QUALIFICATION AND QUANTIFICATION OF DISSOLVED ORGANIC MATTERS IN BREWERY WASTEWATERS AND THEIR TREATED WASTEWATERS

Miss Tansiphorn Janhom

A Dissertation Submitted in Partial Fulfillment of the Requirements
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การศึกษาปริมาณและคุณภาพของสารอินทรีย์ละลายน้ำในน้ำเสียและน้ำที่ผ่านระบบบำบัดจากโรงเบียร์

นางสาวธัญศิภรณ์ จันทร์หอม

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรดุษฎีบัณฑิต
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ธัญศิภรณ์ จันทร์หอม: การศึกษาปริมาณและคุณภาพของสารอินทรีย์ละลายน้ำในน้ำเสียและน้ำที่ผ่านระบบบำบัดจากโรงเบียร์ (QUALIFICATION AND QUANTIFICATION OF DISSOLVED ORGANIC MATTERS IN BREWERY WASTEWATERS AND THEIR TREATED WASTEWATERS) อ. ที่ปรึกษาวิทยานิพนธ์หลัก: รศ.ดร. ประเสริฐ ภวสันต์, อ. ที่ปรึกษาวิทยานิพนธ์ร่วม : รศ.ดร. สุรพงษ์ วัฒนะจีระ, 154 หน้า.

การศึกษาปริมาณและคุณภาพของสารอินทรีย์ละลายน้ำในน้ำเสียจากโรงเบียร์ จำนวน 3 โรงงาน ในประเทศไทย (โรงเบียร์ 1, 2 และ 3) โดยการวิเคราะห์ผ่านดรรชนีตัวแทนของสารอินทรีย์ละลายน้ำ (DOM surrogates), การวิเคราะห์สัญญาณ Fluorescent excitation-emission matrix (FEEM), การวิเคราะห์ Fourier transform infrared (FTIR) spectroscopy และ การวิเคราะห์ Pyrolysis gas chromatography mass spectrometry (Pyrolysis GC/MS) และการประเมินสารอินทรีย์ละลายน้ำในน้ำเสียจากโรงเบียร์ที่ผ่านการบำบัดด้วยอนุกรมของระบบชั้นตะกอนจุลินทรีย์ไร้อากาศแบบไหลขึ้น หรือระบบยูเอเอสบี (Upflow Anaerobic Sludge Blanket: UASB) และ ระบบบำบัดน้ำเสียแบบแอกทิเวเต็ดสลัดจ์ หรือระบบเอเอส (Activated Sludge: AS) และเพื่อทำให้สามารถประเมินลักษณะที่จำเพาะเจาะจงยิ่งขึ้น จึงนำเทคนิคการแยกองค์ประกอบสารอินทรีย์ละลายน้ำด้วยการใช้อนุกรมของเรซิ่น DAX-8, AG-MP-50 และ WA-10 สำหรับแยกสารอินทรีย์ละลายน้ำออกเป็น 6 กลุ่ม ประกอบด้วยสารอินทรีย์ละลายน้ำกลุ่ม Hydrophobic neutral (HPON), Hydrophobic base (HPOB), Hydrophobic acid (HPOA), Hydrophilic base (HPIB), Hydrophilic acid (HPIA), และ Hydrophilic neutral (HPIN) ก่อนทำการวิเคราะห์ด้วยเทคนิคต่างๆ พบว่าสารอินทรีย์ละลายน้ำในน้ำเสียจากโรงเบียร์ส่วนใหญ่เป็นกลุ่ม HPOA และ HPIB ซึ่งสารอินทรีย์ละลายน้ำทั้งสองกลุ่มนี้ยังเป็นกลุ่มหลักที่สามารถก่อให้เกิดสารไตรฮาโลมีเทน (THMs) โดยมีสารอินทรีย์ที่เป็นองค์ประกอบหลักของสารอินทรีย์ละลายน้ำทั้งสองกลุ่มนี้เป็นสารกลุ่ม Tryptophan-like substances และ Fulvic and Humic-like substances จากผลศึกษาการบำบัดสารอินทรีย์ละลายน้ำในน้ำเสียจากโรงเบียร์พบว่าสารอินทรีย์ละลายน้ำจะถูกกำจัดด้วยระบบยูเอเอสบีเป็นส่วนใหญ่ โดยค่าการกำจัดเป็นผลจากการลดลงของสารอินทรีย์ละลายน้ำทั้งสองกลุ่มหลัก ซึ่งมีผลโดยตรงต่อการลดโอกาสการก่อตัวของสารไตรฮาโลมีเทน (Trihalomethane Formation Potential: THMFP) ในน้ำเสียจากโรงเบียร์ จึงอาจกล่าวได้ว่าการลดโอกาสการก่อตัวของสารไตรฮาโลมีเทนในน้ำเสียดังกล่าว ส่วนใหญ่เป็นผลจากการลดลงของสารกลุ่ม tryptophan-like substances และจากการลดลงของส่วนที่สามารถย่อยสลายได้ของสาร Fulvic and Humic-like substances ของสารอินทรีย์ละลายน้ำสองกลุ่มหลัก และจากผลการประเมินประสิทธิภาพการบำบัดของระบบยูเอเอสบีและเอเอสในการลดสารอินทรีย์ละลายน้ำในน้ำเสียจากโรงเบียร์ 1, 2 และ 3 พบว่าสามารถลดค่า DOC ได้ร้อยละ 65, 87 และ 79 ค่า UV_{254} ได้ร้อยละ 65, 88 และ 70 และค่าโอกาสการก่อตัวของสารไตรฮาโลมีเทนได้ร้อยละ 71, 90 และ 78 ตามลำดับ แต่อย่างไรก็ตามค่าโอกาสการก่อตัวของสารไตรฮาโลมีเทนในน้ำที่ผ่านกระบวนการบำบัดแล้วยังคงมีค่าสูงเมื่อเปรียบเทียบกับค่าโอกาสการก่อตัวของสารไตรฮาโลมีเทนในน้ำจากแหล่งน้ำดิบสำหรับการทำประปา จากการพิจารณาสารอินทรีย์ละลายน้ำกลุ่ม HPOA ซึ่งมีสาร Fulvic and Humic-like substances เป็นองค์ประกอบหลัก พบว่าสารกลุ่มดังกล่าวมีปริมาณคงเหลือในน้ำที่ผ่านการบำบัดเป็นส่วนใหญ่ และยังจัดเป็นสารกลุ่มที่ยากต่อการบำบัดด้วยกระบวนการบำบัดทางชีวภาพ ดังนั้นจึงอาจจะสรุปได้ว่าสารอินทรีย์ละลายน้ำกลุ่ม HPOA จึงเป็นกลุ่มที่เป็นปัญหาสำหรับการนำน้ำเสียจากโรงเบียร์ที่ผ่านการบำบัดแล้วมาใช้ใหม่ นอกจากนี้ผลการวิจัยยังพบแนวโน้มที่ดีในการนำเทคนิค FEEM มาประยุกต์ใช้เป็นเครื่องมืออย่างง่ายในการวิเคราะห์สารอินทรีย์ละลายน้ำในน้ำเสียโรงเบียร์ได้เป็นอย่างดี เมื่อผลจากการวิเคราะห์สารอินทรีย์ละลายน้ำด้วยเทคนิค FEEM มีความสอดคล้องกับผลการวิเคราะห์ค่าดรรชนีตัวแทนสารอินทรีย์ละลายน้ำทั้งค่า DOC และ UV_{254} ดังจะเห็นได้จากผลการประเมินประสิทธิภาพการบำบัดสารอินทรีย์ละลายน้ำผ่านการวัดค่าความเข้มแสง (Fluorescent Intensity) ที่ลดลงร้อยละ 55, 86 และ 64 สำหรับโรงเบียร์ 1, 2 และ 3 ตามลำดับ

สาขาวิชา การจัดการสิ่งแวดล้อม
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KEYWORDS: TRIHALOMETHAME FORMATION POTENTIAL (THMFP) / DISSOLVED ORGANIC MATTER (DOM) / FRACTIONATION / FLUORESCENT EXCITATION-EMISSION MATRIX (FEEM) / BREWERY WASTEWATER

TANSIPHORN JANHOM: QUALIFICATION AND QUANTIFICATION OF DISSOLVED ORGANIC MATTERS IN BREWERY WASTEWATERS AND THEIR TREATED WASTEWATERS. THESIS ADVISOR: ASSOC. PROF. PRASERT PAVASANT, Ph.D., THESIS CO-ADVISOR: ASSOC. PROF. SURAPHONG WATTANACHIRA, D.Eng., 154 pp.

Dissolved organic matter (DOM) in wastewater from three breweries in Thailand, namely Sites 1, 2 and 3, was qualified and quantified through DOM surrogates, fluorescent excitation-emission matrix (FEEM), fourier transform infrared (FTIR) spectroscopy, and pyrolysis gas chromatography mass spectrometry (pyrolysis GC/MS), stepwise along the treatment train which typically comprises a series of biological processes, i.e. upflow anaerobic sludge blanket (UASB) followed by activated sludge (AS). To evaluation DOM characteristics in greater detail, DOM in all samples was isolated into six DOM fractions viz. hydrophobic neutral (HPON), hydrophobic base (HPOB), hydrophobic acid (HPOA), hydrophilic base (HPIB), hydrophilic acid (HPIA) and hydrophilic neutral (HPIN) using a series of DAX-8, AG-MP-50, and WA-10 resins prior to further analyses. The results revealed that major organic fractions in brewery wastewater were HPOA and HPIB which were also found to be the main trihalomethane (THM) precursors for all three studied breweries. The major DOM components in brewery wastewater from three sites (both light and lager beers) were groups of tryptophan-like substances and fulvic and humic-like substances. The reduction of DOM was mainly found to occur during the UASB treatment which was attributed to the removal of these two major DOM fractions. This resulted in a direct reduction in trihalomethane formation potential (THMFP). In other words, the reduction in THMFP was mainly due to the disappearance of tryptophan-like substances and partially occurred from decreases of degraded fulvic and humic-like substances of the two main THM precursors. The effectiveness of the UASB and AS treatments on the reductions in DOC, UV_{254}, and THMFP were comparable, i.e. 65, 87, 79 for DOC; 65, 88, 70, for UV_{254}, and 71, 90, and 78% for THMFP were observed for Sites 1, 2 and 3, respectively. However, the existing THMFP of the final effluent from all three breweries was still high when compared to THMFP in the water supply facilities. Among all organic fractions, HPOA, particularly fulvic and humic-like substances, was of particular concern for water reclamation process of treated brewery wastewater, since it was still relatively predominated in residual DOM in the effluents and it was considered likely to be refractory in biological treatments. In addition, FEEM analytical results were consistent with the results from conventional DOM analyses such as DOC and UV_{254} with certain level of confidence, where FEEM was reduced by 55, 86, and 64% for Sites 1, 2 and 3, respectively. Hence, FEEM could be potentially employed as a simple monitoring technique for DOM in brewery wastewater.

Field of Study: Environmental Management
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LIST OF ABBREVATIONS

abs.	Absorbance
amu	Apparent Molecular Unit
amw	Average Molecular Weight
AWWA	American Water Works Association
AS	Activated Sludge
BOD	Biochemical Oxygen Demand
$CHBr_3$	Bromoform
$CHCl_2Br$	Bromodichloromethane
$CHCl_3$	Chloroform
$CHClBr_2$	Dibromochloromethane
Cl_2	Chlorine
cm	Centimeter
COD	Chemical Oxygen Demand
°C	Degree Celsius
D/DBP	Disinfection /Disinfection by product ratio
DBPs	Disinfection by Products
DOC	Dissolved Organic Carbon
DOM	Dissolved Organic Matter
DPD	*N*, *N*-diethyl-*p*-phenylenediamine
ECD	Electron Capture Detector
EDTA	Disodiumethylenediamine Tetraacetate Dehydrate
EPA	Environmental Protection Agency
FAS	Ferrous Ammonium Sulfate
FEEM	Fluorescent Excitation–Emission Matrix
FTIR	Fourier Transform Infrared Spectroscopy
g/cm^3	Gram per Cubic Centimeter
g/L	Gram per Liter
g/mol	Gram per Molar
GC	Gas Chromatograph
GC/MS	Gas Chromatograph Mass Spectrometry

hr	Hour
HA	Humic Acid
HAAs	Haloacetic acid
HANs	Haloacetonitrile
HPIA	Hydrophilic acid
HPIB	Hydrophilic base
HPIN	Hydrophilic neutral
HPOA	Hydrophobic acid
HPOB	Hydrophobic base
HPON	Hydrophobic neutral
KHP	Potassium Hydrogen Phthalate
KI	Potassium Iodide
L/mg-m	Liter per milligram-meter
m	Meter
M	Molar
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
μg/L	Microgram per Liter
mg/L	Milligram per Liter
mw	Molecular Weight
nm	Nanometer
NOM	Natural Organic Matter
NTU	Nepheo Turbidity Unit
ppm	Part per Million
$SUVA_{254}$	Specific Ultraviolet Absorbance at wavelength of 254 nanometers
THMFP	Trihalomethanes Formation Potential
THMs	Trihalomethanes
TOC	Total Organic Carbon
TTHM	Total Trihalomethanes
UASB	Upflow Anaerobic Sludge Blanket
USEPA	United States Environmental Protection Agency
UV_{254}	Ultraviolet Absorbance at wavelength of 254 nanometers

CHAPTER I

INTRODUCTION

1.1 Motivations

High strength organic wastewater is rather difficult to be treated by common wastewater treatment systems, and even with the most efficient treatment facility, the effluent still contains small amount of organic constituents or commonly known as dissolved organic matter (DOM). This residual DOM is of particular concern as they could potentially react with chlorine during the disinfection process in the typical water treatment facility and formed halogenated disinfection by-products (DBPs), e.g. trihalomethanes (THMs) and haloacetic acids (HAAs) which are classified as carcinogenic substances (Rook, 1974). The U.S. Environmental Protection Agency (USEPA) has issued the drinking water standard under the Disinfectants/Disinfection By-Products (D/DBP) Rule with a THMs Maximum Contaminant Level (MCL) of 80 μg/L for Stage 1 and 40 μg/L for Stage 2 which is due to be deployed in the near future. 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 a thorough investigation of the formation of DBPs 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. Biochemical oxygen demand (BOD), chemical oxygen demand (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. More complicated techniques have been utilized to qualify DOM in terms of their physical and chemical natures including resin fractionation, elemental analyses; ^{13}C- and ^{1}H-nuclear magnetic resonance (NMR) spectroscopy, fourier transform infrared (FTIR) spectroscopy, and pyrolysis gas chromatography mass spectrometry (pyrolysis GC/MS). Three-dimensional fluorescent spectroscopy technique--fluorescent excitation-emission matrix (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 humiclike fluorophores and the proteinlike fluorophores (Chen et al., 2003; Leenheer and Croue, 2003; Sierra et al., 2005). The application of FEEM is becoming increasingly widespread for river or fresh water (Coble, 1996; Croue, et al., 2000; 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; Saadi et al., 2006).

Brewery, one of the main generators of organic pollutants with high organic loading, not only produces a massive amount of wastewater, typically 3–12 hectoliters of wastewater for every hectoliter of beer produced (Luc Fillaudeau et al., 2006) but also requires an enormous amount of water, with more or less 7 hectoliters for each hectoliter of beer production. Therefore, reuse of treated brewery wastewater is of high importance for brewery. Unfortunately, water reuse is not common in this type of industry due to public perception and possible product quality deterioration problems. However, the future reuse of water seems to be unavoidable, as the issue of water shortage has become a serious global and environmental problem. Nevertheless, leaving a considerable amount of DOM in the treated wastewater is still a problematic issue for reuse purposes as mentioned above. Accordingly, a thorough comprehension of both the characteristics of the DOM and the process ability to treat is essential for establishing proper management of treated wastewater prior to reuse.

In this work, the brewery wastewater was characterized stepwise along the treatment train. Typically the wastewater treatment process of breweries comprises a series of different processes, i.e. upflow anaerobic sludge blanket (UASB) followed by activated sludge (AS). The approaches herein were to isolate DOM in influent and effluents from UASB and AS using the resin adsorption method and to investigate their surrogate parameters of DOM and DOM fractions. Spectrofluorometry was utilized to fingerprint DOM and DOM fractions in influents and effluents from each treatment step. Furthermore, functional groups, chemical classes and important pyrolysis fragments of DOM and DOM fractions of the influent wastewater and the effluents from each treatment step were introduced to identify and confirm the fluorescent organic compounds. The reduction of DOM and DOM fractions during the treatment course was also appraised. Wastewaters from three major local breweries in Thailand with a total beer production rate of more than a half of the overall beer production rate in the country were selected as a modeled system for this study.

1.2 Objectives

Main objectives were:

- To characterize DOM and DOM fractions in brewery wastewaters and in the effluents from UASB and AS treatments through DOM surrogates.
- To quantify and qualify the DOM and DOM fractions using FEEM together with identification and confirmation of the fluorescent DOM and DOM fractions by pyrolysis-GC/MS analysis, and also to examine their functional groups with FTIR.

- To appraise the reduction of THMFP in brewery wastewaters through UASB and AS treatments.

Sub objectives were:

- To characterize DOM in brewery wastewaters and the effluents from UASB and AS treatments using fractionation method and to determine the potential of each DOM fraction to form Trihalomethanes (THMs) during disinfection process.
- To fingerprint DOM and DOM fractions in brewery wastewaters and the effluents from UASB and AS treatment using FEEM.
- To introduce functional groups, chemical classes and important pyrolysis fragments of DOM and DOM fractions of the influent wastewater and the effluents from UASB and AS to identify and confirm the fluorescent organic compounds.

1.3 Scopes of Study

- Influent wastewater and effluents from each treatment step of the wastewater treatment system of three local breweries in Thailand with a total production rate of more than a half of the overall country beer production rate were studied.
- The resin fraction technique developed by Leenheer (1981) and Marhaba et al. (2003) was utilized as a fractionation method for all collected water sample.
- All water samples were analyzed through DOM surrogate parameters including DOC, UV_{254}, $SUVA_{254}$, and THMFP.
- A FEEM was utilized to qualify and quantify fluorescent organic matters of DOM and DOM fractions.

- A FTIR analysis was employed to introduce and identify functional groups of DOM and their DOM fractions of all water samples.
- A pyrolysis GC/MS was used to introduce and identify chemical classes and pyrolysis fragments of DOM and their DOM fractions of all water samples.
- The problematic DOM fractions of brewery wastewaters and the effluents from UASB and AS treatments were determined.
- The performance capability of UASB and AS for reducing DOM and DOM fractions of brewery wastewaters was evaluated.

CHAPTER II

BACKGROUNDS AND LITERATURE REVIEWS

2.1 Trihalomethanes (THMs)

2.1.1 Background

Chlorination has made the water supply safe from bacteria, viruses, and parasites, as it has almost completely eliminated risks of deadly waterborne diseases such as typhoid fever, cholera, and dysentery. However, 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) present in the source water. Different disinfectants produce different types or amounts of disinfection by-products (DBPs), the most common of which being THMs. THMs are typically considered to include four chemicals: chloroform, bromodichloromethane, dribromochloromethane, and bromoform. The first identification of chloro- and bromo-trihalomethanes (THMs) was done by J.J. Rook in 1974. The first class of halogenated DBPs was 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, and it was reported that THMs were found to be the most widespread organic contaminants in drinking water, and occurred at higher concentrations than other DBPs. 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 and Travis, 1986). Chloroform ($CHCl_3$), the most common form of THMs, is a proven animal carcinogen and a suspected human carcinogen.

THMs can be taken into body by drinking the water and breathing its vapors (for example when showering). They are then metabolized and eliminated 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 induce cytotoxicity in the liver and kidneys of rodents 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. However, there are some reports on the investigation of THMFP in different types of water. For instance, Musikavong et al. (2005) revealed that the level of THMFP in the treated wastewater of the industrial estate in northern Thailand was moderately high when compared with other surface waters in Thailand (Wattanachira et al., 2003; Homklin, 2004; Janhom et al., 2005; Panyapinyopol et al., 2005; Phumpaisanchai, 2005; Musikavong, 2006). This could pose serious concerns for the authorities and further examination of the effect of such THMs on human and environment should be conducted.

2.1.2 Possible reaction pathways of THMs in water treatment

Reckhow and Singer (1990) demonstrated a possible reaction that illustrates steps by which chloroform can be produced during water treatment as shown in Figure 2.1 whereas the National Environmental Board (1984) demonstrated a series of reactions of chloroform that may be created during water treatment as shown in Figure 2.2.

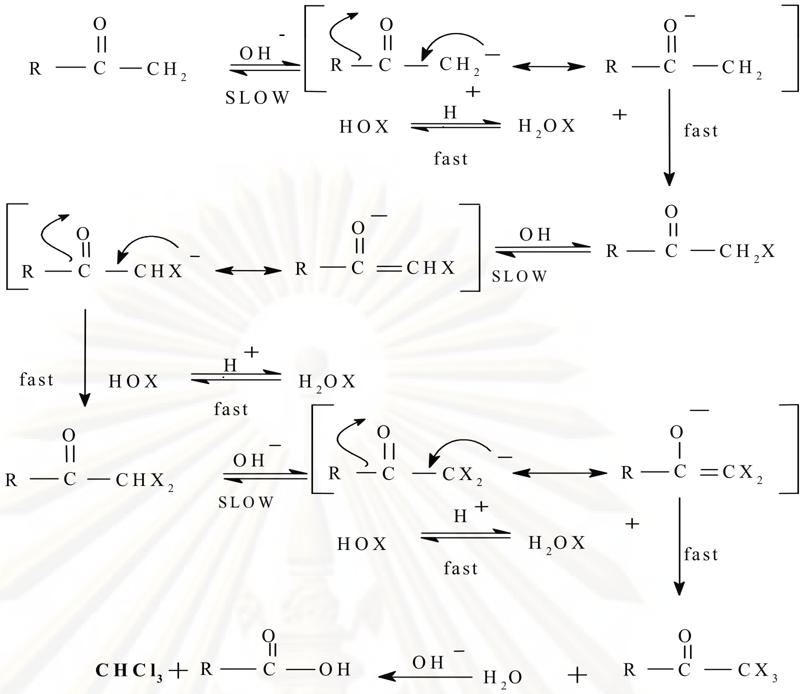
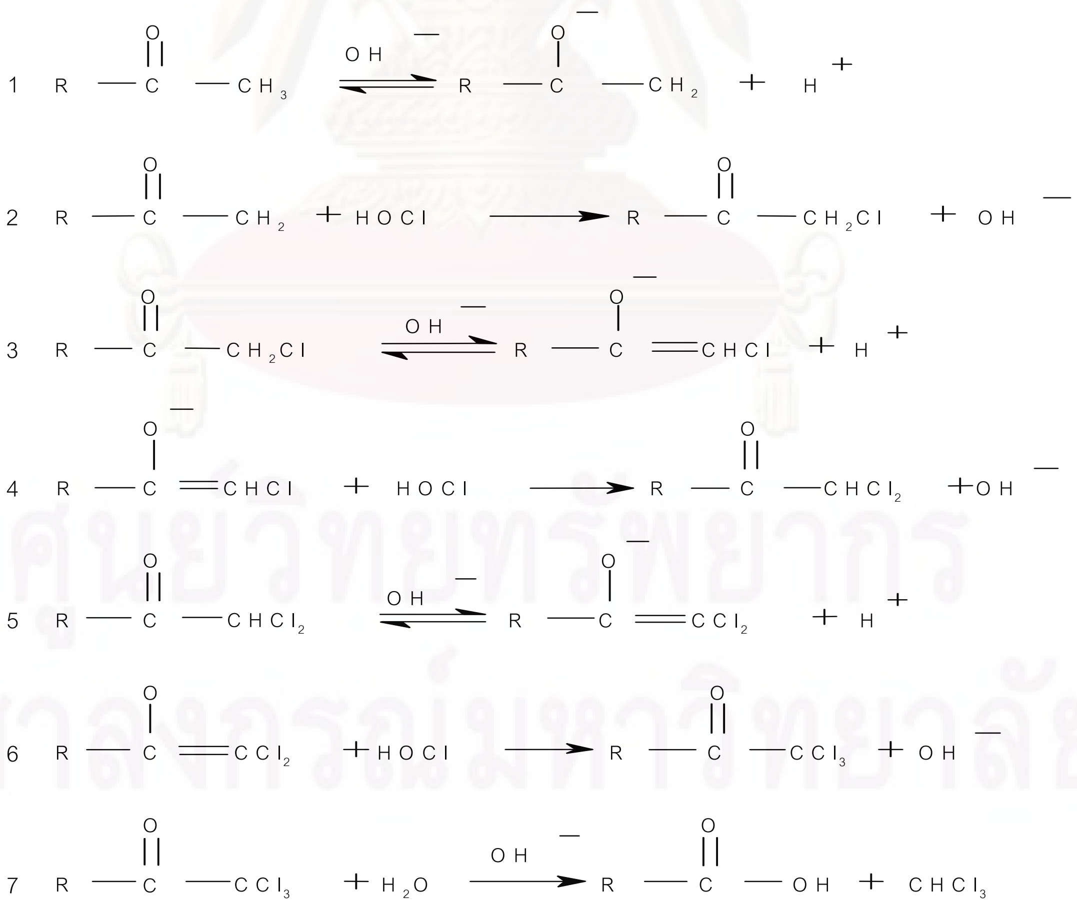


Figure 2.1 Chloroform reaction pathways



$$1\quad R-\overset{O}{\overset{\|}{C}}-CH_3 \overset{OH^-}{\rightleftharpoons} R-\overset{O^-}{\overset{|}{C}}-CH_2 + H^+$$

$$2\quad R-\overset{O}{\overset{\|}{C}}-CH_2 + HOCl \longrightarrow R-\overset{O}{\overset{\|}{C}}-CH_2Cl + OH^-$$

$$3\quad R-\overset{O}{\overset{\|}{C}}-CH_2Cl \overset{OH^-}{\rightleftharpoons} R-\overset{O^-}{\overset{|}{C}}=CHCl + H^+$$

$$4\quad R-\overset{O^-}{\overset{|}{C}}=CHCl + HOCl \longrightarrow R-\overset{O}{\overset{\|}{C}}-CHCl_2 + OH^-$$

$$5\quad R-\overset{O}{\overset{\|}{C}}-CHCl_2 \overset{OH^-}{\rightleftharpoons} R-\overset{O^-}{\overset{|}{C}}=CCl_2 + H^+$$

$$6\quad R-\overset{O}{\overset{|}{C}}=CCl_2 + HOCl \longrightarrow R-\overset{O}{\overset{\|}{C}}-CCl_3 + OH^-$$

$$7\quad R-\overset{O}{\overset{\|}{C}}-CCl_3 + H_2O \xrightarrow{OH^-} R-\overset{O}{\overset{\|}{C}}-OH + CHCl_3$$

Figure 2.2 Reaction steps of chlorofrom produced during water treatment

2.1.3 Factors influencing THM formation

There have been extensive investigations on the formation of THMs in disinfected source waters and controls of THMs by various treatment processes which were testified to a wide variety of factors. Variables including pH, concentration and characteristics of organic precursor materials, chlorine concentration, water temperature and contact time all play an important role in controlling THM formation reactions.

2.1.3.1 pH

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

Rook (1976) suggested that THM formation increased significantly at pH values of 8 to 10, whereas in the range pH 1 to 7, pH had less influence on THM formation. Liang and Singer (2003) presented that increasing pH from 6 to 8 increased trihalomethane formation. Carlson and Hardy (1998) reported that at pH levels greater than 9.0, THM formation decreased with increasing pH. It was possible that the shift in chlorine species from hypochlorous acid to hypochlorite affected THM formation. AWWARF (1991) observed no relationships between pH and the concentrations of THMs, suggesting that although THM concentrations for particular water were known to be pH dependent, factors other than pH might have influenced THM concentrations over a variety of source waters.

2.1.3.2 Organic precursor concentration and characteristics

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) found that chloroform production from organic matter followed linear relationship with concentration up to 250 mg/l TOC. Young and Singer (1979) showed that quantity of chloroform produced depended upon TOC concentration in raw water since chloroform formation increased as non-volatile TOC increased. Milter et al. (1994) present that the removal of TOC was a conservative indicator of the removal of the precursors of THMs.

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.

2.1.3.3 Chlorine concentration

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

Muttamara et al. (1995) showed the relationship between THM concentrations and chlorine dosages. THM concentrations increased as the chlorine dosages increased. At dosages of 7 and 10 mg/L chlorine, the total THM concentrations at the end of the test run were found to be 124.5 and 158.3 μg/L, respectively. The level of THM concentration increased with respect to the level of THM precursors.

2.1.3.4 Temperature

On a conceptual basis, it may be that rapidly forming compounds are more reactive and form DBPs regardless of temperature. On the other hand, slowly forming compounds require higher activation energy, and an increase in the temperature supplies that extra energy. In addition, the temperature of source water can also affect disinfection efficiency. The formation rates of THMs have been shown to increase with temperature (AWWARF, 1991; Siddiqui and Amy, 1993). 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).

2.1.3.5 Contact time

After the addition of chlorine, there is a period of rapid THM formation which is the initial few hours (e.g. 4 h), followed by a decline in the rate of THM formation, suggesting fast and slow DOM reactive sites. Recknow and Singer (1984) ran a few sets of experiments. One of these experiments studied the formation of these chlorinated products as a function of the reaction time. They found that by varying the chlorine contact time, chloroform and total THM increased rapidly in the first few hours and then slowed down until the organic in the water source was totally removed. 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).

2.1.4 Trihalomethane 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 ± 2° C and the recommended pH is 7.0 ± 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.

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.

$TTHM_7$ is the total concentration of all four THMs compounds that are formed when the sample is incubated at 25± 2°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 ΔTHMFP is the difference between the final $TTHM_T$ concentration and the initial $TTHM_0$ concentration as shown in Figures 2.3 and 2.4, respectively. THMFP determinations provide a worst-case scenario of the concentration of THMs that may be formed.

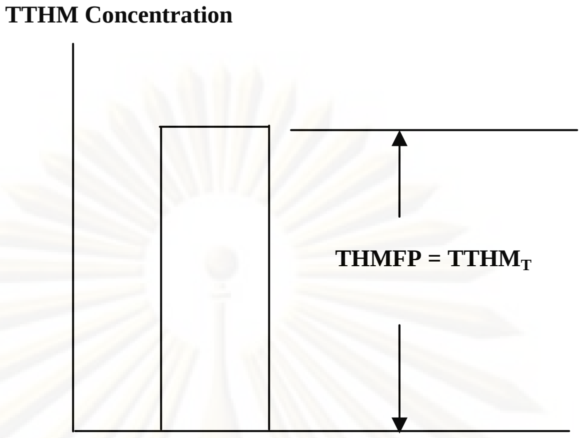


Figure 2.3 Definition used in the formation potential test of a sample without free chlorine at the time of sampling

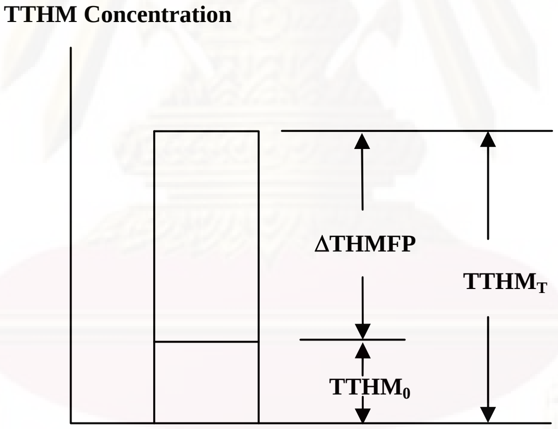


Figure 2.4 Definition used in the formation potential test of a sample with free chlorine at the time of sampling

2.2 Dissolved Organic Matter (DOM)

Dissolved organic matter (DOM) is defined as a complex mixture of aromatic and aliphatic hydrocarbon structures that have attached amide, carboxyl, hydroxyl, ketone, and various minor functional groups (Leenheer and Croue, 2003). The increased DOM complexity depends upon these heterogeneous molecular aggregates.

Normally, DOM can be distinguished into humic and non-humic substances (Pirnie, 1993). The Humic substances, usually described as heterogeneous poly-functional polymers formed through the breakdown of plant and animal tissues by chemical and biological processes, include humic and fulvic acids causing natural color in water. The humic acids are mentioned to the fraction of humic substances that is not soluble in water under acidic conditions (pH < 2) but is soluble at higher pH values. They are dark brown to black in color. Fulvic acids are referred to the fraction of humic substances that is soluble in water under all pH conditions. They remain in solution after removal of humic acid by acidification. Fulvic acids are light yellow to yellow-brown in color. While non-humic substances include hydrophilic acids, proteins, carbohydrates, carboxylic acids, amino acids, hydrocarbons, and a large number of organic molecules (Thurman, 1985; Amy, 1993). In fact, operationally defined humic substances generally comprise one-third to one-half of the DOM in natural waters (Thurman, 1985). However, DOM characteristics are highly variable and depend upon the sources of organic matter in both watershed surrounding a water source (allochthonous) and within the water source itself (autochthonous); on the temperature, ionic strength, pH, major cation composition of the water; on the surface chemistry of sediment sorbents that act as solubility controls; and on the presence of photolytic and microbiological degradation processes (Leenheer and Croue, 2003).

Many studies have shown the importance of monitoring and characterizing DOM in aquatic environments. DOM plays a role in many aspects of water treatment, as it is capable of forming complexes with metals such as iron. It can also serve as a substrate for microbial growth and can exert significant oxidant demand, thereby interfering with both oxidation and disinfection during drinking water treatment. DOM in drinking water resources is of significant concern as it influenced disinfection by-products (DBPs), colors and odors in drinking water and bacterial regrowth in distribution systems (Williamson et al., 1999). Rook (1974) was the pioneer researcher who discovered the disinfection by-products (DBPs) in chlorinated drinking water generated from DOM. There are then several subsequent reports that have led to a better understanding of DBPs, their precursors and the kinetic yield of DBPs forming reactions, the active chemical classes for forming DBPs (Kavanaugh et al., 1980; Christman et al., 1989; Miller and Uden, 1983; Steven, 1982; White et al., 2003). Marhaba and Washington (1998) proposed that DOM contained precursors for disinfection by-product formation during water treatment disinfection operation. Sirivedhin and Gray (2005) revealed that DOM in water served as a precursor to the formation of potentially harmful disinfection by-products (DBPs) in the chlorination process. The major halogenated DBPs commonly identified from chlorine treatment consisted of trihalomethans (THMs), haloacetic acids (HAAs), haloacetronitriles (HANs), haloketones (HKs), cyanogen halides, and halopicrins (Krasner et al., 1989; Stevens et al., 1989). The DBPs in drinking water were considered to be carcinogenic, mutagenic, and teratogenic (Black et al., 1996; Kanitz et al., 1996; Singer, 1999; Zavaleta et al., 1999), and therefore they posed adverse health effects in both human and animals (Bull and Kopfler, 1991; Morris et al., 1992). Much of the study of health risks associated with DBP has been historically centered on THMs; however, there was a growing concern about the health risks associated with HAAs (Sirivedhin and Gray, 2005).

