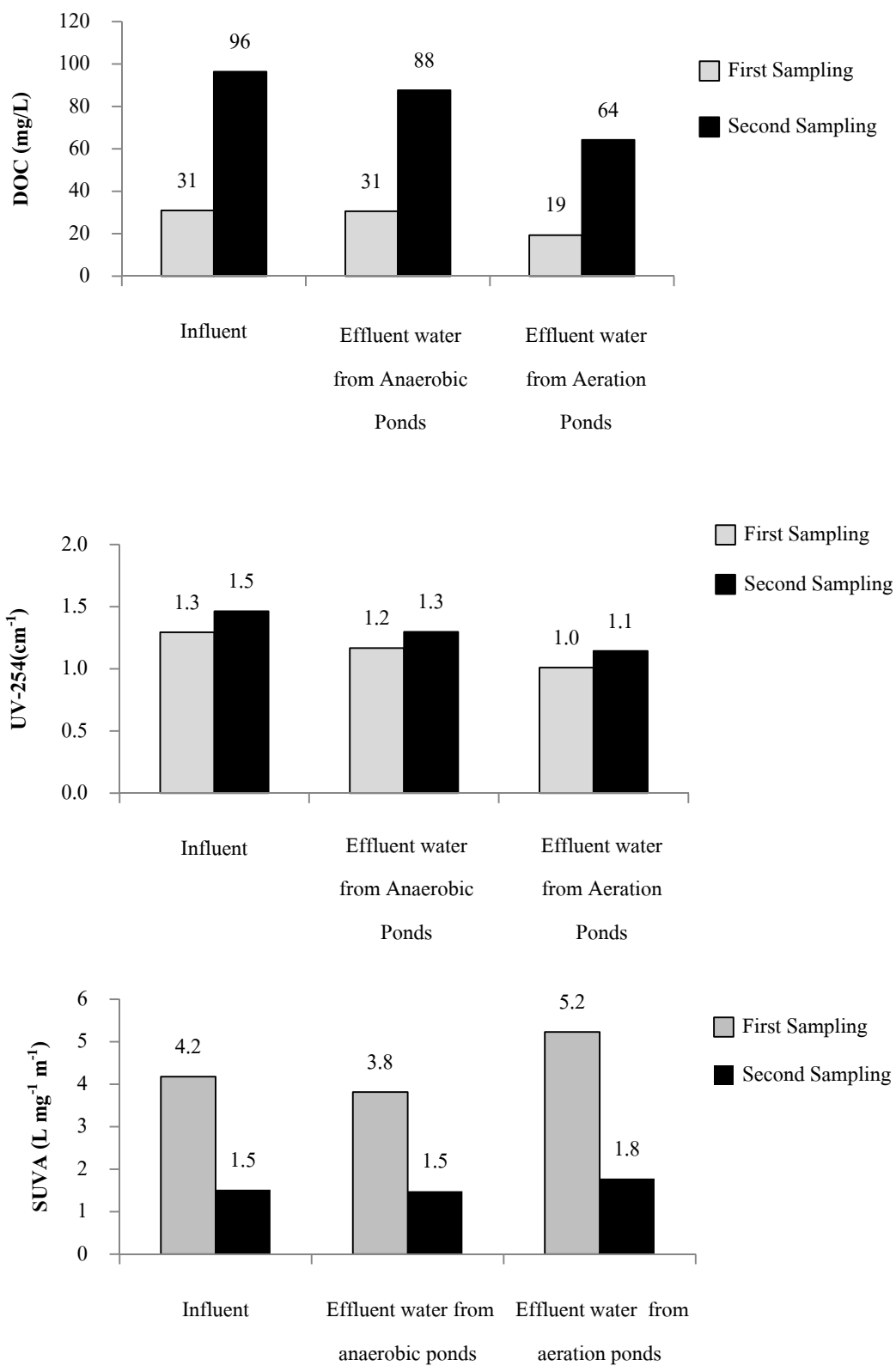
**Table 4.4** Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant C on BOD and COD

Parameters	Reduction efficiency		Accumulated reduction efficiency	
	Aeration Ponds		Aeration Ponds	
	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling
BOD	29	24	29	24
COD	12	5	12	5

For the conclusion of this part, the wastewater treatment process with consist of anaerobic ponds + aeration ponds in Plant A could be reduced high level of BOD and COD. DAF + aeration ponds of Plant B could reduce COD better than BOD. This could be because the COD values of water sample in this study were the unfiltered COD. In the process of DAF the bubbles adhere to the suspended matter, causing the suspended matter to float to the surface and form a froth layer which is then removed by a skimmer. So, DAF could be reduced COD in the form of suspended solid, whereas the aeration ponds could be used to treat the wastewater with low BOD and COD values.

#### 4.3.3 The reduction of DOC, UV-254 and SUVA

DOC is commonly used to present the level of aliphatic and aromatic hydrocarbons in the water whereas UV-254 is used to represent the level of aromatic in water. SUVA presents the ratio between aromatic hydrocarbon and the summation of aromatic hydrocarbon and aliphatic hydrocarbon. Figure 4.4 presents the DOC, UV-254 and SUVA of influent water of each wastewater treatments plant of Plant A.



**Figure 4.4** DOC, UV-254 and SUVA of influent and effluent water of each wastewater treatment systems of Plant A



For the first sampling, DOC of 31 mg/L was observed in the influent wastewater. The anaerobic ponds were considered to be not removed DOC. The value of DOC in the effluent water after the anaerobic pond was 30.6 mg/L. The aeration ponds were able to reduce DOC by 37 percent. The DOC in the effluent water from the aerobic ponds was 19 mg/L. In the second sampling, the DOC of the influent wastewater was 96 mg/L. The anaerobic ponds reduced DOC by 9 percent. The DOC in the effluent water after the anaerobic ponds was 88 mg/L. The aeration pond reduced DOC by 27 percent; DOC in the effluent water from the aerobic ponds was 64 mg/L.

UV-254 of  $1.3 \text{ cm}^{-1}$  was observed in the influent wastewater. The anaerobic ponds could reduce UV-254 by 10 percent. The value of UV-254 in the effluent water after the anaerobic pond was  $1.2 \text{ cm}^{-1}$ . The aeration ponds were also able to reduce UV-254 by 13 percent. The UV-254 in the effluent water from the aerobic ponds was  $1 \text{ cm}^{-1}$ . In the second sampling, the UV-254 of the influent wastewater was  $1.5 \text{ cm}^{-1}$ . The anaerobic ponds reduced UV-254 by 11 percent. The UV-254 in the effluent water after the anaerobic ponds was  $1.3 \text{ cm}^{-1}$ . The aeration pond reduced UV-254 by 12 percent; UV-254 in the effluent water from the aerobic ponds was  $1.1 \text{ cm}^{-1}$ .

The SUVA value for the first and second sampling in the effluent water from aeration ponds increased moderately to 5.2 and  $1.8 \text{ L mg}^{-1} \text{ m}^{-1}$ , respectively. These values were higher than their influent wastewater. Imai *et al.* (2002) reported that when a biological treatment had been employed in the sewage treatment plants, the SUVA value for its effluent should have been higher than that of its influent.

Given the total DOC and UV-254 reduction; the wastewater treatment process of Plant A by anaerobic and aerobic ponds could reduce average DOC and UV-254 by 34 and 21 percent, respectively. The aerobic pond was the main course of action that reduced DOC and UV-254. It can be stated that the aromatic compound was considerably difficult to reduce by anaerobic and aerobic ponds.

Tambo (1989) classified organic substances in DOC on the basis of their ability to adsorb light in the UV range. He divided them into two fractions: UV-sensitive and UV-insensitive. McKnight *et al.*, (1994) proposed that UV-sensitive fraction was mostly hydrophobic or aromatic in nature. According to the UV-254 reduction results in Table 4.5, the anaerobic and aeration ponds had moderate difficulty removing UV-sensitive organic fraction with aromatic characteristics when compared with the overall reduction of DOC.

In general, SUVA could be utilized to provide the relative index of humic content of the DOC in water (AWWA 1993). When the SUVA value in the effluent from aeration pond was increased, it was suspected that the biological process in the aeration ponds easily removed the UV-insensitive fraction from the effluent water after the anaerobic pond; Therefore, the remaining dissolved organic matter in the treated wastewater was mainly composed of more UV-sensitive fractions that provided a high relative index of DOC humic content (Musikavong and Wattanachira, 2007).

**Table 4.5** Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant A on DOC, UV-254 and SUVA

Parameters	Reduction efficiency <sup>a</sup>				Accumulated reduction efficiency <sup>b</sup>			
	Anaerobic Ponds		Aeration Ponds		Anaerobic Ponds		Aeration Ponds	
	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling
DOC	1	9	37	27	1	9	38	33
UV-254	10	11	13	12	10	11	22	22
SUVA	9	2	(-)	(-)	9	2	(-)	(-)

**Remark:** <sup>a</sup> DOC reduction efficiency = ((DOC influent water to pond – DOC effluent water from pond)/ DOC influent water to pond)\*100.

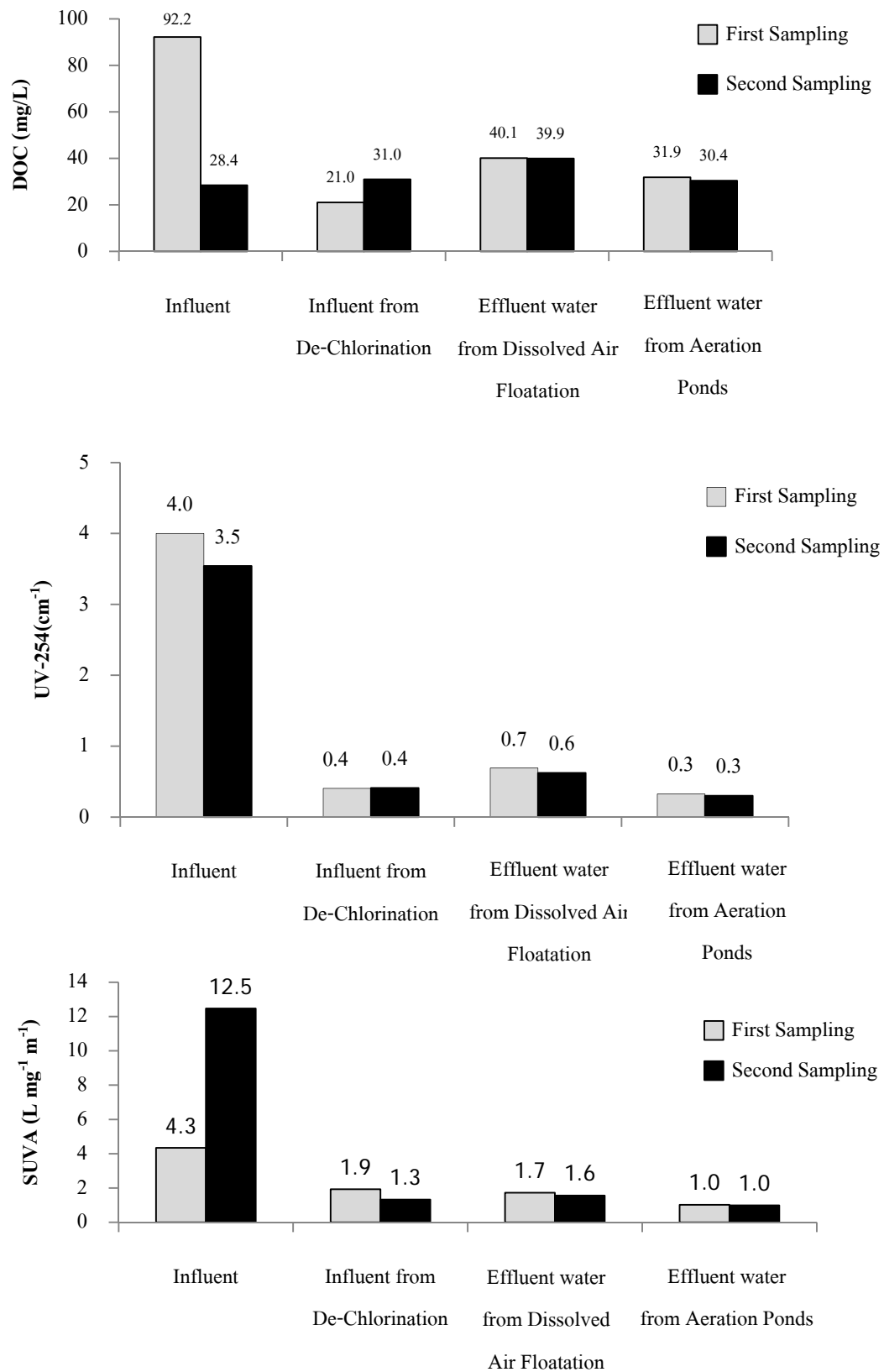
<sup>b</sup> Accumulated DOC reduction efficiency = ((DOC influent wastewater – DOC effluent water from pond)/ DOC influent wastewater )\*100 (The reduction efficiency and accumulated reduction efficiency of the stabilization pond process on UV-254 and SUVA were calculated using the mentioned equations.).

In the case of Plant B (Figure 4.5), for the first sampling, DOCs of wastewater and de-chlorination wastewater were 92.2 and 21 mg/L, respectively. By using equation (1) to calculate the DOC value,  $DOC_{\text{summation}}$  of influent wastewater for first and second sampling were 66 and 67 mg/L, respectively. DOC of 40.1 mg/L was observed in the effluent water from DAF. DAF reduced DOC by 39 percent. The aeration ponds could reduction DOC by 21 percent as show in table 4.6. The value of DOC in the effluent water after the aeration ponds was 31.9 mg/L. In the second sampling, DOCs of wastewater and de-chlorination wastewater were 28.4 and 31 mg/L, respectively. The DOC of the effluent water from DAF was 39.9 mg/L. The aeration ponds reduced DOC by 24 percent. The DOC in the effluent water after the aeration ponds was 30.4 mg/L. The DAF could reduction DOCs by 39 and 36 percent, respectively.

UV-254 of 4 and  $0.41 \text{ cm}^{-1}$  were detected in wastewater and de-chlorination wastewater, respectively. The  $UV-254_{\text{summation}}$  of influent wastewater for the first and second sampling were  $1.29$  and  $1.46 \text{ cm}^{-1}$ , respectively. UV-254 of  $0.69 \text{ cm}^{-1}$  was observed in the effluent water from DAF. DAF effectively reduced UV-254. The aeration ponds could reduction UV-254 by 53 percent. The value of UV-254 in the effluent water after the aeration ponds was  $0.3 \text{ cm}^{-1}$ . In the second sampling, UV-254 of wastewater and de-chlorination wastewater were  $3.5$  and  $0.40 \text{ cm}^{-3}$ , respectively. The UV-254 of the effluent water from DAF was  $0.6 \text{ cm}^{-1}$ . The aeration ponds reduced UV-254 by 52 percent. The UV-254 in the effluent water after the aeration ponds was  $0.30 \text{ cm}^{-1}$ .

**Table 4.6** Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant B on DOC, UV-254 and SUVA

Parameters	Reduction efficiency				Accumulated reduction efficiency			
	DAF		Aeration Ponds		DAF		Aeration Ponds	
	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling
DOC	39	36	21	24	39	36	52	55
UV-254	74	74	53	52	74	74	88	87
SUVA	50	81	41	37	50	81	70	88



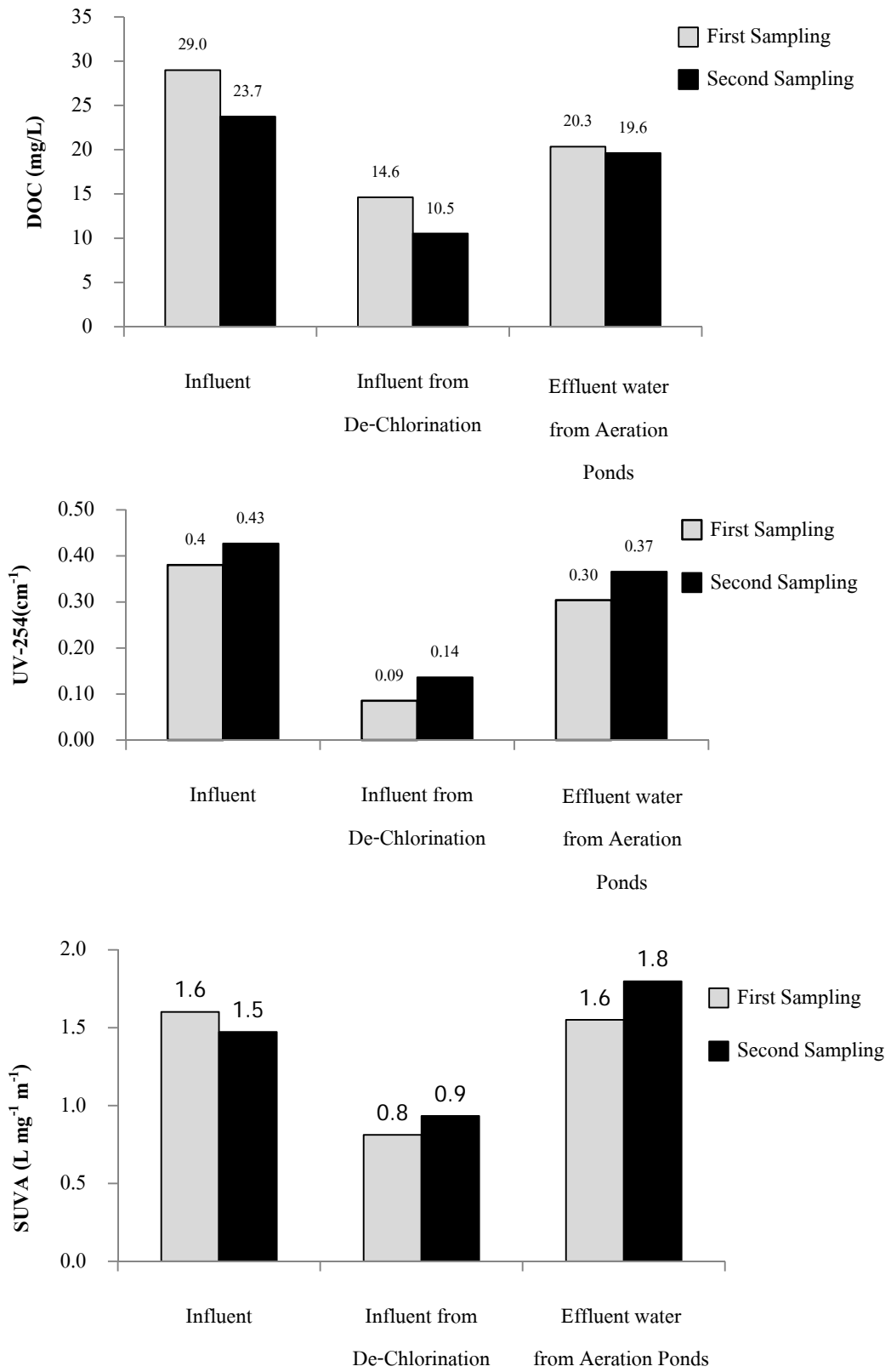
**Figure 4.5** DOC, UV-254 and SUVA of the water sample in the wastewater treatment plant of Plant B

Based on the DOC and UV-254 reduction results that show in Table 4.6, it can be stated that the DAF was the main course of action that reduced DOC and UV-254.