In view of substances contained in DOM, the humic substances are reactive components for interactions with many inorganic and organic pollutants, and may decrease toxicities of these pollutants; however, they are precursors of numerous chlorination by-products that can cause certain cancers. Humic acids have generally been found to be more reactive with chlorine than fulvic acids. The non-humic substances have also been shown to be precursors to THMs (Morris and Baum, 1978; Oliver and Shindler, 1980).

2.3 DOM surrogate parameters

DOMs are highly heterogeneous consisting of various molecular weight compounds from simple structure to very complex polymers (Henze, 1992). Normally, DOMs are analyzed by combining nonspecific or surrogate parameters because no single analytical technique is capable of measuring the wide characteristics of DOMs. Commonly used DOM surrogates include dissolved organic carbon (DOC), ultraviolet absorbance at wavelength of 254 nm (UV- 254) and specific ultraviolet absorbance (SUVA).

2.3.1 Dissolved Organic Carbon (DOC)

Total organic carbon TOC in water can be classified into two fractions, particulate organic carbon (POC) and dissolved organic carbon (DOC). DOC is defined as the organic carbon fraction of (TOC) that passes through a 0.45 μm in diameter of filter paper (Leenheer and Croue, 2003). Since some types of 0.45 μm 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 μm in diameter was therefore proposed to replace cellulose based membranes in DOC analysis (Musikavong, 2006).

2.3.2 UV absorbance at wavelength 254 nm (UV_{254})

Ultraviolet (UV) absorbance is one of spectrophotometric analyses. Absorption of both visible and UV is widely considered to be attributed to the aromatic chromophores present in DOM—primarily humics—dissolved in the water. Most research has utilized the measurement of UV-visible at the wavelength of 254 nm as the representative for the relative quantity of aromatic-humic organic substances (APHA, AWWA, WEF, 1995; Leenheer and Croue, 2003). UV_{254} is a well-known technique for measuring the presence of naturally occurring organic matter such as humic substances. UV_{254} analysis is also affected by pH and turbidity (Edzwald et al., 1985). UV absorption is a useful surrogate measurement for DOM or precursor of THMs because humic substrates strongly absorb ultraviolet radiation (Eaton, 1995). As noted by Edzwald et al. (1985), humic aromatic compounds and molecules with conjugated double bonds absorbed UV light, whereas simple aliphatic acids, alcohol, and sugars did not. However, most aquatic researches have limited data collection to UV_{254} as it was a rough indicator of overall DOMs concentration (Leenheer and Croue, 2003).

2.3.3 Specific Ultraviolet Absorbance (SUVA$_{254}$)

Specific ultraviolet absorbance (SUVA or SUVA$_{254}$) is referred to “the sample’s UV$_{254}$ divided by the DOC concentration of the solution” (Leenheer and Croue, 2003). SUVA$_{254}$ indicates aromatic compounds in the DOC and can be used to estimate the chemical nature of the DOC at a given location. SUVA$_{254}$ could inform the nature of DOM and its consequent THM formation (Krasner et al., 1996). The water industry also used SUVA$_{254}$ as a surrogate parameter to monitor sites for disinfection byproducts precursors (Croue et al., 2000). The higher SUVA$_{254}$ values tended to indicate a higher humic content. SUVA$_{254}$ of a humic sample depended upon the molecular weight of the substances (Petterson et al., 1995).

SUVA$_{254}$ can be used as an indicator of its coagulation (or softening) ability to remove THM precursors. Water having high SUVA$_{254}$ (> 3 L/mg-m) have been found to contain organic matter that was more humic-like in character, higher in apparent molecular weight (AMW), and more readily removed by coagulation (Edzwald, 1993) whereas lower SUVA$_{254}$ values (< 3 L/mg-m) indicated the presence of organic matter of lower AMW that was more fulvic-like in character and more difficult to remove.

2.4 Characterization of Dissolved Organic Matter (DOM)

Characterization of DOMs from physical, chemical and biological perspectives is crucial not only in water treatment but also in water resource management. Several parameters have been used to categorize these various complex compositions of DOMs. Biochemical oxygen demand (BOD) and chemical oxygen demand (COD) have typically been employed for this purpose particularly for indicating wastewater quality. Normally, DOM is characterized by combining surrogate parameters because no single analytical technique is capable of measuring the widely varied characteristics of DOM. The DOM surrogates as explained in previous section are commonly used including DOC, UV$_{254}$ and SUVA$_{254}$. 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, including resin fractionation, ^{13}C- and ^{1}H-neuclear magnetic resonance (NMR) spectroscopy, fourier transform infrared (FTIR) spectroscopy, pyrolysis gas chromatography mass spectrometry (pyrolysis GC/MS), Three-dimensional fluorescent spectroscopy technique--fluorescent excitation-emission matrix (FEEM) etc (Croue et al., 2000; 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.

The resin fractionation, FEEM, FTIR, and pyrolysis GC/MS have been utilized more regularly as these could characterize DOMs simply and clearly. These selected techniques are detailed as follows.

2.4.1 Resin Fractionation

Resin fractionation technique is to separate DOM into each fraction that are chemically similar (AWWA, 1993). Fractionation of DOM using the resin adsorption technique was developed for characterizing DOM and differentiating the problematic organic fractions from other organic fractions (Leenheer, 1981; and Marhaba et al. 2003). DOM is commonly characterized by fractionating it into distinct categories with resin sorbents. A protocol with XAD-8 resin has been widely used to isolate humic substances-- humic and fulvic acids (Thurman and Malcolm, 1981) and is the basis of a simple DOC analysis that determines the so-called humic/non-humic distribution (DOC profiling) of raw and treated waters (Leenheer and Croue, 2003). Leenheer (1981) firstly developed the resin fractionation procedure for the separate of DOM into six fractions including hydrophobic neutral (HPON), hydrophobic base (HPOB), hydrophobic acid (HPOA), hydrophilic base (HPIB), hydrophilic acid (HPIA) and hydrophilic neutral (HPIN) by using a series of three resins (DAX-8, AG-MP-50 and Duolite A7). Imai et al. (2001) modified the resin fractionation procedure developed by Leenheer (1981) by replacing Duolite A7 to AG-MP-1 resin. Later on, Marhaba et al. (2003) adjusted the resin fractionation procedure proposed by Leenheer (1981) by replacing the resins from Duolite A7 to WA-10 as summarized in Figure 2.5.

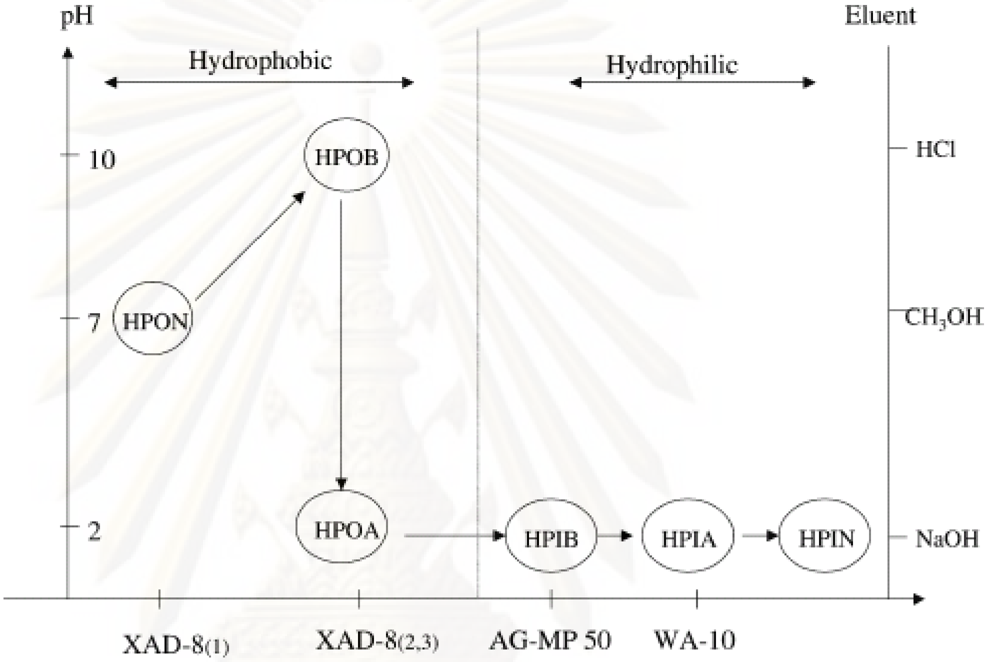


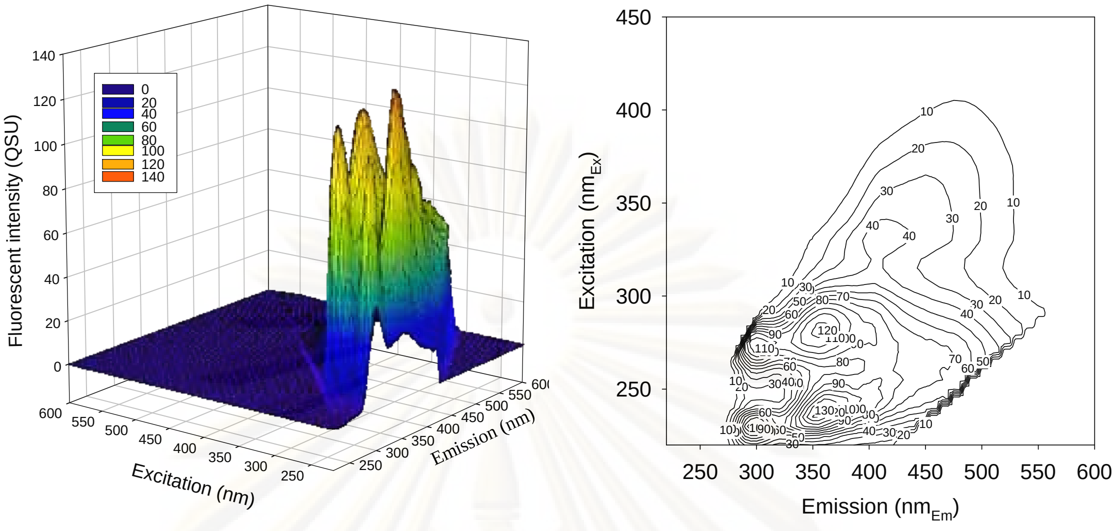
Figure 2.5 Resin fractionation process (Marhaba et al., 2003)

Resin fractionation technique has been utilized by many researchers for characterizing DOM in water sources for drinking water facilities such as underground water (Swietlik et al., 2004), reservoir and lake waters (Imai et al., 2001; 2003; Janhom et al., 2005) and river water (Day, 1991; Marhaba and Van, 1999; Croue et al., 2000; Marhaba and Van, 2000; Imai et al., 2001; Kimura et al., 2004; Panyapinyopol et al., 2005).

2.4.2 Three-Dimensional Fluorescence Spectroscopy

Three-dimensional fluorescence spectroscopy or fluorescent excitation - emission matrix (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). The application of FEEM becomes increasingly widespread for river or fresh water (Croue et al., 2000), marine water (Coble et al., 1990), wastewater (Baker, 2001; 2002; Musikavong et al., 2006), and leachate (Baker and Curry, 2004) as the method is a versatile, simple, rapid and sensitive, requiring only a small volume of sample (Nakajima et al., 2002; Yamashita and Tanoue, 2003; Musikavong et al., 2006).

Fluorescence occurs when molecules which, having been previously excited by a high-energy light source that raised the energy levels of the electrons within the molecule, release energy in the form of light (Baker and Genty, 1999). The fluorescent matrix is constructed by scanning sequential and simultaneous of fluorescent intensity in coordinates of excitation and emission wavelengths (Coble et al., 1990; Coble, 1996; Nakajima et al., 2000). FEEM obtained could provides information on fluorescent organic matter in water as fluorescent peaks as depicted in Figure 2.6. The results in excitation-emission matrices provided highly detailed information as fluorescent peaks which could be used to identify fluorescent compounds present in complex mixtures (Christian et al., 1981; Lochmuller and Saavedra, 1986; Leiner and Wolfbeis, 1988).



(a) (b)

Figure 2.6 FEEM view in 3-D (a) and FEEM view in 2-D (top view) (b)

Since Kalle (1949) firstly studied on fluorescence properties of DOM in water, study on fluorescence properties of DOM was then become interested (Willey, 1984; Hayase et al., 1987, 1988; Chen and Bada, 1989, 1992; Momzikoff et al., 1992; Hayase and Shinozuka, 1995). The FEEM has been widely utilized by many active researchers in several circumstances including ocean (Kalle, 1949, 1966; Zepp and Schlotzhauer, 1981; Ewald et al., 1983; Coble et al., 1990, 1993; Green, 1992; Mopper and Schultz, 1993; Sierra et al., 1994; Coble, 1996; Baker and Spencer,2004), freshwater (Coble, 1993; Baker and Genty, 1999; Nakajima et al., 2002; Reynolds, 2003, Wu et al., 2003, Yamashita and Tanoue, 2003, Baker et al., 2004; Homklin 2004; Zepp et al., 2004; Baker and Spencer,2004; Komatsu et al., 2005; Janhom et al., 2005; Phumpaisanchai, 2005; Elliott et al., 2006), wastewater and treated wastewater (Baker, 2001; Baker, 2002; Her et al., 2003; Chen et al., 2003; Baker et al., 2003, 2004; Musikavong, 2006), and leachate (Baker and Curry, 2004).

In FEEM technique, the features from several past reports are consistent with the presence of two primary groups of fluorescent DOM; the first has been ascribed to humic-like substances (namely humic acid-like or fulvic-like) source, the latter was ascribed to protein-like substances (namely tyrosine-like or tryptophan-like). The FEEM regions of these four compound-likes which were identified are compared with the standard representing actual humic acid, fulvic acid, tyrosine, and tryptophan as illustrated in Table 2.1. Other FEEM regions ($\text{nm}_{ex}/\text{nm}_{em}$) were identified such as algae-derived DOM at 225/295 and 270/295 (Nakajima et al., 2003), lake fulvic acid at 320/406 and 230/412 (Mcknight et al., 2001), human urine 270/380 and 320/410 (Nakajima et al., 2003), laundry detergent 230/285, 240/435, 225/565 and 350/430 (Nakajima et al., 2003), marine humic-like 310-320/380-420 (Leenheer, 2003) and 312/380-420 (Coble, 1996), and xenobiotic organic matter (XOM) such as naphthalene at 220-230/230-260 (Baker, 2004).

Factors that may influence the fluorescence intensity and wavelength of DOM include: degree of aromaticity, pH, metal-ion interaction, and climate (Baker and Genty, 1999).

2.4.3 Pyrolysis Gas Chromatography-Mass Spectrometry

Pyrolysis Gas Chromatography-Mass Spectrometry (pyrolysis GC/MS) is an analytical technique which has been used to study the structure of complex, non-volatile, organic macromolecules and recently has been applied to the study of DOM occurring in systems of interest to environmental engineers (Gray et al., 1996). Pyrolysis is a method that thermally cleaves an organic molecule into volatile fragments which are then separated by gas chromatography (GC) and identified by mass spectrometry (MS). Under controlled conditions, this technique yields a reproducible fragmentation pattern or fingerprint, which is highly the characteristics of the parent organic matter. Pyrolysis of DOM produces a complex chromatogram, or ‘‘pyrogram’’, containing hundreds of peaks as depicted in Figure 2.7.

Table 2.1 Summary of FEEM regions of fluorescent DOM substances from previous reports

Substances	Excitation (nm)/Emission (nm)	Source	References
Tyrosine	270-275/300-302	Authentic standard	Yamashita and Tanoue, 2003
Tyrosine-like proposed	220-275/300-305	-	Wolfbeis, 1985
	275/310	Bulk seawater	Coble, 1996
	230/300	Lake water, Japan	Komatsu et al., 2005
	230/295, 275/300	Industrial estate Wastewater and its treated wastewater, Lamphun, Thailand	Musikavong, 2006
Tryptophan	280/342-346	Authentic standard	Yamashita et al., 2003
Tryptophan-like proposed	220-275/340-350	-	Wolfbeis, 1985
	275/340	Bulk seawater	Coble, 1996
	265-280/300-370	Groundwater, from Sutherland, Scotland; Derbyshire, England; Dordogne, France; Wiltshire, England	Baker and Genty, 1999
	278-279/340-353	Discharge from Sewage treatment plants, England	Baker, 2001
	277/351	Discharge from Tissue mill, Northumberland, England	Baker, 2002
	278/353	Natural water and wastewater, USA	Her et al., 2003
	280/320	Lake water, Japan	Komatsu et al., 2005
	240/355, 280/355	Industrial estate Wastewater and its treated wastewater, Lamphun, Thailand	Musikavong, 2006
Fulvic acids	350/450	Suwannee River, Peat and Soil standards, IHSS	Marhaba and Kochar, 2000
	315/437-441	Extracted from forest soil in Dando, Japan	Yamashita and Tanoue, 2003
	245/445, 320/443	Suwannee River fulvic acid (SRFA, with lower MW and high aromaticity)	Her et al., 2003
	220/445	Standard fulvic acid (SFA)	Chen et al., 2003
	255/455, 320/450	Suwannee River Fulvic Acid (1S101F), IHSS	Sierra et al., 2005
	265/475, 325/440	Elliot Soil Fulvic Acid (1S102F), IHSS	Sierra et al., 2005
Humic acids	250/450	Suwannee River, Peat and Soil standards, IHSS	Marhaba and Kochar, 2000
	235-255/435-465	Commercially available humic acid, Wako Pure Chemical Industries Ltd.	Nakajima et al., 2002
	260/485, 330/470	Suwannee River Humic Acid (1S101H), IHSS	Sierra et al., 2005
	270/550, 360/560	Elliot Soil Humic Acid (1S102H), IHSS	Sierra et al., 2005
	261/457, 325/452	Suwannee River humic acid (SRHA, with larger MW and high aromaticity)	Her et al., 2003
Fulvic acid and Humic acid-like proposed	275/410,330/410	Industrial estate Wastewater and its treated wastewater, Lamphun, Thailand	Musikavong, 2006
	235/435,320/430	Lake water, Japan	Komatsu et al., 2005
	290-340/395-430	Groundwater from Sutherland, Scotland; Derbyshire, England; Dordogne, France; Wiltshire, England	Baker and Genty, 1999
	230/440, 340/440	Hawaiian River water	Coble, 1993
	260/380-460, 350/420-480	Bulk seawater	Coble, 1996
	339/420-422	Discharge from Sewage treatment plants, England	Baker, 2001
	343/433	Discharge from Tissue mill, Northumberland, England	Baker, 2002
	320-360/400-470	Landfill leachates, England	Baker and Curry, 2004
	337/423	Natural water and wastewater, USA	Her et al., 2003

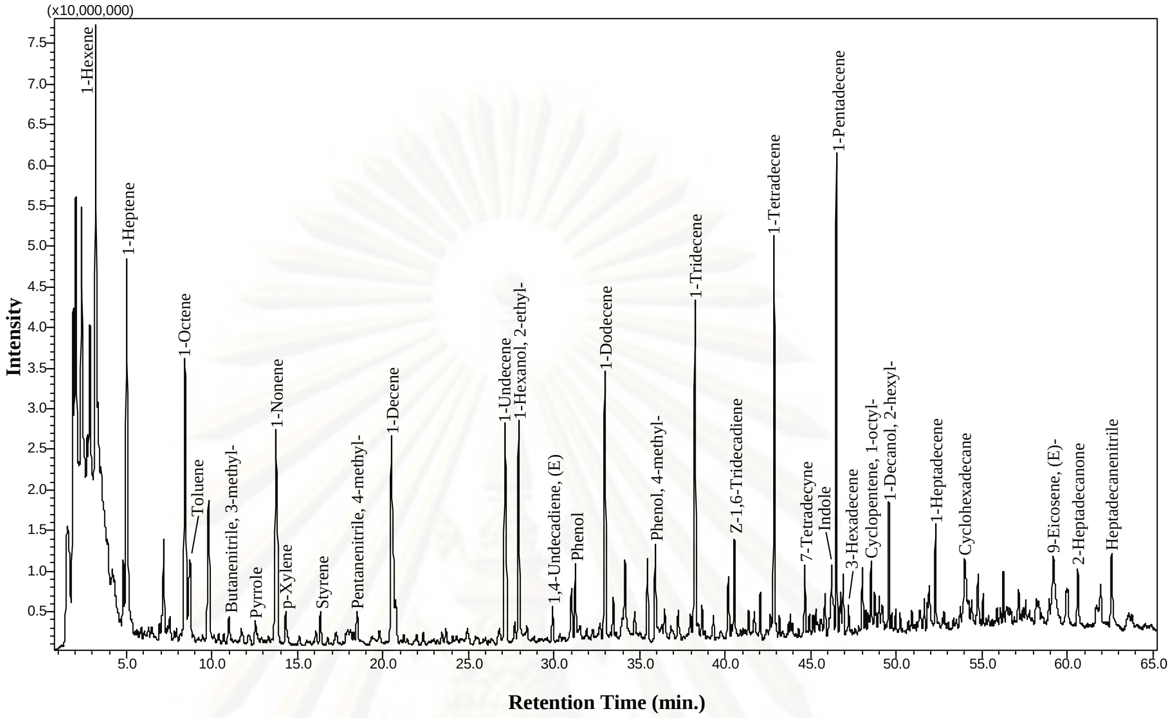


Figure 2.7 Example of Pyrogram of industrial estate wastewater (Musikavong, 2006)

Utilization of pyrolyzer coupling with GC/MS could provide a chemical fingerprint (pyrolysis fragments) of both chromatographable and non-chomatographable fractions. It, therefore, could be used to identify the original mixture of DOM in water. The qualitative identification of polysaccharides, proteins, lipids, lignins and other biomarkers could be accomplished by using pyrolysis GC/MS. (Almedros et al., 1997; Fabbri et al., 1998; Hatcher et al., 2001; Kogel-Knabner, 2000; Pouwels et al., 1989 and, Ralph and Hatfield, 1991). Although pyrolysis technique has many advantages, it is not without limitations. In particular, pyrolysis is a destructive technique where organic molecules can undergo side reactions that form new compounds (e.g. ring structures) (Bracewell et al., 1984; Jimenez, 1994). However, it has been widely used to characterize numerous DOMs from various sources, such as wood (Alen et al.,1996; Aspax and Baldellou,1985), fossil objects (Wilson et al., 1987), soil sediments (Jimenez, 1992; Bracewell et al., 1984); in river waters (Bruchet et al., 1990 and White et al., 2003), lake water (Biber et al., 1996 and White et al., 2003), groundwater (White et al., 2003), treated wastewater (Dignac et al., 2000; Sirivedhin and Gray, 2005; Musikavong, 2006) and wastewater (Dignac et al., 2000; Musikavong, 2006).

Recently, pyrolysis GC/MS technique was used to identify biopolymer comprising DOM. Biber et al. (1996) demonstrated five main groups of biopolymer including polysaccharides, proteins, lignins, amino sugars, and polyhydroxy aromatics in a eutrophic lake AWWA (1998) identified chemical classes in water samples from Ohio River, Mississippi River, Passaic River, Lake Gailland and groundwater in USA where the pyrolysis fragments were classified into five categories: aromatic, aliphatic, nitrogen containing, halogen substituted and unknown compounds. Christy et al. (1999) characterized DOM from 9 different water sources in Norway and the pyrolysis fragments were identified as carbohydrates, proteins, amino sugars, polyhydroxy aromatics and others. Komatsu et al. (2005) also utilized the pyrolysis-GC/MS to characterize the complex position of DOM in a eutrophic lake in Japan where 16 fragment compounds were detected and some of them were possibly originated from polyhydroxy aromatics (PHA), polysaccharides (Ps), proteins (Pr) and amino sugars (As).

Regarding the applications of pyrolysis GC/MS, Musikavong (2006) used pyrolysis GC/MS coupled with FEEM technique to characterize wastewater of northern-region industrial estate, Thailand. In this work, FEEM was used to characterize the major compounds containing DOM while pyrolysis GC/MS was used to confirm the major fragment of each compound. The analysis demonstrated that phenol, p-cresol, pyrrole, nitrile and indole were the major pyrolysis fragments of the tyrosine-like substance; indole was the major pyrolysis fragment of tryptophan-like substances; and $C_3 \leq$Aliphatic hydrocarbon $\leq C_{20}$, alkyl-benzenes, naphthalene, and nitrogen containing compounds were found as major pyrolysis fragments of humic and fulvic acids-like substances. The summary of fluorescent peak positions and major pyrolysis fragments of major fluorescent components is shown in Table 2.2.

Table2.2 Fluorescent peak positions and major pyrolysis fragments of major fluorescent components from literature

Substance	**Majors pyrolysis fragments**
Tyrosine-like and protein-like substances	Phenol and p-cresol (phenol, 4 methyl) (Bruchet et al., 1990) Pyridines, pyrroles, indoles, nitriles, phenol and p-cresol (equal quantities from tyrosine) (AWWA, 2000)
Tryptophan-like and protein-like substances	Indole (AWWA, 2000) Acetronitrile, benzonitrile, phenylacetonitrile, pyridine, methylpyridine, pyrrole, indole and methylindole (Leenheer and Croues, 2003)
Fulvic acids and fulvic-like substances	**Humic acids;** Highly aliphatic (Bruchet, 1986; Gadel and Bruchet, 1987) (1) n-alk-1-ene/n-alkane with 8-29 carbon presenting the limited odd over predominance in the C_{24}-C_{29} range (2) alkyl-benzenes, naphthalene, alkyl-naphthalene (3) phenol (Faure et al.2006) **Fulvic acids;** Highly peaks of butenal, acetic acid, 2-fufural, methyl furfural, levoglucosenone, 5-(Hydroxymethyl) 2 fufaral (Bruchet,1986; Gadel and Bruchet,1987) Large peaks of phenol and cresol (Croue et al., 1993) **Humic substances;** (1) Nitrogen containing compounds (such as pyrrole and pyridine), aliphatic products (such as n-alk-1-ene/n-alkane with 5-29 carbon) (2) aromatic products (such as alkyl-benzenes, naphthalene and alkyl-naphthalene, (4) lignin products (such as o-cresol, m cresol, catechol, dimethylphenol) (5) carbohydrate product (such as furan, 2-methyl proppenal, dimethyfuran, vinyfuran, 2-fufaraldehyde. (Lu et al., 2006)
Humic acids, Fulvic and humic-like substances	

Source: Musikavong (2006)

2.4.4 Fourier Transform Infrared Spectroscopy

A large number of research works have been allocated to the identification of functional groups that could potentially lead to the formation of DBPs. This helped in the future development of the abatement technology to prevent the formation of compounds such as amino acid, aromatic characteristic organics, etc. In the interpretation of the functional groups, Fourier transform infrared (FTIR) is a crucial instrument. FTIR has been widely used for the structural investigation of humic substances. Fundamentally, 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(s). FTIR analysis allows the identification of inorganic and organic functional groups as well as elemental composition. The recording of FTIR spectra of freeze dried water samples was another possibility to investigate the DOM composition of small sample amounts (Benke et al., 1998). This was similarly performed by Capriel (1997) with bulk soil. Kanokkantapong et al. (2006) presented that the investigation of the formation of HAAs could be achieved by tracking the changes in the FTIR results of the same water sample before and after the chlorination reaction. The study illustrated that carboxylic acids, ketone, amide, amino acids and aromatic characteristic organics seemed to be the main precursors to HAA formation in the water samples from Bangkhen water treatment facility in Bangkok.

CHAPTER III

METHODOLOGY

3.1 Detail of the selected breweries

Three breweries in Thailand (namely Sites 1, 2 and 3) with a total production rate of more than a half of the overall beer production rate in the country were selected as the modeled system in this study (see more details on all three breweries in Appendix B). As shown in Figure 3.1, the first two Sites, 1 and 2, are located in the middle part of Thailand whereas Site 3 is situated in the north-eastern province. The studied Sites 1 and 3 commonly produce the lager beer whereas the studied Site 2 produces light beer. In brewing processes, not only an intensive groundwater and water supply consumption is required with more or less 7 hectoliters of fresh water needed for each hectoliter of beer production but also large quantities of wastewater are produced, typically 3–12 hectoliters of wastewater for every hectoliter of beer produced. Generally the water is used in washing activities and the resulting wastewater is treated before being discharged to environment. The wastewater treatment system of all three breweries consists of equalization unit, upflow anaerobic sludge blanket (UASB) and activated sludge (AS) connected in series. The influent and effluent from each treatment step were collected at sampling positions as indicated in Figure 3.2.

All experiments and parameter analyses of this research were conducted in the laboratory at the Department of Environmental Engineering, Faculty of Engineering, Chiang Mai University, Chiang Mai, Thailand.

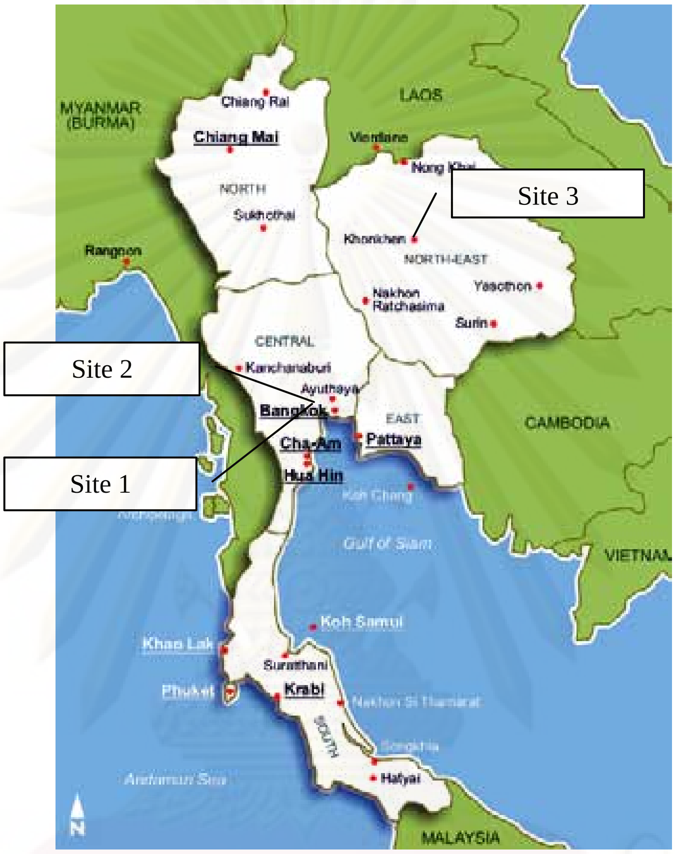
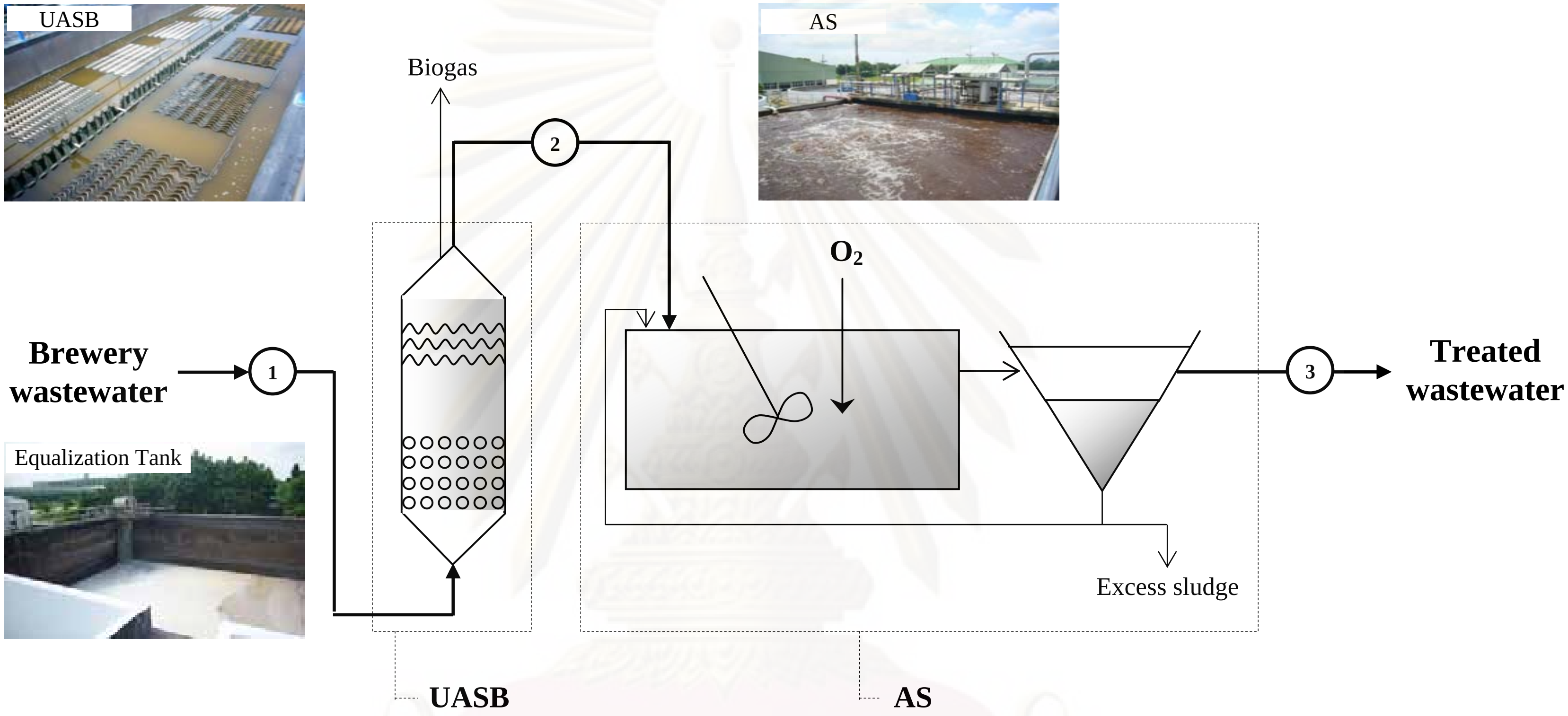


Figure 3.1 Location of three studied breweries



Remarks: UASB = Upflow anaerobic sludge blanket process
AS = Activated sludge process

①, ② and ③ = Sampling points

Figure 3.2 Typical wastewater treatment system for all three breweries

3.2 Experiments

3.2.1 Overall experimental plan

Twenty liters of grab samples of the influent and effluent from each treatment step, i.e., UASB and AS from the three selected breweries, Sites 1, 2, and 3, were collected three times on the sampling day. All water samples were then filtered through a pre-combusted (550°C for 2 h) Whatman GF/F filter (nominal pore size of 0.7µm). The filtered samples were placed into amber glass bottles with TFE-lined screw caps and stored at 4°C before being further analyzed through the following procedure (See Figure 3.3 for a schematic diagram of the experimental procedure).