SUVA of 4.3 and 1.9  $\text{L mg}^{-1} \text{m}^{-1}$  were detected in wastewater and de-chlorination wastewater, respectively. SUVA of 1.7  $\text{L mg}^{-1} \text{m}^{-1}$  was observed in the effluent water from DAF. DAF could reduce SUVA by 50 percent. The aeration ponds could reduce SUVA by 41 percent. The value of SUVA in the effluent water from the aeration ponds was 1  $\text{L mg}^{-1} \text{m}^{-1}$ . In the second sampling, SUVA of wastewater and de-chlorination wastewater were 12.5 and 1.3  $\text{L mg}^{-1} \text{m}^{-1}$ , respectively. The SUVA of the effluent water from DAF was 1.6  $\text{L mg}^{-1} \text{m}^{-1}$ . DAF could reduce SUVA by 80 percent. The aeration ponds reduced SUVA by 37 percent. The SUVA in the effluent water from the aeration ponds was 1  $\text{cm}^{-1}$ .

It can be stated that DAF was the main course of action that could reduce DOC, UV-254, and SUVA. Interestingly, the aeration pond after DAF could reduce DOC, UV-254 and SUVA. This observation corresponded with previous study (Imai, 2002). The installation of DAF before the biological treatment should support the reduction of aromatic compounds.

In the case of Plant C (Figure 4.6), for the first sampling, DOC of wastewater and de-chlorination wastewater were 29 and 14.6 mg/L, respectively. The  $\text{DOC}_{\text{summation}}$ ,  $\text{UV-254}_{\text{summation}}$ ,  $\text{SUVA}_{\text{summation}}$  for the first sampling were 44 mg/L, 0.5  $\text{cm}^{-1}$ , 2  $\text{L mg}^{-1} \text{m}^{-1}$ , respectively. In the second sampling,  $\text{DOC}_{\text{summation}}$ ,  $\text{UV-254}_{\text{summation}}$ ,  $\text{SUVA}_{\text{summation}}$  were 34 mg/L, 0.6  $\text{cm}^{-1}$ , 2  $\text{L mg}^{-1} \text{m}^{-1}$ , respectively. DOC of 20.3 mg/L was observed in the effluent water from aerated lagoon system. In the second sampling, DOCs of wastewater and de-chlorination wastewater were 23.7 and 10.5 mg/L, respectively. The DOC of the effluent water from aeration ponds was 19.6 mg/L. The aeration ponds could reduce DOC by 14 percent. UV-254 of 0.38 and 0.09  $\text{cm}^{-1}$  were detected in wastewater and de-chlorination wastewater, respectively. The value of UV-254 in the effluent water after the aeration ponds was 0.30  $\text{cm}^{-1}$ . In the second sampling, UV-254s of wastewater and de-chlorination wastewater were 0.43 and 0.14  $\text{cm}^{-1}$ , respectively. The UV-254 of the effluent water from aeration ponds was 0.37  $\text{cm}^{-1}$ . The aeration ponds could not reduce UV-254. Aeration ponds may have less capability of reducing DOM.



**Figure 4.6** DOC, UV-254 and SUVA of the water sample in the wastewater treatment plant of Plant C

Based on the DOC, UV-254 and SUVA reduction results that show in Table 4.7, it can be stated that the treatment wastewater system of Plant C could not reduce DOM in influent wastewater.

**Table 4.7** Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant C on DOC, UV-254 and SUVA

Parameters	Reduction efficiency		Accumulated reduction efficiency	
	Aeration Ponds		Aeration Ponds	
	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling
DOC	16	(-)	14	(-)
UV-254	(-)	(-)	(-)	(-)
SUVA	(-)	(-)	(-)	(-)

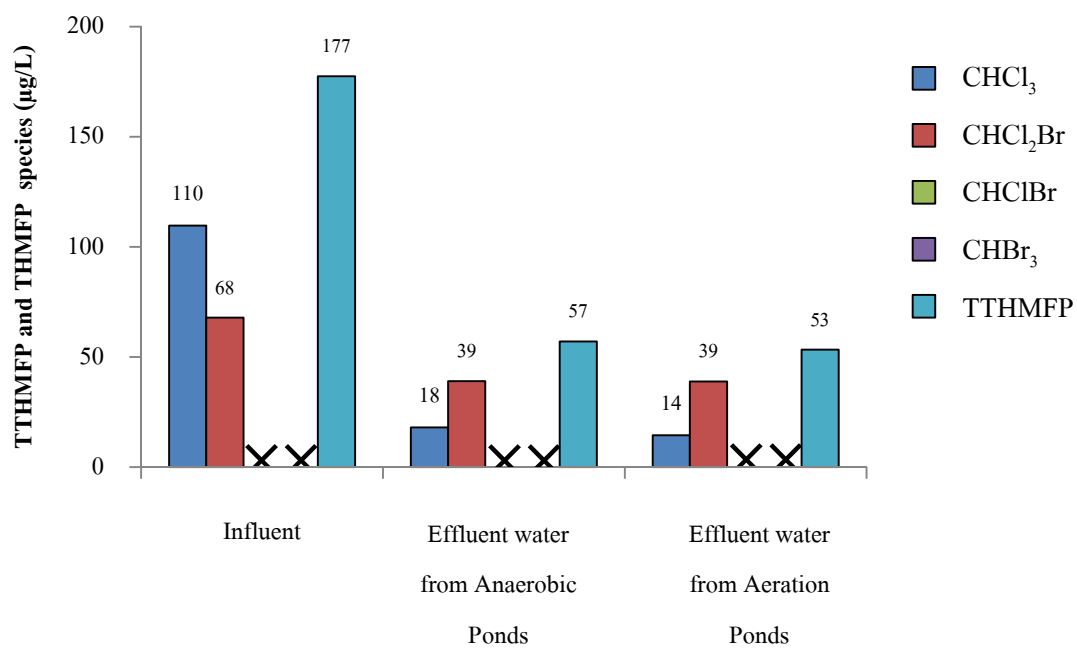
#### 4.3.4 The reduction of THMFP

In general, THMs refers to the concentration of THMs in the water measured at the time of the sampling. This value represents the amount of THMs that could adversely affect the consumers who utilize the water. THMs have recently been promulgated under regulation in the USEPA disinfectant/Disinfection By-Products (D/DBPs) Rule (United States Environmental Protection Agency or USEPA, 1998). The current drinking water maximum contaminant level for four THMs, chloroform ( $\text{CHCl}_3$ ), dichlorobromoform ( $\text{CHCl}_2\text{Br}$ ), dibromochloroform ( $\text{CHClBr}_2$ ) and bromoform ( $\text{CHBr}_3$ ), is set at 80  $\mu\text{g}/\text{L}$ . The THMFP has been commonly utilized to determine the THMs at the completion of the reaction condition between DOM and the excess amount of chlorine. THMFP was utilized to monitor the highest possible concentrations of THMs in the water (Musikavong and Wattanachira, 2007).

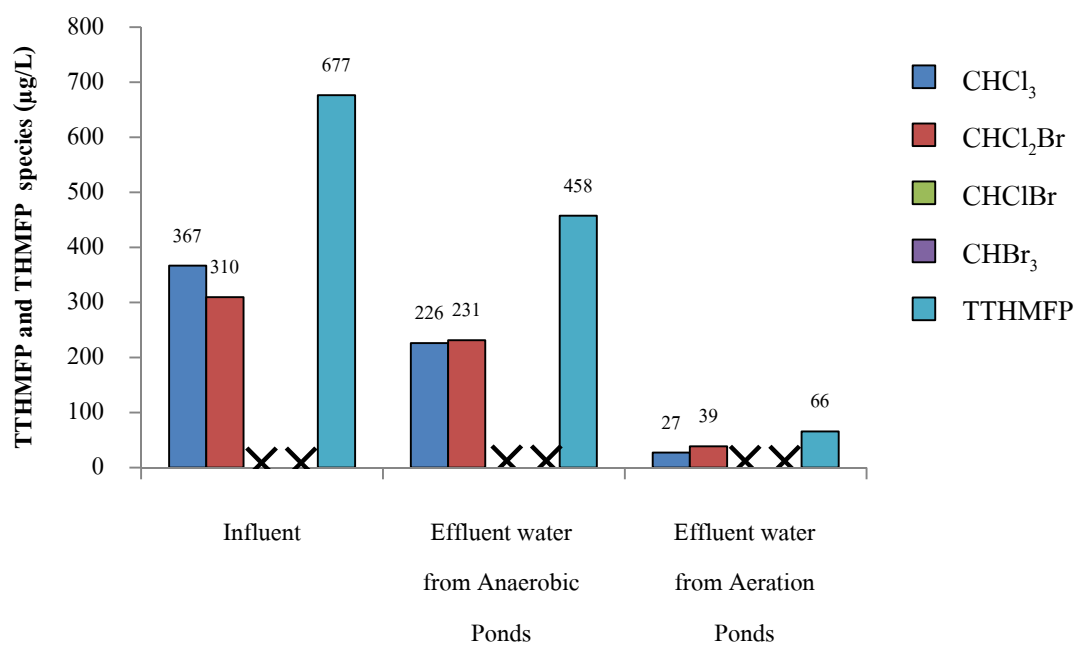
Figure 4.7 presents the THMFP and THMFP species in influent and effluent water from each water treatment systems of Plant A. For Plant A THMFP of 177  $\mu\text{g}/\text{L}$  was observed in the influent wastewater at the first sampling. This value came from the summation of the  $\text{CHCl}_3$ -FP at 110  $\mu\text{g}/\text{L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 68  $\mu\text{g}/\text{L}$ . After wastewater was treated by anaerobic ponds, the THMFP,  $\text{CHCl}_3$ -FP and  $\text{CHCl}_2\text{Br}$ -FP were reduced by 68, 84, 43 percents,

respectively as show in Table4.8. The THMFP of 57  $\mu\text{g/L}$  was found in effluent water from anaerobic ponds. This came from the summation of  $\text{CHCl}_3$ -FP at 18  $\mu\text{g/L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 39  $\mu\text{g/L}$ . The effluent water from the aeration ponds had THMFP of 53  $\mu\text{g/L}$ , it composed of  $\text{CHCl}_3$ -FP at 14  $\mu\text{g/L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 39  $\mu\text{g/L}$ . The aeration ponds slightly reduced THMFP.





a) First Sampling



b) Second Sampling

**Figure 4.7** THMFP and THMFP species of the water sample from the wastewater treatment plant of Plant A

**Table 4.8** Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant A on THMFP.

Parameters	Reduction efficiency <sup>a</sup>				Accumulated reduction efficiency <sup>b</sup>			
	Anaerobic Ponds		Aeration Ponds		Anaerobic Ponds		Aeration Ponds	
	1 <sup>st</sup>	2 <sup>nd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>
	sampling	sampling	sampling	sampling	sampling	sampling	sampling	sampling
TTHMFP	68	32	7	86	68	32	70	90
CHCl <sub>3</sub>	84	38	20	88	84	38	87	93
CHCl <sub>2</sub> Br	43	25	0	83	43	25	43	88

**Remark:** <sup>a</sup>THMFP reduction efficiency = ((THMFPinfluent water to pond – THMFP effluent water from pond)/THMFPinfluent water to pond)\*100.

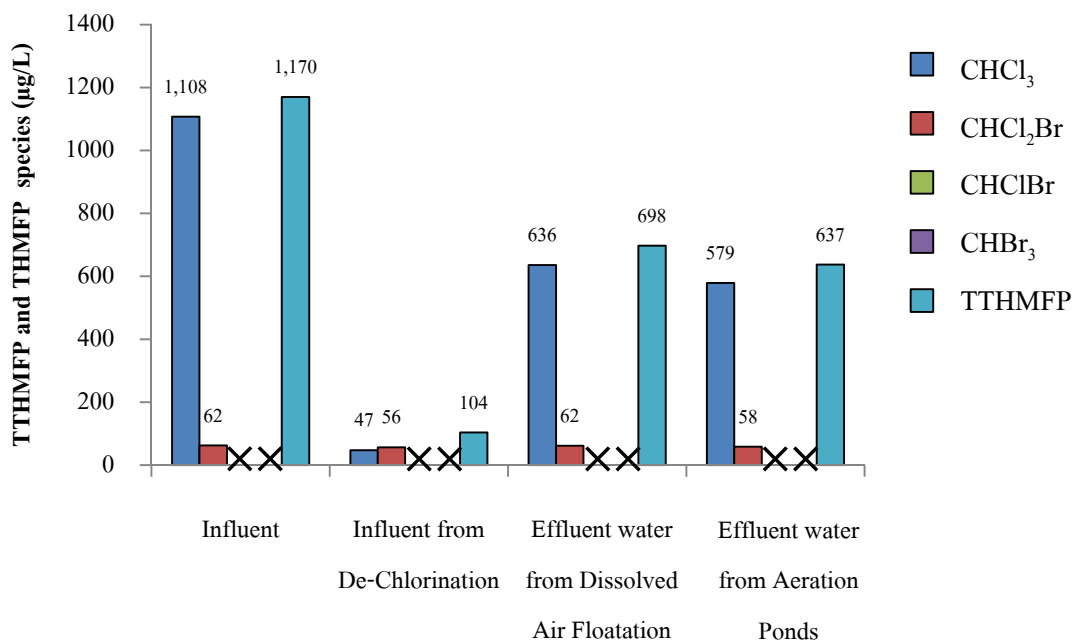
<sup>b</sup>AccumulatedTHMFP reduction efficiency =((THMFPinfluent wastewater – THMFPeffluent water from pond)/THMFP influent wastewater )\*100.

In the second sampling, THMFP in influent wastewater was as high as 677 µg/L. This value came from the summation of the CHCl<sub>3</sub>-FP at 367 µg/L and CHCl<sub>2</sub>Br-FP at 310 µg/L. After wastewater was treated by anaerobic ponds, the THMFP, CHCl<sub>3</sub>-FP and CHCl<sub>2</sub>Br-FP were reduced by 32, 38 and 25 percents, respectively. The THMFP of 458 µg/L was detected in effluent water from anaerobic ponds. This came from the summation of CHCl<sub>3</sub>-FP at 226 µg/L and CHCl<sub>2</sub>Br-FP at 231 µg/L.

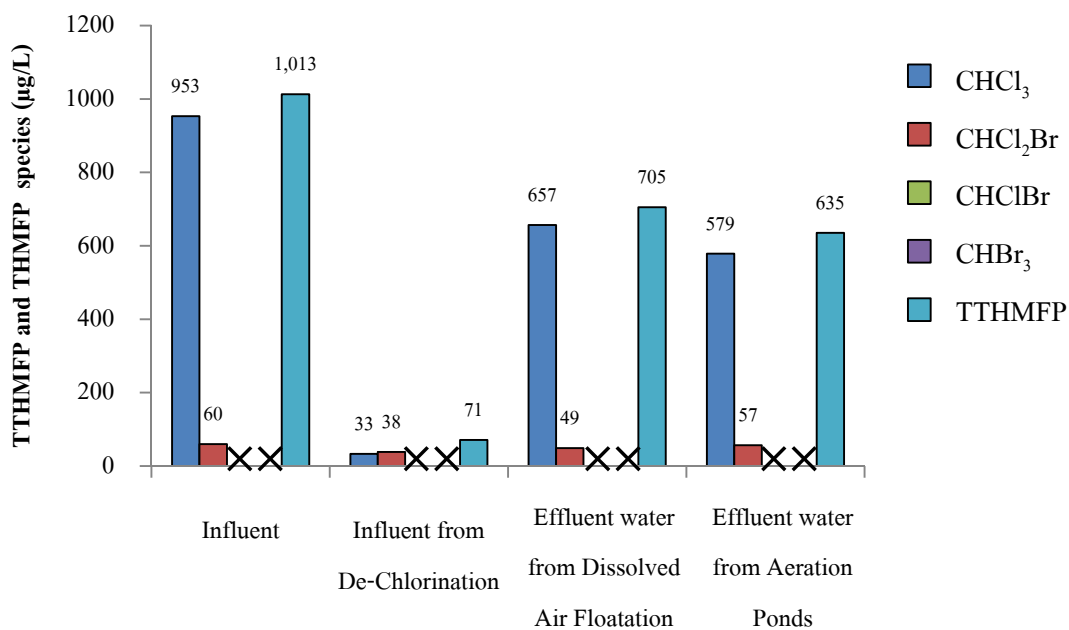
The effluent water from the aeration ponds had THMFP of 66 µg/L, it composed of CHCl<sub>3</sub>-FP at 27 µg/L and CHCl<sub>2</sub>Br-FP at 39 µg/L. The aeration ponds reduced THMFP, CHCl<sub>3</sub>-FP and CHCl<sub>2</sub>Br-FP by 86, 88, 83 percents, respectively. It could be stated that the anaerobic and aeration pond could reduce THMFP to the lower than THMs standard. It must be noted that for low THMFP in influent wastewater (first sampling), anaerobic pond was the main course of action that reduced THMFP. In the case of high THMFP (second sampling) anaerobic ponds could reduce THMFP in some levels but aerobic ponds have a high ability to reduce THMFP.

By considering the THMFP species,  $\text{CHCl}_3$ -FP was the major THMFP species in the wastewater. Interestingly, in the effluent water from anaerobic and aerobic ponds, the  $\text{CHCl}_2\text{Br}$ -FP was slightly higher than  $\text{CHCl}_3$ -FP. This observation was not matched with previous works. Musikavong and Wattanachira (2008) found that  $\text{CHCl}_3$ -FP was the major THMFP species in wastewater and treated wastewater from stabilization ponds of industrial state.

For Plant B (Figure 4.8), in the first sampling, THMFP in influent wastewater was as high as 1,170  $\mu\text{g/L}$ . This value came from the summation of the  $\text{CHCl}_3$ -FP at 1,108  $\mu\text{g/L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 62  $\mu\text{g/L}$ . THMFP of 104  $\mu\text{g/L}$  were detected in influent from de-chlorination. It composed of the summation of the  $\text{CHCl}_3$ -FP at 47  $\mu\text{g/L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 56  $\mu\text{g/L}$ . By using equation (1) to calculate the THMFP value,  $\text{THMFP}_{\text{summation}}$  of influent wastewater for the first sampling was 738  $\mu\text{g/L}$ . After wastewater was treated by DAF, the THMFP of 698  $\mu\text{g/L}$  was detected in effluent water from DAF. This came from the summation of  $\text{CHCl}_3$ -FP at 636  $\mu\text{g/L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 62  $\mu\text{g/L}$ . DAF could reduce THMFP,  $\text{CHCl}_3$ -FP and  $\text{CHCl}_2\text{Br}$ -FP by 5, 14, 92 percents, respectively as show in Table 4.9. The effluent water from the aeration ponds had THMFP of 637  $\mu\text{g/L}$ , it composed of  $\text{CHCl}_3$ -FP at 579  $\mu\text{g/L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 58  $\mu\text{g/L}$ . The aeration ponds reduced THMFP by 9 percent.



a) First Sampling



b) Second Sampling

**Figure 4.8** THMFP and THMFP species of the water sample from the wastewater treatment plant of Plant B

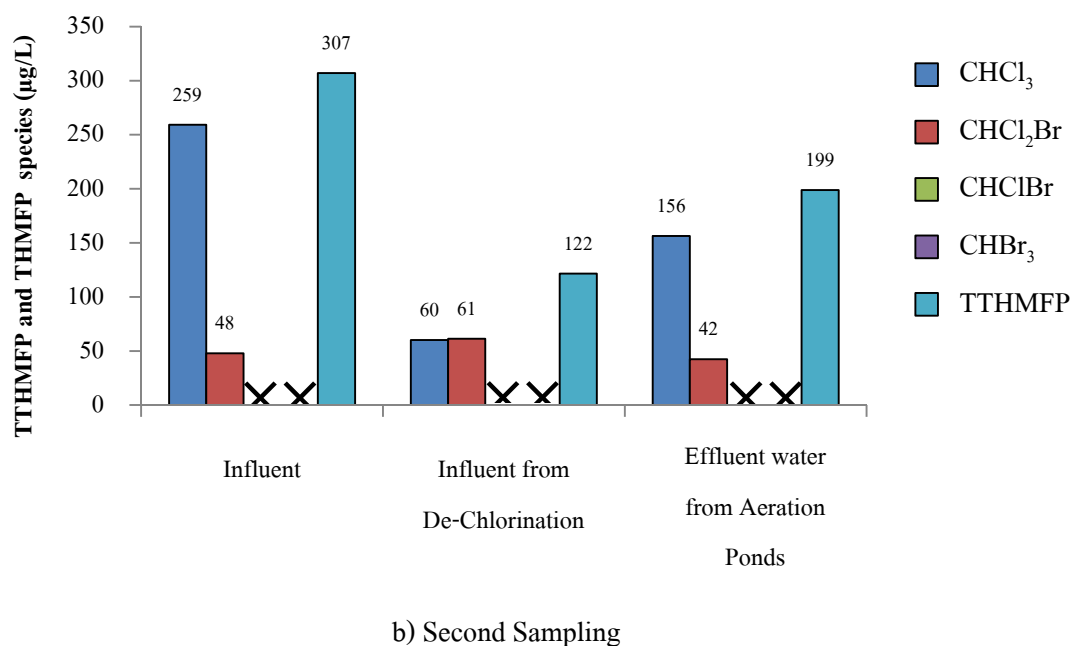
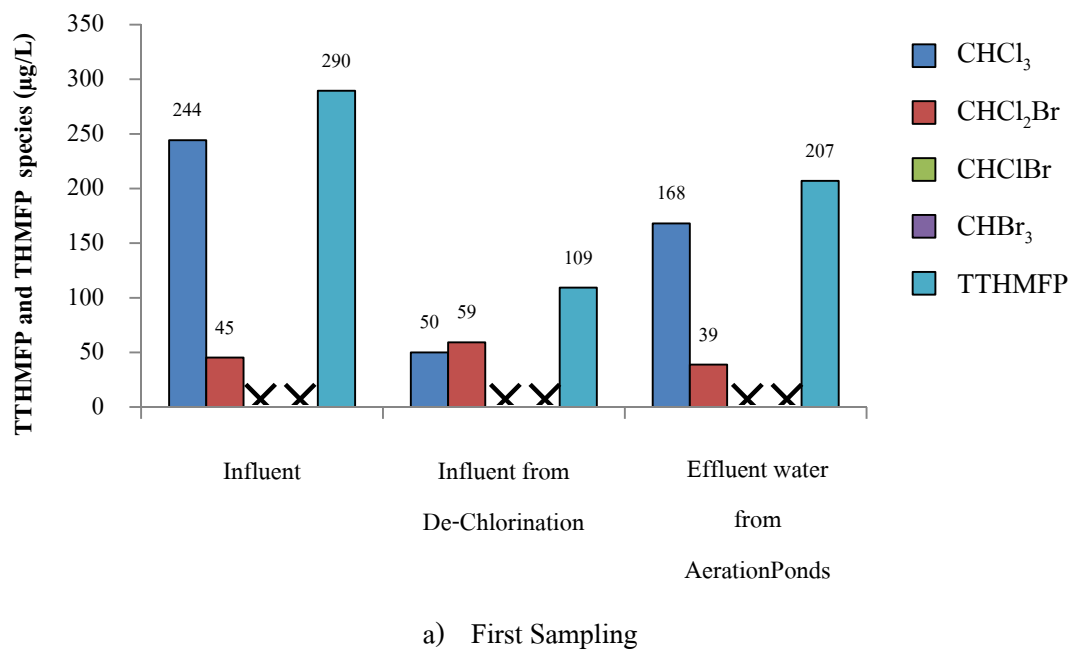
**Table 4.9** Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant B on THMFP

Parameters	Reduction efficiency <sup>a</sup>				Accumulated reduction efficiency <sup>b</sup>			
	DAF		Aeration Ponds		DAF		Aeration Ponds	
	1 <sup>st</sup>	2 <sup>nd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>	1 <sup>st</sup>	2 <sup>nd</sup>
	sampling	sampling	sampling	sampling	sampling	sampling	sampling	sampling
TTHMFP	5	(-)	9	10	5	(-)	14	5
CHCl <sub>3</sub>	14	1	9	12	14	1	9	13
CHCl <sub>2</sub> Br	92	93	5	(-)	92	93	92	91

THMFP of 1,013  $\mu\text{g/L}$  was detected in influent wastewater at the second sampling. This value came from the summation of the CHCl<sub>3</sub>-FP at 953  $\mu\text{g/L}$  and CHCl<sub>2</sub>Br-FP at 60  $\mu\text{g/L}$ . THMFP of 71  $\mu\text{g/L}$  was detected in influent from de-chlorination. It composed of the summation of the CHCl<sub>3</sub>-FP at 33  $\mu\text{g/L}$  and CHCl<sub>2</sub>Br-FP at 38  $\mu\text{g/L}$ . By using equation (1) to calculate the THMFP value, THMFP<sub>summation</sub> of influent wastewater for the second sampling was 666  $\mu\text{g/L}$ . After wastewater was treated by DAF, the THMFP of 705  $\mu\text{g/L}$  was detected in effluent water from DAF. DAF could reduce CHCl<sub>3</sub>-FP and CHCl<sub>2</sub>Br-FP by 1 and 93 percents, respectively. This came from the summation of CHCl<sub>3</sub>-FP at 657  $\mu\text{g/L}$  and CHCl<sub>2</sub>Br-FP at 49  $\mu\text{g/L}$ . The effluent water from the aeration ponds had THMFP of 635  $\mu\text{g/L}$ , it composed of CHCl<sub>3</sub>-FP at 579  $\mu\text{g/L}$  and CHCl<sub>2</sub>Br-FP at 57  $\mu\text{g/L}$ . The aeration ponds reduced THMFP by 10 percent. It could be stated that treated wastewater from Plant B had extremely high THMFP value than THMs standard.

The THMFP in treated wastewater from DAF + aeration ponds was greatly higher than that of treated wastewater by anaerobic and aerations ponds. It may due to the different in raw material in the production process. In the rubber glove manufacturing process, the raw material can be the para rubber or synthesis rubber. The raw material used in Plant B may have a high reactivity to form THMs than raw material used in Plant A. To reduce the THMFP discharged to water source, the major focus should be on the reduction of THMFP of treated wastewater from Plant B.

Figure 4.9 presents THMFP and THMFP species of the water sample in the wastewater treatment plant of Plant C. In the first sampling, THMFP of influent wastewater was 290  $\mu\text{g/L}$ . This value came from the summation of the  $\text{CHCl}_3$ -FP at 244  $\mu\text{g/L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 45  $\mu\text{g/L}$ . THMFP of 109  $\mu\text{g/L}$  was detected in de-chlorination wastewater. It composed of the summation of the  $\text{CHCl}_3$ -FP at 50  $\mu\text{g/L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 59  $\mu\text{g/L}$ . By using equation (1) to calculate the THMFP value,  $\text{THMFP}_{\text{summation}}$  of influent wastewater for first was 186  $\mu\text{g/L}$ . After wastewater was treated by aeration pond, the THMFP of 207  $\mu\text{g/L}$  was detected. This came from the summation of  $\text{CHCl}_3$ -FP at 168  $\mu\text{g/L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 39  $\mu\text{g/L}$ . The aeration ponds reduced  $\text{CHCl}_3$ -FP and  $\text{CHCl}_2\text{Br}$ -FP were reduced by 10 and 79 percents, respectively as show in Table 4.10. For the second sampling, THMFP of 307  $\mu\text{g/L}$  was detected in influent wastewater. This value came from the summation of the  $\text{CHCl}_3$ -FP at 259  $\mu\text{g/L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 48  $\mu\text{g/L}$ . The de-chlorination wastewater had a THMFP of 122  $\mu\text{g/L}$ , it composed of  $\text{CHCl}_3$ -FP at 60  $\mu\text{g/L}$  and  $\text{CHCl}_2\text{Br}$ -FP at 61  $\mu\text{g/L}$ . After wastewater was treated by aeration pond system, the THMFP of 199  $\mu\text{g/L}$  was detected. The aeration ponds could not reduce THMFP. It can be stated that THMFP in treated wastewater from Plant C was moderately higher than THMs standard. For the THMFP species in wastewater from Plant B and Plant C,  $\text{CHCl}_3$  was detected as major THMFP species.  $\text{CHCl}_2\text{Br}_3$  was detected in low level in compared with  $\text{CHCl}_3$ .



**Figure 4.9** THMFP and THMFP species of the water sample from wastewater treatment plant of Plant C

**Table 4.10** Reduction efficiency and accumulated reduction efficiency of wastewater treatment system of Plant C on THMFP

Parameters	Reduction efficiency <sup>a</sup>		Accumulated reduction efficiency <sup>b</sup>	
	Aeration Ponds		Aeration Ponds	
	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling	1 <sup>st</sup> sampling	2 <sup>nd</sup> sampling
TTHMFP	(-)	(-)	(-)	(-)
CHCl <sub>3</sub>	10	(-)	10	(-)
CHCl <sub>2</sub> Br	79	(-)	79	(-)

The obtained THMFP of the treated wastewater in this study was compared with raw water supply of Thailand (as shown in Table 4.11). It was found that the THMFP values of the treated wastewater from plant A and C were considerably lower than that of raw water supply from other sources in Thailand. Treated wastewater of plant B was considerably high in compared with THMFP of raw water supply from other sources.

**Table 4.11** THMFP in the treated effluent of this study compared with the values from raw water supply sources in southern of Thailand

Water source	THMFP ( $\mu\text{g L}^{-1}$ )
Raw water U-Tapao Canal, songkhla, Thailand (Srimuang K., 2011)	729
The Chao Phraya River Bangkok, Thailand (Panyapinyopolet <i>et al.</i> , 2005)	313
Mae-Kuang Reservoir, Chiang Mai, Thailand (Homklin, 2004)	236
Mae-Sa River, Chiang Mai, Thailand (Homklin, 2004)	113
Plant A (first)	53-66
Plant B (second)	635-637
Plant C (Third)	199-207



#### 4.4 Correlation between THMFP and DOC, and THMFP and UV-254

Regression and correlation coefficients between THMFP and DOM surrogate parameters were presented in Table 4.12. In the case of Plant A, moderate correlations were obtained from relationships between THMFP and DOC, ( $R^2$  of 0.7256) and between THMFP and UV-254 ( $R^2$  of 0.7769). The fitting equation for predicting THMFP in wastewater from Plant A could be expressed as follows:  $\text{THMFP } (\mu\text{g L}^{-1}) = 1465.3 \text{ UV-254 } (\text{cm}^{-1}) - 1553.5$ . In case of Plant B, a poor correlation and a fair correlation ( $R^2 = 0.5840$ ) were observed from relationships between THMFP and DOC and THMFP and UV-254, respectively. For plant C, moderate correlations of THMFP and DOC and THMFP and UV-254 were found with  $R^2$  of 0.8365 and 0.8690, respectively. The appropriate equation for predicting THMFP in the wastewater from Plant C could be expressed as follows:  $\text{THMFP } (\mu\text{g L}^{-1}) = 546.96 \text{ DOC } (\text{mg/L}) + 50.639$ . In conclusion, DOC and UV-254, moderately correlated with THMFP in wastewater from Plant A and C. White et al (White *et al.*, 2003) studied natural organic matter and DBP formation potential of water resources for different drinking water systems in Alaska. By using the data from fifteen surface water sources, regression values ( $R^2$ ) of THMFP and UV-254 and of THMFP and DOC, were 0.99, and 0.87, respectively. On this basis, it can be stated that DOC and UV-254 could be used to preliminary predict the THMFP.

**Table 4.12** Correlation coefficient between THMFP and DOC, and THMFP and UV-254

Y	X	Source	n	R <sup>2</sup>	equation	correlation
THMFP	DOC	Plant A	6	0.7256	THMFP ( $\mu\text{g L}^{-1}$ ) = 6.8191 DOC (mg/L) - 126.02	Moderate
		Plant B	8	0.4171	THMFP ( $\mu\text{g L}^{-1}$ ) = 11.2 DOC (mg/L) + 188.23	Poor
		Plant C	6	0.8365	THMFP ( $\mu\text{g L}^{-1}$ ) = 11.513 DOC (mg/L) - 20.607	Moderate
THMFP	UV-254	Plant A	6	0.7769	THMFP ( $\mu\text{g L}^{-1}$ ) = 1465.3 UV-254 ( $\text{cm}^{-1}$ ) - 1553.5	Moderate
		Plant B	8	0.5840	THMFP ( $\mu\text{g L}^{-1}$ ) = 190.64 UV-254 ( $\text{cm}^{-1}$ ) + 383.65	Fair
		Plant C	6	0.8690	THMFP ( $\mu\text{g L}^{-1}$ ) = 546.96 UV-254 ( $\text{cm}^{-1}$ ) + 50.639	Moderate

#### 4.5 Concluding remarks

The wastewater and treated wastewater from three rubber glove manufacturing processes were collected and determined the performance capability of BOD, COD, DOC, UV-254, and THMFP reductions. 1) DAF and aeration ponds of Plant B and 2) Aeration ponds of Plant C could reduce high BOD and COD values in wastewater to be lower than effluent standard. Aeration ponds could also reduce low BOD and COD in wastewater to be lower than standard. For DOC and UV-254 reduction, the anaerobic and aeration pond could reduce DOC and UV-254 by 34 and 21 percents, respectively. The DOC and UV-254 in the treated wastewater by DAF and aeration ponds were lower than treated wastewater by anaerobic and aerobic ponds. The level of DOC and UV-254 in the treated wastewater by aeration ponds was slightly lower than the influent wastewater.