1. Filtered samples were split into 2 portions:
   -Portion 1: For determination of unfractionated water characteristics.
   -Portion 2: For determination of fractionated water characteristics.
2. Filtered water in Portion 1 was analyzed for pH, dissolved organic carbon (DOC), ultraviolet-visible at the wavelength of 254 nm (UV_{254}), specific ultraviolet absorbance at the wavelength of 254 nm ($SUVA_{254}$), trihalomethane formation potential (THMFP), fluorescent excitation - emission matrix (FEEM), fourier transform infrared spectroscopy (FTIR) and pyrolysis gas chromatography-mass spectrometry (Pyrolysis GC/MS).
3. Five liters of the filtered water in Portion 2 were fractionated into 6 fractions as described in Section 3.2.2 and analyzed for pH, DOC, UV_{254}, $SUVA_{254}$, THMFP, FEEM, FTIR and Pyrolysis GC/MS.
4. The major DOMs of HPOA, HPOB, HPON, HPIA, HPIB, and HPIN fractions in water samples were investigated and defined.

3.2.2 Resin Fractionation procedure

Resin adsorption procedure was employed to fractionate five liters of filtered water in Portion 2 into six DOM fractions, viz. hydrophobic neutral (HPON), hydrophobic base (HPOB), hydrophobic acid (HPOA), hydrophilic base (HPIB), hydrophilic acid (HPIA), and hydrophilic neutral (HPIN) fractions by using a series of DAX-8 resin (SuperliteTM DAX-8, SUPELCO, Supelco Park, Bellefonte, PA), AG-MP-50, a cationic resin, (BIO-RAD, Hercules, CA) (Leenheer, 1981) and WA-10 resin (SUPELCO), a weak anion exchange resin, respectively (Marhaba et al., 2003). The diagram of the resin fractionation procedure is presented in Figure 3.4 and is described as follows:

1. The filtered water sample of which pH is adjusted to 7 by 5 and 0.1 N NaOH was pumped through the 1st DAX-8 column (Ø: 2.5 cm. × H: 120 cm.) with a flow rate of less than 12 bed volume per hour (BV/h) (0.25 mL/s). The retained HPON fraction in DAX-8 resin was extracted by methanol (CH_3OH). The rotary evaporator was utilized to get rid of the methanol from the extracted sample.
2. The effluent from Step 1 was adjusted to pH 10 by 5 and 0.1 N NaOH and then pumped through the 2nd DAX-8 resin column (Ø: 2.5 cm. × H: 120 cm.) with the flow rate of less than 12 BV/h (0.25 mL/s). The retained HPOB fraction in DAX-8 resin was eluted by 0.25 BV of 0.1 N hydrochloric acid (HCl) followed by 1.5 BV of 0.01 N HCl with the flow rate of less than 2 BV/h (0.04 mL/s).
3. The effluent from Step 2 was acidified to pH 2 by 5 and 0.1 N $H_2SO_4$and pumped into the 3rd DAX-8 resin (Ø: 2.5 cm. × H: 120 cm.) with the flow rate of less than 12 BV/h (0.25 mL/s). The retained HPOA was eluted from the DAX-8 resin by 0.25 BV of 0.1 N (sodium hydroxide: NaOH) followed by 1.25 BV of 0.01 N NaOH with a flow rate of less than 2 BV/h (0.04 mL/s).
4. The effluent from Step 3 was directly pumped into the AG-MP-50 resin column (Ø: 2.5 cm. × H: 120 cm.) with the flow rate of less

than 5 BV/h (0.06 mL/s). The retained HPIB fraction in AG-MP-50 resin was then eluted by 1 BV of 1 N NaOH with the flow rate of less than 2 BV/h (0.02 mL/s).

5. The effluent from Step 4 was then pumped through the WA-10 resin column (Ø: 2.5 cm. × H: 120 cm.) with the flow rate of less than 8 BV/h (0.8 mL/s). The retained HPIA fraction in the WA-10 resin was eluted by 1.5 BV of 0.1 N NaOH followed by 1 BV of 0.01 N NaOH with the flow rate of less than 2 BV/h (0.24 mL/s) while the final effluent contained the HPIN fraction.

Remarks:

1. The ratios between the resin volume and the water sample volume were:

15 mL:1L was used for DAX-8
4 mL:1L was used for AG-MP-50
85 mL:1L was used for WA-10

2. Specifications of the three resins

DAX-8

- Nonionic resin (SUPELCO)
- 60% porosity
- 40-60 mesh
- 160 square meters per dry gram

AG-MP-50

- Strong acid cation exchange resins (BIO-RAD)
- Sulfonic acid functional groups attached to a styrene divinylbenzene copolymer lattice
- Effective surface area approximates 35 m^2/ g as dry weight
- 30-50% porosity

WA-10 (SUPELCO)

- Weak anionic resin (SUPELCO)
- Strong physical and chemical chemistry

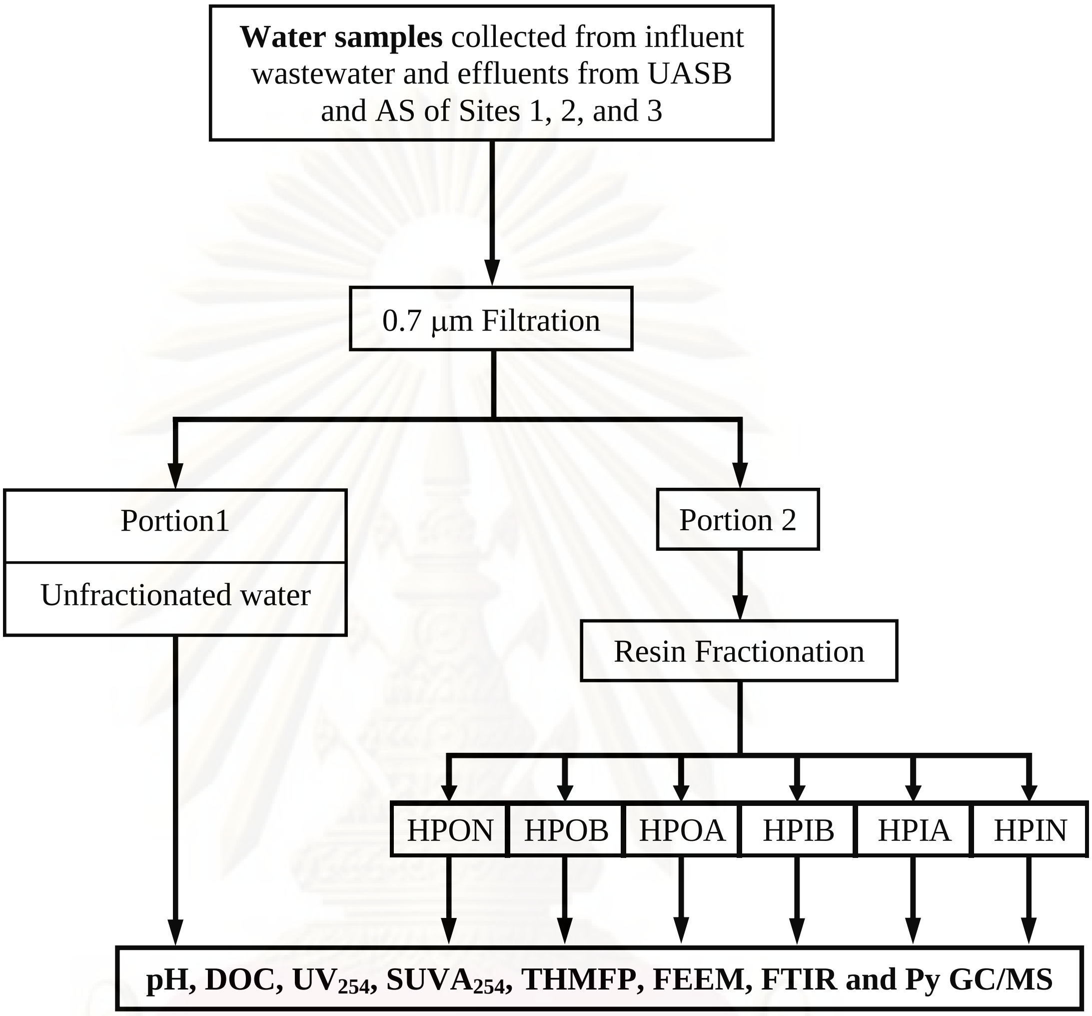


Figure 3.3 Experimental procedure

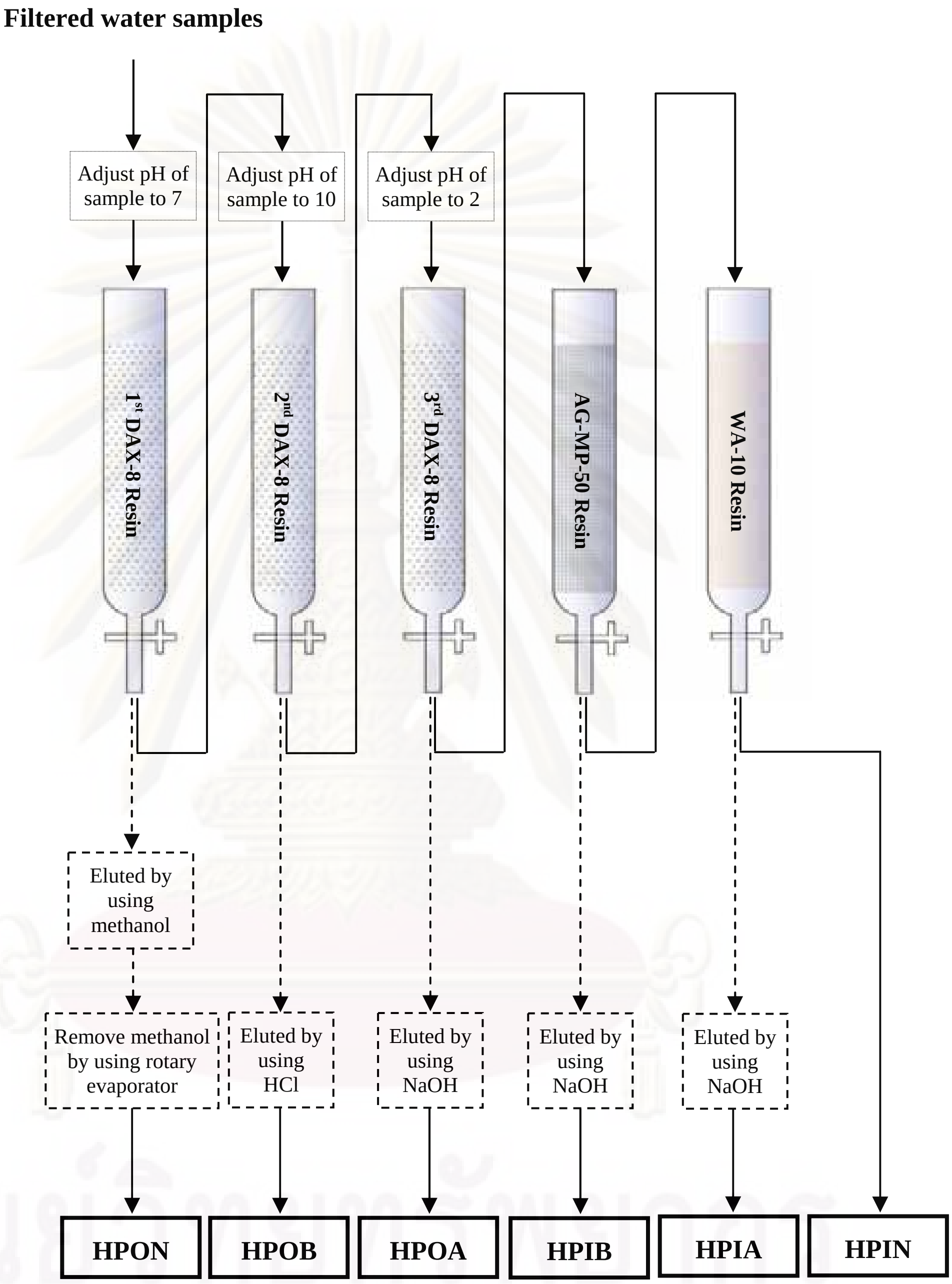


Figure 3.4 Resin fractionation procedure

3.2.3 Resin Preparations

1. DAX-8

- Refine DAX-8 resin by soaking DAX-8 with 0.1N NaOH for 24 h
- Purify the refined DAX-8 resin with acetone for 24 h followed by hexane for 24 h in a set of soxhlet extraction apparatus as shown in Figure 3.5
- Soak the purified DAX-8 resin in methanol
- Transfer the ready DAX-8 resin in slurry of methanol into columns lined with glass wool packed at the bottom
- Rinse the packed resin in column with two times 2.5 BV of 0.1 N NaOH, followed by 0.1 N HCl and then flushed with Milli-Q water until the conductivity and DOC of the effluents were lower than 10 μs/cm and 0.2 mg/L, respectively

2. AG-MP-50

- Purify AG-MP-50 resin with methanol for 24 hrs in a set of soxhlet extraction apparatus.
- Transfer the purified resin in slurry of methanol into column lined with glass wool packed at the bottom.
- Rinse the packed resin in column with more than 2 BV of 1 N NaOH followed by more than 2 BV of 2 N HCl and Milli-Q water, respectively until the DOC and conductivity of the effluent water were lower than 0.1 mg/L and 10 μs/cm, respectively

3. WA-10

- Soak WA-10 resin with methanol for 24 hours.
- Transfer the soaked resin in slurry of methanol into column lined with glass wool packed at the bottom.
- Rinse the packed resin in column with more than 1 BV of 1 N HCl followed by more than 2.5 BV of 1 N NaOH and Milli-Q water, respectively until DOC and conductivity of the effluent water were lower than 0.1 mg/L and 10 μs/cm, respectively

Figure 3.5 Soxhlet extraction apparatus

3.3 Analytical Methods

Unfractionated water (Portion 1) and six fractionated water including HPON, HPOB, HPOA, HPIB, HPIA, and HPIN of all three studied sites were analyzed for their pH, DOC, UV_{254}, $SUVA_{254}$, THMFP, FEEM, FTIR and Pyrolysis GC/MS. All these parameters are described below and the summary of analytical methods and standards used for analyzing the mentioned parameters is conclusively demonstrated in Table 3.1.

A duplication of all analyses was carried out for each sample in this study. The results of these analyses should be within ±5%, or otherwise more repetition was necessary (Kebbekus and Mitra, 1998).

3.3.1 pH

The pH of water samples were measured by a Horiba pH meter, Model D-13E with an accuracy of ± 0.01 pH unit.

3.3.2 DOC

DOC of water samples were measured in accordance with Standard Method 5310D (Standard Method, 1995) using a TOC analyzer (O.I. analytical, College Station, Texas, USA).

Table 3.1 Analytical parameters, analytical methods, standards and instruments used in this study

Parameters	Analytical Method	Standard	Instruments
pH	Direct Measurement	-	Horibra pH-meter Model F-21
UV-254	Ultraviolet Absorption Method	Standard method 5910 B	Jasco V-350 UV/VIS spectrophotometer
DOC	Wet - Oxidation Method	Standard method 5310 D	O.I. Analytical 1010 TOC Analyzer
THMFP	Formation of Trihalomethanes and Other Disinfection By-Products and Liquid-Liquid Extraction Gas Chromatography Method	Standard method 5710 and 6232 B	Gas Chromatography with electron capture detector (GC/ECD)
FEEM	-	-	JASCO FP-6200 Spectrofluorometer
FTIR	-	-	Jasco FTIR-460 spectrometer
Pyrolysis GC/MS	-	-	Shimadzu GC/MS QP-5050

Analyzing in accordance with Standard method or USEPA method (Standard Methods, 1995)

3.3.3 UV$_{254}$

UV$_{254}$ of water samples were measured in accordance with Standard Method 5910B (Standard Methods, 1995) using a UV/VIS spectrometer, Jasco V-350 spectrophotometer (Jasco Corporation, Tokyo, Japan) at 253.7 nm, with matched quartz cells, providing a path length of 10 mm.

3.3.4 SUVA$_{254}$

SUVA$_{254}$ is defined as the UV absorbance at 254 nm measured in inverse meters (1/m) divided by the DOC concentration measured in milligrams per liter (mg/L) (Weishaar et al., 2003).

3.3.5 THMFP

THMFP measurement was done in accordance with Standard Method 5710B (Standard Method, 1995). 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 chlorine residual was measured according to the procedures mentioned in Standard Method 4500-Cl G, the *N*,*N*-dechthyl-p-phenylenediamine colorimetric method. The level of chlorine was determined by the light absorbance at 515 nm using a UV/VIS spectrometer, Jasco V-350 spectrophotometer with matched quartz cells with a path length of 10 mm. The samples contained free chlorine residual of between 3 and 5 mg/L, acceptable range for determining THMs, were extracted with pentane in accordance with Standard Method 6232B (Standard Method, 1995). 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 μm film were used to analyze THMs under the following operating conditions:

Inlet Condition

Mode: Split
Initial Temperature: 225^{o}C.
Pressure: 31.33 psi,
Split ratio: 10:1
Split flow 15.9 mL/min
Gas Type: Helium
Total flow: 20.5 mL/min

Oven Condition

The temperature programs of oven adjusted for analyzing THMs are conclusively shown in Table 3.2.

Table 3.2 Temperature programs for analyzing THMs

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

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

Detector Condition

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

Free Chlorine Residual

Free chlorine residual was determined in accordance with Standard method 4500-Cl G. DPD Colorimetric Method. Due to THMFP analysis, the chlorinated water samples must have 3 to 5 mg/L free chlorine residual.

Liquid-Liquid Extraction

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

3.3.6 Three-dimensional fluorescence spectroscopy (fluorescent excitation-emission matrix, FEEM)

FEEM is the recorded matrix of fluorescent intensity in coordinates of excitation (EX) and emission (EM) wavelengths in a definite spectral window by fluorescent spectrometry. The FFEMs of this study were obtained by using JASCO FP-6200 Spectrofluorometer. The water samples were adjusted their pH to be 7±0.2 prior to being analyzed by FEEM technique using the following operating conditions:

Spectrofluorometer Operating Condition

Measurement Mode: Emission
Band width excitation: 5 nm
Band width emission: 5 nm
Response: Fast
Sensitivity: High
Scanning speed: 2000 nm/min
Excitation wavelength: Start at 220 nm, end at 720 nm
Emission wavelength: Start at 220 nm, end at 720 nm
Excitation wavelength interval: 5 nm
Emission wavelength interval: 5 nm

FEEM of each sample was figured out using a JASCO FP-6200 spectrofluorometer with a wavelength range of 220 to 730 nm (with 5 nm intervals) for excitation and emission. All slit widths were set to 5 nm. FEEM spectra of all water samples were subtracted by the FEEM spectra of Milli-Q water and converted to quinine sulfate units (QSU) where 10 QSU is equivalent to the fluorescence spectra of 10 μg/L quinine sulfate solution at 450 nm with an excitation wavelength of 345 nm. In order 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 (Ex) ≥ emission wavelength (Em) or Ex × 2 ≤ Em (Komatsu et al. 2005). In addition, the Rayleigh and Raman scattering peaks at peak Em ±10-15nm of each Ex were removed from the FEEM (Zepp et al., 2004).

3.3.7 FTIR Analysis

All water samples were frozen (a pre-freeze unit at -20 °C for at least 12 h) and freeze-dried under -57°C and 0.004 bar for at least 24 h in order to gain a uniform fine powder for determining the organic composition. The FTIR analysis samples were prepared using the standard KBr pellet procedure for freeze dried sample (freeze-dried sample:KBr mixture at a 1:100 ratio). The FTIR spectra were analyzed on a Jasco FTIR-460 spectrometer at a resolution of 4 cm^{-1} by collecting 16 scans per sample in a wave number range of 4000–400 cm^{-1}.

3.3.8 Pyrolysis GC/MS Analysis

All water samples were frozen (a pre-freeze unit at -20°C for at least 12 h) and freeze-dried under -57°C and 0.004 bar for at least 24 h in order to gain a uniform fine powder for determining the organic composition. A few milligrams of freeze-dried powder of all the water samples were put in platinum buckets attached to sample holders in the quartz tube of the pyrolyzer. The pyrolyzer is connected to the injection port of a Shimadzu GC/MS QP-5050 equipped with the Rtx-VMS column (Restek, thickness: 1.4µm, length: 30m, diameter: 0.25mm, maximum usable temp: 240°C). The compounds were interpreted by comparing the mass spectra with those of the NIST mass spectral database. The operating pyrolyzer, GC and MS conditions used in this study are:

Pyrolysis Condition

Presure:150 psi
Spilt flow: 8 cm/s
Intermediate temp: 220°C
Initial temperature: 220°C
Final temperature: 700°C, final time 10 seconds
Gas type: Helium

GC Condition

Initial temp: 40°C
Ramp#1: Rate 2.0°C/min, final temperature 80°C
Ramp#2: Rate 3.0°C/min, final temperature 140°C
Ramp#3: Rate 5.0°C/min, final temperature 230°C
Final holding time: 30 min.
Run time: 88.0 min

MS Condition

Acquisition mode: Scan

Interface Temperature: 220°C

Solvent cut time: 0.1 min

Detector voltage: Relative to tuning results

Start time: 0.1 min

End time: 86 min

Start (m/z): 40

End (m/z): 650

Scan speed: 2000

CHAPTER IV

CONVENTIONAL SURROGATE ANALYSES OF DISSOLVED ORGANIC MATTER IN BREWERY WASTEWATER

In this chapter, the qualitative and quantitative information of DOM in brewery wastewater and treated brewery wastewater from three studied breweries were investigated through DOM surrogates: dissolved organic carbon (DOC), ultraviolet absorbance at a wavelength of 254 nm (UV_{254}), and specific ultraviolet absorbance ($SUVA_{254}$). For the specific details on DOM characteristics, DOM in all samples was isolated into six DOM fractions based on its chemical characteristics via resin fractionation method prior to further analyze. The appraisal of the performance of upflow anaerobic sludge blanket (UASB) and activated sludge (AS) on reducing DOM and DOM fractions of brewery wastewaters are also elucidated through these DOM surrogate parameters.

4.1 DOM in brewery wastewater and its treated wastewater

DOC, UV_{254} and $SUVA_{254}$ are commonly utilized as surrogate parameters for DOM in water and wastewater. These parameters are capable of providing significant information on DOM properties. DOC has been typically used as an aggregate measure of the organic content in water while UV_{254} has been used to represent the presence of aromatic structures incorporated into the molecules of humic substances composed of DOM. $SUVA_{254}$, on the other hand, is generally utilized to provide a relative index of the humic content of the DOC in water. These parameters are used to qualify DOM and DOM fractions in brewery wastewater and treated wastewater in this section.

4.1.1 Surrogate properties of DOM

DOC of 52.4, 39.8 and 99.9 mg/L with their UV_{254} of 1.53, 1.21 and 1.98 were observed in the influent wastewater from Sites 1, 2 and 3, respectively. These high levels of DOC and UV_{254} indicated that the discharges from breweries contained high level of organic content, especially of aromatic structure. In addition, $SUVA_{254}$ of the influent wastewaters from Sites 1, 2 and 3 were 2.92, 3.05 and 1.99, respectively. Edzwald (1993) reported that fresh water with high $SUVA_{254}$ (>3 L/mg-m) contained organic matter of more humic-like in character and higher in average molecular weight (AMW) whereas lower SUVA values (< 3 L/mg-m) indicated the presence of organic matter of lower AMW with more fulvic character. Although $SUVA_{254}$ was often employed to characterize fresh water quality, analogy could imply that the characteristics of influent wastewater from Sites 1 and 3, or that from lager beer production, might contain organic content with low AMW, fulvic character. On the other hand, the influent wastewater from Site 2, or that from light beer production, might contain organic content which was more humic-like in character and higher in AMW.

4.1.2 Specific characteristics of DOM

In order to obtain specific details on DOM characteristics, DOM in all samples was isolated into six DOM fractions viz. hydrophobic neutral (HPON), hydrophobic base (HPOB), hydrophobic acid (HPOA), hydrophilic base (HPIB), hydrophilic acid (HPIA), and hydrophilic neutral (HPIN) fractions via resin fractionation method prior to be further analyzed. The mass distribution of all six DOM fractions in the filtered samples from Sites 1, 2 and 3 are demonstrated in Table 4.1. According to the fractionation results, the weight totals of the six DOC fractions in each of the filtered samples were about 2 to 15% higher than their initial values. This total weight surplus was explained by Leenheer (1981) to be the possible result of resin bleeding during the elution process, where Day et al. (1991) and Marhaba and Pipada (2000) demonstrated that the level of inaccuracy was acceptable as this fractionation technique had often been reported to be given as much as a 10% to 15% tolerance for DOM recovery.

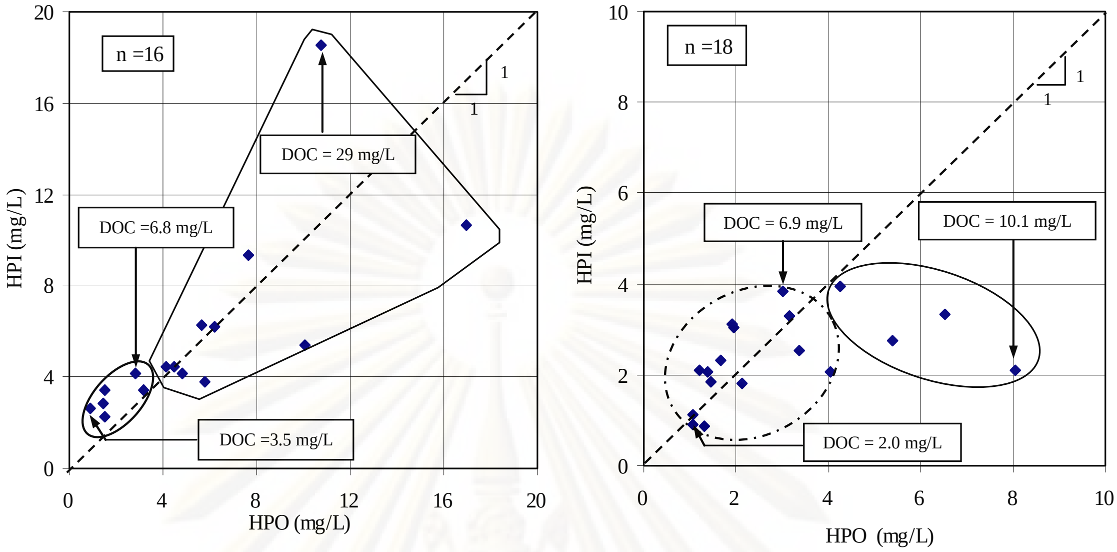
From the mass distribution results, the hydrophobic organic fraction (HPO) of the influent wastewater and effluents from the UASB and AS treatments of Sites 1, 2 and 3 accounted for more than 50% of the total DOC mass. The HPO fraction of the influent wastewater from Sites 1, 2 and 3 collectively accounted for 54.4%, 56.1% and 53.8% of total DOC, respectively. This agrees with the reports from Barber et al. (2001) and Hu et al. (2003) who demonstrated that the HPO fraction often dominated in high DOC wastewaters. For the treated wastewater, the HPO fraction of the effluents from the UASB and AS treatments of Sites 1, 2 and 3 was also predominated as it accounted for more than 50% of the total DOC.

The unpublished data in Musikavong (Ph.D. Dissertation, Chulalongkorn University, Thailand, 2007) illustrated the relationship between HPI and HPO of treated wastewater and reservoir water sources which was conclusively gathered from many researches as shown in Figure 4.1. In case of treated wastewater, HPI fraction was found to be dominant in treated wastewater with low DOC concentration, while in treated wastewater with high DOC concentration, no distinguished trend on HPO and HPI fractions was observed. This might be due to the different characteristics of wastewater and performance capability of the wastewater treatment process for removing DOM from the wastewater. In case of the reservoir water, HPO which is representative of humic substances was found as the major DOM fraction in reservoir with high DOC concentration condition. This reported data strongly support the findings in this presented study as all collected samples had high DOC concentration where HPO dominated.

Table 4.1 DOC mass distribution of DOM

	Water sources	DOC concentration (mg/L)	Mass of DOM (mg DOC)		DOC Surplus (%)	Mass of DOM fractions (mg DOC)							
			UW	FW		HPON ^{1}	HPOB ^{2}	HPOA ^{3}	HPIB ^{4}	HPIA ^{5}	HPIN ^{6}	HPO	HPI
Site 1	Influent wastewater	52.4	261.8	298.6	+ 14.1	32.6	11.3	118.5	76.1	14.4	45.7	162.4	136.2
	Effluent from UASB	21.6	107.8	124.1	+ 15.2	14.5	5.9	54.6	17.7	4.1	27.3	75.0	49.1
	Effluent from AS	18.4	91.9	102.9	+ 12.0	14.2	2.6	43.6	16.0	14.1	12.4	60.4	42.5
Site 2	Influent wastewater	39.8	199.2	202.3	+ 1.5	44.1	11.8	57.4	56.9	4.6	27.4	113.4	88.9
	Effluent from UASB	8.8	44.0	45.1	+ 2.7	8.7	1.2	20.9	8.5	2.6	3.2	30.9	14.3
	Effluent from AS	5.1	25.4	28.3	+ 11.4	6.7	0.9	9.6	3.0	4.6	3.4	17.3	11.0
Site 3	Influent wastewater	99.9	499.6	545.4	+ 9.2	64.3	12.4	216.7	139.1	16.4	96.5	293.5	251.9
	Effluent from UASB	50.1	250.7	270.3	+ 7.8	30.6	6.7	120.4	32.9	5.1	74.7	157.7	112.6
	Effluent from AS	21.1	105.4	108.3	+ 2.8	26.4	1.9	28.2	22.5	14.7	14.6	56.5	51.8

Note:
UW = Unfractionated water = DOC (mg/L) × 5 L
HPO = 1+2+3 or HPON+ HPOB+ HPOA
HPI = 4+5+6 or HPIB+ HPIA+ HPIN
FW = Fractionated water = 1+2+3+4+5+6 or HPO + HPI
DOC Surplus (%) = (FW – UW) / UW × 100



(a) (b)

Figure 4.1 Relationship between HPI and HPO in treated wastewater (a) and reservoir water (b)

Remarks: DOC refers to DOC of unfractionated water

: n refers to the number of DOC data used for graph plotting

(Source: Musikavong, Ph.D. Dissertation, Chulalongkorn University, Thailand, 2007)

Among the mass distribution of the six DOM fractions, the sequences from high to low of each DOM fraction of the influent wastewater and effluents from the UASB and AS treatments for Sites 1, 2 and 3 are as follows.

Site 1

- Influent wastewater:

  HPOA > HPIB > HPIN > HPON > HPIA > HPOB

- Effluent from UASB:

  HPOA > HPIN > HPIB > HPON > HPOB > HPIA

- Effluent from AS:

  HPOA > HPIB > HPON > HPIA > HPIN > HPOB

Site 2

- Influent wastewater:

  HPOA > HPIB > HPON > HPIN > HPOB > HPIA

- Effluent from UASB:

HPOA > HPON > HPIB > HPIN > HPIA > HPOB

- Effluent from AS:

  HPOA > HPON > HPIA > HPIN > HPIB > HPOB

Site 3

- Influent wastewater:

  HPOA > HPIB > HPIN > HPON > HPIA > HPOB
- Effluent from UASB:

  HPOA > HPIN > HPIB > HPON > HPOB > HPIA
- Effluent from AS:

  HPOA > HPON > HPIB > HPIA > HPIN > HPOB

Single or multiple DOM fractions which accounted for more than 50% of the total DOC mass were considered as the major DOM fractions in the brewery wastewater. HPOA and HPIB fractions were the major DOM fractions of the brewery wastewater from Site 1; where HPOA accounted for 41.4% of total DOC, followed by HPIB which accounted for 23.8% of total DOC. HPIA and HPOB fractions were the lowest two DOM fractions found. Similar findings are observed for the DOM fractions of Site 3, i.e. HPOA and HPIB fractions were the major DOM fractions of the brewery wastewater where HPOA accounted for 39.7% of total DOC, followed by HPIB which accounted for 25.5% of total DOC, and HPIA and HPOB fractions were the lowest two DOM fractions. For Site 2, HPOA and HPIB also were the two major DOM fractions where HPOA accounted for 28.4% followed by HPIB at 28.1% of total DOC, whereas HPOB and HPIA were the lowest two DOM fractions.

To further analyze the major components in each DOM fraction, the relationships between the organic compounds and the DOM fractions were analyzed through infrared and ^{13}C-NMR spectral characterization proposed by Leenheer and Croué (2003), and the results are described as follows.

HPON: contained hydrocarbons/tannins

HPOB: contained aromatic amines

HPOA: contained fulvic acid

HPIB: contained peptides/aminos

HPIA: contained polyuronic acids

HPIN: contained sugars

Since HPOA and HPIB fractions were the major DOM fractions in the wastewater of all three breweries, it could be implied that most of the organic compounds contained in breweries wastewater of all three sites might consist of fulvic acids and peptides/aminos.