The THMFP in the treated wastewater by anaerobic and aerations ponds was lower than 80  $\mu\text{g/L}$ . However, the THMFP of treated wastewater from 1) the DAF and aeration ponds of Plant B and 2) aeration ponds of Plant C were 635 and 205  $\mu\text{g/L}$  respectively. The

wastewater characteristics to DAF and aeration ponds and to aeration ponds have high reactivity to from THMFP. Therefore, it resulted in high THMFP in treated wastewater.  $\text{CHCl}_3$  was the major THMFP species in influent wastewater from three plants. In treated wastewater from Plant A,  $\text{CHCl}_2\text{Br}$  was the major THMFP species, whereas  $\text{CHCl}_3$  was the major THMFP species in treated wastewater from Plant B and C.

## CHAPTER 5

### CHARACTERIZATION OF TRIHALOMETHANE PRECURSORS IN RUBBER GLOVE MANUFACTURING PROCESSES BY FLUORESCENT EXCITATION-EMISSION MATRIX AND FOURIER TRANSFORM INFRARED ANALYSIS

#### 5.1 Introduction and Objective

Dissolved organic matter (DOM) even present a tiny quantity in water can react with chlorine in the chlorination process of water treatment plant to form carcinogenic disinfection by-products (DBPs), e.g. trihalomethanes (THMs), haloacetic acids (HAAs) and haloacetonitriles (HANs) (Krasner,1989) (Marhaba and Washington,1998) and (Rook ,1974). The formation of disinfection by-products (DBPs) is normally depended on the quantity and nature of DOM in water. The primary surrogate parameters that have been used to evaluate the quantity of DOM are dissolved organic carbon (DOC), ultraviolet adsorption at wavelength 254-nm (UV-254), specific ultraviolet adsorption (SUVA) and trihalomethanes formation potential (THMFP). The ratio between THMFP and DOC can be used to determine the reactivity of DOM for the formation of THMs. Water sample that has a high THMFP/DOC value may contains the specific DOM type which related to react with chlorine to form THMs. For qualitative characterization of DOM, three dimensional florescent spectroscopy analysis by a fluorescent excitation-emission matrix (FEEM) and fourier transform infrared (FTIR) can be used to provide the information on the putative origin of DOM. FTIR can be used to identify nature and abundance of structure units in DOM molecule (Chen *et al.*, 2002). Another technique is FEEM which provides the information on the putative origin of the fluorescent organic matter in water. FEEM has been widely utilized for identifying the matter as a tyrosine-like substance, tryptophan-like substances, humic and fulvic acid-like substances, and so on (Coble,1996; Nakajima *et al.*, 2002; Chen *et al.*, 2003; Sierra *et al.*, 2005; Musikavong *et al.*, 2007).

In the previous chapter, the level of DOM surrogates parameters including DOC, UV-254, THMFP and their reductions by three wastewater treatment processes of rubber glove manufacturing was determined. In this chapter, the major objective is to evaluate the reactivity of influent wastewater and treated wastewater of three rubber glove manufacturing processes for the formation of THMs. In addition, the nature of DOM in influent wastewater and treated wastewater was identified by using the FEEM and FTIR analysis.

## 5.2 Material and Methods

### 5.2.1 Sample Collection and Experiment Procedure

The wastewater samples were collected from each treatment step of the wastewater treatment system of three rubber glove manufacturing plants for twice times in January 6 and April 9, 2010 for Plant A, March 2 and July 6, 2010 for Plant B and Plant C. The wastewater treatment process and sampling points were presented in Chapter 3. All water samples were filtered through a pre-combusted ( $550^{\circ}\text{C}$  for 2 h) Whatman GF/F (nominal pore size  $0.7\ \mu\text{m}$ ) filter. The filtered waters were kept at  $4^{\circ}\text{C}$  until analysis. All water samples were measured for DOC and THMFP. The reactivity of DOM to form THMFP is determined by ratio of THMFP/DOC.

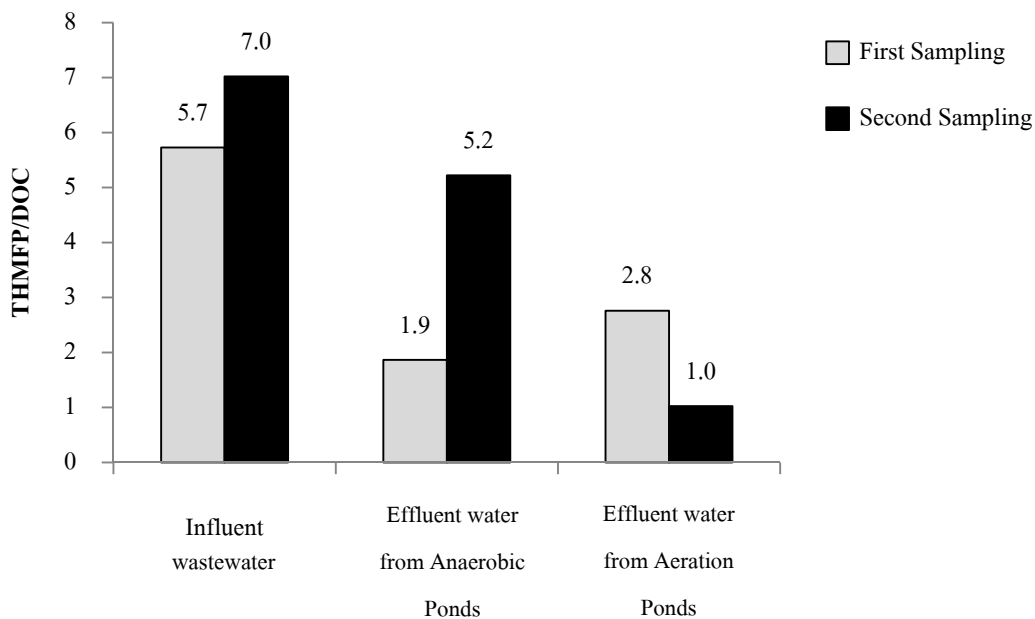
For analysis of the characteristic of DOM, filtered water samples were measured for FEEM and FTIR. FEEMs were measured using a JASCO FP-6200 spectrofluorometer with a wavelength range between 220nm to 600 nm for excitation and emission. FEEM spectra of all water samples were subtracted by the FEEM spectra of Milli-Q water and converted to quinine sulfate units (QSU). Basically, 10 QSU is equivalent to the fluorescence spectra of  $10\ \mu\text{g/L}$  quinine sulfate solution at 450 nm with an excitation wavelength of 345 nm. To eliminate the influence of the primary and secondary scattered fluorescence and to highlight the targeted peaks, FEEM data were discarded when the excitation wavelength ( $\text{Ex}$ )  $\geq$  emission wavelength ( $\text{Em}$ ) or  $\text{Ex} \times 2 \leq \text{Em}$  (Komatsu *et al.*, 2005). In addition, the Rayleigh and Raman scattering peaks at peak  $\text{Em} \pm 10\text{-}15\text{nm}$  of each excitation wavelength were removed from the FEEM (Zeppet *et al.*, 2004).

For FTIR analysis, filtered water samples were pre-frozen at  $-20\text{ }^{\circ}\text{C}$  for at least 12 h. Then they were placed in freeze-drying unit at  $-57^{\circ}\text{C}$  and 0.004 bars until the uniform powder was obtained. For each water sample, this process was repeated several times to produce sufficient amount uniform powder for FTIR analysis. Pellets were made using 1-2 mg of powder combined with 150 mg of KBR. The FTIR spectra were analyzed on a Jasco FTIR-460 spectrometer at a resolution of  $4\text{ cm}^{-1}$  by collecting 16 scans per sample in a wave number range of  $4000 - 400\text{ cm}^{-1}$ .

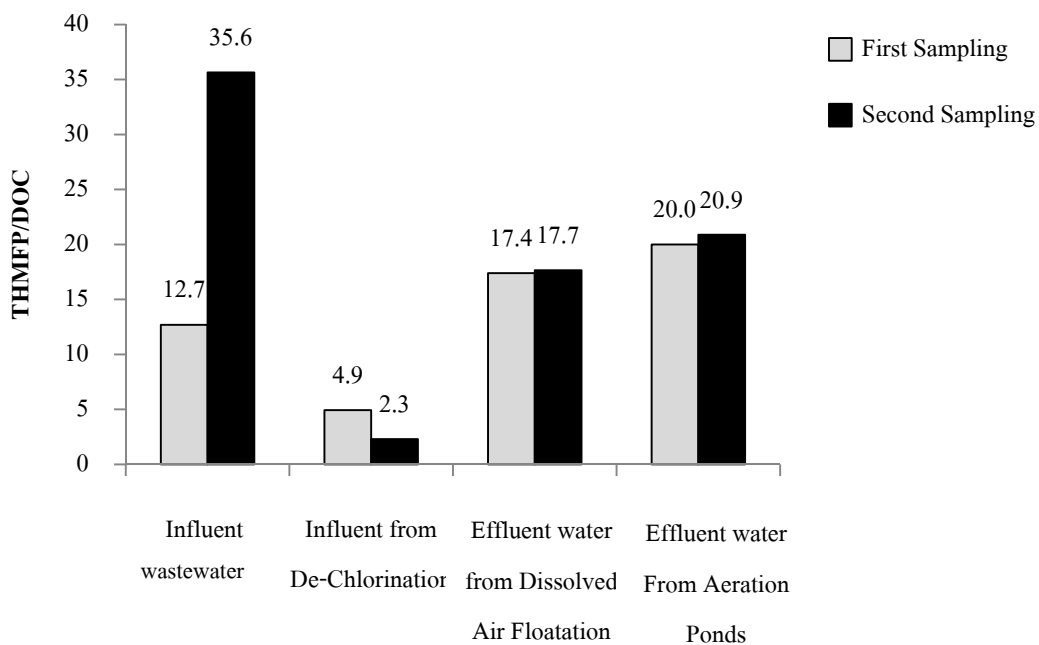
### 5.3 Results and Discussions

#### 5.3.1 THMFP /DOC

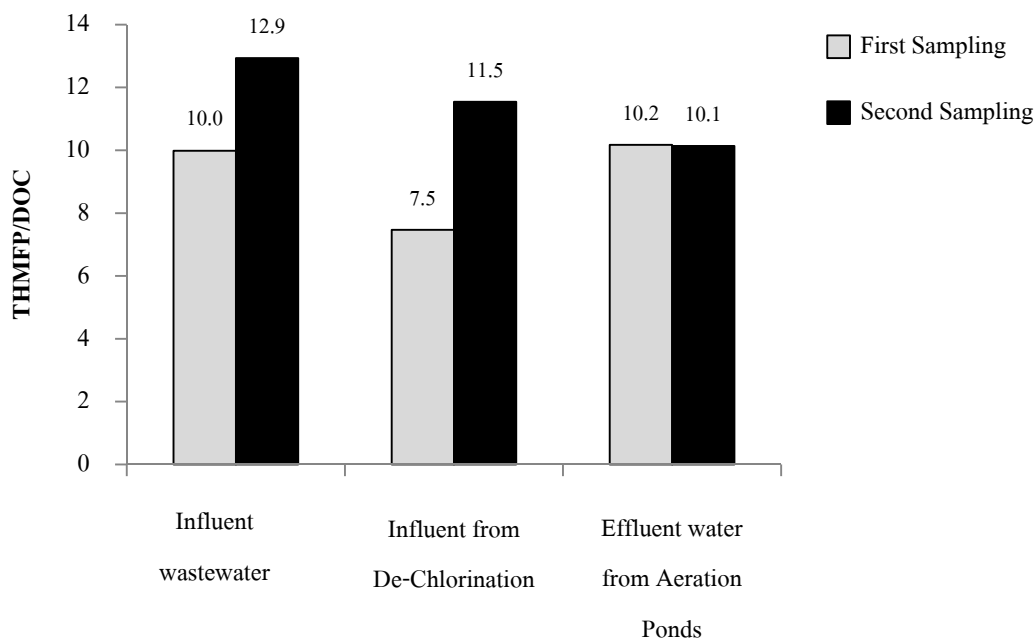
The ratio of THMFP/DOC of influent wastewater and effluent water of Plant A, B and C is presents in Figure 5.1, 5.2, and 5.3, respectively. The THMFP/DOC of the influent wastewater from the first sampling and second samplings of Plant A was 5.7 and 7.0  $\mu\text{g THMFP/mg DOC}$  respectively. The THMFP/DOC of influent wastewater and de-chlorination wastewater from Plant B of the first sampling was 12.7 and 4.9  $\mu\text{g THMFP/mg DOC}$ , respectively, whereas that of the second sampling was 35.6 and 2.3  $\mu\text{g THMFP/mg DOC}$ , respectively. In the case of Plant C, THMFP/DOC of influent and de-chlorination wastewater from Plant C in the first sampling was 10.0 and 7.5  $\mu\text{g THMFP/mg DOC}$ , respectively, whereas that of the second sampling was 12.9 and 11.5  $\mu\text{g THMFP/mg DOC}$ , respectively. It was found that the influent wastewater from Plant B and C had a higher THMFP/DOC values than that of plant A. The nature of DOM in this influent wastewater should have a high ability to react with chlorine to form THMFP and should be seriously concerned. The THMFP/DOC of de-chlorination wastewater from Plant B was detected in low level, whereas, that of plant C was moderately high. The nature of DOM in the de-chlorination wastewater from Plant C should be concerned. When compared THMFP/DOC of influent wastewater from Plant A with that of Plant B and C, it was detected in the low level.



**Figure 5.1** THMF/DOC of wastewater and treated wastewater from the rubber glove manufacturing process of Plant A



**Figure 5.2** THMF/DOC of wastewater and treated wastewater from the rubber glove manufacturing process of Plant B



**Figure 5.3** THMFP/DOC of wastewater and treated wastewater from the rubber glove manufacturing process of Plant C

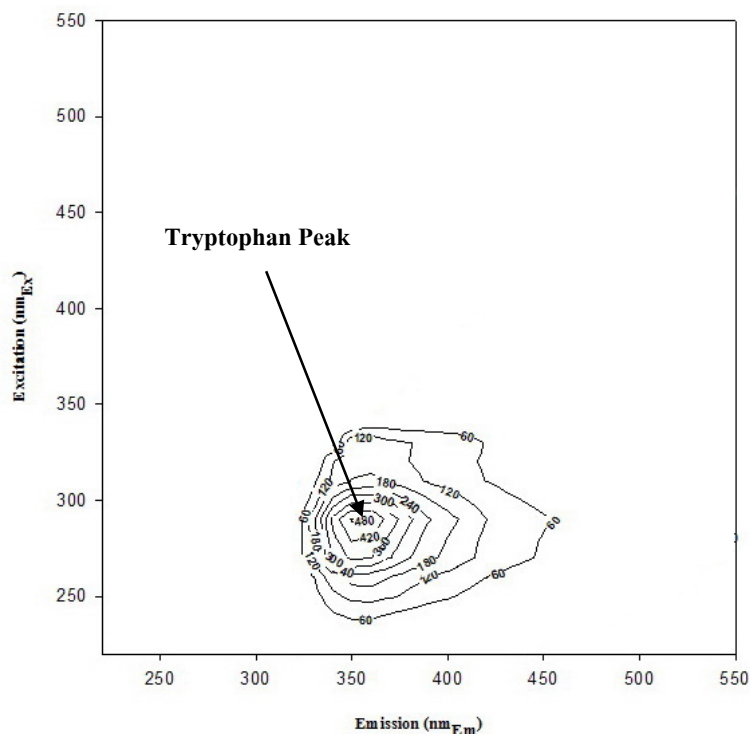
Considering THMFP/DOC in treated wastewater, THMFP/DOC of treated wastewater by anaerobic and aerobic ponds in the first and second sampling of Plant A were 2.8 and 1.0  $\mu\text{g THMFP/mg DOC}$ , respectively. THMFP/DOC in treated wastewater from dissolved air flotation (DAF) at the first and second samplings were 17.4 and 17.7  $\mu\text{g THMFP/mg DOC}$ , respectively, whereas, that of from aeration ponds were 20.0 and 20.9  $\mu\text{g THMFP/mg DOC}$ , respectively. The aeration ponds after DAF system may reduce the DOM that had a low reactivity to form THMs, the remaining DOM in treated wastewater had a high ability to form THMs. THMFP/DOC in treated wastewater from aeration ponds, therefore, was higher than that of DAF. The treated wastewater from plant B had a high THMFP/DOC value. The nature of DOM in this wastewater should be seriously identified. For plant C, THMFP/DOC in treated wastewater by aerated lagoon system in the first and second sampling were 10.2 and 10.1  $\mu\text{g THMFP/mg DOC}$ , respectively. This value was close to THMFP/DOC in influent wastewater. The aeration ponds reduced DOM that had a low reactivity to form THMs, the remaining DOM in treated wastewater had a high ability to form THMs.