During biological treatment processes, DOM characteristics were directly affected, as observed by the variations in the DOM fractions. For Sites 1, 2 and 3, HPOA was the predominant DOM fraction (44.0%, 46.4% and 44.6% of total DOC, respectively) in the effluent water of the UASB treatment. HPOA was also found to be the dominant DOM fraction in the AS treatment effluent from all three sites (42.3%, 34.0% and 26.0% of total DOC, respectively). This finding agrees with a finding by Barber et al. (2001) who reported that the HPOA fraction was the dominant DOM fraction in the effluent resulting from an AS treatment. The HPOA fraction was also found to be the prominent DOM fraction in the effluent from other biological treatment processes, such as stabilization ponds (unpublished data of Musikavong, Ph.D. Dissertation, Chulalongkorn University, Thailand, 2007). It may be stated that HPOA (or fulvic acid) seems to be recalcitrant to the biological process treatments.

4.2 Analyses of treatment processes on the reduction of brewery DOM

DOM in brewery wastewater and its treated wastewater consists of various organic compounds from simple structures to very complex polymers. In this section, the effectiveness of each treatment unit on the reduction of DOM surrogates was evaluated.

4.2.1 Reduction of DOM through UASB and AS treatments

DOC, UV_{254} and $SUVA_{254}$ of unfractionated wastewater samples from Sites 1, 2 and 3 are conclusively summarized in Table A-1 (Appendix A). Figure 4.2 demonstrates the performance of the wastewater treatment system of all three breweries in terms of DOC, UV_{254} and $SUVA_{254}$ reductions. UASB could remove DOC of influent wastewater from Sites 1, 2 and 3 with the removal efficiencies of around 59, 78 and 50% respectively, and the AS treatment further augmented approx. 6, 9 and 29% to the overall DOC reduction efficiency. In terms of UV_{254}, UASB could bring this parameter down by 57, 80, and 29% for Sites 1, 2 and 3 respectively, and these were further removed at another 8, 9 and 41% as the wastewater passed through AS treatment. UASB could lower $SUVA_{254}$ of the wastewater from Site 2 down from 3.05 to 2.81 L/mg-m, even though only slightly. On the other hand, an increase in $SUVA_{254}$ after passing through UASB from 2.92 to 3.03 L/mg-m and from 1.99 to 2.82 L/mg-m was observed for Sites 1 and 3, respectively. An only marginal decrease in the $SUVA_{254}$ after passing through AS from 3.03 to 2.93 L/mg-m, from 2.81 to 2.80 L/mg-m and from 2.82 to 2.81 L/mg-m was found for Sites 1, 2 and 3, respectively. This effectively means that $SUVA_{254}$ remained almost constant for all wastewaters.

At Sites 1 and 2, the percent reduction of DOM through UASB and AS in terms of DOC was comparably close to those of UV_{254}. These observations suggest that the biological process in the UASB and AS treatments could remove DOM mainly with aromatic structure. For Site 3, the percent reduction of DOM through UASB in terms of DOC was slightly more than the reduction of UV_{254} while the percent reduction of DOM though AS in terms of DOC and UV_{254} was comparable. This means that aromatic organics were not as effectively removed as other types of organic compounds, and therefore, the remaining DOM in the treated wastewater was still composed of aromatic DOM.

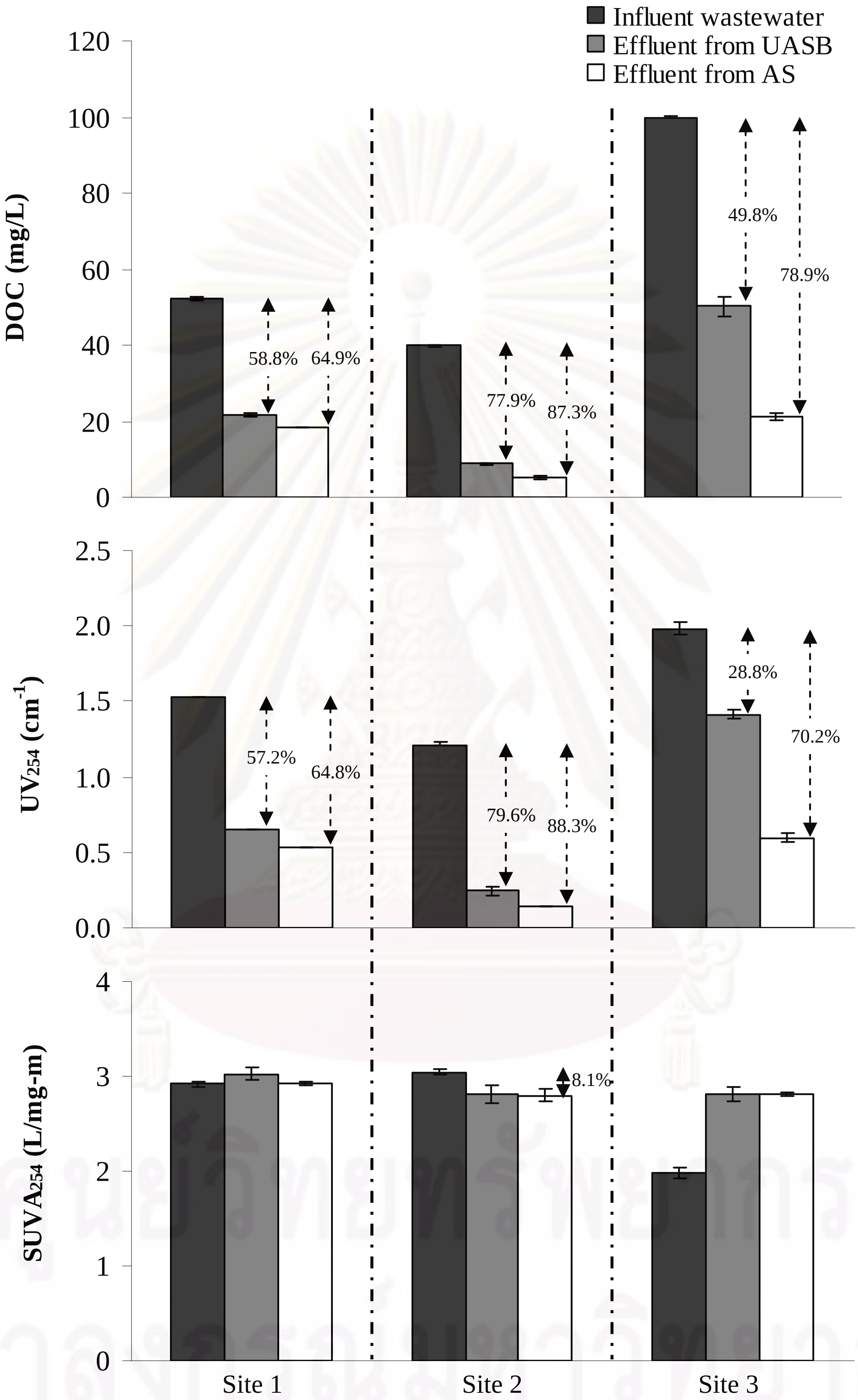


Figure 4.2 Changes in DOM surrogate parameters through UASB and AS treatments

Changes in $SUVA_{254}$ are more difficult to interpret as $SUVA_{254}$ is the ratio between UV_{254} to DOC which is a measure of the relative contents of aromatic structures in the overall DOM (Weishaar et al., 2003). It was observed that $SUVA_{254}$ of all effluents were rather high, which indicated high content of aromatic compounds when compared with the total organic matters. The fact that $SUVA_{254}$ was not reduced suggested the all types of organic matters were removed at a comparable rate, resulting in an approximately constant $SUVA_{254}$ level.

4.2.2 Reduction of DOM fractions through UASB and AS treatments

For specific details of DOM reduction, one liter of each DOM fraction was rationally prepared by diluting the eluted solution in accordance with their fractionation ratios obtained from the fractionation procedure as shown in the mass distribution of all six DOM fractions (Table 4.2). Figures 4.3, 4.4 and 4.5 demonstrate the analytical results of DOC, UV_{254} and $SUVA_{254}$, for the six DOM fractions of the wastewater and the effluents from UASB and AS of all studied sites. In terms of DOC reduction (mg/L) for the six DOM fractions, the reduction of DOM was mainly due to the disappearance of the two major DOM fractions, HPOA and HPIB which accounted for 65 and 76% for Site 1, 84 and 94% for Site 2, and 85 and 82% for Site 3, respectively. More than half of the DOC reduction of each DOM fraction occurred during the UASB treatment, except the HPIN fraction of wastewater from Sites 1 and 3 which were more effectively removed by the AS treatment. Interestingly, HPIA was the only fraction that displayed a different behavior as it increased after passing through the AS treatment unit. It might be that HPIA was formed as a result of biological transformations of other degraded DOM fractions. This finding agreed with the unpublished data in Musikavong (Ph.D. Dissertation, Chulalongkorn University, Thailand, 2007) who stated that the DOC levels of HPIA slighly increased after the facultative and oxidation ponds. Imai et al. (2001; 2002) reported that HPIA was a dominate DOM fraction in the effluent water from the AS treatment plant in Japan, and was considered to be mostly microbial origin and was recalcitrant for bacterial degradation. HPOA is the fraction of most concern because, despite of being removed by more than 80%, it was still a relatively dominant DOM fraction in the effluents.

Similar findings with the treatment of DOC are observed for the treatment of UV_{254}, the DOM fractions in terms of UV_{254} (cm^{-1}) was mainly reduced by decreases in the two major DOM fractions, HPOA and HPIB. The reduction in UV_{254} of HPOA and HPIB fractions of the three breweries were 64 and 81%, respectively, for Site 1, 84 and 94% for Site 2, and 67 and 88% for Site 3. The UASB treatment could reduce more than half of the UV_{254}, except HPIN fraction of wastewater from Sites 1 and 3 which was mostly treated by the AS treatment. HPIA, again, displayed different removal behavior as it increased after passing through the AS treatment unit for all three studied sites. The biological transformation of other degraded DOM fractions could also play significant role on generating more HPIA (polyuronic acid) as discussed in the previous paragraph.

$SUVA_{254}$ (L/mg-m) was found to increase for all DOM fractions of Sites 1 and 3 after passing through the UASB, while $SUVA_{254}$ of each DOM fraction was slightly changed for Site 2 after passing through the UASB and AS. The increase may have caused by the biotransformation of other organic matter to a more UV-sensitive fraction such as organics with aromatic structure. However, as mentioned earlier, the fact that $SUVA_{254}$ was not reduced suggested the all types of organic matters were removed at a comparable rate, resulting in an approximately constant $SUVA_{254}$ level.

These findings could imply that HPOA was of particular concern as a problematic DOM fraction for water reclamation process of treated brewery wastewater, since it was still relatively predominated in residual DOM in the effluents and it was considered likely to be refractory in biological treatments.

Table 4.2 DOC distribution of DOM fractions

	Water sources	DOC concentration (mg/L)	Percentage of DOM fractions (%)					
			HPON	HPOB	HPOA	HPIB	HPIA	HPIN
Site 1	Influent wastewater	52.4	10.9	3.8	41.4	23.8	4.8	15.3
	Effluent from UASB	21.6	11.7	4.8	44.0	14.2	3.3	22.0
	Effluent from AS	18.4	13.8	2.5	42.3	15.6	13.8	12.0
Site 2	Influent wastewater	39.8	21.8	5.8	28.4	28.1	2.3	13.6
	Effluent from UASB	8.8	19.3	2.7	46.4	18.7	5.7	7.2
	Effluent from AS	5.1	23.7	3.3	34.0	10.8	16.2	12.0
Site 3	Influent wastewater	99.9	11.8	2.3	39.7	25.5	3.0	17.7
	Effluent from UASB	50.1	11.3	2.5	44.6	12.2	1.9	27.6
	Effluent from AS	21.1	24.4	1.7	26.0	20.8	13.6	13.5

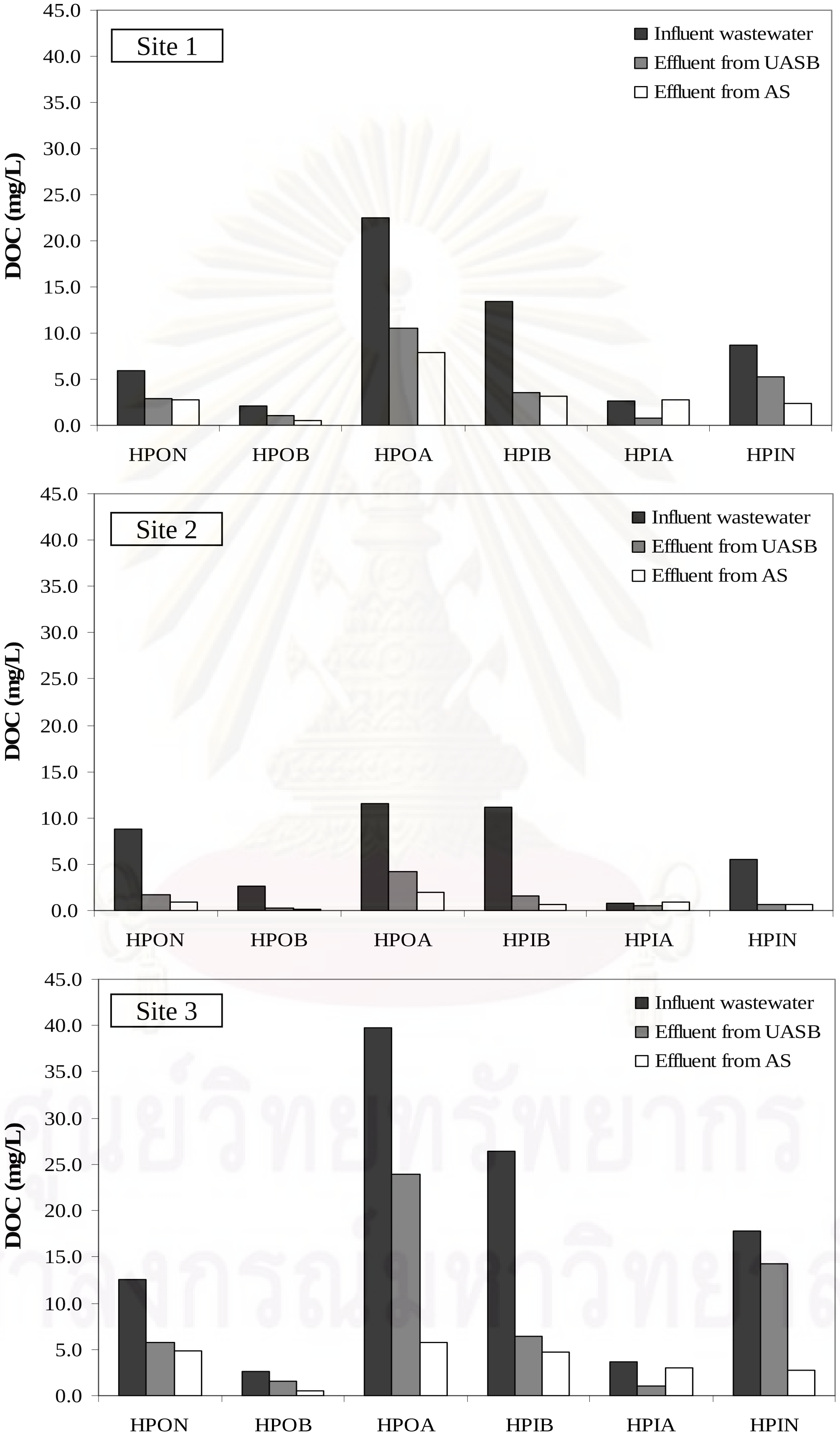


Figure 4.3 Changes in DOC of six DOM fractions by UASB and AS treatments

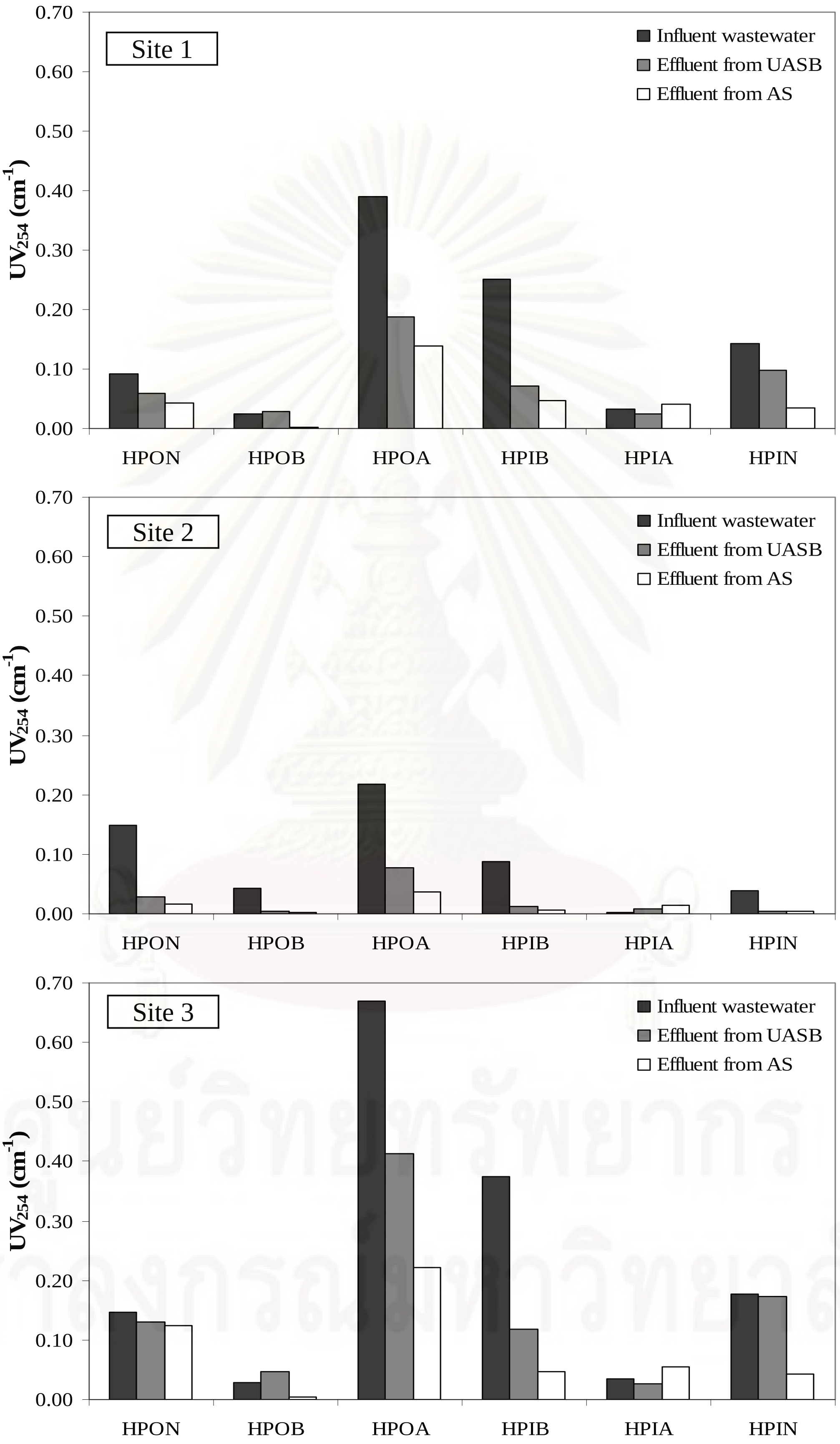


Figure 4.4 Changes in UV_{254} of six DOM fractions by UASB and AS treatments

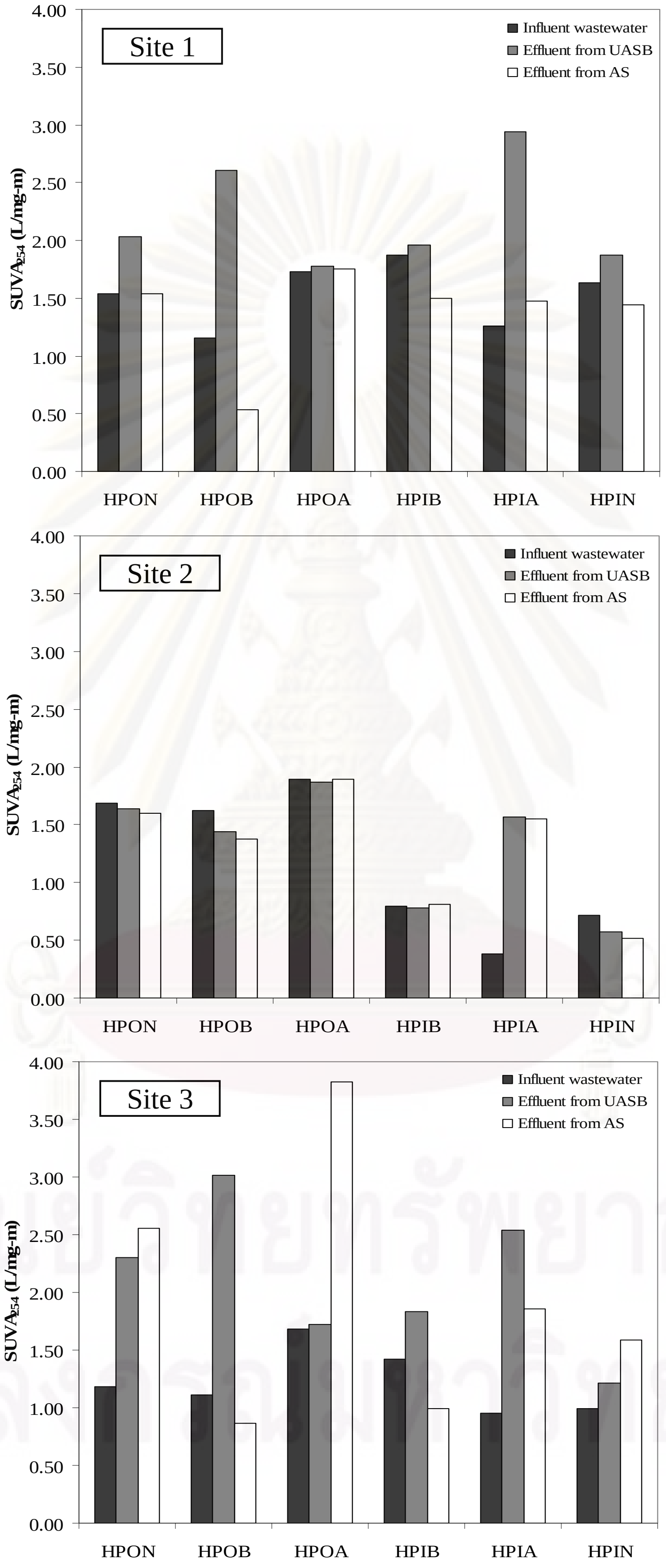


Figure 4.5 Changes in $SUVA_{254}$ of six DOM fractions by UASB and AS treatments

4.2.3 Relationships among DOM surrogate parameters

In unfractionated water samples, the tendency of DOC and UV_{254} reduction through UASB and AS from all three sites followed the same trend. Both DOC and UV_{254} were actually removed more effectively through the UASB unit. This result agreed with previous observations that brewery wastewater was easily biodegradable and amenable using anaerobic treatment (Etheridge and Leroff, 1994; Hanqing and Guowei, 1996; Leal et al., 1998; Parawira et al., 2005). However, the residual DOM in effluents from UASB of all sites was still rather high as represented by the high levels of DOC, UV_{254} and $SUVA_{254}$. As UV_{254} indicates the presence of aromatic structures incorporated into the molecules of humic substances (Weishaar et al., 2003), it might be that the DOM from the wastewater samples after UASB contained dissolved aromatic humic and fulvic-type molecules which were relatively stable against microbial degradation (Saadi et al., 2006). Consequently, the aerobic AS treatment could only slightly further remove DOC and UV_{254}. A good correlation (R^2=0.9209) obtained from the relationship between DOC and UV_{254} of unfractionated water samples (Figure 4.6) suggested that both DOC and UV_{254} could well be employed as surrogate parameters for brewery wastewater

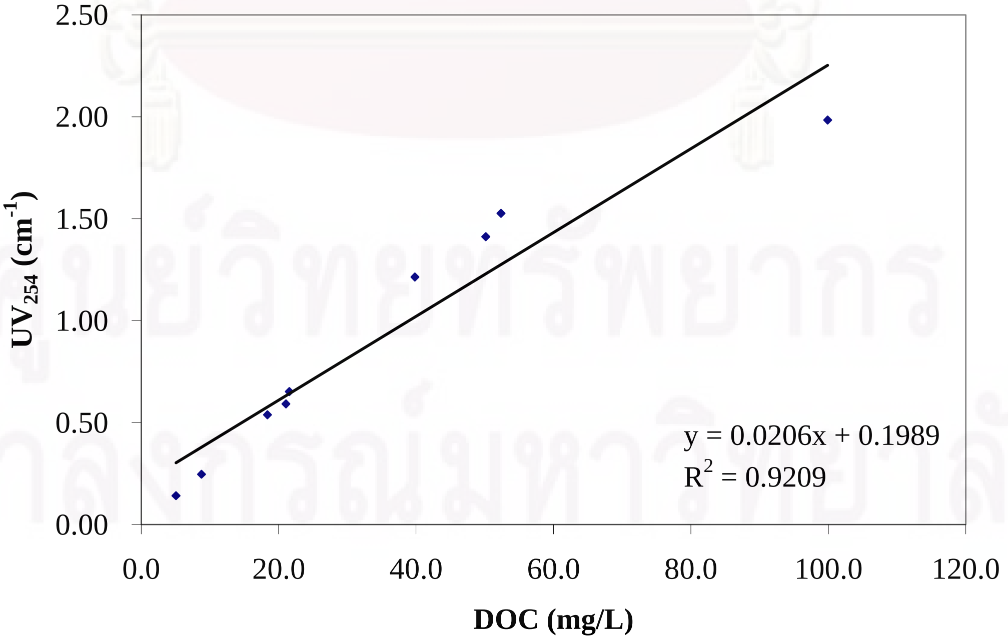


Figure 4.6 Relationship between DOC and UV_{254} of unfractionated water samples

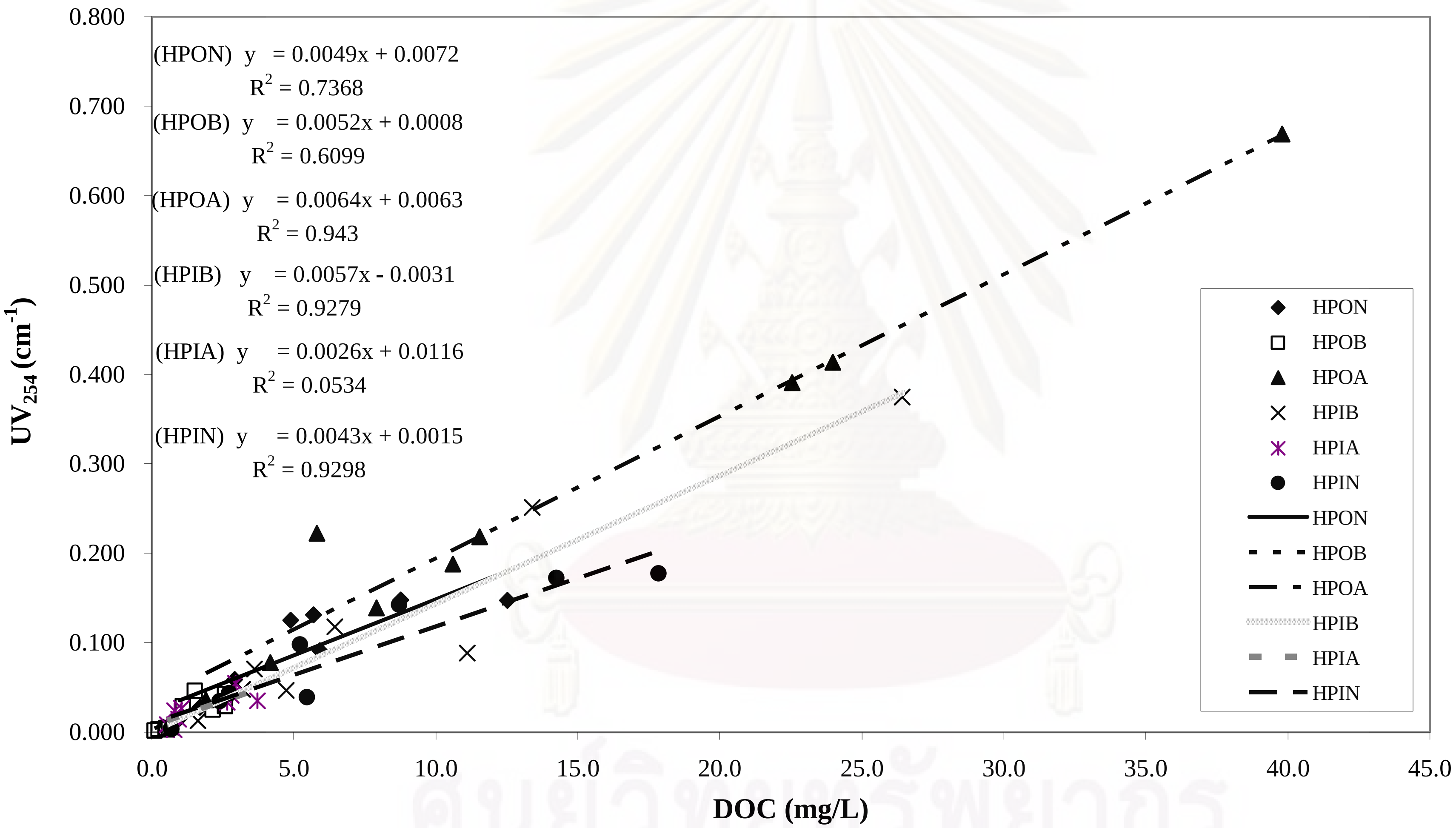


Figure 4.7 Relationships between DOC and UV$_{254}$ of six DOM fractions for all fractionated samples

Similar conclusion could be drawn for the relationships between DOC and UV_{254} of all the major DOM fractions, i.e. HPOA and HPIB, and also HPIN (see Figure 4.7). This meant that the variations in major DOM fractions were due to the changes in their aromatic components.

4.3 Concluding remarks

The aims of this chapter were to qualify and quantify of DOM in brewery wastewater and treated wastewater by DOM surrogate parameters viz. DOC, UV_{254} and $SUVA_{254}$. The appraisal of the performance capability of UASB and AS in the treatment of DOM and in brewery wastewaters was also evaluated through DOM surrogate analyses. The utilization of resin fractionation coupled with DOM analyses could help to provide more specific details on the characteristics and the reduction of DOM in each specific chemical group. This work demonstrates that the major organic fractions in brewery wastewater were found to be HPOA and HPIB. The reduction of DOM was mainly found to occur during the UASB treatment. This reduction was attributed to the removal of two major DOM fractions, i.e. HPOA and HPIB. The HPOA fraction is of particular concern because it was recalcitrant during the UASB and AS treatments of the two breweries studied. In addition, a considerable quantity of this organic compound still remained in the effluents. From a water reuse perspective, the HPOA fraction might be a problematic DOM for treated brewery wastewater reclamation.

CHAPTER V

FLUORESCENT EXCITATION-EMISSION MATRIX ANALYSIS OF DISSOLVED ORGANIC MATTER IN BREWERY WASTEWATER

In this chapter, the qualitative and quantitative information of DOM in brewery wastewater and treated brewery wastewater from three studied breweries were investigated through three-dimensional fluorescent spectroscopy technique – fluorescent excitation–emission matrix (FEEM). Furthermore, the performance of upflow anaerobic sludge blanket (UASB) and activated sludge (AS) for reducing DOM and DOM fractions of brewery wastewaters are also appraised through the FEEM technique.

5.1 DOM and DOM fractions in brewery wastewater and its treated wastewater

FEEM technique has recently been developed to describe the complex composition of DOM. In fact, 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 the water samples. This technique was employed to identify 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). The application of FEEM has become increasingly widespread for river or fresh water (Croue et al., 2000), marine water (Coble et al., 1990), wastewater (Baker, 2001, 2002; Musikavong et al., 2006), and leachate (Baker and Curry, 2004) as the method is fast, simple, and requires a minimal sample amount and pre-treatment. In addition, this technique is nondestructive and can be adapted to real-time, in situ, and unmanned instrumentation. Thus the FEEM technique was employed to characterize DOM and DOM fractions in brewery wastewater and its treated wastewater in this work.

5.1.1 FEEM profiles of DOM

An example of an FEEM of the wastewater from Site 2 where the 5 FEEM peak positions viz. (C) 230nm$_{\mathrm{Ex}}$/340-365nm$_{\mathrm{Em}}$, (D) 265-295nm$_{\mathrm{Ex}}$/315-390nm$_{\mathrm{Em}}$, (E) 290nm$_{\mathrm{Ex}}$/400nm$_{\mathrm{Em}}$, (F) 330-335nm$_{\mathrm{Ex}}$/395-410nm$_{\mathrm{Em}}$, and (G) 255-265nm$_{\mathrm{Ex}}$/435-455nm$_{\mathrm{Em}}$ were identified is shown in Figure 5.1. Literature recommended the potential origins of fluorescent spectra as summarized in Table 5.1. These fluorescent peaks could be further categorized into three main regions as shown in Figure 5.2. Peaks A and B in Region I represented tyrosine-like substances, Peaks C and D in Region II for tryptophan-like substances, and Peaks E, F and G in Region III for humic and fulvic acid-like substances.

FEEM spectra of unfractionated water sample including influent and effluent wastewater after UASB and AS of Sites 1, 2 and 3 are presented in Figure 5.3. All FEEM peak positions found in unfractionated water samples, which were categorized into their associated putative regions, are also conclusively illustrated in Table 5.2. In the influent wastewater from Site 1, Peaks C, D and F were observed, while Peaks C, D, F, and G were detected in the influent wastewater from Site 2. Peaks C, D, E, and F were observed in the wastewater from Site 3. This led to a potential conclusion that Peaks C, D and F represented common organic compositions found in all brewery wastewaters. In other words, it can be implied that the wastewater from three sites (both light and lager beers) were mainly composed of tryptophan-like substances (as represented by Peaks C and D) and fulvic and humic-like substances (as represented by Peak F). In the effluents from the UASB and AS treatments of Sites 1, 2 and 3, Peak F was found to be a common group. This means that fulvic and humic-like substances, as represented by Peak F, were the major component which could not be treated through the treatment units typically employed in the brewery factories.

Table 5.1 Summary of proposed mapping of FEEM regions and fluorescent DOM substances

Substances	Excitation (nm)/Emission (nm)	Source	References
Tyrosine	270-275/300-302	Authentic standard	Yamashita and Tanoue, 2003
Tyrosine-like proposed	220-275/300-305	-	Wolfbeis, 1985
	275/310	Bulk seawater	Coble, 1996
	230/300	Lake water, Japan	Komatsu et al., 2005
	230/295, 275/300	Industrial estate Wastewater and its treated wastewater, Lamphun, Thailand	Musikavong, 2006
Tryptophan	280/342-346	Authentic standard	Yamashita et al., 2003
Tryptophan-like proposed	220-275/340-350	-	Wolfbeis, 1985
	275/340	Bulk seawater	Coble, 1996
	265-280/300-370	Groundwater, from Sutherland, Scotland; Derbyshire, England; Dordogne, France; Wiltshire, England	Baker and Genty, 1999
	278-279/340-353	Discharge from Sewage treatment plants, England	Baker, 2001
	277/351	Discharge from Tissue mill, Northumberland, England	Baker, 2002
	278/353	Natural water and wastewater, USA	Her et al., 2003
	280/320	Lake water, Japan	Komatsu et al., 2005
	240/355, 280/355	Industrial estate Wastewater and its treated wastewater, Lamphun, Thailand	Musikavong, 2006
Fulvic acids	350/450	Suwannee River, Peat and Soil standards, IHSS	Marhaba and Kochar, 2000
	315/437-441	Extracted from forest soil in Dando, Japan	Yamashita and Tanoue, 2003
	245/445, 320/443	Suwannee River fulvic acid (SRFA, with lower MW and high aromaticity)	Her et al., 2003
	220/445	Standard fulvic acid (SFA)	Chen et al., 2003
	255/455, 320/450	Suwannee River Fulvic Acid (1S101F), IHSS	Sierra et al., 2005
	265/475, 325/440	Elliot Soil Fulvic Acid (1S102F), IHSS	Sierra et al., 2005
Humic acids	250/450	Suwannee River, Peat and Soil standards, IHSS	Marhaba and Kochar, 2000
	235-255/435-465	Commercially available humic acid, Wako Pure Chemical Industries Ltd.	Nakajima et al., 2002
	260/485, 330/470	Suwannee River Humic Acid (1S101H), IHSS	Sierra et al., 2005
	270/550, 360/560	Elliot Soil Humic Acid (1S102H), IHSS	Sierra et al., 2005
	261/457, 325/452	Suwannee River humic acid (SRHA, with larger MW and high aromaticity)	Her et al., 2003
Fulvic acid and Humic acid-like proposed	275/410,330/410	Industrial estate Wastewater and its treated wastewater, Lamphun, Thailand	Musikavong, 2006
	235/435,320/430	Lake water, Japan	Komatsu et al., 2005
	290-340/395-430	Groundwater from Sutherland, Scotland; Derbyshire, England; Dordogne, France; Wiltshire, England	Baker and Genty, 1999
	230/440, 340/440	Hawaiian River water	Coble, 1993
	260/380-460, 350/420-480	Bulk seawater	Coble, 1996
	339/420-422	Discharge from Sewage treatment plants, England	Baker, 2001
	343/433	Discharge from Tissue mill, Northumberland, England	Baker, 2002
	320-360/400-470	Landfill leachates, England	Baker and Curry, 2004
	337/423	Natural water and wastewater, USA	Her et al., 2003

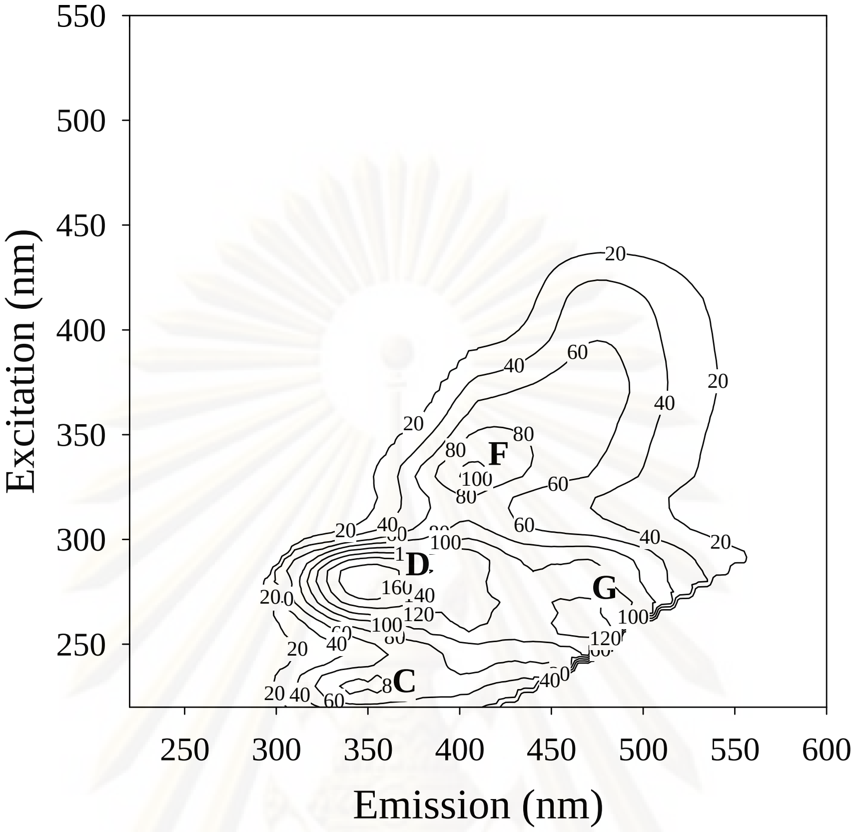


Figure 5.1 Example of FEEM of wastewater from Site 2 (20 QSU)

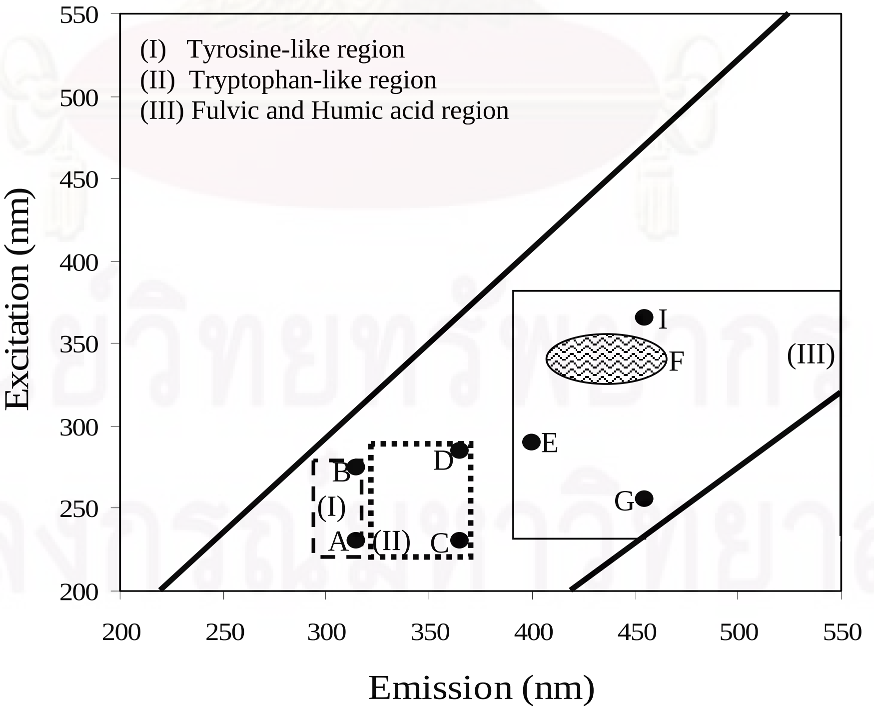


Figure 5.2 Proposed FEEM peak positions in the FEEM regions and their putative origins

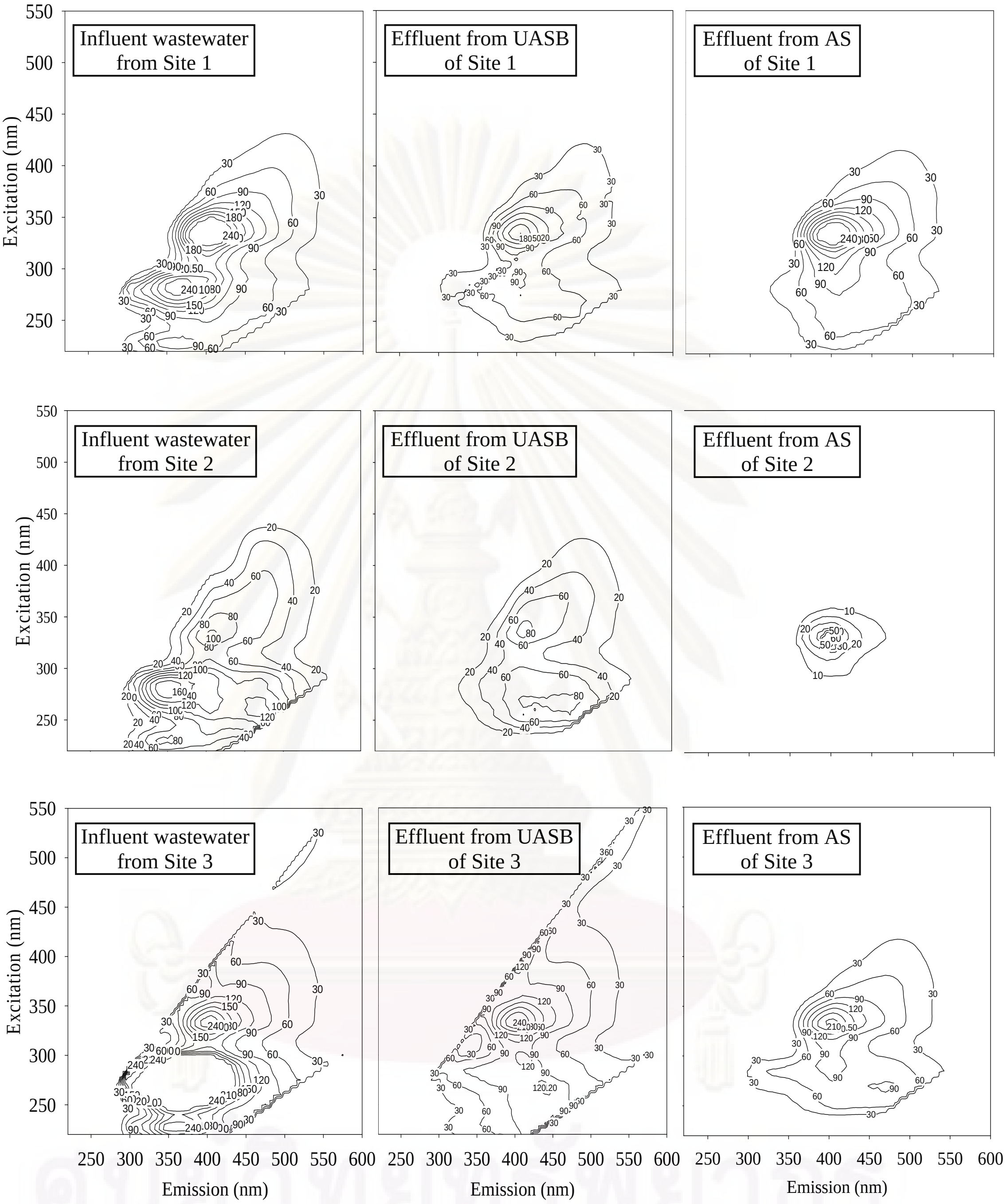


Figure 5.3 FEEM spectra of unfractionated water samples (wastewater and effluent wastewater after UASB and AS) of Sites 1 (30QSU), 2 (20QSU) and 3 (30QSU)

Table 5.2 FEEM peak positions in unfractionated water samples

Water Samples		FEEM peak positions							
		Tyrosine-like region		Tryptophan-like region		Fulvic and Humic acid region			
		A	B	C	D	E	F	G	I
nm_{Ex}/nm_{Em}		230/315	275/315	230/340-365	265-295/315-390	290/400	330-335/395-465	255-265/435-455	365/455
Site 1	Influent wastewater			●	●		●		
	Effluent from UASB					●	●	●	
	Effluent from AS						●		
Site 2	Influent wastewater			●	●		●	●	
	Effluent from UASB						●	●	
	Effluent from AS						●		
Site 3	Influent wastewater			●	●	●	●	●	
	Effluent from UASB				●	●	●	●	
	Effluent from AS					●	●	●	

Figures 5.4, 5.5 and 5.6 summarize FEEM spectra of unfractionated influent wastewater and effluents from UASB and AS with their six DOM fractions from Site 3, respectively. For brevity purpose, FEEM spectra of unfractionated influent wastewater and effluents from UASB and AS with their six DOM fractions from Sites 1 and 2 are given in Appendix A. For fractionated water samples, a total of 6 fluorescent peaks were detected at: (C) 230nm$_{Ex}$/340-365nm$_{Em}$, (D) 265-295nm$_{Ex}$/315-390nm$_{Em}$, (E) 290nm$_{Ex}$/400nm$_{Em}$, (F) 330-335nm$_{Ex}$/395-410nm$_{Em}$, (G) 255-265nm$_{Ex}$/435-455nm$_{Em}$, and (I) 3650nm$_{Ex}$/455nm$_{Em}$. Table 5.3 conclusively illustrates all FEEM peak positions found from DOM fractions of the influent wastewater and effluents from UASB and AS, which were categorized into their associated putative regions.

Based on the results, FEEM spectra of unfractionated wastewater and its six DOM fractions from Site 3 demonstrate that the appearances of high strength intensities at the major FEEM peaks viz. tryptophan-like substances, as represented by Peaks C and D, and humic-like substances as represented by Peaks E, F, and G in the wastewaters were mainly found in FEEM peaks of HPOA and HPIB fractions which were recognized as the major DOM fractions in the wastewater. Similar findings were found for Sites 1 and 2 where the major FEEM peak intensities of the unfractionation sample could be described using the major FEEM peaks found in HPOA and HPIB fractions. The FEEM Peak F (representing humic-like substances) was found to be the main component in HPOA fraction which was the major component of the effluents from the UASB and AS treatments of all three sites. This finding reveals that the wastewater from the various breweries had similar characteristics which could be represented by similar groups of FEEM components.

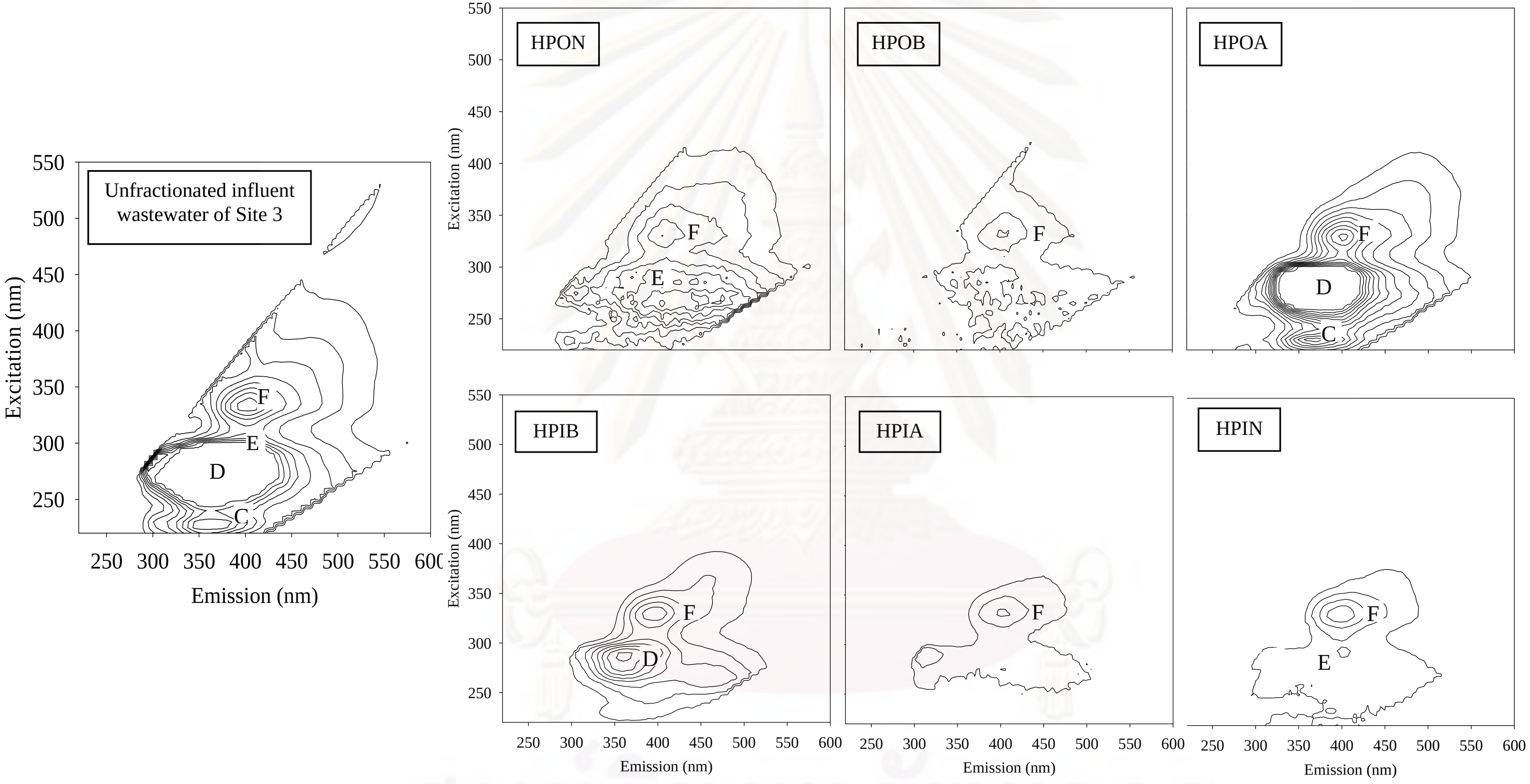


Figure 5.4 FEEMs of unfractionated influent wastewater (30 QSU) from Site 3 and its six DOM fractions(10 QSU)

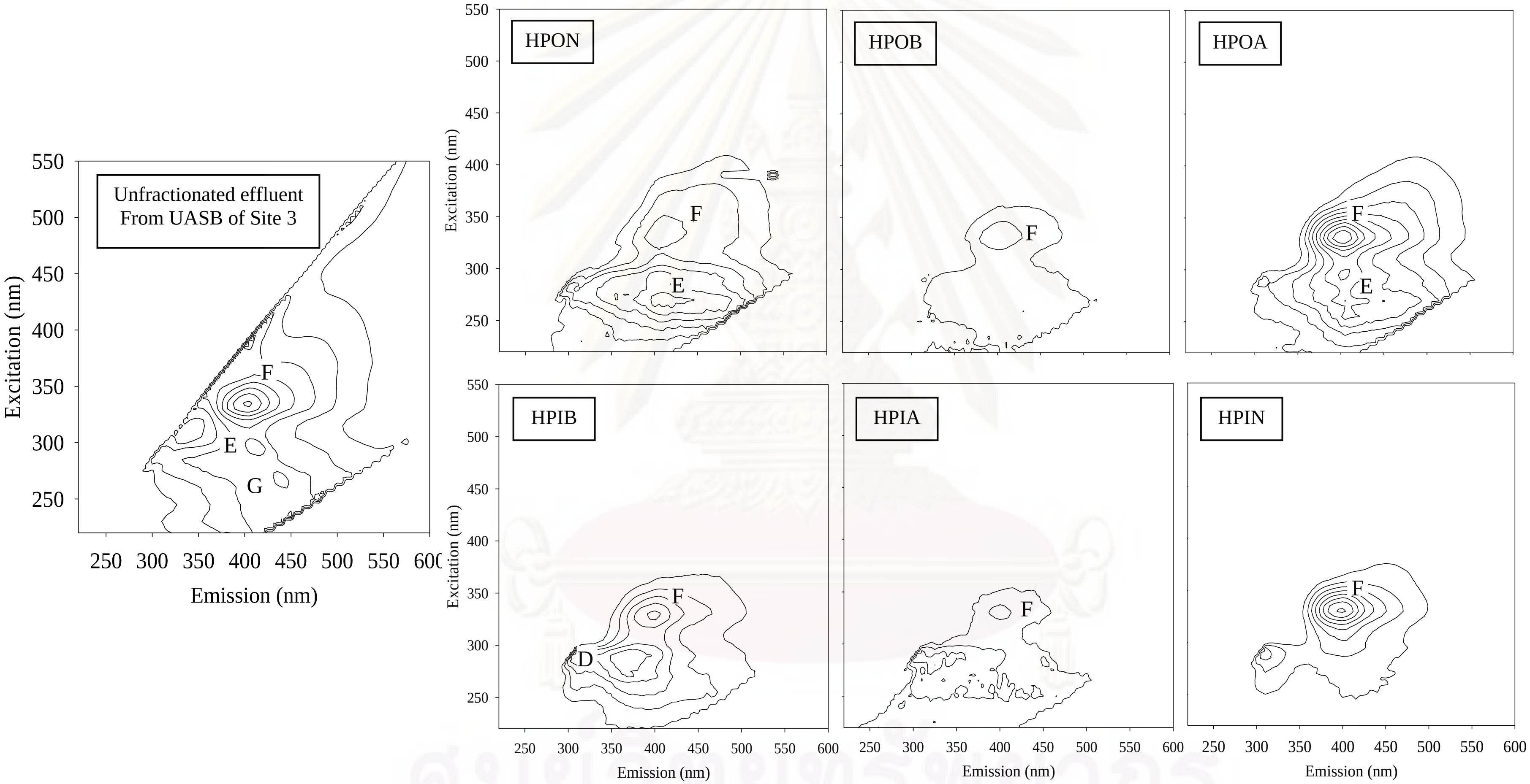


Figure 5.5 FEEMs of unfractionated effluent from UASB (30 QSU) from Site 3 and its six DOM fractions (10 QSU)

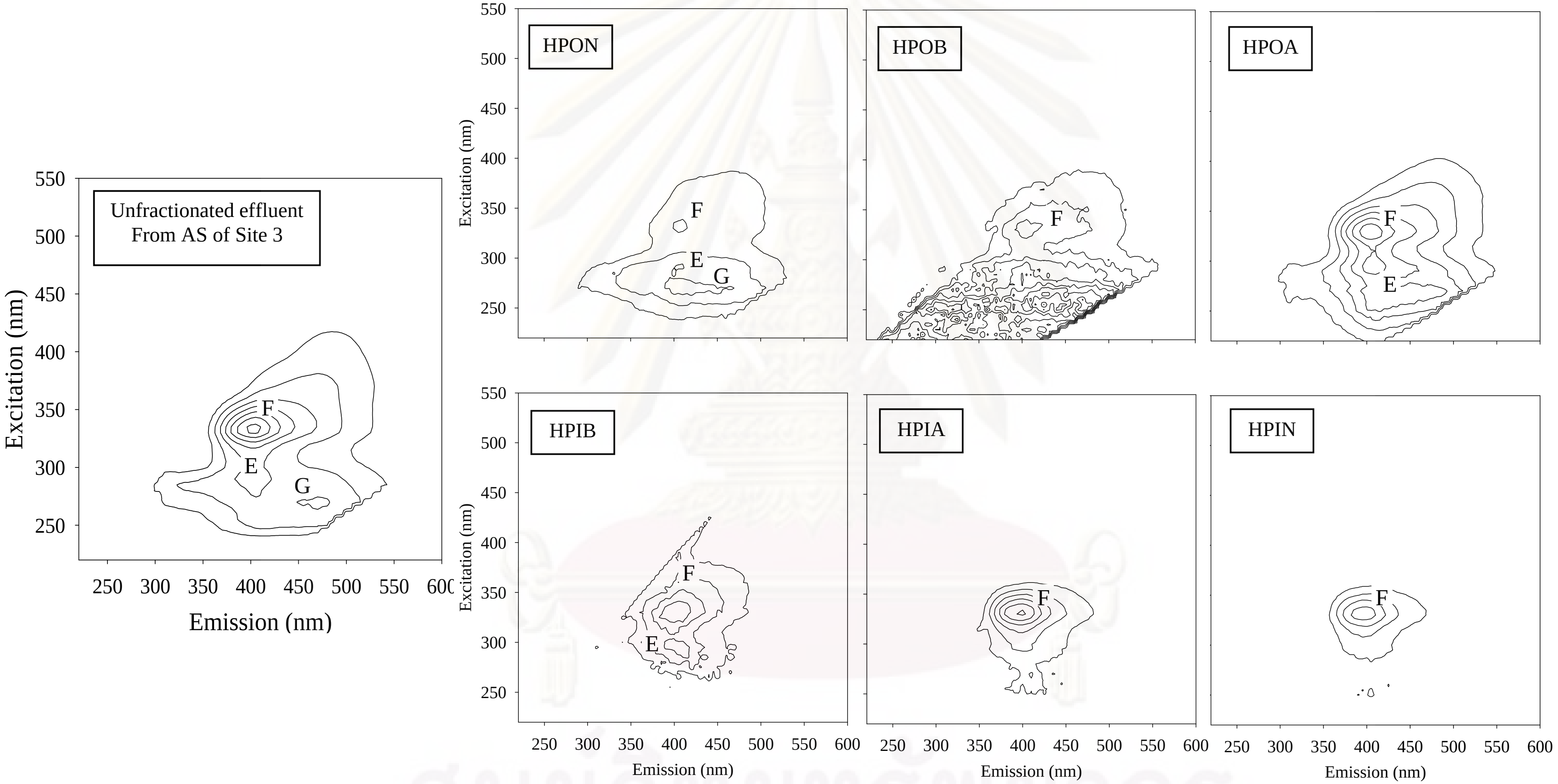


Figure 5.6 FEEMs of unfractionated effluent from AS (30 QSU) from Site 3 and its six DOM fractions (10 QSU)

Table 5.3 FEEM peak positions observed from FEEMs of all unfractionated samples and their DOM fractions

Water Samples	Site 1						Site 2						Site 3					
	FEEM Peak Positions																	
	Tryptophan-like region		Humic-like region				Tryptophan-like region		Humic-like region				Tryptophan-like region		Humic-like region			
	C	D	E	F	G	I	C	D	E	F	G	I	C	D	E	F	G	I
Influent wastewater	●	●		●			●	●		●	●		●	●	●	●	●	
HPON			●	●				●	●	●	●	●			●	●		
HPOB				●							●					●		
HPOA	●	●		●			●	●		●			●	●		●		
HPIB	●	●		●			●	●		●	●			●		●		
HPIA				●						●	●					●		
HPIN			●	●					●	●					●	●		
Effluent from UASB			●	●	●					●	●			●	●	●	●	
HPON			●	●					●	●	●	●			●	●		
HPOB				●						●	●					●		
HPOA			●	●	●				●	●	●	●			●	●		
HPIB				●					●	●				●		●		
HPIA				●					●	●						●		
HPIN				●					●	●						●		
Effluent from AS				●						●					●	●	●	
HPON				●					●	●	●				●	●	●	
HPOB				●												●		
HPOA			●	●						●					●	●		
HPIB				●						●					●	●		
HPIA				●					●	●						●		
HPIN				●												●		

5.1.2 Comparison of DOM characterization in wastewaters by DOM surrogates and FEEM

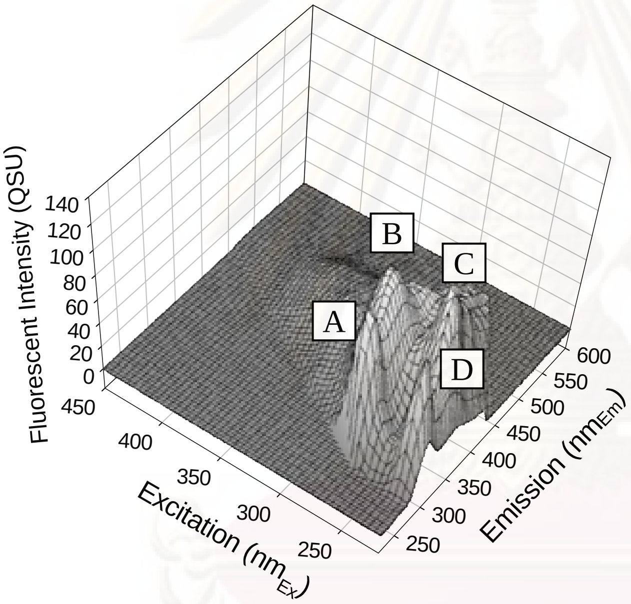
The use of DOM surrogate parameters and FEEM analysis to qualify the organic composition of DOM in brewery wastewater and the treated wastewater was found to be consistent (Table 5.4). Based on our findings and those in the literature, it can be concluded that the major DOM components in brewery wastewater are groups of humic substances and proteins. Humic substances are of significance because they are recalcitrant materials represented by the HPOA fraction and the FEEM position of Peak F. These humic substances can be seen as problematic DOM for UASB and AS treatments as they could not be effectively treated with these typical treatment processes.

Table 5.4 Comparison of DOM characterization in wastewaters by DOM surrogate parameters and FEEM

Profiling Techniques	Characterization of DOM	
	Major organic composition found in this study	Organic compounds based on literatures
DOM surrogates	*Wastewater* 1. HPOA 2. HPIB	 1. Fulvic acid 2. Peptide or amino
	Effluent from UASB 1. HPOA	 1. Fulvic acid
	Effluent from AS 1. HPOA	 1. Fulvic acid
FEEM	*Wastewater* 1. Peaks C and D 2. Peaks E, F and G	 1. Tryptophan-like substances 2. Humic and fulvic acid-like substances
	Effluent from UASB 1. Peaks E, F and G	 1. Humic and fulvic acid-like substances
	Effluent from AS 1. Peaks E, F and G	 1. Humic and fulvic acid-like substances

5.2 Analyses of the effectiveness of treatment processes on the reduction of brewery DOM

FEEM spectra could be utilized to quantify all fluorescent organic matters in water by summarizing the maximum fluorescent intensities of all FEEM peaks (Musikavong et al. 2007; Janhom et al. 2008). Figure 5.7 shows an example of FEEM for Sample X. The total fluorescent intensity is obtained by summarizing the highest value of FEEM intensities of Peaks A, B, C, and D.



Fluorescent intensity of Sample X
(QSU) = A+B+C+D

Figure 5.7 Example of quantification of FEEM for Sample X

The distribution of FEEM peaks of unfractionated samples and their DOM fractions in wastewater and effluent from UASB and AS treatments of all three sites based on their intensities (QSU) are illustrated in Table 5.5, and this is described in more detail as follows.

5.2.1 Reduction of FEEM intensities of DOM through UASB and AS treatments

The DOM in unfractionated water samples was quantified through FEEM technique and the reduction of the fluorescent organic matter was reflected by the difference in the total fluorescent intensities of the total fluorescent organic matter obtained from wastewaters after the UASB and AS treatments. The summation of fluorescent intensities of the FEEM peaks found in the wastewater and the effluents from the UASB and AS treatments are depicted in Figure 5.8 and this can be used to evaluate the reduction of fluorescent organic compounds in brewery wastewaters of all three studied sites.

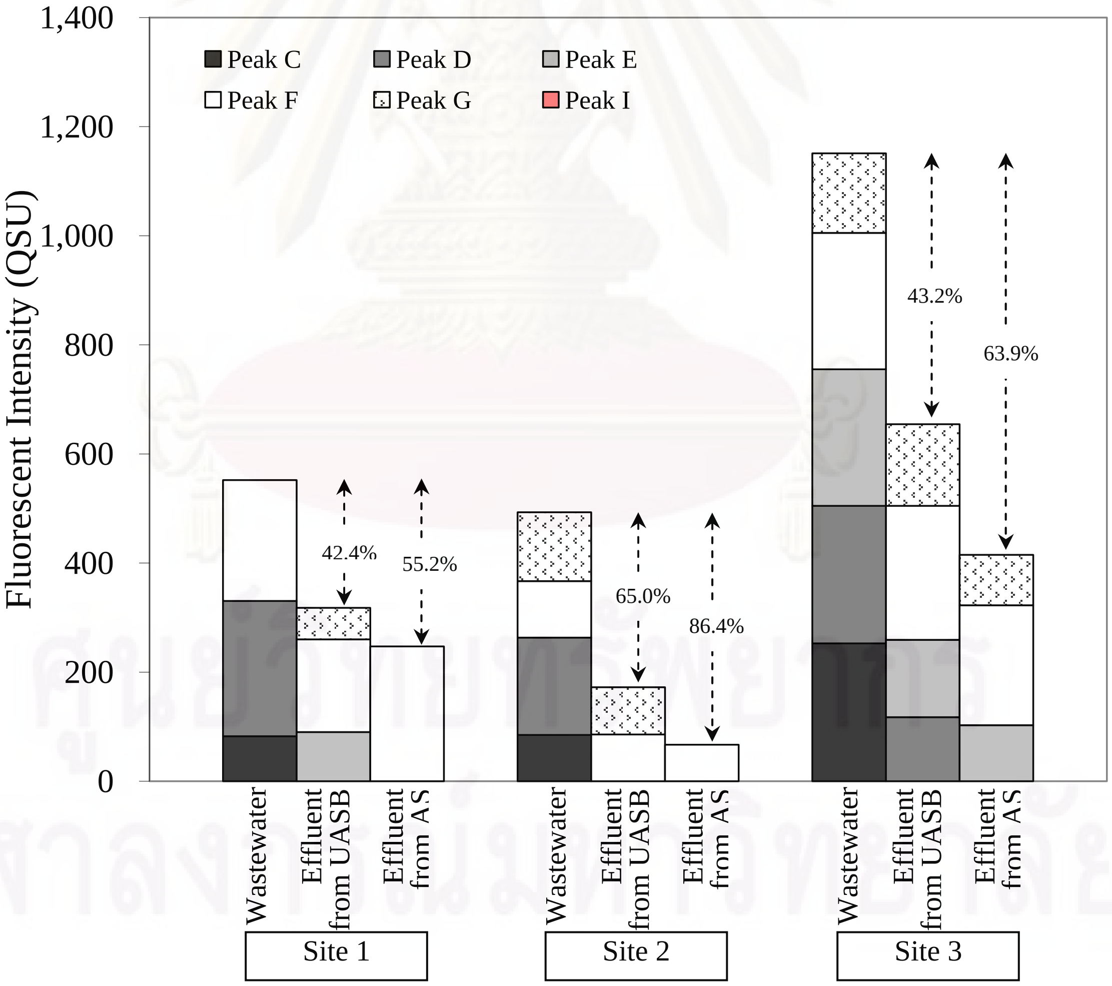


Figure 5.8 Reduction of FEEM peaks of brewery wastewater by UASB and AS treatments

The UASB treatment could remove around 42%, 65% and 43% of the fluorescent organic matter from the wastewaters for Sites 1, 2 and 3 respectively. The AS treatment further augmented the reductions of the fluorescent organic matter of Sites 1, 2 and 3 by about 13%, 21% and 21%. Based on the observation, the reduction of DOM was mainly found to occur during the UASB treatment where the one of two common organic compounds, tryptophan-like substances, represented by Peaks C and D could mostly reduced. This finding was supported by the report from Stevenson (1994) that typical tryptophan-like substances were proteinaceous materials which could be biodegradable in typical wastewater treatment systems. Peaks E and G were generally not found in the brewery wastewater but they were generated from the treatment with UASB. The AS treatment seemed to be able to treat some of the compounds in these two peaks as seen in the case of Site 1 (lager beer) and Site 2B (light beer), but not so well for Site 3 (lager beer). This means that the organic compositions in wastewater from Brewery 3 could well be different to those from Brewery 1, despite of being the same lager beer production facility. One common conclusion from this investigation was that fulvic and humic-like substances as represented by Peak F were hardly biodegraded by UASB and AS treatments, regardless of the type of breweries, and thus they remained in the water along the treatment process.