### 5.3.2 Characterization of THMFP precursors using FEEM

The sample of pattern of FEEMs of influent wastewater of Plant A is illustrated in Figure 5.4. One strong peak was exhibited at  $290\text{nm}_{\text{Ex}}/355\text{nm}_{\text{Em}}$  for both first and second samplings. For the treated wastewater after anaerobic ponds and aeration ponds, similarly, one strong peak at  $290\text{nm}_{\text{Ex}}/355\text{nm}_{\text{Em}}$  was exhibited for the first and second samplings. In comparison with the study of Chen *et al.* (2003) and Musikavong *et al.* (2007), the putative origin of fluorescent organic matter in wastewater and treated wastewater of Plant A was the tryptophan like substances. Musikavong *et al.* (2007) utilized the fluorescent intensity of each fluorescent peak to determine the reduction of fluorescent organic matter by the wastewater treatment plant. The fluorescent intensity of wastewater and treated wastewater of Plant A is presented in Figure 5.5. The fluorescent intensities of tryptophan-like substances of influent wastewater at the first and second samplings were 478 and 487 QSU, respectively. After the wastewater was treated by anaerobic ponds, it could reduce fluorescent intensities of tryptophan-like substances of the first and second samplings by 18 and 33 percent, respectively. After the treated wastewater by anaerobic ponds was treated by aeration ponds, it could reduce fluorescent intensities of tryptophan-like substances of the first and second samplings by 45 and 25 percents, respectively.

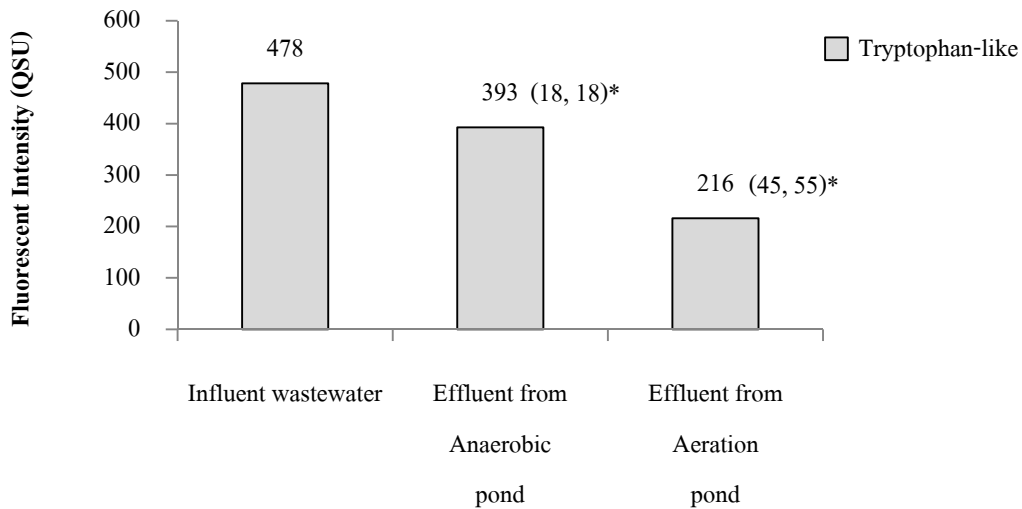
Considering the total reduction of tryptophan like substances, the anaerobic and aeration ponds can reduce fluorescent intensities of tryptophan like substances by 55 and 50 percents at the first and second samplings, respectively. These values were higher than the DOC and UV-254 reduction as previously found but it was lower than the reduction of THMFP. In addition, aeration ponds were the main course of action that reduced tryptophan-like substances.



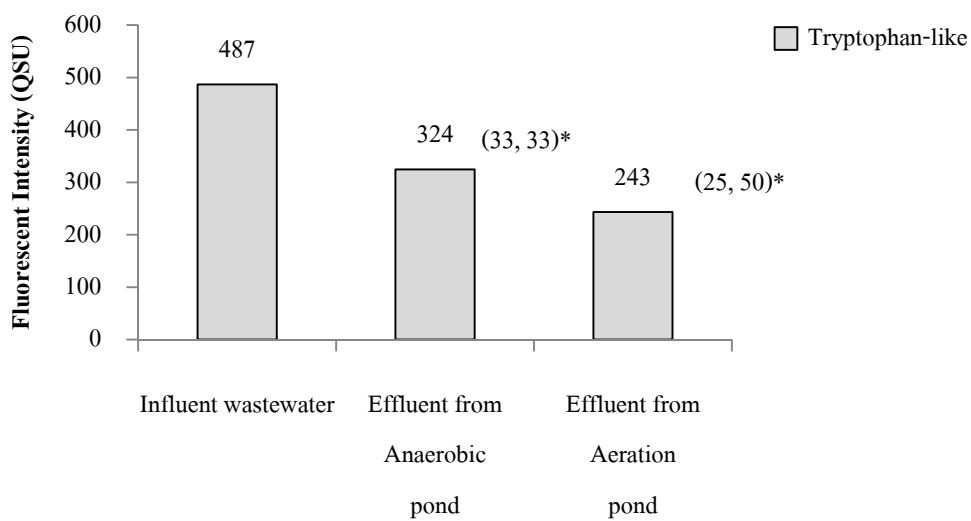
**Figure 5.4** Sample of FEEM of influent wastewater from Plant A

For the FEEM of Plant B as shown in Figure 5.6, interestingly, three fluorescent peaks at  $230\text{nm}_{\text{Ex}}/290\text{nm}_{\text{Em}}$ ,  $240\text{nm}_{\text{Ex}}/350\text{nm}_{\text{Em}}$ , and  $290\text{nm}_{\text{Ex}}/350\text{nm}_{\text{Em}}$  were detected in de-chlorination wastewater for the first and second sampling. The putative fluorescent organic matter of peak  $230\text{nm}_{\text{Ex}}/290\text{nm}_{\text{Em}}$  was tyrosine-like substance whereas that of  $240\text{nm}_{\text{Ex}}/350\text{nm}_{\text{Em}}$ , and  $290\text{nm}_{\text{Ex}}/350\text{nm}_{\text{Em}}$  was tryptophan-like substances. For influent wastewater, tryptophan-like substances was exhibited at  $285\text{nm}_{\text{Ex}}/355\text{nm}_{\text{Em}}$  at the first and second sampling.

For the fluorescent peaks of treated wastewater after DAF, only the tryptophan peak at  $290\text{nm}_{\text{Ex}}/350\text{nm}_{\text{Em}}$  was detected. The tyrosine-like substance peaks at  $230\text{nm}_{\text{Ex}}/290\text{nm}_{\text{Em}}$ , and tryptophan-like substances peak at  $240\text{nm}_{\text{Ex}}/350\text{nm}_{\text{Em}}$  were removed. DAF can completely remove tyrosine-like substances. As can be seen from Figure 5.7, the aeration ponds reduced fluorescent intensity of tryptophan - like substance by 29 and 20 percents, respectively, for the first and second samplings.



**a) First Sampling**



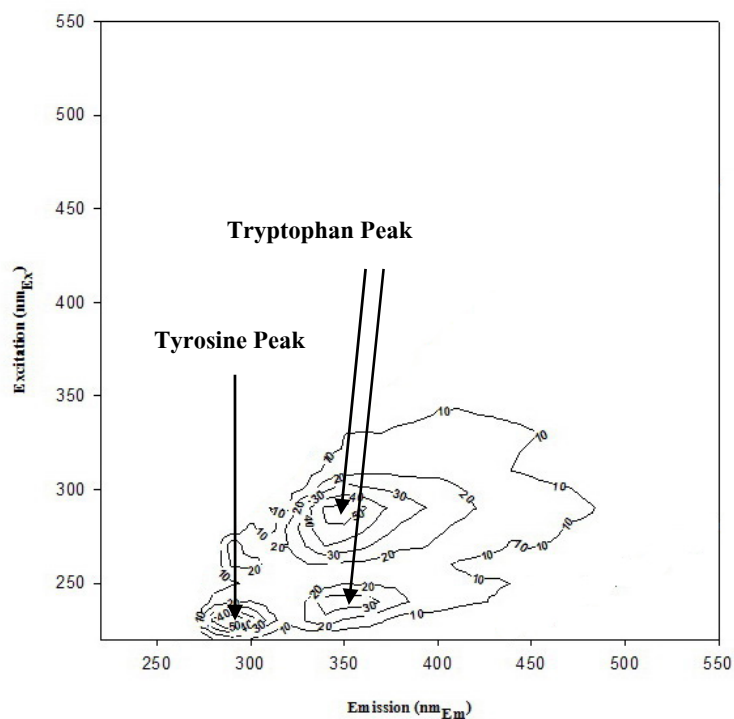
**b) Second Sampling**

Remark: (x, y)\*

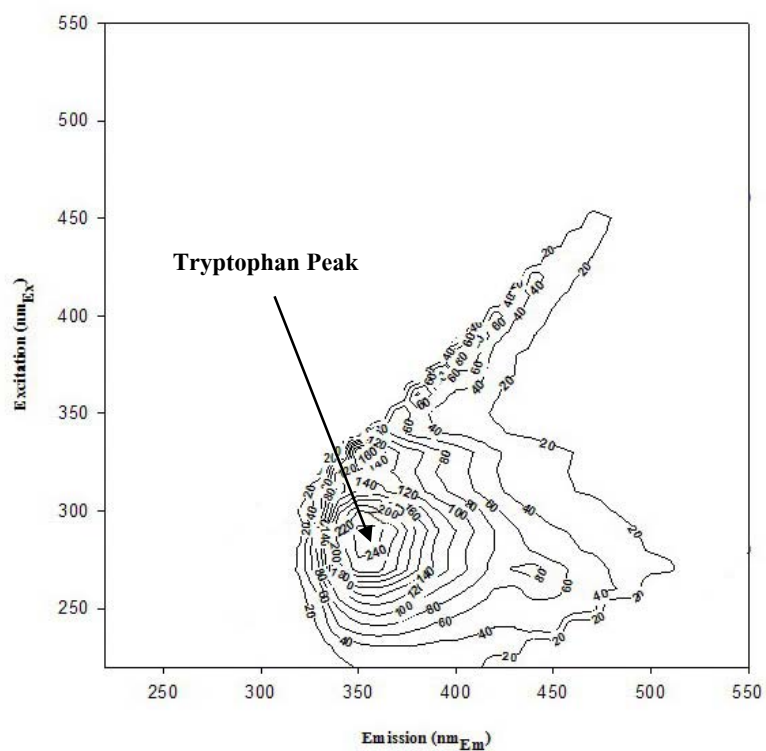
x; Percent reduction of tryptophan-like

y; Accumulated percent reduction of tryptophan-like

**Figure 5.5** Fluorescent intensity of influent wastewater and effluent water from Plant A

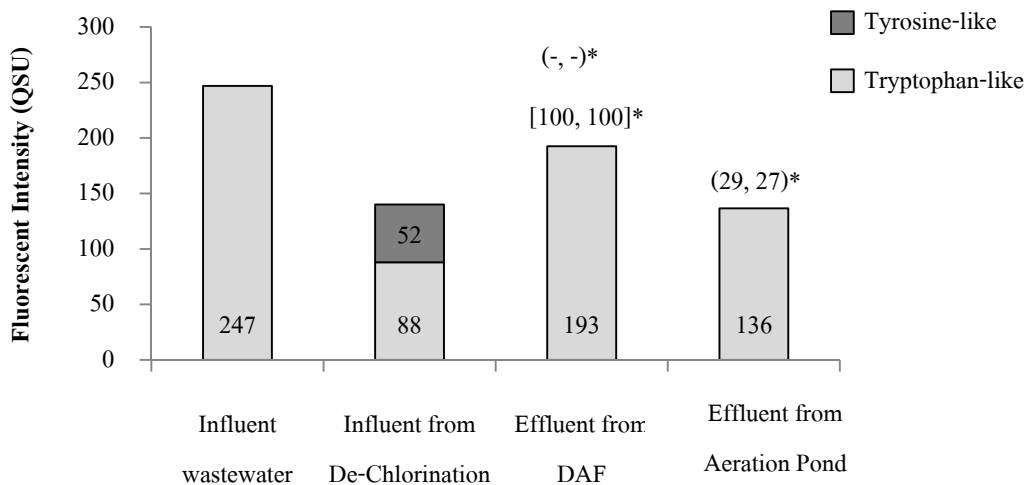


a) De-chlorination wastewater

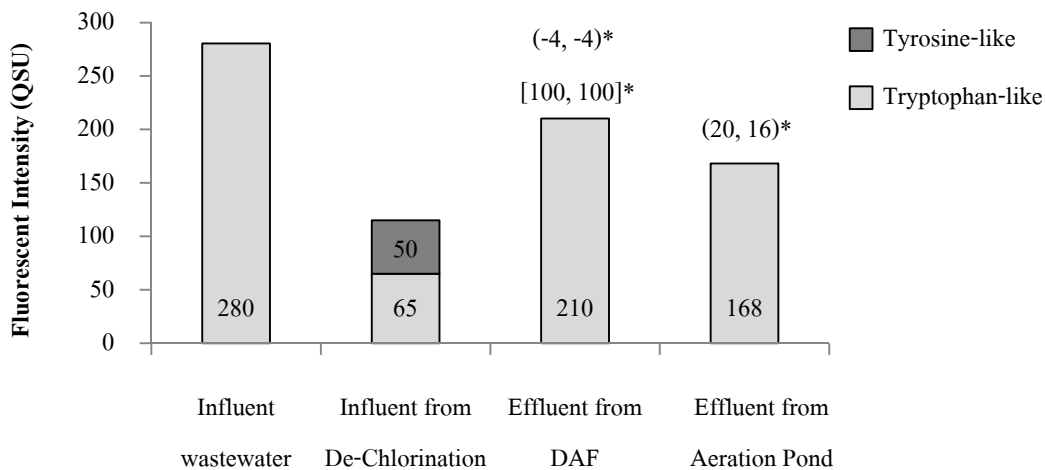


a) Influent wastewater

**Figure 5.6** Sample of FEEM of influent wastewater from Plant B



**First Sampling**



**Second Sampling**

Remark: (x, y)\*

x; Percent reduction of tryptophan-like

y; Accumulated percent reduction of tryptophan-like

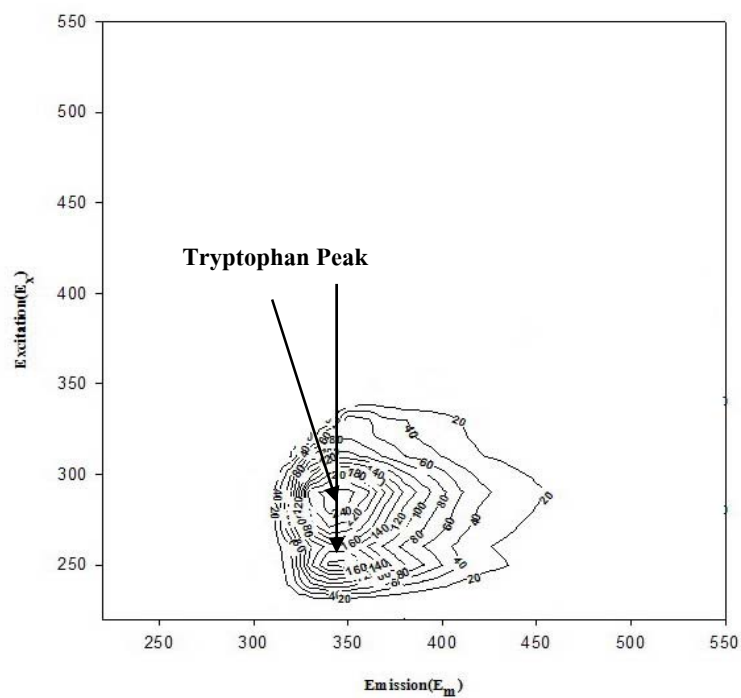
[A, B]\*

A; Percent reduction of tyrosine-like

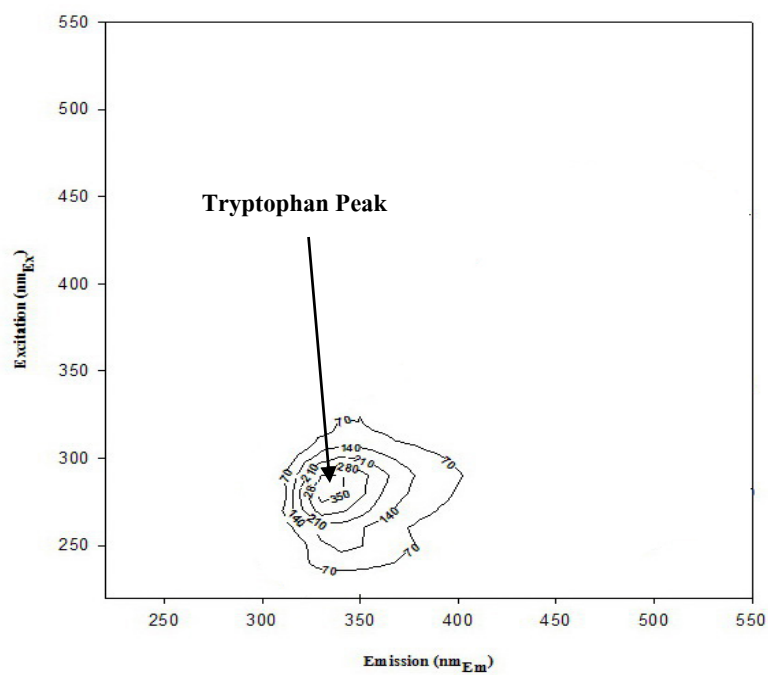
B; Accumulated percent reduction of tyrosine-like

**Figure 5.7** Fluorescent intensity of influent wastewater and effluent water from Plant B

As stated previously, the aeration ponds in Plant B can reduce THMFP, DOC, and UV-254 at the first sampling by 9, 21 and 53 percents respectively, whereas that of the second sampling were 10, 24 and 52percent, respectively. The reduction of tryptophan of 29 and 20 percents for the first and second samplings was corresponded with UV-254 reduction in this case. Figure 5.8 presents the sample of FEEM of de-chlorination wastewater and influent wastewater of Plant C whereas the fluorescent intensity of wastewater and treated wastewater is shown in Figure 5.9.

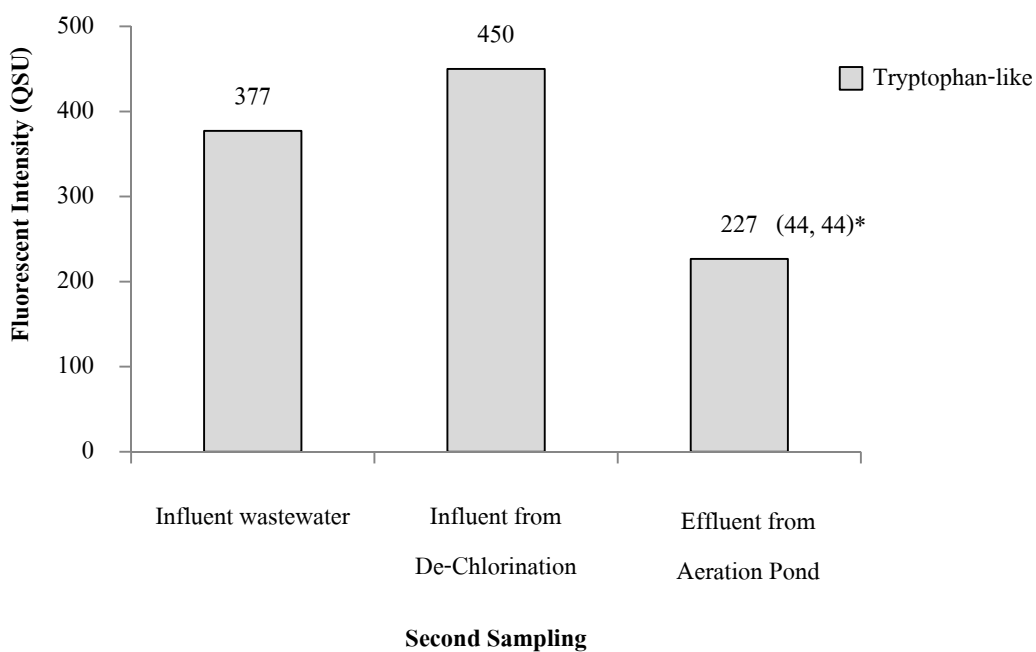
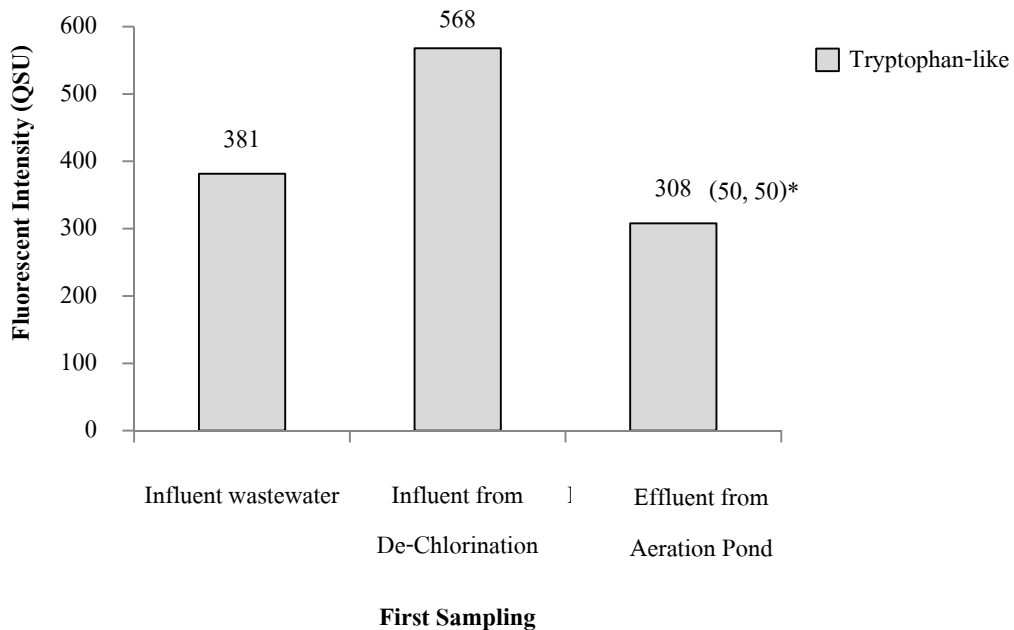


a) De-chlorination wastewater



b) Influent wastewater

**Figure 5.8** Sample of FEEM of wastewater from Plant C



Remark: (x, y)\*

x; Percent reduction of tryptophan-like

y; Accumulated percent reduction of tryptophan-like

**Figure 5.9** Fluorescent intensity of influent wastewater and effluent water from Plant C



For the FEEM of Plant C as shown in Figure 5.6, interestingly, two fluorescent peaks at  $240\text{nm}_{\text{Ex}}/350\text{nm}_{\text{Em}}$ , and  $285\text{ nm}_{\text{Ex}}/350\text{ nm}_{\text{Em}}$  were detected in de-chlorination wastewater for the first and second samplings. The putative fluorescent organic matter of found peaks was tryptophan-like substances. For influent wastewater, tryptophan-like substances was exhibited at  $285\text{nm}_{\text{Ex}}/340\text{nm}_{\text{Em}}$  at the first and second samplings. After wastewater was treated by aerated lagoon system, the tryptophan-like substances at peak  $240\text{nm}_{\text{Ex}}/350\text{nm}_{\text{Em}}$ , was removed.

It can be stated that tryptophan-like substances was the major THMFP precursors in the wastewater and treated wastewater of rubber glove manufacturing process. For the de-chlorination wastewater, it is possible to detect the tyrosine-like substance; however, it was completely remove by DAF unit. The series of anaerobic and aerobic pond can reduce tryptophan-like substances better than DOC and UV-254, whereas, the aeration ponds after DAF slightly reduce tryptophan-like substances.

### 5.3.3 Characterization of THMFP precursors using FTIR

The FTIR analysis can provide the distribution of functional groups of DOM in the water samples. The general assignment of FTIR spectra developed by Charonpun Musikavong and Suraphong Wattanachira (2012) is presented in Table 5.1. The FTIR spectras of influent wastewater and treated wastewater of Plant A, B, and C are shown in Table 5.2, 5.3, and 5.4, respectively.

For Plant A, C=O stretching of amide group (amide-I), C-O stretching and O-H deformation of  $-\text{COOH}$ , and hydrogen-bonded OH stretching were detected in the influent wastewater from the first and second samplings. The anaerobic and aeration ponds could remove C-O stretching and O-H deformation of  $-\text{COOH}$  formation from the wastewater in the first and the second sampling. The major functional group of DOM in treated wastewater were C=O stretching of amide group (amide-I), hydrogen-bonded OH stretching, and deformation of COOH.

By considering the functional group of DOM in wastewater from Plant B which had the high reactivity to form THMFP, C=O stretching of amide group, and salts of carboxylic acids were found in the influent wastewater of the first and second samplings. Hydrogen-bonded

OH stretching was detected in the first sampling and N-H bending vibration and deformation of COOH were detected only in the second sampling. The DAF and aeration system can remove the functional group of aliphatic stretching vibration of benzene and pyridine, salts of carboxylic acids, hydrogen-bonded OH stretching and deformation of COOH from the wastewater in the first sampling. In the second sampling, it can reduce only C-O stretching and O-H deformation of –COOH, C-O stretching of esters, ethers, and phenols.

For Plant C, C=O stretching of amide group (amide-1), salts of carboxylic acids, hydrogen-bonded OH stretching, N-H bending vibration of amide group (amide-2) were detected in the influent wastewater from the first and second samplings. The aeration ponds could remove C=O stretching vibration of double bonds in cyclic and acyclic compound, ketones and quinines, aromatic C=C vibration, C-O stretching and O-H deformation of –COOH, C-O stretching of esters, ethers, and phenols, deformation of COOH and hydrogen-bonded OH stretching from the wastewater in the first and the second sampling. The major functional group of DOM in treated wastewater were C=O stretching of amide group (amide-1), N-H bending vibration of amide group (amide-2) and salts of carboxylic acids.

As stated previously, the nature of DOM in the treated wastewater from Plant B and C had a high value of THMFP/DOC. The specific functional group that were detected only in the treated wastewater of Plant B and C were N–H bending vibration of amide group (amide-2), aliphatic C-H deformation or C–CH<sub>3</sub> of methyl ester, C-O stretching and O-H deformation of –COOH, C-O stretching of esters, ethers, and phenols

**Table 5.1** General assignment of FTIR spectra of tryptophan, humic acid and Suwannee River NOM

Peak No	Wavenumber (cm <sup>-1</sup> )				Assignments
	Tryptophan <sup>1</sup>	Humic acid <sup>1</sup>	ISHH <sup>1</sup>	DOM <sup>2</sup>	
1	3404	3670-3300	3655-3439	3670-3300	Hydrogen-bond O—H groups, Free O—H group, intermolecular-bond O—H or H-bonded NH
2	3078-3037	N.D.	N.D.	3100 – 3000	Aromatic C—H stretching
3	N.D.	2950-2850	2950-2850	2950-2850	Aliphatic C—H, C—H <sub>2</sub> , C—H <sub>3</sub> stretching
4	2564	2850-2500	N.D.	2850-2500	Carboxylate ion
5	N.D.	N.D.	1717	1730-1700	C=O stretching of carboxylic acids, aldehydes, ketones and ester
6	1700-1668	N.D.	N.D.	1690-1650	C=O stretching of amide group (amide-1)
7	1589	1618	1635	1640-1585	C=O stretching vibration of double bonds in cyclic and acyclic compound, ketones and quinines, aromatic C=C vibration
8	N.D.	N.D.	N.D.	1570-1550	N—H bending vibration of amide group (amide-2)
9	N.D.	N.D.	N.D.	1515	Aliphatic stretching vibration of benzene and pyridines
10	1456	N.D.	N.D.	1465-1440	Aliphatic C-H deformation or C—CH <sub>3</sub> of methyl ester
11	1414	N.D.	N.D.	1420-1400	O—H bending vibration of carboxylic groups, C—O stretching of alcohols
12	N.D.	N.D.	1397	1400-1390	O—H-deformation and C—O stretching of phenolic, O—H, C—H deformation of C—H <sub>3</sub> groups
13	1357-1315	1375	N.D.	1390-1322	Salts of carboxylic acids
14	1231-1157	1280-1137	1210	1280-1137	C-O stretching and O-H deformation of —COOH, C-O stretching of esters, ethers, and phenols
15	1099-1007	1090-1040	1080	1090-1040	C-O stretching of alcohols, ethers, and carbohydrates
16	919	912	N.D.	919-730	C-H bending vibration of aromatic rings
17	744	N.D.	N.D.	880-750	Hydrogen-bonded OH stretching vibration of carboxylic groups
18	650-510	535	N.D.	650-510	deformation of COOH

**Source:**<sup>1</sup>Charongpun Musikavong and Suraphong Wattanachira (2012). <sup>2</sup>The FTIR peak position of DOM was obtained from Kannokkantonget *et al.* (2006), Kim and Yu (2005); Barber *et al.* (2001); Lin *et al.* (2001); Davis *et al.* (1999); Sposito,(1989); Aiken *et al.*(1985); N.D. = Not detectable

**Table 5.2** Functional group of DOM in the influent wastewater and treated wastewater of rubber glove manufacturing Plant A

	<b>Influent</b>	<b>Effluent water from anaerobic pond</b>	<b>Effluent water from aeration ponds</b>	<b>Remark</b>
<b>First Sampling</b>				
Functional groups	6.C=O stretching of amide group (amide-I)(Wavenumber 1649 cm <sup>-1</sup> ) 14.C-O stretching and O-H deformation of -COOH,C-O stretching of esters, ethers, and phenols(Wavenumber 1138 cm <sup>-1</sup> ) 17.Hydrogen-bonded OH stretching(Wavenumber 872 cm <sup>-1</sup> )	6.C=O stretching of amide group (amide-I) (Wavenumber 1663 cm <sup>-1</sup> ) 9.Aliphatic stretching vibration of benzene and pyridine(Wavenumber 1509 cm <sup>-1</sup> ) 14.C-O stretching and O-H deformation of -COOH,C-O stretching of esters, ethers, and phenols(Wavenumber 1148 cm <sup>-1</sup> ) 17.Hydrogen-bonded OH stretching(Wavenumber 874 cm <sup>-1</sup> ) 18.Deformation of COOH (Wavenumber 669 cm <sup>-1</sup> )	6.C=O stretching of amide group (amide-I) (Wavenumber 1653 cm <sup>-1</sup> ) 9.Aliphatic stretching vibration of benzene and pyridine (Wavenumber 1508 cm <sup>-1</sup> ) 17.Hydrogen-bonded OH stretching(Wavenumber 870 cm <sup>-1</sup> ) 18.Deformation of COOH (Wavenumber 618cm <sup>-1</sup> )  <b>Removal</b> 14.C-O stretching and O-H deformation of -COOH,C-O stretching of esters, ethers, and phenols	<b>Treatment process removal</b> 14.C-O stretching and O-H deformation of -COOH,C-O stretching of esters, ethers, and phenols

**Table 5.2** Functional group of DOM in the influent wastewater and treated wastewater of rubber glove manufacturing Plant A (Cont.)

	Influent	Effluent water from anaerobic pond	Effluent water from aeration ponds	Remark
<b>Second Sampling</b>				
Functional groups	6.C=O stretching of amide group (amide-I) (Wavenumber 1652 cm <sup>-1</sup> ) 11.O-H bending vibration of carboxylic groups, C-O stretching of alcohols(Wavenumber 1419 cm <sup>-1</sup> ) 14.C-O stretching and O-H deformation of -COOH,C-O stretching of esters, ethers, and phenols(Wavenumber 1139 cm <sup>-1</sup> ) 17.Hydrogen-bonded OH stretching(Wavenumber 874 cm <sup>-1</sup> )	6.C=O stretching of amide group (amide-I) (Wavenumber 1644 cm <sup>-1</sup> ) 11.O-H bending vibration of carboxylic groups, C-O stretching of alcohols(Wavenumber 1410 cm <sup>-1</sup> ) 14.C-O stretching and O-H deformation of -COOH,C-O stretching of esters, ethers, and phenols(Wavenumber 1133 cm <sup>-1</sup> ) 17.Hydrogen-bonded OH stretching(Wavenumber 871 cm <sup>-1</sup> ) 18. Deformation of COOH (Wavenumber 616cm <sup>-1</sup> )	6.C=O stretching of amide group (amide-I) (Wavenumber 1649 cm <sup>-1</sup> ) 13.Salts of carboxylic acids(Wavenumber 1384 cm <sup>-1</sup> ) 15.C-O stretching of alcohols, ethers, and carbohydrates(Wavenumber 1074cm <sup>-1</sup> ) 17.Hydrogen-bonded OH stretching(Wavenumber 864 cm <sup>-1</sup> ) 18. Deformation of COOH (Wavenumber 565 cm <sup>-1</sup> )	<b><u>Treatment process removal</u></b> 11.O-H bending vibration of carboxylic groups, C-O stretching of alcohols 14.C-O stretching and O-H deformation of -COOH,C-O stretching of esters, ethers, and phenols
			<b><u>Removal</u></b> 11.O-H bending vibration of carboxylic groups, C-O stretching of alcohols 14.C-O stretching and O-H deformation of -COOH,C-O stretching of esters, ethers, and phenols	

**Table 5.3** Functional group of DOM in the influent wastewater and treated wastewater of rubber glove manufacturing Plant B

	Influent	Influent from De-Chlorination	Effluent water from Dissolved Air Flotation	Effluent water from aeration ponds	Remark
<b>First Sampling</b>	6.C=O stretching of amide group (amide-I) (Wavenumber 1654 cm <sup>-1</sup> )	6.C=O stretching of amide group (amide-I) (Wavenumber 1649 cm <sup>-1</sup> )	7.C=O stretching vibration of double bonds in cyclic and acyclic compound, ketones and quinines,	6.C=O stretching of amide group (amide-I)(Wavenumber 1651 cm <sup>-1</sup> )	<b><u>Treatment process</u></b> <b><u>removal</u></b>
Functional groups	13.Salts of carboxylic acids (Wavenumber 1384cm <sup>-1</sup> )	9.Aliphatic stretching vibration of benzene and pyridine (Wavenumber 1509 cm <sup>-1</sup> )	aromatic C=C vibration (Wavenumber 1635 cm <sup>-1</sup> )	10.Aliphatic C-H deformation or C- CH <sub>3</sub> of methyl ester(Wavenumber 1488 cm <sup>-1</sup> )	
	17.Hydrogen-bonded OH stretching (Wavenumber 826 cm <sup>-1</sup> )	13.Salts of carboxylic acids (Wavenumber 1393 cm <sup>-1</sup> )	13.Salts of carboxylic acids(Wavenumber 1388 cm <sup>-1</sup> )	14.C-O stretching and O-H deformation of –COOH,C-O stretching of esters, ethers, and phenols(Wavenumber 1136 cm <sup>-1</sup> )	9.Aliphatic stretching vibration of benzene and pyridine 13.Salts of carboxylic acids 17.Hydrogen-bonded OH stretching
		14.C-O stretching and O-H deformation of –COOH,C- O stretching of esters, ethers, and phenols (Wavenumber 1139 cm <sup>-1</sup> )	14.C-O stretching and O-H deformation of –COOH,C-O stretching of esters, ethers, and phenols(Wavenumber 1144 cm <sup>-1</sup> )	17.Hydrogen-bonded OH stretching (Wavenumber 865cm <sup>-1</sup> )	18.Deformation of COOH
		18. Deformation of COOH (Wavenumber 622 cm <sup>-1</sup> )	17.Hydrogen-bonded OH stretching(Wavenumber 824 cm <sup>-1</sup> )	<b><u>Removal</u></b>	
			18.Deformation of COOH (Wavenumber 669 cm <sup>-1</sup> )	7.C=O stretching vibration of double bonds in cyclic and acyclic compound, ketones and quinines, aromatic C=C vibration	
			<b><u>Removal</u></b>	13.Salts of carboxylic acids	
			6.C=O stretching of amide group	18.Deformation of COOH	
			9.Aliphatic stretching vibration		

**Table 5.3** Functional group of DOM in the influent wastewater and treated wastewater of rubber glove manufacturing Plant B (Cont.)