This finding was similar to previous reports where the effluent DOM originated from biological wastewater treatment schemes could have included organic compounds of different groups, from easily biodegradable carbohydrates and proteins to more biologically resistant components known as fulvic and humic materials (Rebhun and Manka, 1971; Manka et al., 1974; Ma et al., 2001; Imai et al., 2002; Ilani et al., 2005).

For water reclamation perspective, fulvic and humic-like substances, represented by Peak F are of considerable concern, since they were likely to be refractory through biological treatments and it was still relatively predominated in residual DOM in the effluents.

Table 5.5 Distribution of FEEM intensities of DOM and DOM fractions

Water sources		FEEM intensities of DOM (QSU)		Surplus	FEEM intensities of DOM fractions (QSU)					
		UW	FW	(%)	HPON [1]	HPOB [2]	HPOA [3]	HPIB [4]	HPIA [5]	HPIN [6]
Site 1	Influent wastewater	551.9	586.9	+ 6.3	65.3	22.9	239.2	136.4	28.6	94.5
	Effluent from UASB	318.0	380.5	+ 19.6	48.2	23.3	158.9	55.3	15.6	79.2
	Effluent from AS	247.2	277.1	+ 12.1	38.2	10.7	113.7	46.5	36.4	31.7
Site 2	Influent wastewater	492.9	536.6	+ 8.9	91.7	29.6	175.3	170.6	8.5	60.8
	Effluent from UASB	172.4	194.6	+ 12.9	57.6	2.3	79.1	19.7	17.2	18.7
	Effluent from AS	67.0	78.2	+ 16.7	24.0	ND	47.0	1.2	6.0	ND
Site 3	Influent wastewater	1151.4	1159.6	+ 0.7	38.3	6.2	611.9	418.8	16.6	67.9
	Effluent from UASB	654.4	787.6	+ 20.4	75.4	23.1	259.9	177.0	6.8	245.5
	Effluent from AS	415.2	458.5	+ 10.4	117.8	3.0	188.3	71.9	49.5	27.9

Note: UW = Unfractionated water
FW = Fractionated water = 1+2+3+4+5+6
Surplus (%) = (FW – UW) / UW × 100
ND = Not detect

5.2.2 Reduction of FEEM intensity of DOM fractions through UASB and AS treatments

The distribution of FEEM peaks of unfractionated samples and their DOM fractions based on their intensities (QSU) as illustrated in Table 5.5 suggests that the summation of the FEEM peak intensities of fractionated water was slightly higher (1% to 20%) than those of unfractionated water. The surplus might be due to the isolation of the DOM which separates the overlapping peaks of the unfractionated sample and the signals from each isolated peak emerged.

Similar findings with DOC and UV_{254} are observed using quantified FEEM. DOM fractions in terms of FEEM peak intensities were mainly reduced by decreases in the two major DOM fractions, HPOA and HPIB which accounted for 52 and 66% reductions in HPOA and HPIB, respectively, for Site 1, 73 and 99% for Site 2, and 69 and 83% for Site 3 (Figure 5.9). UASB was also the main treatment unit for the reduction of these two major fractions. With FEEM measuring technique, HPIA was also shown to display different treatment behavior as it increased after passing through the AS treatment unit for all three studied sites. The results suggest that the reduction of DOM through UASB treatment was mainly occurred by decreases of tryptophan-like substances, represented by Peaks C and D existed in each fraction. The residual DOM, i.e. fulvic and humic-like substances represented by Peaks E and G, was being transferred to AS and was further treated while Peak F could not (see Fig. 5.8).

HPOA fraction or the group of fulvic and humic-like substances represented by Peaks F was recalcitrant during the UASB and AS treatments of all three studied breweries. This is of particular concern as considerable quantity of this organic compound still remained in the effluents which could affect the possibility of reusing the water.

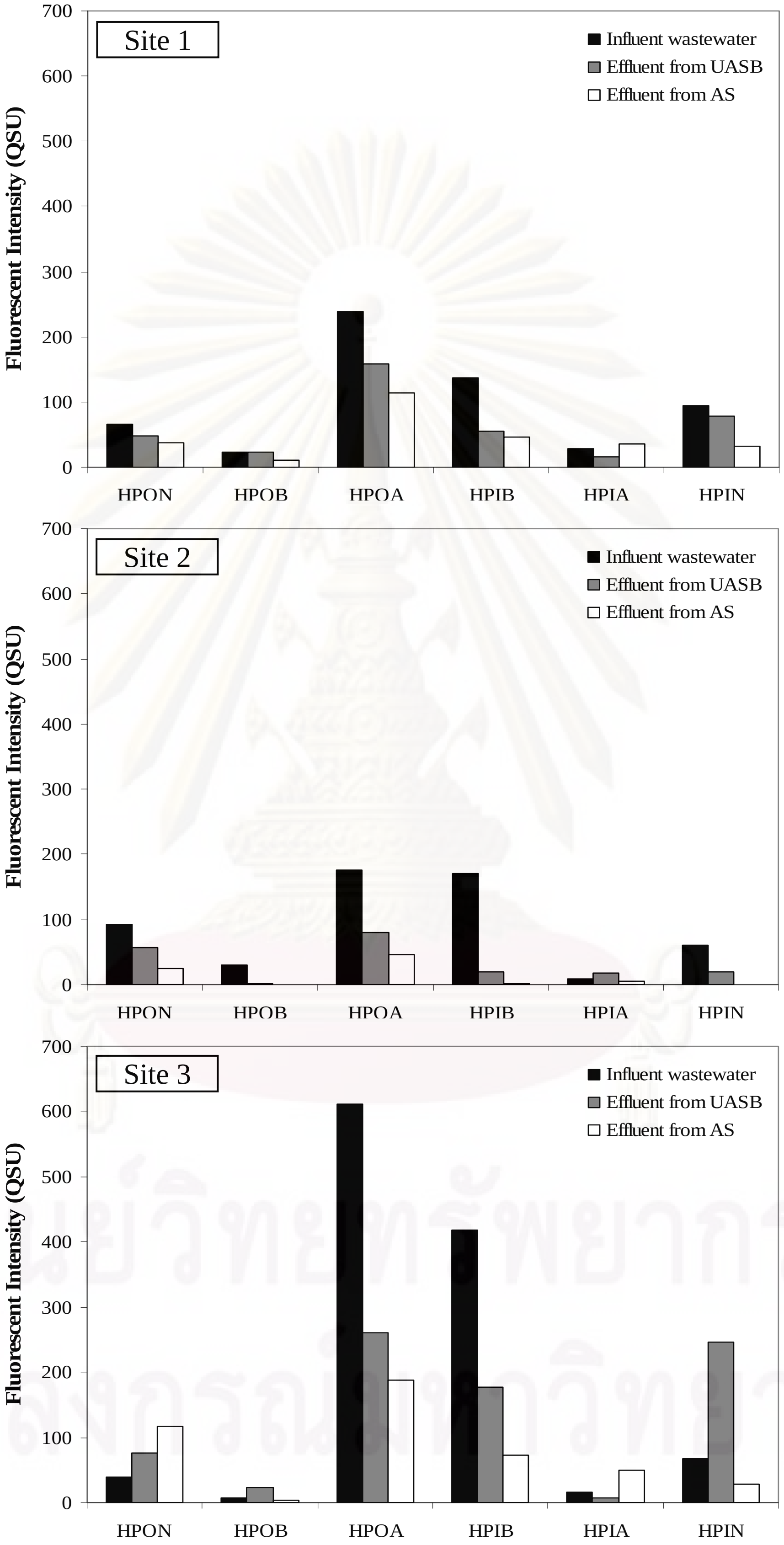


Figure 5.9 Reduction of FEEM peak intensities of DOM fractions through UASB and AS treatments at Sites 1, 2 and 3

5.2.3 Relationships between FEEM intensities and DOM surrogate parameters

The reduction potential of organic constituent in the wastewater obtained from quantifying FEEM corresponded well with the reductions in DOC and UV_{254} of DOM, where major degradation was observed in the UASB. Table 5.6 compares the wastewater treatment characteristics from UASB and AS of the breweries using the three surrogates examined in this work. Major difference was found for the effluent from the UASB of Brewery 3 as the treatment of UV_{254} seemed not to be as effective as the other two surrogates. This suggested that there could be some aromatic organic in the influence of wastewater from Brewery 3 which was slightly biorecalcitrant than the wastewaters from the other two breweries. Figures 5.10 and 5.11 illustrates linear relationships between FEEM and DOC and UV_{254} where a good correlation between FEEM intensity and DOC (R^2=0.9678), and FEEM intensity and UV_{254} (R^2=0.8789), respectively, could be observed. This, to some extent, verifies the use of FEEM as an organic surrogate for the wastewater from Brewery.

Table 5.6 Comparison of DOM reduction monitored by FEEM, DOC and UV_{254}

Site	Treatment Unit	Percent reduction (%)		
		FEEM	DOC	UV_{254}
1	UASB	42	59	57
	AS	55	65	65
2	UASB	65	78	80
	AS	86	87	88
3	UASB	43	50	29
	AS	64	79	70

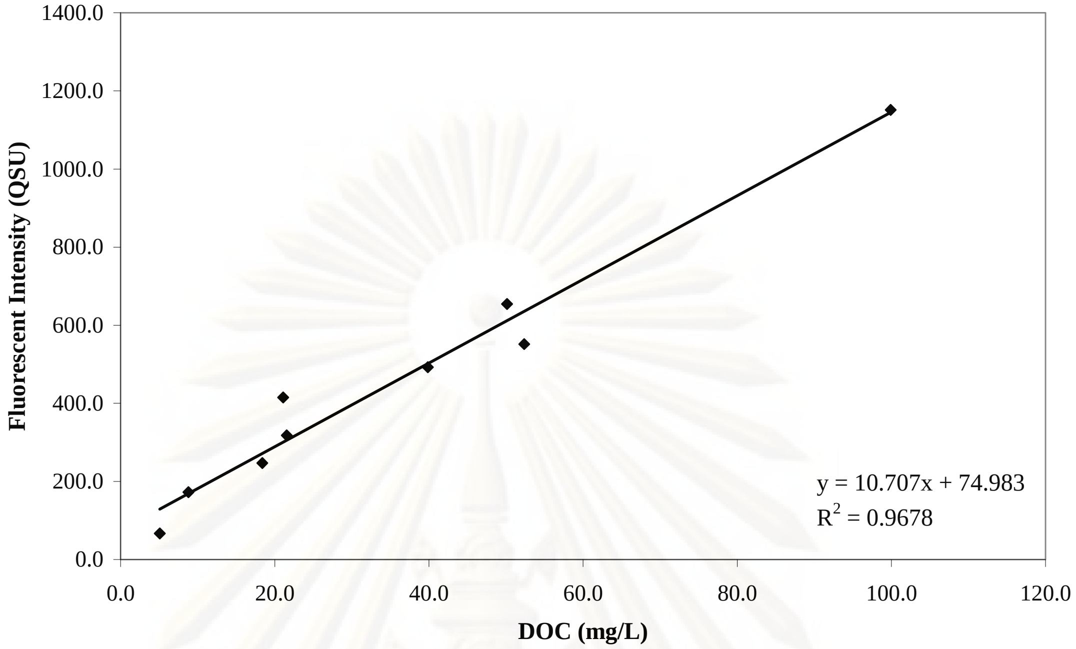


Figure 5.10 Relationship between FEEM intensity and DOC of unfractionated samples

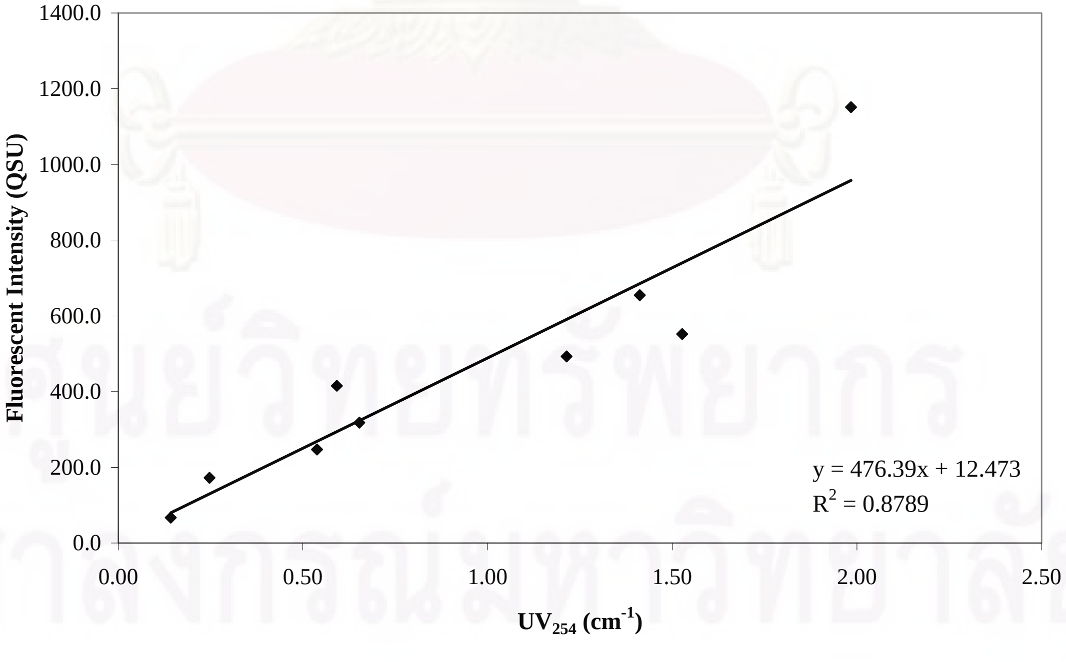


Figure 5.11 Relationship between FEEM intensity and UV_{254} of unfractionated samples

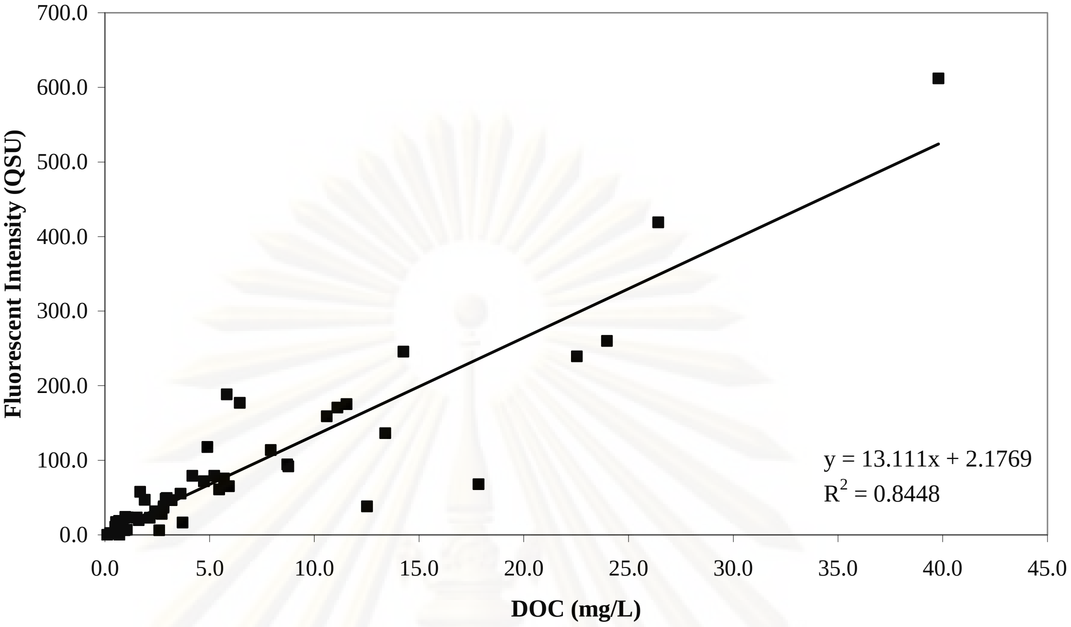


Figure 5.12 Relationship between FEEM intensity and DOC of fractionated samples

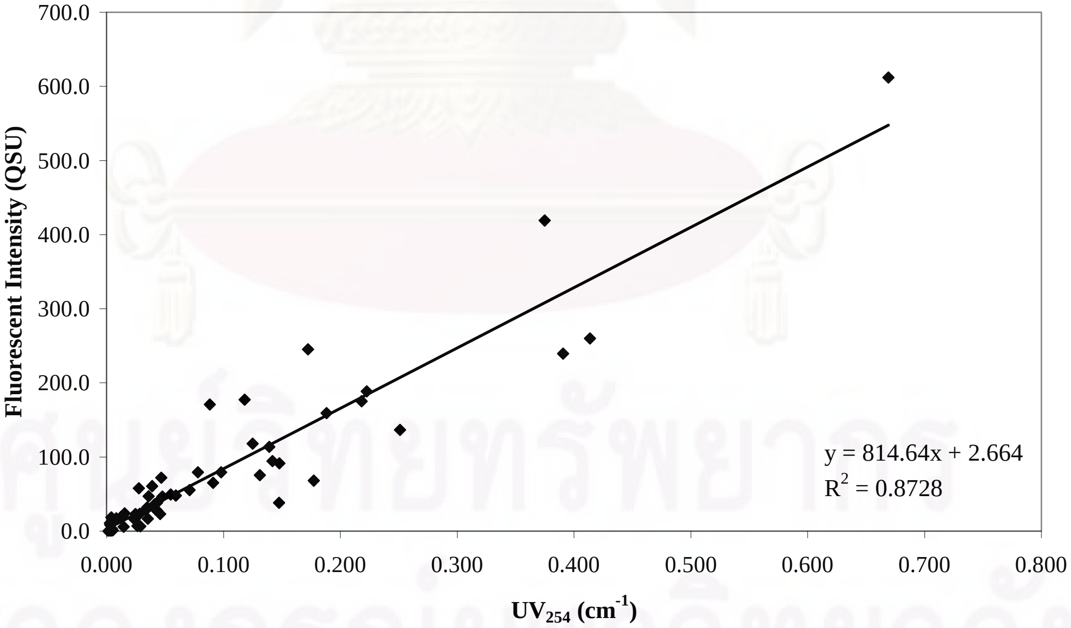


Figure 5.13 Relationship between FEEM intensity and UV_{254} of fractionated samples

The percent reductions of the two major DOM fractions monitored through the FEEM technique also corresponded well with the reductions in DOC and UV_{254}. Linear relationships with a good correlation between FEEM intensity and DOC (R^2=0.8448) and FEEM intensity and UV_{254} (R^2=0.8728) for these major DOM fractions are demonstrated in Figures 5.12 and 5.13, respectively. This implies that the use of the resin fractionation technique coupled with FEEM analysis could well be used to determine DOM variation during the treatment sequence of the brewery facilities.

5.3 Classification of fluorescent organic compounds

5.3.1 Pyrolysis Gas Chromatography-Mass Spectrometry (Pyrolysis GC/MS)

In this research, the Py-GC/MS was used to identify and confirm the kinds of the major chemical classes and pyrolysis fragments of DOMs in the wastewaters and the treated wastewater from that three selected breweries. The programs of brewery wastewater and effluents from UASB and AS treatments of all three sites are illustrated in Appendix A (from Table A-7 to A-15). It was found that the group of ketone, acid and alcohol were the major chemical class of DOM of all brewery wastewater from Sites 1, 2 and 3, this group was accounted more than 60% of DOMs, followed by aliphatic hydrocarbon (C_3-C_{19}) and aromatic hydrocarbon, respectively, whereas, organic nitrogen class was only slightly detected. Similar observations were found for the effluents of UASB and AS treatments. Interestingly, the first two major chemical classes including of the groups of ketone, acid and alcohol and the groups of aliphatic hydrocarbon and aromatic hydrocarbon considerably existed along the USAB and AS treatment since they was found to be the major chemical class of DOM in the effluents. This observation corresponded with the report from Dignac et.al. (2000), that the major fragments from the pyrochromatograms of wastewater and treated wastewater from activated sludge treatment processes were not different

To further analyze for the chemical classes of FEEM results, Musikavong (2006) used pyrolysis GC/MS in order to characterized wastewater of northern-region industrial estate, Thailand, according to the FEEM characteristics of the same water samples. In other words, the notion was to use FEEM to characterize major DOM compounds while pyrolysis GC/MS to confirm the major fragment of each compound comprising DOM. With this technique, the fluorescent peak positions could be further characterized according to their major pyrolysis fragments as shown in Table 5.7.

For this work, the fluorescent peak positions of DOMs from all three brewery wastewaters and theirs putative of fluorescent organic matters could be matched with the pyrolysis fragments. The results are concisely illustrated in Table 5.8. These findings agreed quite well with the reported matching characteristics in Musikavong (2006).

Table5.7 Fluorescent peak positions and major pyrolysis fragments of major fluorescent components from literature data

Substance	Majors pyrolysis fragments
Tyrosine-like and protein-like substances	Phenol and *p*-cresol (phenol, 4 methyl) (Bruchet *et al.*, 1990) Pyridines, pyrroles, indoles, nitriles, phenol and *p*-cresol (equal quantities from tyrosine) (AWWA, 2000)
Tryptophan-like and protein-like substances	Indole (AWWA, 2000) Acetronitrile, benzonitrile, phenylacetonitrile, pyridine, methylpyridine, pyrrole, indole and methylindole (Leenheer and Croues, 2003)
Fulvic acids and fulvic-like substances	Humic acids; Highly aliphatic (Bruchet, 1986; Gadel and Bruchet 1987) (1) n-alk-1-ene/n-alkane with 8-29 carbon presenting the limited odd over predominance in the C_{24}-C_{29} range (2) alkyl-benzenes, naphthalene, alkyl-naphthalene (3) phenol (Faure *et al.*2006) Fulvic acids; Highly peaks of butenal, acetic acid, 2-fufural, methyl furfural, levoglucosenone, 5-(Hydroxymethyl) 2 fufaral (Bruchet,1986; Gadel and Bruchet,1987) Large peaks of phenol and cresol (Croue *et al.*, 1993) Humic substances; (1) Nitrogen containing compounds (such as pyrrole and pyridine), aliphatic products (such as n-alk-1-ene/n-alkane with 5-29 carbon) (2) aromatic products (such as alkyl-benzenes, naphthalene and alkyl-naphthalene, (4) lignin products (such as o-cresol, m-cresol, catechol, dimethylphenol) (5) carbohydrate product (such as furan, 2-methyl proppenal, dimethyfuran, vinyfuran, 2-fufaraldehyde. (Lu *et al.*, 2006)
Humic acids, Fulvic and humic-like substances	

Source: Musikavong, 2006

Table 5.8 Fluorescent peak positions of DOM and theirs putative of fluorescent organic matter with pyrolysis fragments

Water Sample	Peak C	Peak D	Peak E	Peak F	Peak G	Pyrolysis fragments of putative fluorescent organic matter obtained in this study
Site 1						
Influent wastewater	●	●		●		***Tryptophan-like substances, Peaks C and D:*** Indole, Acetronitrile and Pyrrole ***Humic-like substances, Peaks F:*** $C_3 \leq$ Aliphatic hydrocarbon $\leq C_{17}$, alkyl-benzenes, nitrogen containing compounds, phenol and cresol
Effluent from UASB			●	●	●	***Humic-like substances, Peaks E, F and G:*** $C_5 \leq$aliphatic hydrocarbon fragments$\leq C_{15}$, alkyl-benzenes, naphthalene, phenol and cresol, and nitrogen containing compounds
Effluent from AS				●		***Humic-like substances, Peaks F:*** $C_5 \leq$ Aliphatic hydrocarbon $\leq C_{15}$, alkyl-benzenes, and nitrogen containing compounds
Site 2						
Influent wastewater	●	●		●	●	***Tryptophan-like substances at peaks C and D:*** Indole and Pyrrole, ***Humic-like substances, Peaks F and G:*** $C_3 \leq$ Aliphatic hydrocarbon $\leq C_{16}$, alkyl-benzenes, phenol and cresol
Effluent from UASB				●	●	***Humic-like substances, Peaks F:*** $C_3 \leq$ Aliphatic hydrocarbon $\leq C_{14}$, alkyl-benzenes, nitrogen containing compounds, and aldehydes
Effluent from AS				●		***Humic-like substances, Peaks F:*** $C_5 \leq$ Aliphatic hydrocarbon $\leq C_{14}$, phenol and nitrogen containing compounds
Site 3						
Influent wastewater	●	●	●	●	●	***Tryptophan-like substances at peaks C and D:*** Indole, Acetronitrile, Benzonitrile and Pyrrole ***Humic-like substances, Peaks F:*** $C_3 \leq$ Aliphatic hydrocarbon $\leq C_{19}$, alkyl-benzenes, nitrogen containing compounds, phenol and cresol, and aldehydes
Effluent from UASB		●	●	●	●	***Tryptophan-like substances at peaks C and D:*** Indole, Benzonitrile and Pyrrole ***Humic-like substances, Peaks F:*** $C_3 \leq$ Aliphatic hydrocarbon $\leq C_{16}$, alkyl-benzenes, nitrogen containing compounds, phenol and cresol
Effluent from AS			●	●	●	***Humic-like substances, Peaks F:*** $C_3 \leq$ Aliphatic hydrocarbon $\leq C_{16}$, alkyl-benzenes, nitrogen containing compounds, phenol and cresol and aldehydes

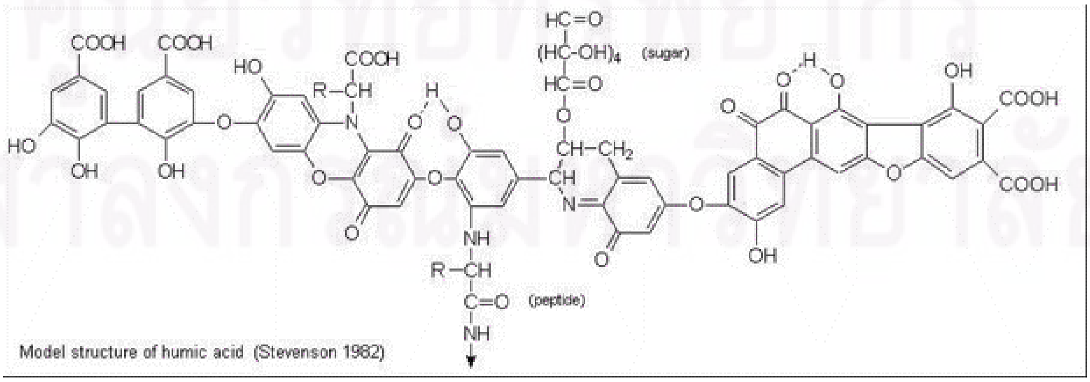
5.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIRs of brewery wastewater and effluents from UASB and AS treatments of all three sites are illustrated in Appendix A (from Table A-16 to A-24). Table 5.9 presents the possible functional groups present in the water samples. The results suggest that common functional groups of DOM in brewery wastewater and treated wastewater were carboxylic acid, amide, ketone, alcohol, and aromatic characteristics. These common functional groups particularly associated with the structural compositions comprising the common fluorescent organic compounds in brewery wastewater, i.e. tryptophan-like substances and. fulvic and humic-like substances as displayed in Figures 5.14 and 5.15.

Table 5.9 Possible functional groups present in the water samples

Water Sample	Possible functional groups
Site 1	
Influent wastewater	Carboxylic acid, Amide, Ketone, AL alcohol, AL HC, AR HC
Effluent from UASB	Carboxylic acid, Amide, Ketone, Mono substituted AR HC, AL HC
Effluent from AS	Carboxylic acid, Amide, Mono substituted AR HC, Amino acids, AL HC
Site 2	
Influent wastewater	Carboxylic acid, Amide, Ketone, AL alcohol, AL HC, AR HC
Effluent from UASB	Carboxylic acid, Amide, Ketone, AL alcohol, Aldehyde, AL HC, AR HC
Effluent from AS	Carboxylic acid, Amide, Ketone, AL HC, AR HC
Site 3	
Influent wastewater	Carboxylic acid, Amide, Ketone, AL alcohol, AL HC, AR HC
Effluent from UASB	Carboxylic acid, Amide, Ketone, AL alcohol, Mono substituted AR HC, AL HC
Effluent from AS	Carboxylic acid, Amide, Ketone, AL alcohol, Mono substituted AR HC, AL HC

Remarks: AL= Aliphatic, AR = Aromatic, HC = Hydrocarbon



Model structure of humic acid (Stevenson 1982)

Figure 5.14 Structural Model of Humic acid

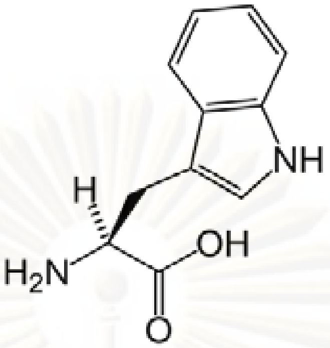


Figure 5.15 Skeletal of Tryptophan

Table 5.10 presents the possible functional groups of DOM fractions in brewery wastewater and treated wastewater. Based on the FEEM results, it showed that tryptophan-like substances and humic and fulvic acids-like substances in the wastewaters were mainly found in FEEM peaks of HPOA and HPIB fractions which were recognized as the major DOM fractions in the wastewater. The functional groups found for each DOM fraction were also related since carboxylic acid, amide, aromatic characteristics, particularly for the two major DOM fractions, mainly composed of tryptophan-like and humic and fulvic acids-like substances. Based on this characterization, it may be stated that the major organic components in brewery wastewater were the humic and proteineous substances. Furthermore, the problematic organics for the future reclamation process were the humic substances.

Table 5.10 Possible functional groups of DOM fractions

DOM fractions	Possible functional groups
HPON	Ketone, AL alcohol
HPOB	Amide, Amine, AR characteristics
HPOA	Carboxylic acid, Amide, AR characteristics, AL alcohol, Phenol, Amino acids
HPIB	Carboxylic acid, Amide, AR characteristics, Amino acids
HPIA	Carboxylic acid, AR characteristics
HPIN	Carboxylic acid, Amine, AL alcohol

Remarks: AL= Aliphatic, AR = Aromatic, HC = Hydrocarbon

5.4 Concluding Remarks

This chapter was to qualify and quantify DOM in brewery wastewater and treated brewery wastewater from three studied breweries through FEEM analysis. The results suggest that the major DOM components in brewery wastewater from three sites were groups of tryptophan-like substances and fulvic and humic-like substances. The investigation was also illustrated that fulvic and humic-like substances as represented by Peak F were hardly biodegraded by UASB and AS treatments, regardless of the type of breweries, and thus they remained in the water along the treatment process. The utilization of FEEM could yield the specific information on the organic composition of brewery wastewater and its treated effluent, and the FEEM intensities could be used to monitor the variations of DOM and DOM fractions during treatment process. Furthermore, the FEEM analytical results were consistent with the results from conventional DOM analyses such as DOC and UV_{254}, with certain level of confidence, FEEM analysis can be potentially employed as a simple monitoring technique for DOM analysis. To further analyze the FEEM results, pyrolysis-GC/MS and FTIR could be employed to identify the chemical classification of the fluorescent DOM in the wastewater and treated wastewater, it may be concluded that the major organic components in brewery wastewater were the humic substances and proteineous substances, and the problematic organics for the future reclamation process were the humic substances.

CHAPTER VI

TRIHALOMETHANES FORMATION POTENTIAL OF DISSOLVED ORGANIC MATTER IN BREWERY WASTEWATER

This chapter demonstrates the potential of DOM and DOM fractions in brewery wastewater and treated wastewater in forming trihalomethanes (THMs). The reactivity to form THMs of DOM and its fractions which are useful for predicting and control the possible formation of disinfection by-product (DBPs) are also presented. The performance capability of upflow anaerobic sludge blanket (UASB) and activated sludge (AS) for trihalomethane formation potential (THMFP) reduction are then evaluated.