	Influent	Influent from De-Chlorination	Effluent water from Dissolved Air Flotation	Effluent water from aeration ponds	Remark
<b>Second Sampling</b>					
Functional groups	6.C=O stretching of amide group (amide-1) (Wavenumber 1649 cm <sup>-1</sup> ) 8.N-H bending vibration of amide group (amide-2)(Wavenumber 1541 cm <sup>-1</sup> ) 13.Salts of carboxylic acids (Wavenumber 1385 cm <sup>-1</sup> ) 18. Deformation of COOH (Wavenumber 668 cm <sup>-1</sup> )	6.C=O stretching of amide group (amide-1) (Wavenumber 1663cm <sup>-1</sup> ) 8.N-H bending vibration of amide group (amide-2)(Wavenumber 1554 cm <sup>-1</sup> ) 13.Salts of carboxylic acids (Wavenumber 1385 cm <sup>-1</sup> ) 14.C-O stretching and O-H deformation of -COOH,C-O stretching of esters, ethers, and phenols (Wavenumber 1147 cm <sup>-1</sup> ) 18. Deformation of COOH (Wavenumber 619 cm <sup>-1</sup> )	6.C=O stretching of amide group (amide-1) (Wavenumber 1685cm <sup>-1</sup> ) 8.N-H bending vibration of amide group (amide-2)(Wavenumber 1541 cm <sup>-1</sup> ) 13.Salts of carboxylic acids(Wavenumber 1384 cm <sup>-1</sup> ) <b>Removal</b> 14.C-O stretching and O-H deformation of -COOH,C-O stretching of esters, ethers, and phenols 18. Deformation of COOH	6.C=O stretching of amide group (amide-1) (Wavenumber 1649 cm <sup>-1</sup> ) 8.N-H bending vibration of amide group (amide-2)(Wavenumber 1545 cm <sup>-1</sup> ) 13.Salts of carboxylic acids(Wavenumber 1384 cm <sup>-1</sup> ) 18. Deformation of COOH(Wavenumber 599cm <sup>-1</sup> )	<b>Treatment process removal</b> 14.C-O stretching and O-H deformation of -COOH,C-O stretching of esters, ethers, and phenols

**Table 5.4** Functional group of DOM in the influent wastewater and treated wastewater of rubber glove manufacturing Plant C

	<b>Influent</b>	<b>Influent from De-Chlorination</b>	<b>Effluent water from aeration ponds</b>	<b>Remark</b>
<b>First Sampling</b>				
Functional groups	6.C=O stretching of amide group (amide-1) (Wavenum 1652 cm <sup>-1</sup> ) 13.Salts of carboxylic acids (Wavenumber 1384 cm <sup>-1</sup> ) 17.Hydrogen-bonded OH stretching (Wavenumber 825 cm <sup>-1</sup> )	6.C=O stretching of amide group (amide-1) (Wavenumber 1649 cm <sup>-1</sup> ) 13.Salts of carboxylic acids (Wavenumber 1384 cm <sup>-1</sup> ) 14.C-O stretching and O-H deformation of –COOH, C-O stretching of esters, ethers, and phenols (Wavenumber 1127 cm <sup>-1</sup> )	6.C=O stretching of amide group (amide-1) (Wavenumber 1649 cm <sup>-1</sup> ) 8.N-H bending vibration of amide group (amide-2) (Wavenumber 1540 cm <sup>-1</sup> ) 13.Salts of carboxylic acids (Wavenumber 1384 cm <sup>-1</sup> ) 18. Deformation of COOH (Wavenumber 669 cm <sup>-1</sup> )  <b>Removal</b> 14.C-O stretching and O-H deformation of –COOH, C-O stretching of esters, ethers, and phenols 17.Hydrogen-bonded OH stretching	<b>Treatment process removal</b> 14.C-O stretching and O-H deformation of –COOH, C-O stretching of esters, ethers, and phenols 17.Hydrogen-bonded OH stretching



**Table 5.4** Functional group of DOM in the influent wastewater and treated wastewater of rubber glove manufacturing plant C (Cont.)

	Influent	Influent from De-Chlorination	Effluent water from aeration ponds	Remark
<b>Second Sampling</b>				
Functional groups	6.C=O stretching of amide group (amide-1) (Wavenumber 1658 cm <sup>-1</sup> ) 8.N-H bending vibration of amide group (amide-2)(Wavenumber 1554 cm <sup>-1</sup> ) 13.Salts of carboxylic acids (Wavenumber 1383 cm <sup>-1</sup> )	7.C=O stretching vibration of double bonds in cyclic and acyclic compound, ketones and quinines, aromatic C=C vibration(Wavenumber 1625 cm <sup>-1</sup> ) 13.Salts of carboxylic acids (Wavenumber 1384 cm <sup>-1</sup> ) 14.C-O stretching and O-H deformation of –COOH,C-O stretching of esters, ethers, and phenols(Wavenumber 1145 cm <sup>-1</sup> ) 18. Deformation of COOH (Wavenumber 602 cm <sup>-1</sup> )	6.C=O stretching of amide group (amide-1) (Wavenumber 1649 cm <sup>-1</sup> ) 8.N-H bending vibration of amide group (amide-2) (Wavenumber 1540 cm <sup>-1</sup> ) 13.Salts of carboxylic acids(Wavenumber 1384 cm <sup>-1</sup> ) <b>Removal</b> 7.C=O stretching vibration of double bonds in cyclic and acyclic compound, ketones and quinines, aromatic C=C vibration 14.C-O stretching and O-H deformation of –COOH,C-O stretching of esters, ethers, and phenols 18.Deformation of COOH	<b>Treatment process removal</b> 7.C=O stretching vibration of double bonds in cyclic and acyclic compound, ketones and quinines, aromatic C=C vibration 14.C-O stretching and O-H deformation of –COOH,C-O stretching of esters, ethers, and phenols 18. Deformation of COOH

#### 5.4 Concluding Remarks

The wastewater and treated wastewater from three rubber glove manufacturing processes were collected to determine the reactivity for forming THMFP and to identify the nature of THMFP precursors. The influent wastewater and treated wastewater from 1) the DAF and aeration ponds of Plant B and 2) aeration ponds of Plant C had high reactivity to form THMFP due to their high THMFP/DOC value. Influent wastewater and treated wastewater from Plant A had a low THMFP/DOC value when compared with that of Plant B and C. The fluorescent of tryptophan-like substances at  $285\text{-}290\text{ nm}_{\text{EX}}/350\text{ nm}_{\text{EM}}$  was detected in all influent wastewater and treated wastewater. The tryptophan-like substance, therefore was the major THMFP precursors in the wastewater and treated wastewater of rubber glove manufacturing process. For the de-chlorination wastewater, the tyrosine-like and tryptophan-like substances were detected; however, tyrosine-like substance was completely removed by DAF unit. The series of anaerobic and aeration ponds can reduce the tryptophan-like substance better than DOC and UV-254, whereas, the aeration ponds after DAF slightly reduced tryptophan-like substance.

The functional groups that were reduced by wastewater treatment system of plant A, B, and C were O-H bending vibration of carboxylic groups, C-O stretching of alcohols and C-O stretching, aliphatic stretching vibration of benzene and pyridine, salts of carboxylic acids, hydrogen-bonded OH stretching, deformation of COOH and C-O stretching and O-H deformation of  $\text{-COOH}$ , C-O stretching of esters, ethers, and phenols, C=O stretching vibration of double bonds in cyclic and acyclic compound, ketones and quinines and aromatic C=C vibration.

The general functional groups that were detected in the treated wastewater of plant A, B and C were C=O stretching of amide group (amide-1), salts of carboxylic acids, hydrogen-bonded OH stretching vibration of carboxylic groups, deformation of COOH.

The specific functional group that were detected only in the treated wastewater of plant B and C were N-H bending vibration of amide group (amide-2), aliphatic C-H deformation or C-CH<sub>3</sub> of methyl ester, C-O stretching and O-H deformation of  $\text{-COOH}$ , C-O stretching of esters, ethers, and phenols. This could related to the high value of THMFP.

The results obtained present the prominent DOM in the wastewater and treated wastewater from rubber glove industry that had relation to the formation of THMs. This DOM must be seriously monitor prior to discharging treated wastewater to natural water way.

## REFERENCES

- Aiken, G. R., McKnight D. M., Wershaw, R. L. & MacCarthy, P. (1985) Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation and Characterization. Wiley, New York, NY.
- Amy, G.L. (1994). Using NOM characterization for the evaluation of treatment. In Natural organic matter in drinking water: origin, characterization, and removal. Workshop Proceedings, AWWRF, September 19-22, (1993) Chamonix, France, 19-26.
- Amy, G.L. and Chadik, P.A.(1983). Cationic polyelectrolytes as primary coagulants for removing trihalomethane precursors, J.AWWA. :527-531.
- APHA, AWWA and WPCF. (1995). Standard methods for the examination of water and wastewater. 19<sup>th</sup> ed. Washington D. C., U.S.A.
- AWWARF (1991).Disinfection by products database and model project, American Water Works Association Research Foundation, Denver, Colorado.
- Baber, L.B., Leenheer, J.A., Noyes, T.I., & Stiles, E.A. (2001) Nature and transformation of dissolved organic matter in treatment wetlands. *Environmental Science and Technology*. 35 (24), 4805-4816.
- Baker, A. (2001). Fluorescence excitation-emission matrix characterization of some sewage-impacted rivers. *Water Sci Technol*. 35: 948-953.
- Baker, A. (2002). Fluorescence excitation–emission matrix characterization of river waters impacted by a tissue mill effluent. *Environ. Sci. Technol*. 36, 1377–1382.
- Baker, A., Curry, M. (2004). Fluorescence of leachates from three contrasting landfills. *Water Res*. 38:2605-2613.
- Carlson, M.; and Hardy, D. 1998. Controlling DBPs with monochloramine. *Journal of AWWA* 90(2): 95-106.

- Chen, J., Gu, B., LeBoeuf, E.J., Pan, H., & Dai, S. (2002) Spectroscopic characterization of the structure and functional properties of natural organic matter fractions. *Chemosphere* 48 (1), 59-68.
- Chen, W., Westerhoff, P., Leenheer, J.A., & Booksh, K. (2003). Fluorescence excitation - emission matrix regional integration to quantify spectra for dissolved organic matter. *Environmental Science and Technology*. 37(24), 5701-5710.
- Coble, P.G. (1996). Characterization of marine and terrestrial DOM in seawater using excitation-emission matrix spectrometry. *Marine Chemistry*. 51, 325-346.
- Coble, P. G.; Green, S. A.; Blough, N. V.; et al. (1990). Characterization of dissolved organic matter in Black Sea by fluorescence spectroscopy. *Nature* 48: 432-435.
- Coble, P.G., Schultz, C.A., and Mopper, K. (1993). Fluorescence contouring analysis of DOC intercalibration experiment samples: a comparison of techniques. *Marine Chemistry*. 41: 173-178.
- Coelho, R.R., Sacramento, D.R., and Linhares, L.F. (1997). Amino Sugars in Fungal Melamins and Soil Humic Acids. *The European J. Soil Sci.* 48(3), 435.
- Collins, M., Amy, G., and Steelink, C. (1986). Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter: Implications for removal during water treatment. *Envi Sci and Technol.* 20(10): 1028-1032.
- Cotruvo, J.A. (1981). THMs in drinking water. *Environ Sci&Tech.* 15(3): 268-274.
- Croue, J.P., Korshin, G.V., Benjamin, M., (2000). Characterization of Natural Organic Matter in Drinking Water. American Water Works Association, United States of America. 324.
- Department of Environmental and Labour. Water Resources Management Division. 2000. Trihalomethanens level in public water supplies of Newfoundland and Labrador[Online]. Available from: <http://www.hc-sc.gc.ca>[2001 January 25].

- Debroux, J.-F. (1998). The physical–chemical and oxidantreactive properties of effluent organic matter (EfOM) intended for potable reuse. Ph.D. Thesis, University of Colorado, Boulder.
- Dignac, M.F., Ginestet, P., Rybacki, D., Bruchet, A., Urbain, V., and Scribe, P. (2000). Fate of wastewater organic pollution during activated sludge treatment: nature of residual organic matter. *Water Research*. 34 (17): 4185-4194.
- Eaton, A. (1995). Measuring UV-absorbing organic: a standard method. *Journal of American Water Works Association*. 2: 86-90.
- Edzwald, J. K. (1993). Coagulation in drinking water treatment: particles, organics and coagulants. *Water Science and Technology*. 27(11): 21–35.
- Edzwald, J. K.; Becker, W. C.; and Wattier, K. (1985). Surrogate parameters for monitoring organic matter and THM precursors. *Journal of AWWA* 77(4): 122.
- El-Shahat, M.F., Abdel-Halim, S.H., and Hassan, G.A. (1998). Evaluation of trihalomethanes in water treatment plants' outputs in Cairo, Egypt during 1991-1993, *Bull. Environ. Contam. Toxicol* 60: 502-506.
- El-Shahat, M.F., Abdel-Halim, S.H., and Hassan, G.A. (2001). Factors influencing the formation of trihalomethanes in drinking water treatment plants. *Bull. Environ. Contam. Toxicol* 67: 549-553.
- Fukushima, T., Park, J., Imai, A., & Matsushige, K. (1996). Dissolved organic carbon in a eutrophic lake: Dynamics, biodegradation and origin. *Aquatic Sciences*, 58, 139–157.
- Ghazali, Zainuddin Bin Md. (1989). Trihalomethane formation in Bangkok Water Treatment Plant. Thailand. Master's Thesis, Asian Institute of Technology Thailand.
- Gould, J.P., Fitchorn, L.E. and Urheim, E.(1983). Formation of brominated trihalomethanes: extent and kinetics. *Water chlorination: Environmental Impact and Health Effects*, eds. R. L. Jolley *et al.*, Vol. 4. Ann Arbor Science Publishers, Ann Arbor, MI.

- Gray, K.A., McAuliffe, K.S., Bornick, R., Horne, A.J., and Bachand, P. (1996). Evaluation of organic quality in Prado Wetlands and Santa Ana River by Pyrolysis-GC/MS (Final Report). Orange County Water District, CA.
- Henze, M. (1992). Characterization of wastewater for modeling of activated sludge processes. *Water Sci. Technol.* 25, 1–15.
- Hubel, E.R. and Edward, K.J. (1987). Removing Trihalomethanes Precursor by Coagulation. *J.AWWA* .(6): 98-106.
- Imai, A., Fukushima, T., Matsushige, K., Kim, Y-H., and Choi, K. (2002). Characterization of dissolved organic matter in effluent from wastewater treatment plant. *Water Research.* 36: 859-870.
- Janhom, T. (2004). Reduction of trihalomethane created from six fractions of dissolved organic matters in raw water supply by alum coagulation. Master thesis. Inter-Department Program in Environmental Management, Chularongkorn University.
- Kanokkantapong, V., Marhaba, T.F., Panyapinyophol, B., & Pavasant P., (2006). FTIR evaluation of functional groups involved in formation of haloacetic acids during chlorination of raw water. *Journal of Hazardous Materials.* 136(2), 188-196.
- Kim, H.C., Yu, M.J., & Han I. (2006). Multi-method study of the characteristic chemical nature of aquatic humic substances isolated from Han River, Korea. *Applied Geochemistry.* 21(7), 1226-1339.
- Komatsu, K., Nakajima, F., Furumai, H. and Miki, O. (2005). Characterization of dissolved organic matter (DOM) removed by iron coagulation using spectrofluorimetry and pyrolysis GC/MS analysis. *Journal of Water Supply Research and Technology.-AQU,* 54 (3), 157-163.