6.1 THMFP of DOM and DOM fractions in brewery wastewater and treated wastewater

THMFP results of DOM and DOM fractions in brewery wastewater and effluents from typical brewery treatment processes are reported in Table 6.1. Based on these results, DOM in the influent wastewater of all three sites could vastly create THMs since their high THMFP was detected. This may have caused by the high organic loading concentration contained in the resulting wastewater from brewing activities. THMFP created from DOM in the effluents from UASB and AS treatments of all three sites was also high as a result of high residual DOM left in those treated wastewaters. THMs created by residual DOM in the treated brewery wastewater in this study was noticeably higher than that of DOM in raw water used for water supply from other water resources as shown in Table 6.2. This should be aware of when the treated wastewater is to be reclaimed for further use.

Table 6.1 THMFP of unfractionated and fractionated water samples

Water sources		av THMFP (µg/L)							
		UW	FW						Σ FW
			HPON	HPOB	HPOA	HPIB	HPIA	HPIN	
Site 1	Influent wastewater	3281.2	511.3	389.7	2632.8	1924.5	246.8	489.6	6194.7
	Effluent from UASB	1183.6	201.4	195.4	1178.8	451.1	79.6	244.1	2350.4
	Effluent from AS	960.5	181.2	80.6	753.1	438.7	244.4	131.4	1829.4
Site 2	Influent wastewater	2646.2	804.2	493.4	1306.3	1455.6	82.4	328.1	4470.0
	Effluent from UASB	472.8	124.1	43.8	457.9	224.1	51.5	35.9	937.3
	Effluent from AS	257.1	79.0	22.6	194.8	90.6	81.3	29.6	497.9
Site 3	Influent wastewater	5315.8	934.8	488.0	4334.7	3331.7	352.5	792.4	10234.0
	Effluent from UASB	3762.9	515.3	299.8	2694.5	903.7	108.3	889.2	5410.7
	Effluent from AS	1142.1	406.5	94.0	722.3	626.3	278.4	113.4	2240.8

Note: av = Average value
UW = Unfractionated water
FW = Fractionated water

Table 6.2 DOC and THMFP of water samples obtained from this study and raw water used for water supply from other water resources

Water samples	DOC(mg/L)	THMFP (µg/L)	References
Aung-Keaw Reservoir water, Chiang Mai, Thailand	2.4	403	Homklin, 2004
Mae-Kuang Reservoir water, Chiang Mai, Thailand	2.0	236	Homklin, 2004
Mae-Sa River water, Chiang Mai, Thailand	1.8	112	Homklin, 2004
The Chao Phraya River water, Bangkok, Thailand	4.7	313	Panyapinyopol et al., 2005
Mae-Hia Reservoir water, Chiang Mai, Thailand	6.4	583	Pumpaisanchai, 2005
Bhumibol Dam Reservoir water, Tak, Thailand	2.5	317	Pumpaisanchai, 2005
Water supply reservoir water, Northern-Region Industrial Estate, Thailand	5.4	382	Janhom et al., 2005
Effluent from polishing pond of the central wastewater treatment plant	6.8	635	Janhom et al., 2005
Influent wastewater from Northern-Region Industrial Estate, Thailand	10.3	1214	Musikavong, 2007
Effluent water from aeration ponds	5.6	530	Musikavong, 2007
Effluent water from facultative ponds	6.0	564	Musikavong, 2007
Effluent water from oxidation ponds	5.6	572	Musikavong, 2007
Effluent water from detention ponds	6.1	588	Musikavong, 2007
Effluent water from detention ponds	6.8	625	Musikavong, 2007
Influent wastewater from brewery (Site 1)	52.4	3281	Observed in this study
Effluent water from UASB (Site 1)	21.6	1184	Observed in this study
Effluent water from AS (Site 1)	18.4	960	Observed in this study
Influent wastewater from brewery (Site 2)	39.8	2646	Observed in this study
Effluent water from UASB (Site 2)	8.8	473	Observed in this study
Effluent water from AS (Site 2)	5.1	257	Observed in this study
Influent wastewater from brewery (Site 3)	99.9	5316	Observed in this study
Effluent water from UASB (Site 3)	50.1	3763	Observed in this study
Effluent water from AS (Site 3)	21.1	1142	Observed in this study

Since DOM could potentially react with chlorine to form THMs, this DOM is called "THM precursor". The main THM precursor -- a problematic DOM which is mainly the THMFP creator-- have to be investigated and clarified in order to determine the proper management of reclaiming treated brewery wastewater. As the structure of the DOM is an important factor that significantly affects the formation of THMs, fractionation of DOM could facilitate the THM precursor analysis. Therefore the information on the reactivity of each DOM to form THMFP must be examined. Among the distribution of THMFP created from each DOM fraction, the sequences from high to low of THMFP created by all six DOM fractions of the influent wastewater and effluents from the UASB and AS treatments for Sites 1, 2 and 3 are as follows.

Site 1

- Influent wastewater:
  $THMFP_{HPOA} > THMFP_{HPIB} > THMFP_{HPON} > THMFP_{HPIN} > THMFP_{HPOB} > THMFP_{HPIA}$
- Effluent from UASB:
  $THMFP_{HPOA} > THMFP_{HPIB} > THMFP_{HPIN} > THMFP_{HPON} > THMFP_{HPOB} > THMFP_{HPIA}$
- Effluent from AS:
  $THMFP_{HPOA} > THMFP_{HPIB} > THMFP_{HPIA} > THMFP_{HPON} > THMFP_{HPIN} > THMFP_{HPOB}$

Site 2

- Influent wastewater:
  $THMFP_{HPIB} > THMFP_{HPOA} > THMFP_{HPON} > THMFP_{HPOB} > THMFP_{HPIN} > THMFP_{HPIA}$
- Effluent from UASB:
  $THMFP_{HPOA} > THMFP_{HPIB} > THMFP_{HPON} > THMFP_{HPIA} > THMFP_{HPOB} > THMFP_{HPIN}$
- Effluent from AS:
  $THMFP_{HPOA} > THMFP_{HPIB} > THMFP_{HPIA} > THMFP_{HPON} > THMFP_{HPIN} > THMFP_{HPOB}$

Site 3

- Influent wastewater:
  $THMFP_{HPOA} > THMFP_{HPIB} > THMFP_{HPON} > THMFP_{HPIN} > THMFP_{HPOB} > THMFP_{HPIA}$
- Effluent from UASB:
  $THMFP_{HPOA} > THMFP_{HPIB} > THMFP_{HPIN} > THMFP_{HPON} > THMFP_{HPOB} > THMFP_{HPIA}$
- Effluent from AS:
  $THMFP_{HPOA} > THMFP_{HPIB} > THMFP_{HPON} > THMFP_{HPIA} > THMFP_{HPIN} > THMFP_{HPOB}$

Let us first look at the influent wastewater where the main THM precursors from the three sites were HPOA and HPIB fractions (see more details in Chapter 4). For Site 1, $THMFP_{HPOA}$ accounted for 42.5% of total THMFP, followed by $THMFP_{HPIB}$, which accounted for 31.0% of total THMFP. This was similar to Site 3 where $THMFP_{HPOA}$ accounted for 42.4% of total THMFP, followed by $THMFP_{HPIB}$, which accounted for 32.6%. Site 2 exhibited different characteristics where where $THMFP_{HPIB}$ was the highest with 32.6% of total THMFP, followed by $THMFP_{HPOA}$, for another 29.2% of the total THMFP. Similar findings were observed for the effluents from UASB and AS treatments, the main THM precursors were still the same two, HPOA and HPIB, fractions. For Site 1, the effluents from UASB exhibited $THMFP_{HPOA}$ as the major FP component which accounted for 50.2% of total THMFP, followed by $THMFP_{HPIB}$, which accounted for 19.2% of total THMFP. $THMFP_{HPOA}$ and $THMFP_{HPIB}$ of Site 3 were comparably closed to those of Site 1, at 49.8% and 16.7% of total THMFP, respectively. THMFP distribution of Site 2 was commensurate with that of Sites 1 and 3 where $THMFP_{HPOA}$ accounted for 48.9 % of total THMFP, followed by $THMFP_{HPIB}$, which accounted for 23.9% of total THMFP. The effluents from AS from Site 1 saw the main THMFP from HPOA which accounted for 41.2 % of total THMFP, followed by $THMFP_{HPIB}$, at 24.0% of total THMFP. At Site 2, AS effluent had $THMFP_{HPIA}$ at 39.1% followed by $THMFP_{HPOA}$ at 18.2% of the total THMFP. For the effluent from Site 3, $THMFP_{HPOA}$ accounted for 32.2% followed by $THMFP_{HPIB}$ for 27.9% of total THMFP. Note that, HPOA was the first major THM precursor prevalently found in the brewery wastewater and its treated wastewater and also in various kinds of water used for water supply plant as reported in literature (Marhaba and Van, 1999; Imai et al., 2003; Janhom et al., 2005; Musikavong 2007).

Interestingly, HPIB was not considered the major DOM fraction in the effluents from UASB and AS treatments of Sites 1, 2 and 3 since DOC of HPIB was being treated rather effectively by biological process in UASB and AS treatments, i.e. at about 76%, 94% and 82%, respectively (see more details in Chapter 5). However, HPIB fraction was still found to be one of the first two major THM precursors. It is possible that HPIB constituted organic materials with high reactivity with chlorine and this is discussed in the following context.

According to the fractionation results, the THMFP totals of the six DOC fractions in each of the fractionated samples were about 44 to 98% higher than their initial values. This total THMFP surplus was obtained as a result of the high specific reactivity of each fractionated water with chlorine to form THMs when compared to the overall reactivity of DOM in unfractionated water. It could be that the different type of organic species showed some sign of inhibiting effect for the formation of THMs. In the other words, since six DOM fractions were separated into individual DOM fraction; each DOM fraction was capable of reacting more freely with chlorine to form THMs. This also agreed with report from Musikavong (2007) where the extremely high summation value of the THMFP of the six DOM fractions was suspected to be due to the greater ability of DOM fractions to form THMs compared to the ability of the combined DOM. Another possibility would be a change in the complex composition of DOM due to the pH adjustment in the resin fractionation method. The pH adjustment may have created electron-rich sites in organic structures that have a tendency to react with chlorine species, i.e. electrophiles (Rook, 1977; Scully et al., 1988 and Harrington et al., 1996).

Details on THM species are provided in Table 6.3. It was found that $CHCl_3$ was the major THM species in the influent wastewater and the effluents from UASB and AS in this study. This is similar to the findings in other water supply sources in Thailand (Homklin, 2004; Panyapinyopol et al., 2005; Musikavong 2006) and in other countries (Rodriguez et al., 2003; Thacker et al., 2002) Based on the findings, it could be stated that the reduction of THMFP mainly occurred from decreases of $CHCl_3$ species. It is noted that the reduction of $CHCl_3$ species mainly occurred during UASB treatment whilst the reduction of $CHBrCl_2$ occurred better in AS treatment.

Table 6.3 THM species of DOM in wastewater and treated wastewater

	Water sources	**THMFP (μg/L)**				
		$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	**Total THMFP**
Site 1	Influent wastewater	2877.9	301.7	99.8	1.8	3281.2
	Effluent from UASB	936.0	229.0	14.5	4.2	1183.6
	Effluent from AS	775.7	177.0	6.1	1.7	960.5
Site 2	Influent wastewater	2257.1	237.5	145.3	6.3	2646.2
	Effluent from UASB	370.0	95.0	5.3	2.5	472.8
	Effluent from AS	202.1	53.5	1.5	0.0	257.1
Site 3	Influent wastewater	4771.8	410.2	131.5	2.3	5315.8
	Effluent from UASB	3016.3	729.9	15.4	1.2	3762.9
	Effluent from AS	932.8	203.2	5.2	1.0	1142.1

6.2 Reactivity of DOM fractions to form THMs

The ability to form THMs of each DOM fraction termed “Reactivity” is defined as follows:

$$\text{Reactivity of each DOM fraction} = \frac{\text{THMs created from each DOM fraction } (\mu\text{g THMFP/L})}{\text{DOC of each DOM fraction (mg DOC/L)}} \qquad (6.1)$$

Figures 6.1, 6.2 and 6.3 demonstrate the reactivity of DOM and DOM fractions with chlorine in the influent wastewater and effluents from UASB and AS of Sites 1, 2 and 3, respectively. The average reactivity of DOM in the unfractionated influent wastewater and effluents from UASB and AS of all three sites was mostly less than that of DOM fractions, which supported the previous findings that the reactivity with chlorine to form THMs of combined DOM in unfractionated water was less than the sum of isolated THMs of each DOM fraction. Since the reactivity can be utilized to explain THMFP created per mg DOC for each DOM fraction, the THM active precursor can be ordered based on its reactivity. From the averaged reactivity of DOM as shown in Figure 6.4, HPOB had the highest THM active precursor with average reactivity of 184.4 μg THMFP/mg DOC, where HPIB was the second highest with the average reactivity of 134.5 μg THMFP/mg DOC. HPOA and HPIA could moderately create the THMFP at the average reactivity of 110.4 and 95.4 μg THMFP/mg DOC, respectively. The lowest two THM active precursors were HPON and HPIN with average reactivities of 79.4 and 51.3 μg THMFP/mg DOC, respectively. In shorts, the base fractions exhibited the highest reactivity followed by the acid fractions and the least active was the neutral fractions.

These results suggest that HPOB and HPIB fractions in the brewery wastewater even when present in tiny quantity, were more highly active to form THMs than HPOA, and this finding was well supported by literature (Marhaba and Van, 999; Janhom et al., 2005; Panyapinyopol et al., 2005). Fortunately, HPOB fraction did not exist in the large quantity in brewery wastewater and its treated wastewater (only around 1-6 % of total DOC), and therefore the formation of THMFP from HPOB was insignificant. In contrast, HPIB existed in the large quantity (around 11-28 %of total DOC), and with its high reactivity with chlorine, HPIB was therefore considered to be one of the major DOM fractions in brewery wastewater. From the qualification analysis in previous chapters, the tryptophan-like substances and humic-like substances and perhaps their derivatives which mainly composed HPIB fraction, could play an important role in forming THMs.

One of the most important organic fractions that should be mentioned regarding the formation of THMs was HPOA. Although its reactivity was not as high as the basic components, it existed in large quantity and could not be treated via biological treatments. The remaining HPOA in the final treated water still contained fulvic and humic-like substances which could undergo chlorination reaction in the water treatment facility and form THMs.

Note that, when compared the reactivity of unfractionated water with fractionated water, the average reactivity of the six organic fractions was higher than the reactivity of the unfractionated water. In fact, each organic fraction seemed to have higher reactivity with chlorine than the unfractionated water. This clearly explained why THMFP of the unfractionated water was lower than the sum of THMFPs of each fractionated waters.

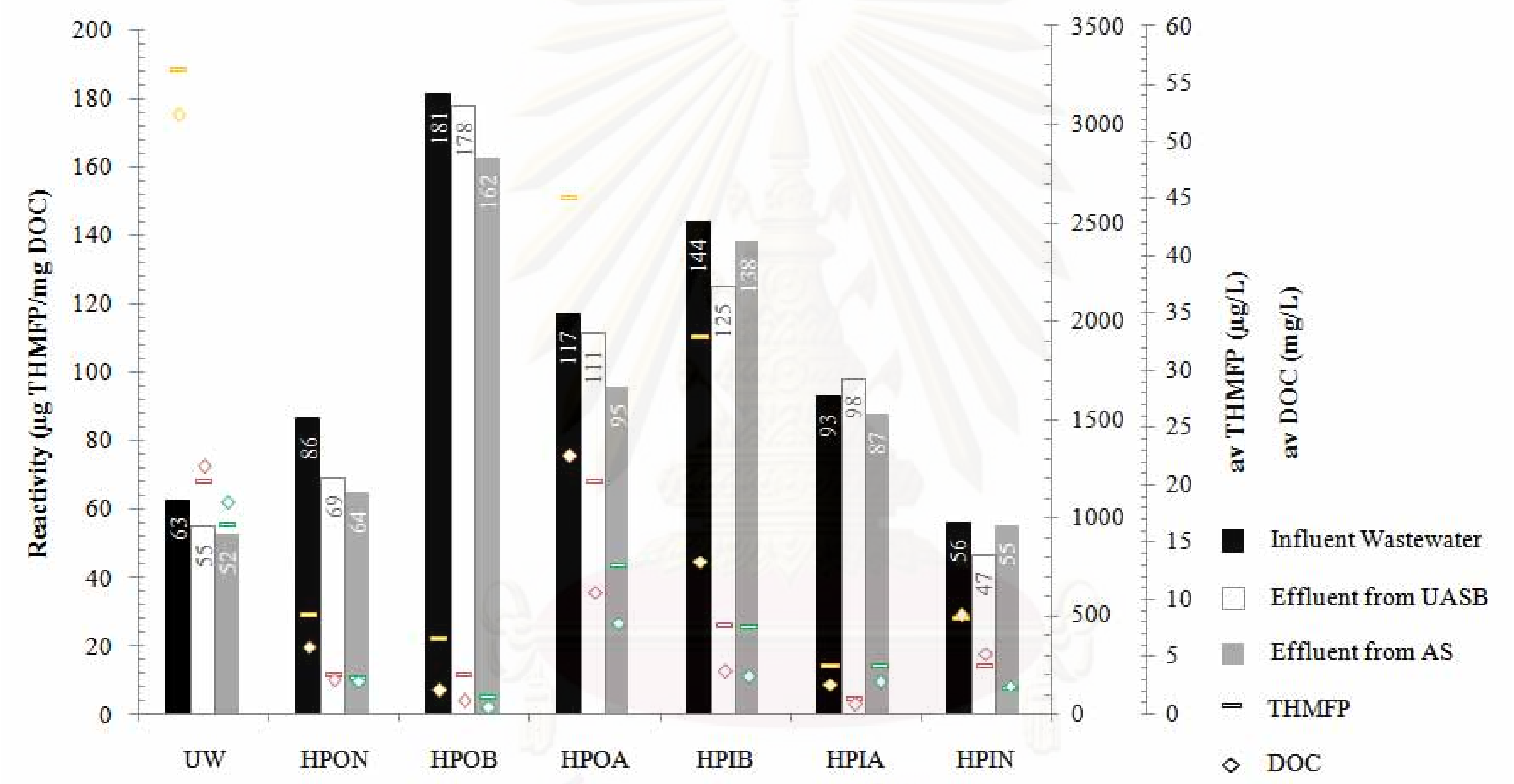


Figure 6.1 Reactivity of DOM (in unfractionated water; UW) and its six DOM fractions of influent wastewater and treated wastewater from Site 1

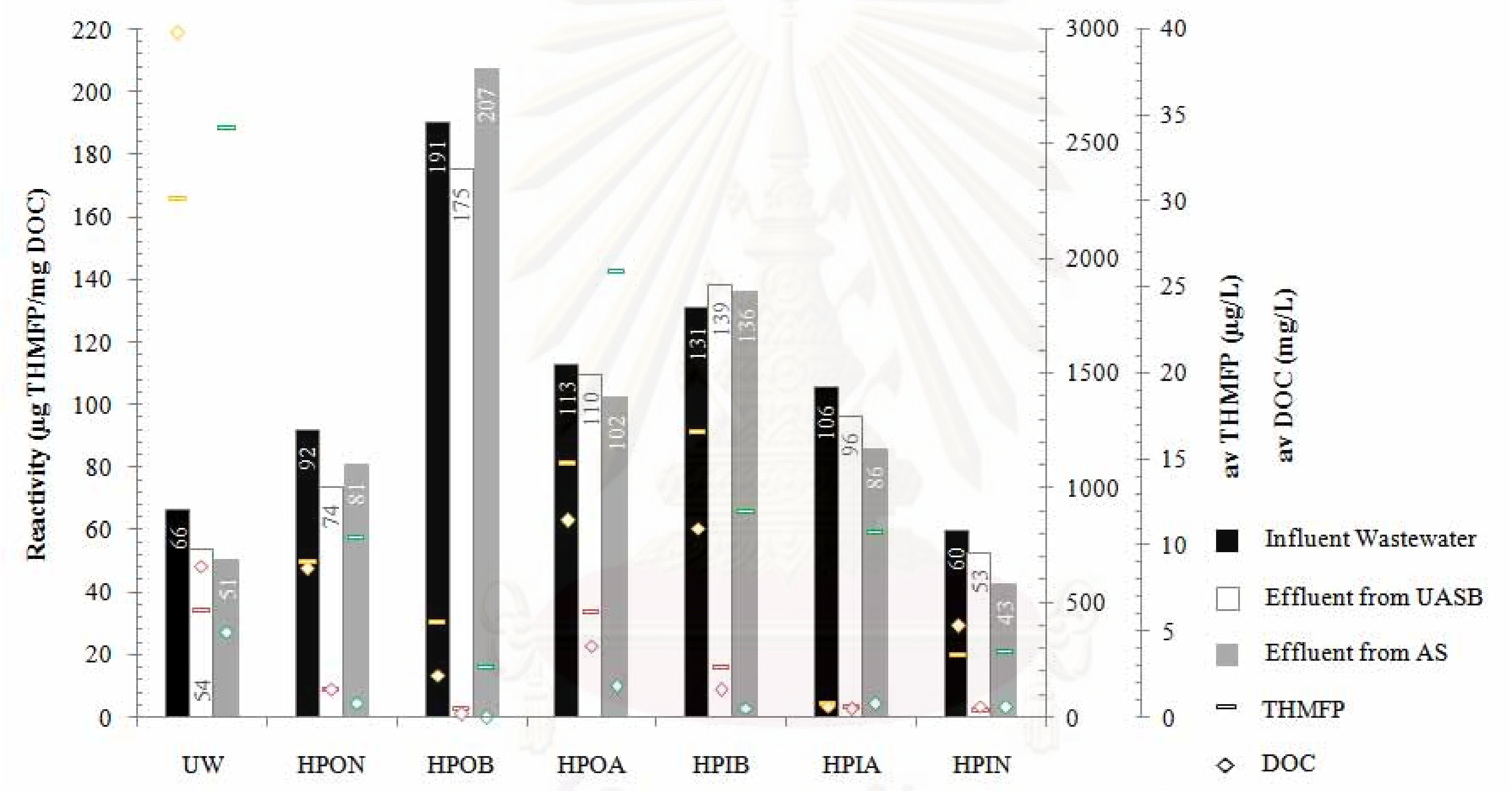


Figure 6.2 Reactivity of DOM (in unfractionated water; UW) and its six DOM fractions of influent wastewater and treated wastewater from Site 2

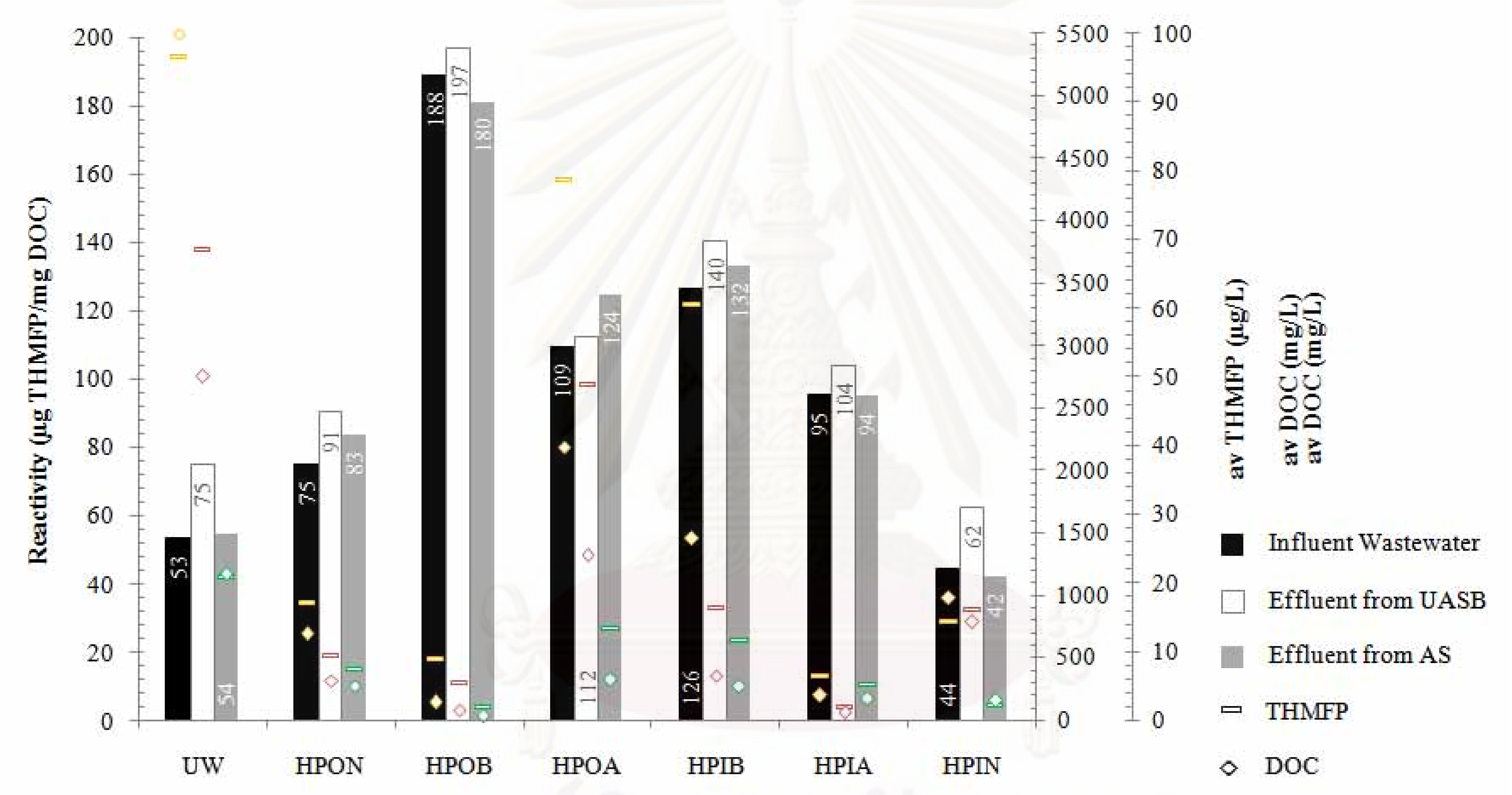


Figure 6.3 Reactivity of DOM (in unfractionated water; UW) and its six DOM fractions of influent wastewater and treated wastewater from Site 3

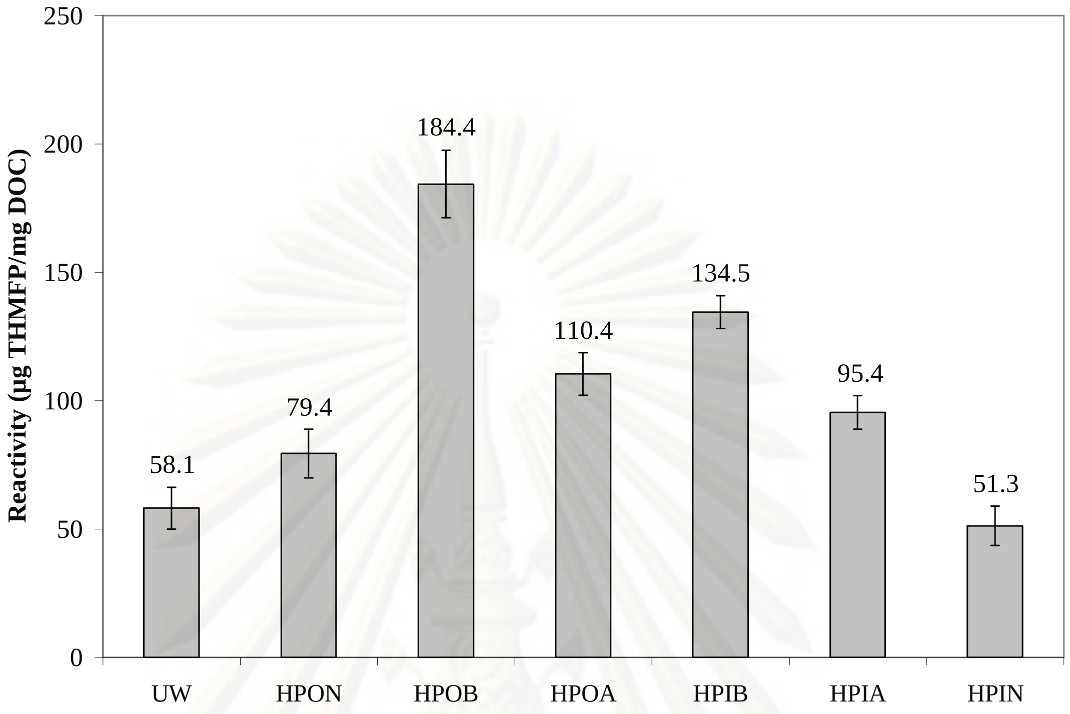


Figure 6.4 Average reactivity of DOM and DOM fractions of unfractionated and fractionated waters

6.3 Reduction of THMFP created from DOM and DOM fractions in brewery wastewater by UASB and AS treatments

Figures 6.5, 6.6 and 6.7 display the performance of biological treatment systems i.e. UASB and AS in reducing THMFP of unfractionated water samples (UW) and fractionated water samples of Sites 1, 2 and 3, respectively.

The UASB could remove THMFP of influent wastewater from Sites 1, 2 and 3 with the removal efficiencies of around 64, 82 and 29% respectively, and these were further removed at another 7, 8 and 49% as the wastewater passed through AS treatment. Note that the overall reduction efficiency of THMFP of more than 70% was observed for all three breweries through biological treatments (UASB and AS). Nevertheless, the existing THMFP of the final effluent from all three breweries was still quite high when compared to THMFP of other resourced water as previous mention.

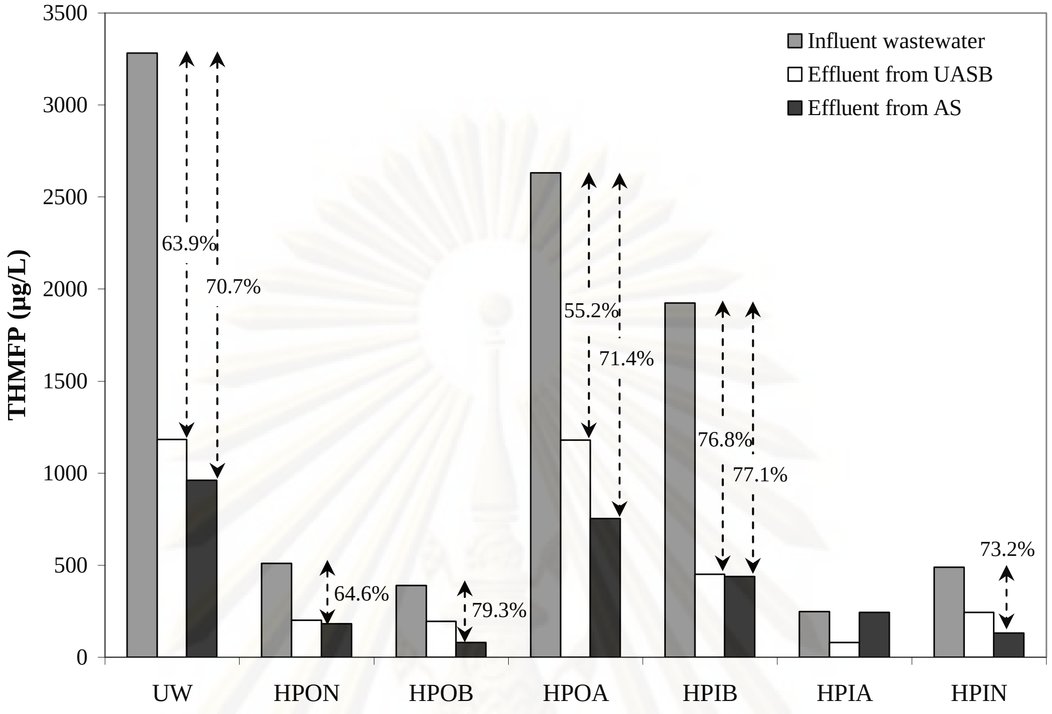


Figure 6.5 THMFP reduction of DOM (in unfractionated water; UW) and its six DOM fractions through UASB and AS treatments of Site 1

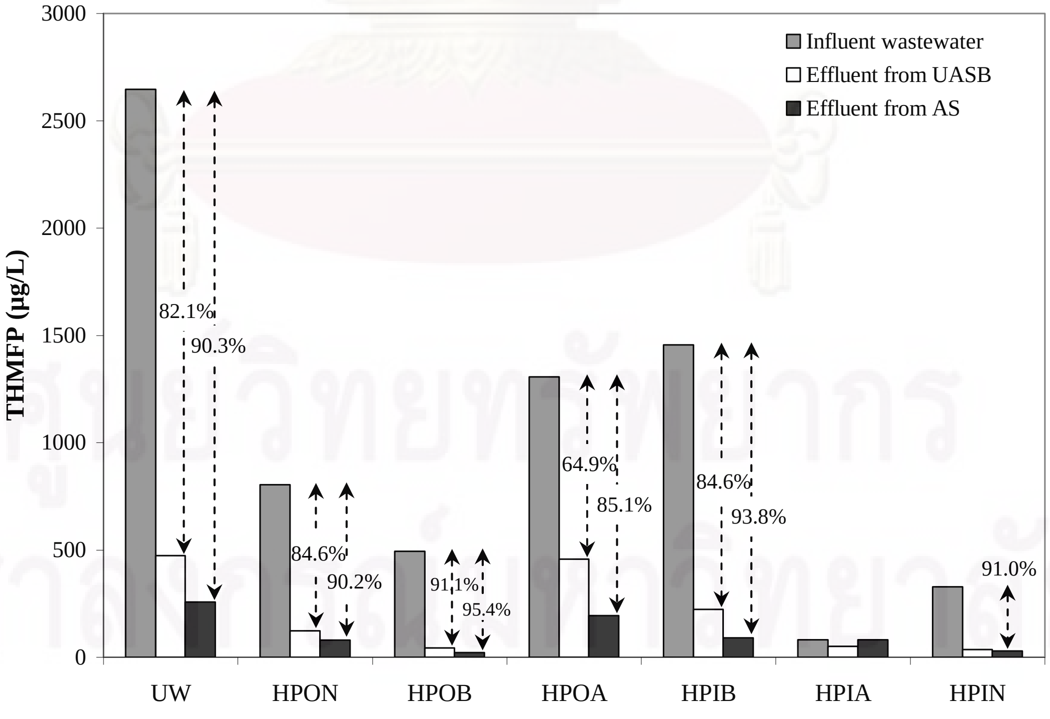


Figure 6.6 THMFP reduction of DOM (in unfractionated water; UW) and its six DOM fractions through UASB and AS treatnments of Site 2

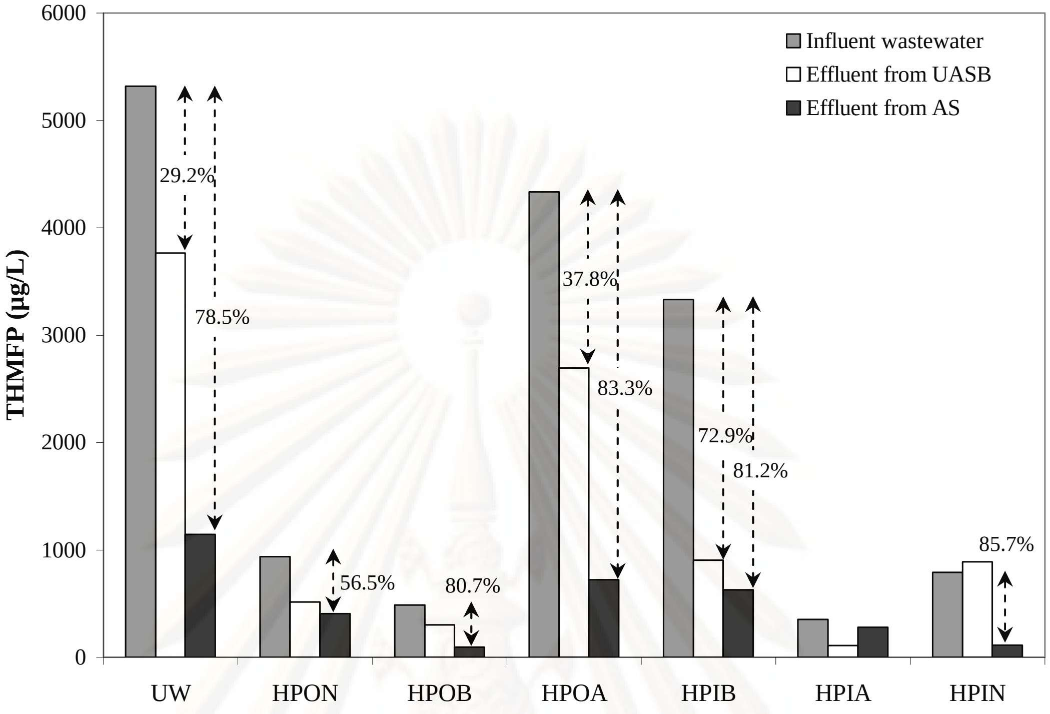


Figure 6.7 THMFP reduction of DOM (in unfractionated water; UW) and its six DOM fractions through UASB and AS treatnments of Site 3

The UASB could remove THMFP of influent wastewater from Sites 1, 2 and 3 with the removal efficiencies of around 64, 82 and 29% respectively, and these were further removed at another 7, 8 and 49% as the wastewater passed through AS treatment. Note that the overall reduction efficiency of THMFP of more than 70% was observed for all three breweries through biological treatments (UASB and AS). Nevertheless, the existing THMFP of the final effluent from all three breweries was still quite high when compared to THMFP of other resourced water as previous mention.