- Krasner, S.W., McGuire, M.J., Jacangelo, J.G., Patania, N.L., Reagan, K.M., and Aietta, E.M. (1989). The Occurrence of Disinfection By-Products in US Drinking Water. *J. Am. Water Works Assoc.* 81(8), 41.
- Lee, S. and Ahn, K.-H. (2004). Monitoring of COD as an organic indicator in wastewater and treated effluent by fluorescence excitation-emission (FEEM) matrix characterization. *Water Science and Technology.* 50 (8): 57-63.
- Leenheer, J.A., and Croué, J.P. (2003). Characterizing dissolved aquatic organic matter. *Envi Sci and Technol.* 1: 19A-26A.
- Lin, C.F., Liu, S.H. & Hao, O.J. (2001). Effect of functional groups of humic substances on UF performance. *Water research,* 35 (4), 985-996.
- Marhaba, T.F. and Kochar, I.H. (2000). Rapid prediction of disinfection by-product formation potential by fluorescence. *Environmental Engineering and Policy.* 2: 29-36.
- Marhaba, T.F., and Washington, M.B. (1998). Drinking Water Disinfection Byproducts:History and Current Practice. *Adv. Env. Res.* 2 (1), 103-115.
- Marhaba, T.F., and Van, D. (1999). Chlorinated Disinfection By-product Formation Potential of Dissolved Organic Matter Fractions at an Ozonation Water Treatment Plant. *Advances in Environmental Research* 3(3): 255-268.
- Musikavong, C. and Wattanachira, S. (2007). Reduction of dissolved organic matter in terms of DOC, UV-254, SUVA and THMFP in industrial estate wastewater treated by stabilization ponds. *Environ Monit Assess.* 134(1-3):489-97.
- Musikavong, C., Wattanachira, S., Marhaba, T.F., and Pavasant, P. (2005). Reduction of organic matter and trihalomethane formation potential in reclaimed water from treated industrial estate wastewater. *Journal of hazardous material.* B127: 48-57.
- Musikavong, C., Wattanachira, S., Nakajima, F. & Furumai, H. (2007). Three-dimensional fluorescent spectroscopy analysis for evaluation of organic matter removal from



- industrial estate wastewater by stabilization ponds. *Water Science and Technology*. 55(11), 201-210.
- Musikavong, C., Wattanachira, S., Nakajima, F., Furumai, H. (2006). Three-dimensional fluorescent spectroscopy analysis for the evaluation of organic matter removal from industrial estate wastewater by stabilization ponds. In: The Seventh IWA Specialist Conference on Waste Stabilization Ponds: Advances in Pond Technology and Management. 25–27 September. AIT, Bangkok, Thailand.
- Musikavong, C. and Wattanachira, S. (2012). Characterization and treatment of Hydrophilic and Hydrophobic Organic Matter in Raw Water Supply from U-Tapao Canal, Songkhla, Thailand. Final report, Thailand research fund.
- Nakajima, F., Hanabusa, M., and Furumai, H. (2002). Excitation-emission fluorescence spectra and trihalomethane formation potential in the Tama River, Japan. *Water Science and Technology: Water Supply*. 2: (5-6), 481-486.
- Nakajima, F., Hanabusa, M., and Furumai, H. (2002). Excitation-emission fluorescence spectra and trihalomethane formation potential in the Tama River, Japan. *Water Science and Technology: Water Supply*. 2 (5-6), 481-486.
- Norin, H. and Renberg, L. (1980). *Determination of trihalomethanes (THM) in water using high efficiency solvent extraction*. *Water Res.* 14:1397.\*
- Oliver, B.G. and Lawrence, J. (1979). Haloform in drinking water: a study of Precursor and precursor removal. *J.AWWA*. 71:3:161.
- Owen, D. M., Pirnie, M. and Amy, G. L. (1993). Characterization of natural organic matter and its relationship to treatability. AWWARF order number: 90631
- Peters, C. J.; Young, R. J.; and Perry, R. (1980). Factors influencing the formation of haloforms in the chlorination of humic materials. *Environ. Sci. & Technol.* 14: 1391-1395.

- Pettersson, C., Bishop, K. H., and Lee, Y. H. (1995). Relations between Organic Carbon and Methylmercury in Humic Rich Surface Waters from Svartberget Catchment in Northern Sweden. *Water Air and Soil Pollution*. 80:971-979.
- Peschel, G. and Wildt, T. (1988). Humic substances of natural and anthropogeneous origin. *Water Research*. 22: 105–108.
- Phumpaisanchai, A. (2005). Removal of Hydrophobic and Hydrophilic Natural Organic Matters in Reservoirs by Alum Coagulation Master Thesis. Graduated School, Chiang Mai University. Thailand.
- Poerschmann, J., Kopinke, F.D., Balcke, G., and Mothes, S. (1998). Pyrolysis pattern of anthropogenic and natural humic organic matter. *Journal of Microcolumn Separations*. 10: 401–411.
- Rook, J.J. (1974). Formation of haloform during chlorination of natural waters. *Journal of the Society for Treatment Examination*. 23: 234-243.
- Rook, J. J. (1977). Formation of haloforms during chlorination of natural water. *Water Treatment and Examinations* 23: 234-243.
- Saadi, I., Borisover, M., Armon, R., Laor, Y. (2006). Monitoring of effluent DOM biodegradation using fluorescence, UV and DOC measurements. *J. Chemosphere*. 63, 530–539.
- Sierra, M.M.D., Giovanela, M., Parlanti, E., Soriano-Sierra, E.J., (2005). Fluorescent fingerprint of fulvic and humic acids from varied origins as viewed by singlescan and excitation/emission matrix techniques. *Chemosphere* 58, 715–733.
- Sirivedhin, T. and Gray, A. (2005). Part I. Identifying anthropogenic markers in surface waters influenced by treated effluents: a tool in potable water reuse. *Water Research*. 39: 1154-1164.
- Shih, Y.H. and Wu, S.C. (2002). Sorption Kinetics of Toluene in Humin under Two Different Levels of Relative Humidity. *J. Environ. Qual.* 31, 970-978.

- Sposito, G. (1989) *The Chemistry of Soils*. Oxford, New York, NY.
- Standard Methods for the Examination of Water and Wastewater* (1995) 19<sup>th</sup> ed, American Public Health Association/American Water Works Association/Water Environment Federation, Washington, DC.
- Stevens, A. A.; Slocum, C. R.; Seeger, D. R. *et al.* (1976). Chlorination of organics in drinking water. *Journal of AWWA* 68: 615-620.
- Thurman, E. M. (1985). *Organic Geochemistry of Natural Waters*. Marinus Nijhoff/Dr.W.Junk, Dordrecht. The Netherlands.
- Trussell, R.R.,and Umphres, M.D.(1978). The formation of trihalomethanes. 70(11):604-611.
- U.S. EPA. (1999). *Enhanced coagulation and enhanced precipitative softening guidance manual: Office of water (4607)[Online]*. Available online from: <http://www.epa.gov> [2010, October 10].
- USEPA (1998). *National Primary Drinking Water Regulation: Disinfectants And Disinfection By-Product (D/DBP), Final Rule*. Fed Register. 63:69389-69476.
- White D. M., Garland D. S., Narr J., and Woolard,C.R. (2003). Natural organic matter and DBP formation potential in Alaskan water supplies.*Water Research*. 37: 939-947.
- Yamashita, Y. and Tanoue, E. (2003). Chemical characterization of protein-like fluorophores in DOM in relation to aromatic amino acids. *Marine Chemistry*. 82: 255-271.
- Zepp, R.G., Sheldon, W.M. and Moran, M.A. (2004) Dissolved organic fluorophores in southeastern US coastal waters: correction methods for eliminating Rayleigh and Raman scattering peaks in excitation-emission matrices. *Marine Chemistry*, 89, 15-36.

**APPENDIX A**  
**CALIBRATION DATA AND CURVES**

**APPENDIX A**  
**CALIBRATION DATA AND CURVES**

**A.1. Calibration data and curves**

**Table A.1** Calibration data of UV-254 nm.

concentration of KHP (mg/L)	Abs (cm <sup>-1</sup> )		
	First Sampling	Second Sampling	Average
2.0	0.03	0.03	0.03
4.0	0.06	0.06	0.06
8.0	0.11	0.11	0.11
16.0	0.20	0.20	0.20
20.0	0.23	0.23	0.23

**Table A.2** Calibration curve of DOC.

concentration(mg/L)	Area (Counts)
0	2028
2.5	29006
5.0	52488
7.5	77264
10.0	103313

## A.2 HP 6890 GC method.

Method: C:\HPCHEM\1\METHODS\TASANA5.M of 10/7/2009 9:45:18 AM

=====  
 HP6890 GC METHOD  
 =====

## OVEN

Initial temp: 60 'C (On)                   Maximum temp: 270 'C  
 Initial time: 1.00 min                   Equilibration time: 3.00 min  
 Ramps:  

#	Rate	Final temp	Final time
1	10.00	100	1.00
2	10.00	130	1.00
3	10.00	180	1.00
4	0.0 (Off)		

 Post temp: 60 'C  
 Post time: 0.00 min  
 Run time: 16.00 min

## FRONT INLET (COOL ON COLUMN)

Mode: Oven track  
 Pressure: 0.00 psi (Off)  
 Gas type: Helium

## BACK INLET (SPLIT/SPLITLESS)

Mode: Split  
 Initial temp: 225 'C (On)  
 Pressure: 31.16 psi (On)  
 Split ratio: 26.885:1  
 Split flow: 96.5 mL/min  
 Total flow: 102.7 mL/min  
 Gas saver: On  
 Saver flow: 20.0 mL/min  
 Saver time: 2.00 min  
 Gas type: Helium

## COLUMN 1

Capillary Column  
 Model Number: HP 19091N-133  
 HP-INNOWax Polyethylene Glycol  
 Max temperature: 260 'C  
 Nominal length: 30.0 m  
 Nominal diameter: 250.00 um  
 Nominal film thickness: 0.25 um  
 Mode: constant flow  
 Initial flow: 3.6 mL/min  
 Nominal init pressure: 31.17 psi  
 Average velocity: 61 cm/sec  
 Inlet: Back Inlet  
 Outlet: Back Detector  
 Outlet pressure: ambient

## COLUMN 2

(not installed)

## FRONT DETECTOR (FID)

Temperature: 250 'C (Off)  
 Hydrogen flow: 40.0 mL/min (Off)  
 Air flow: 450.0 mL/min (Off)  
 Mode: Constant makeup flow  
 Makeup flow: 45.0 mL/min (Off)  
 Makeup Gas Type: Nitrogen  
 Flame: Off  
 Electrometer: Off  
 Lit offset: 2.0

## BACK DETECTOR (μECD)

Temperature: 300 'C (On)  
 Mode: Constant makeup flow  
 Makeup flow: 60.0 mL/min (On)  
 Makeup Gas Type: Nitrogen  
 Electrometer: On

## SIGNAL 1

Data rate: 20 Hz  
 Type: back detector  
 Save Data: On  
 Zero: 0.0 (Off)  
 Range: 0  
 Fast Peaks: Off  
 Attenuation: 0

## SIGNAL 2

Data rate: 20 Hz  
 Type: back detector  
 Save Data: Off  
 Zero: 0.0 (Off)  
 Range: 0  
 Fast Peaks: Off  
 Attenuation: 0

## COLUMN COMP 1

Derive from front detector

## COLUMN COMP 2

Derive from back detector

## POST RUN

Post Time: 0.00 min

Instrument 1 10/8/2009 3:36:41 PM Aroon

Page 2 of 5

Figure A.1 HP 6890 GC method

**APPENDIX B**  
**EXPERIMENTAL DATA**

**B.1. Experimental data****Table B.1** DOC of Plant A.

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	30.98	96.37
<b>Anaerobic Pond</b>	30.58	87.62
<b>Aeration Ponds</b>	19.31	64.22

**Table B.2** BOD of Plant A.

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	229	388
<b>Anaerobic Pond</b>	47	105
<b>Aeration Ponds</b>	15	17

**Table B.3** UV-254 of Plant A.

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	1.29	1.46
<b>Anaerobic Pond</b>	1.17	1.30
<b>Aeration Ponds</b>	1.01	1.14

**Table B.4** COD of Plant A.

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	1513.40	1697.00
<b>Anaerobic Pond</b>	197.40	221.09
<b>Aeration Ponds</b>	89.49	93.44



**Table B-5 THMFP of Plant A.****First Sampling**

	<b>CHCl<sub>3</sub></b>	<b>CHCl<sub>2</sub>Br</b>	<b>CHClBr</b>	<b>CHBr<sub>3</sub></b>	<b>TTHMFP</b>
<b>Influent</b>	109.65	67.85	0.00	0.00	177.50
<b>Anaerobic Pond</b>	18.05	39.00	0.00	0.00	57.05
<b>Aeration Ponds</b>	14.43	38.86	0.00	0.00	53.30

**Second Sampling**

	<b>CHCl<sub>3</sub></b>	<b>CHCl<sub>2</sub>Br</b>	<b>CHClBr</b>	<b>CHBr<sub>3</sub></b>	<b>TTHMFP</b>
<b>Influent</b>	366.97	309.54	0.00	0.00	676.51
<b>Anaerobic Pond</b>	226.17	231.48	0.00	0.00	457.65
<b>Aeration Ponds</b>	27.19	38.61	0.00	0.00	65.80

**Table B.6 DOC of Plant B.**

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	92.163	28.413
<b>Influent from De-Chlorination</b>	21.033	30.968
<b>Dissolved Air Floatation</b>	40.112	39.944
<b>Aerated lagoons</b>	31.873	30.414

**Table B.7** BOD of Plant B.

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	69.8	65.9
<b>Influent from De-Chlorination</b>	20.0	22.5
<b>Dissolved Air Floatation</b>	51.0	49.1
<b>Aerated lagoons</b>	10.0	9.8

**Table B.8** UV-254 of Plant B.

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	4.00	3.54
<b>Influent from De-Chlorination</b>	0.41	0.41
<b>Dissolved Air Floatation</b>	0.69	0.62
<b>Aerated lagoons</b>	0.33	0.30

**Table B.9** COD of Plant B.

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	1798.4	1751.4
<b>Influent from De-Chlorination</b>	156.2	145.8
<b>Dissolved Air Floatation</b>	120.3	114.1
<b>Aerated lagoons</b>	77.6	81.4

**Table B.10** THMFP of Plant B**First Sampling**

	<b>CHCl<sub>3</sub></b>	<b>CHCl<sub>2</sub>Br</b>	<b>CHClBr</b>	<b>CHBr<sub>3</sub></b>	<b>TTHMFP</b>
<b>Influent</b>	1107.68	62.35	0	0	1170.03
<b>Influent from De-Chlorination</b>	47.35	56.21	0	0	103.55
<b>Dissolved Air Floatation</b>	635.97	61.54	0	0	697.51
<b>Aerated lagoons</b>	579.12	58.32	0	0	637.44

**Second Sampling**

	<b>CHCl<sub>3</sub></b>	<b>CHCl<sub>2</sub>Br</b>	<b>CHClBr</b>	<b>CHBr<sub>3</sub></b>	<b>TTHMFP</b>
<b>Influent</b>	953.36	59.55	0	0	1012.90
<b>Influent from De-Chlorination</b>	33.10	38.10	0	0	71.20
<b>Dissolved Air Floatation</b>	656.50	48.58	0	0	705.08
<b>Aerated lagoons</b>	578.51	56.66	0	0	635.17

**Table B.11** DOC of Plant C.

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	28.99	23.74
<b>Influent from De-Chlorination</b>	14.63	10.53
<b>Aerated lagoons</b>	20.35	19.62

**Table B.12** BOD of Plant C.

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	20.0	22.0
<b>Influent from De-Chlorination</b>	9.0	10.8
<b>Aerated lagoons</b>	11.4	13.7

**Table B.13** UV-254 of Plant C.

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	0.38	0.43
<b>Influent from De-Chlorination</b>	0.09	0.14
<b>Aerated lagoons</b>	0.30	0.37

**Table B.14** COD of Plant C.

	<b>First Sampling</b>	<b>Second Sampling</b>
<b>Influent</b>	94.60	100.90
<b>Influent from De-Chlorination</b>	28.80	33.60
<b>Aerated lagoons</b>	62.30	72.20

**Table B.15** THMFP of Plant C.**First Sampling**

	<b>CHCl<sub>3</sub></b>	<b>CHCl<sub>2</sub>Br</b>	<b>CHClBr</b>	<b>CHBr<sub>3</sub></b>	<b>TTHMFP</b>
<b>Influent</b>	244.16	45.34	0	0	289.51
<b>Influent from De-Chlorination</b>	50.05	59.21	0	0	109.25
<b>Aerated lagoons</b>	168.06	38.93	0	0	206.98

**Second Sampling**

	<b>CHCl<sub>3</sub></b>	<b>CHCl<sub>2</sub>Br</b>	<b>CHClBr</b>	<b>CHBr<sub>3</sub></b>	<b>TTHMFP</b>
<b>Influent</b>	259.21	47.81	0	0	307.03
<b>Influent from De-Chlorination</b>	60.23	61.32	0	0	121.55
<b>Aerated lagoons</b>	156.44	42.44	0	0	198.88