In terms of THMFP reduction of the six DOM fractions, it was found that most reduction was mainly due to the disappearance of the two main THM precursors, HPOA and HPIB. The reductions in THMFP of HPOA and HPIB could be summarized as follows: 71 and 77% for Site 1, 85 and 94% for Site 2, and 83 and 81% for Site 3, respectively. The obtained percent THMFP reductions of the main THM precursors (HPOA and HPIB) were comparable to the reductions in DOC, UV_{254} and FEEM intensity (Figures 6.8, 6.9 and 6.10) where more than half of the THMFP reduction of each DOM fraction occurred during the UASB treatment, except the HPIN fraction of wastewater from Site 3 which were more effectively removed by the AS treatment. From the analysis in previous chapters, THMFP reductions were potentially caused by decreases of tryptophan-like substances and partially from decreases of degraded fulvic and humic-like substances. Interestingly, HPIA was also the only fraction that exhibited a different behavior as it increased after passing through the AS treatment unit. It might be due to the fulvic and humic-like derivatives of HPIA itself and other degraded DOM fractions formed during biological transformations as mentioned in Chapters 4 and 5 which could be converted to $THMFP_{HPIA}$. In this case, however, HPIA was only a moderate THM active precursor and a slight increase in the amount of HPIA did not result in a much greater increase in THMFP. Figures 6.11, 6.12 and 6.13 illustrate linear relationships between THMFP and DOC, UV_{254} and FEEM intensity of unfractionated samples (UW) and major DOM fractions (HPOA and HPIB). A very good correlation ($0.933 < R^2 < 0.996$) was obtained from the linear relationships between THMFP and both DOM surrogate parameters i.e. DOC and UV_{254}. The relationships between THMFP and FEEM intensity also provided a good correlation ($0.875 < R^2 < 0.925$). These observations imply that THMFP created from DOM in brewery wastewater and treated wastewater could be well predictable using DOM surrogate parameters i.e. DOC and UV_{254}. Potentially, the FEEM intensity could also be used to predict the THMFP formation from DOM in brewery wastewater but with a slightly lower confidence when compared with other DOM surrogates.

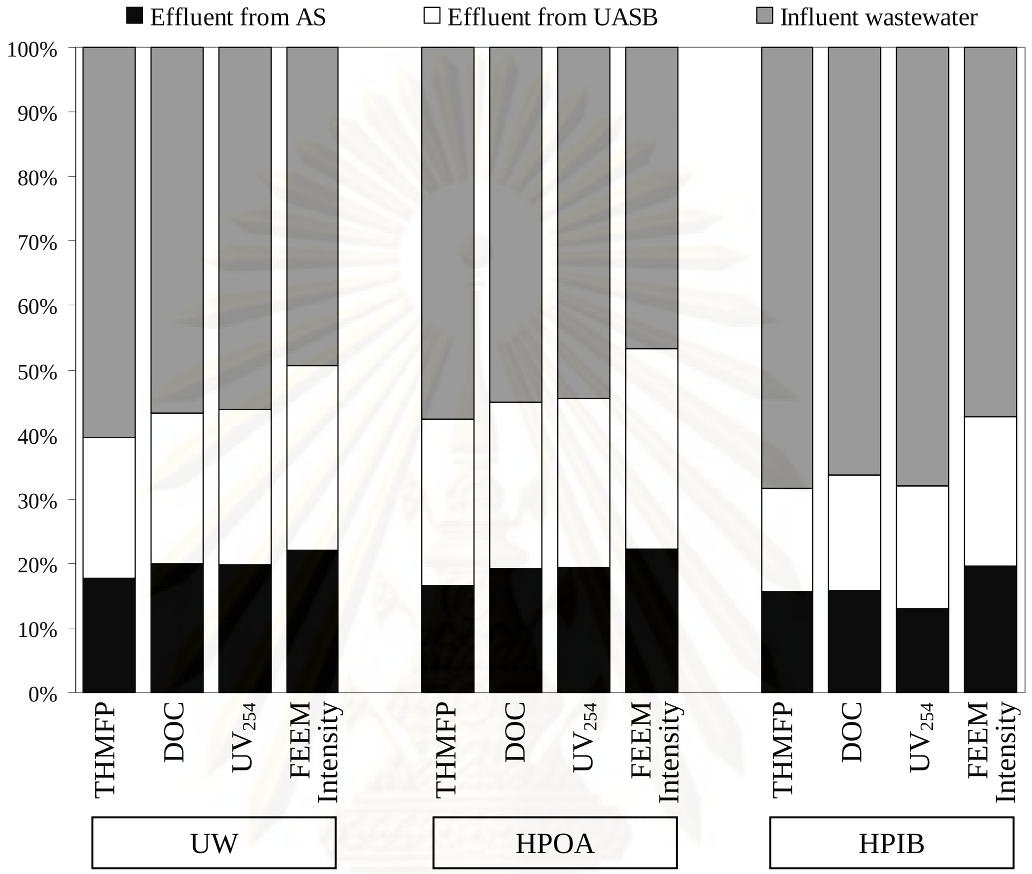


Figure 6.8 Comparison of percent reduction of DOM in unfractionated water (UW) and major DOM fractions (HPOA and HPIB) in terms of THMFP, DOC, UV_{254} and FEEM intensity for Site 1

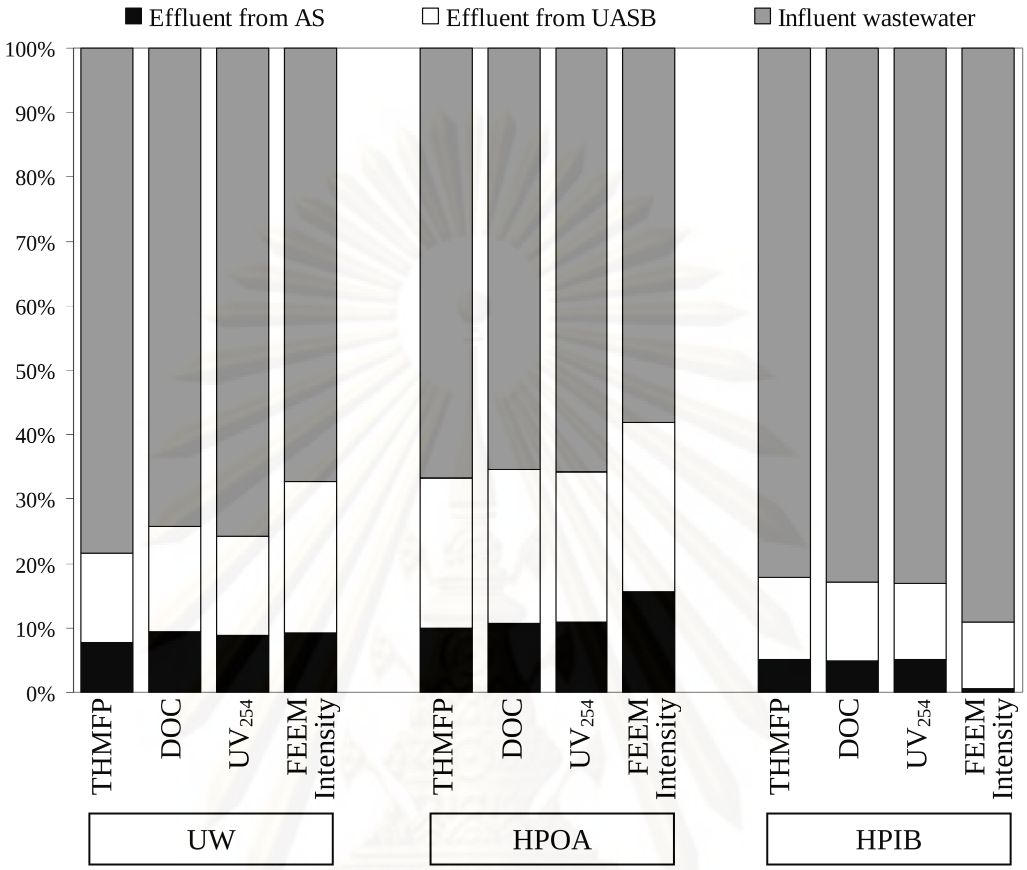


Figure 6.9 Comparison of percent reduction of DOM in unfractionated water (UW) major DOM fractions (HPOA and HPIB) in terms of THMFP, DOC, UV_{254} and FEEM intensity for Site 2

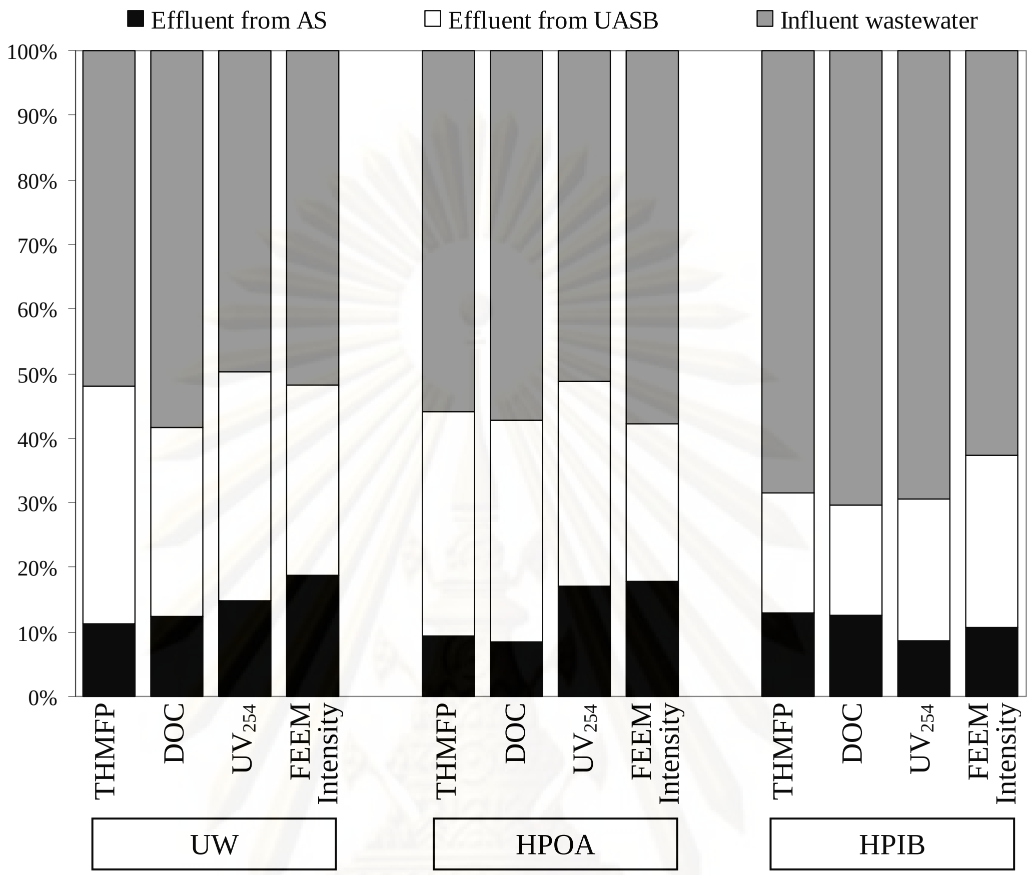


Figure 6.10 Comparison of percent reduction of DOM in unfractionated water (UW) and major DOM fractions (HPOA and HPIB) in terms of THMFP, DOC, UV_{254} and FEEM intensity for Site 3

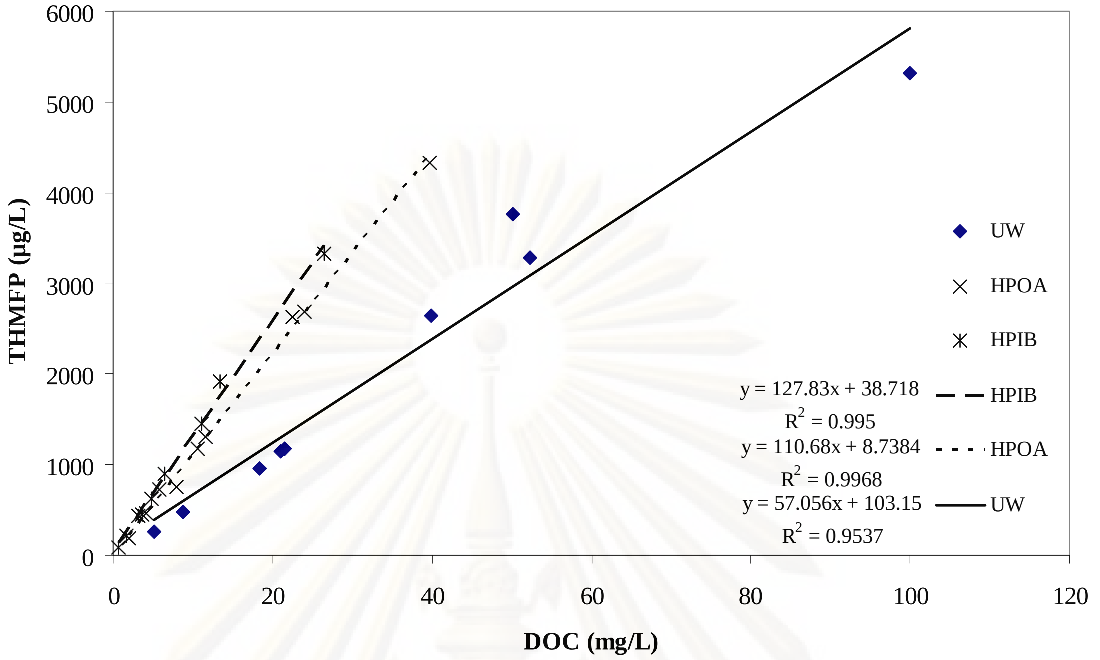


Figure 6.11 Relationship between THMFP and DOC of unfractionated samples (UW) and major DOM fractions (HPOA and HPIB)

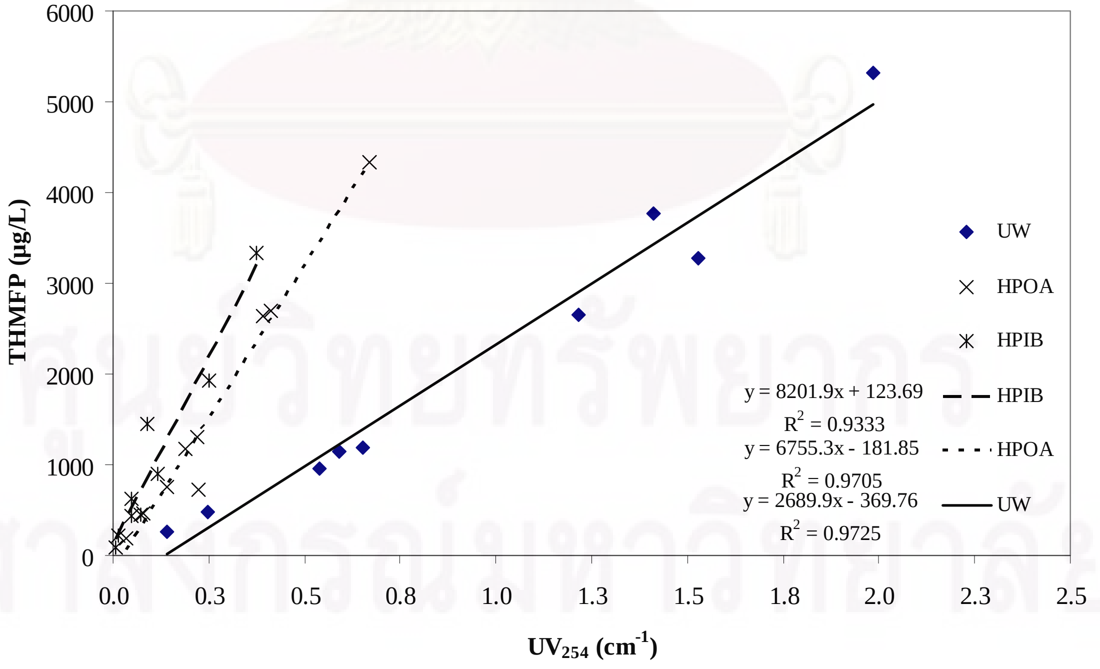


Figure 6.12 Relationship between THMFP and UV_{254} of unfractionated samples (UW) and major DOM fractions (HPOA and HPIB)

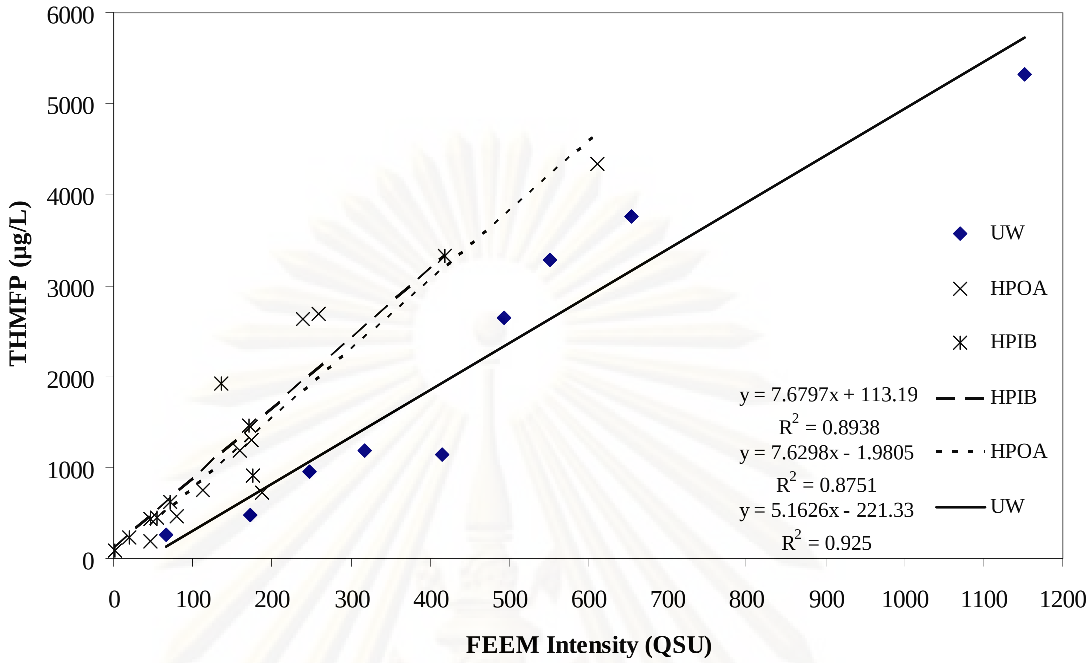


Figure 6.13 Relationship between THMFP and FEEM intensity of unfractionated samples (UW) and major DOM fractions (HPOA and HPIB)

6.4 Concluding remarks

This chapter demonstrated the potential of organic matters in brewery wastewaters in forming THMs. UASB and AS treatments were found to have treatment potential for organic matters which could help prevent the formation of THMs in brewery wastewater effectively. However, the existing THMFP of the final effluent from all three breweries was still high when compared to THMFP of other resourced water. The reduction of THMFP was mainly due to the disappearance of tryptophan-like substances and partially occurred from decreases of degraded fulvic and humic-like substances of the two main THM precursors, HPOA and HPIB. For water reclamation perspective, these two organic precursors are the important DOM fractions to be considered for THMs removal since they were the most outstanding DOM fractions involved in forming THMs in the final treated effluents from all three breweries.

THMFP of reclaimed water should be lessened as much as possible in order to gain more possibility in utilizing such treated wastewater. The treatment technologies used for removing DOM fractions were gathered in Appendix C. According to the literature, HPOA could be successfully removed using coagulation and flocculation processes in water treatment system, whereas, HPIB could not (Marhaba and Pipada, 2000; Marhabar and Van, 2000; Zouboulis et al., 2003; Janhom, 2005; Musikavong et al. 2005, Kim and Yu, 2005; Sharp et al., 2006). In order to reuse the treated brewery wastewater, the enhanced coagulation practices for higher removing HPOA should be further determined and the other processes such as adsorption, ion exchange, membrane filtration, and advanced oxidation processes which enable to remove HPIB (and HPOA) from water should be alternatively selected.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Through the course of research for qualification and quantification of DOM in brewery wastewater and treated brewery wastewater by several DOM analyses and for evaluation of effectiveness of treatment processes on the reduction of brewery DOM and its THMFP, it was learnt that.

1. HPOA and HPIB were identified as the major organic fractions in brewery wastewater which also found to be the main THM precursors for all three studied breweries.
2. The major DOM components in brewery wastewater from three sites (both light and lager beers) were groups of tryptophan-like substances and fulvic and humic-like substances.
3. The reduction of DOM was mainly found to occur during the UASB treatment which was attributed to the removal of two major DOM fractions, i.e. HPOA and HPIB. This resulted in a direct reduction in THMFP. In the other words, the reduction in THMFP was mainly due to the disappearance of tryptophan-like substances and partially occurred from decreases of degraded fulvic and humic-like substances of the two main THM precursors.
4. The effectiveness of the wastewater treatment (UASB and AS) on the reduction in THMFP at around 71, 90, and 78% was observed for Sites A, B and C. However, the existing THMFP of the final effluent from all three breweries was still high when compared to THMFP of other resourced water for water supply plants.
5. HPOA, particularly fulvic and humic-like substances, was of most particular concern as a problematic DOM fraction for water reclamation process of treated brewery wastewater, since it was still relatively predominated in

residual DOM in the effluents and it was considered likely to be refractory in biological treatments and coagulation process in water treatment system.

6. With certain level of confidence, FEEM analysis can be employed as a simple monitoring technique for DOM analysis since the FEEM spectra could well describe the characteristics of organic matters in the wastewater, and the FEEM intensities could be used to monitor the variations of DOM and DOM fractions during treatment process. Furthermore, the FEEM analytical results were consistent with the results from conventional DOM analyses such as DOC and UV_{254}.

7.2 Contributions of this work

This work illustrates that a simple analytical technique such as FEEM could well be utilized to qualify and quantify the organic contaminants in wastewaters. This will facilitate the future monitoring of the wastewater characteristics by reducing the time and cost of analysis. In fact, online monitoring could well be implemented by following the fluorescent matrix of the wastewater. This work focused mainly on the wastewater from the brewery industry where the two types of brewery were investigated, and in all cases, FEEM could well be implemented with reasonable satisfaction. In addition, FEEM could still be used to describe the changes in the chemical characteristics of the wastewater. This will allow the future management of the treatment technique for the removal of the organic matters in the wastewater to ensure high efficiency with maximum safety.

7.3 Recommendations for Further Work

The results from this work showed that HPOA and HPIB were the two most problematic DOMs in brewery wastewater and this, at the moment, caused problems in the reclamation of the wastewater. There is an urgent need for the development of the treatment process that could remove such organic matters to allow the use of the wastewater.

In application perspective, the development of an online system using FEEM as a monitoring means to follow the changes in organic constituents in wastewater should be developed.

Future research could also be developed to further analyze the FEEM matrix in a more comprehensive manner. In other words, with a proper analytical verification, FEEM could be used to indicate more specific organic compounds, and this will allow a development of an even more effective treatment method.

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APPENDICES

APPENDIX A

EXPERIMENTAL DATA

Table A-1: DOM surrogate parameters of unfractionated wastewater samples

	Water samples	Site		
		1	2	3
DOC (mg/L)	Influent wastewater	52.4	39.8	99.9
	Effluent from UASB	21.6	8.8	50.1
	Effluent from AS	18.4	5.1	21.1
UV_{254} (cm^{-1})	Influent wastewater	1.53	1.21	1.98
	Effluent from UASB	0.65	0.25	1.41
	Effluent from AS	0.54	0.14	0.59
$SUVA_{254}$ (L/mg-m)	Influent wastewater	2.92	3.05	1.99
	Effluent from UASB	3.03	2.81	2.82
	Effluent from AS	2.93	2.80	2.81

Table A-2: DOC of unfractionated and fractionated water samples

	Water sources	av DOC (mg/L)						
		UW	FW					
			HPON	HPOB	HPOA	HPIB	HPIA	HPIN
Site 1	Influent wastewater	52.4	5.9	2.1	22.5	13.4	2.7	8.7
	Effluent from UASB	21.6	2.9	1.1	10.6	3.6	0.8	5.2
	Effluent from AS	18.4	2.8	0.5	7.9	3.2	2.8	2.4
Site 2	Influent wastewater	39.8	8.8	2.6	11.5	11.1	0.8	5.5
	Effluent from UASB	8.8	1.7	0.3	4.2	1.6	0.5	0.7
	Effluent from AS	5.1	1.0	0.1	1.9	0.7	0.9	0.7
Site 3	Influent wastewater	99.9	12.5	2.6	39.8	26.4	3.7	17.8
	Effluent from UASB	50.1	5.7	1.5	24.0	6.4	1.0	14.3
	Effluent from AS	21.1	4.9	0.5	5.8	4.7	2.9	2.7

Note: av = Average value
UW = Unfractionated water
FW = Fractionated water

Table A-3: UV_{254} of unfractionated and fractionated water samples

Water sources		av UV_{254} (cm^{-1})						
		UW	FW					
			HPON	HPOB	HPOA	HPIB	HPIA	HPIN
Site 1	Influent wastewater	1.527	0.091	0.025	0.391	0.251	0.034	0.142
	Effluent from UASB	0.653	0.059	0.029	0.188	0.071	0.024	0.098
	Effluent from AS	0.538	0.043	0.003	0.139	0.048	0.041	0.035
Site 2	Influent wastewater	1.214	0.148	0.042	0.218	0.089	0.003	0.039
	Effluent from UASB	0.247	0.028	0.004	0.078	0.013	0.008	0.004
	Effluent from AS	0.142	0.016	0.002	0.036	0.005	0.015	0.004
Site 3	Influent wastewater	1.984	0.148	0.029	0.669	0.375	0.035	0.178
	Effluent from UASB	1.412	0.131	0.046	0.414	0.118	0.027	0.173
	Effluent from AS	0.592	0.125	0.005	0.223	0.047	0.055	0.043

Note:
av = Average value
UW = Unfractionated water
FW = Fractionated water

Table A-4: SUVA$_{254}$ of unfractionated and fractionated water samples

	Water sources	SUVA$_{254}$ (L/mg-m)						
		UW	FW					
			HPON	HPOB	HPOA	HPIB	HPIA	HPIN
Site 1	Influent wastewater	2.917	1.536	1.152	1.733	1.876	1.259	1.631
	Effluent from UASB	3.028	2.031	2.608	1.776	1.962	2.936	1.875
	Effluent from AS	2.929	1.537	0.533	1.757	1.501	1.476	1.442
Site 2	Influent wastewater	3.046	1.688	1.622	1.893	0.797	0.385	0.714
	Effluent from UASB	2.810	1.637	1.440	1.867	0.779	1.570	0.573
	Effluent from AS	2.800	1.602	1.376	1.891	0.812	1.552	0.517
Site 3	Influent wastewater	1.986	1.179	1.109	1.681	1.418	0.949	0.995
	Effluent from UASB	2.816	2.305	3.016	1.726	1.832	2.541	1.211
	Effluent from AS	2.809	2.555	0.864	3.823	0.988	1.857	1.591

Note: UW = Unfractionated water
FW = Fractionated water

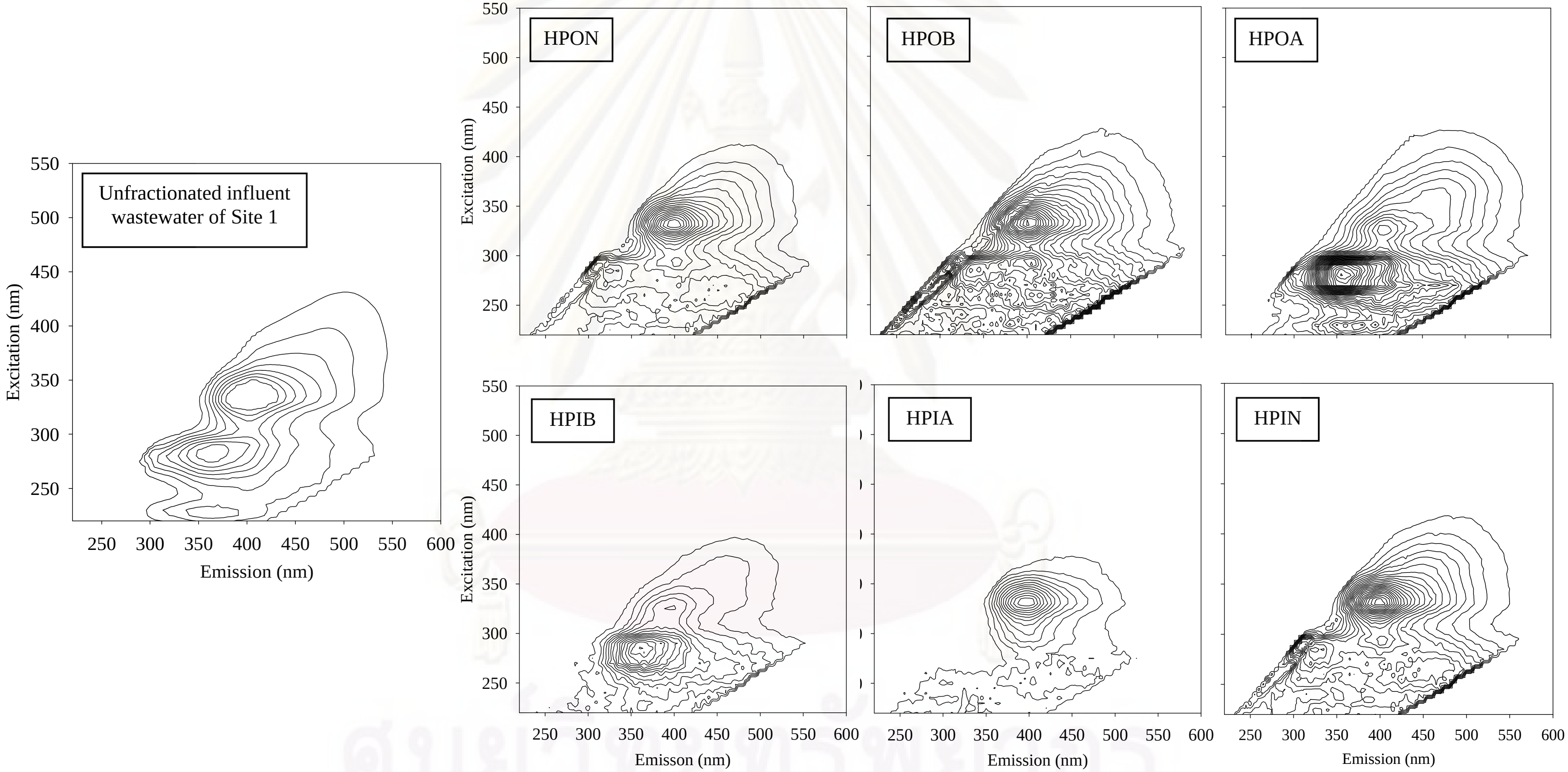

Figure A-1: FEEMs of unfractionated influent wastewater from Site 1 (30 QSU) and its six DOM fractions (5 QSU)

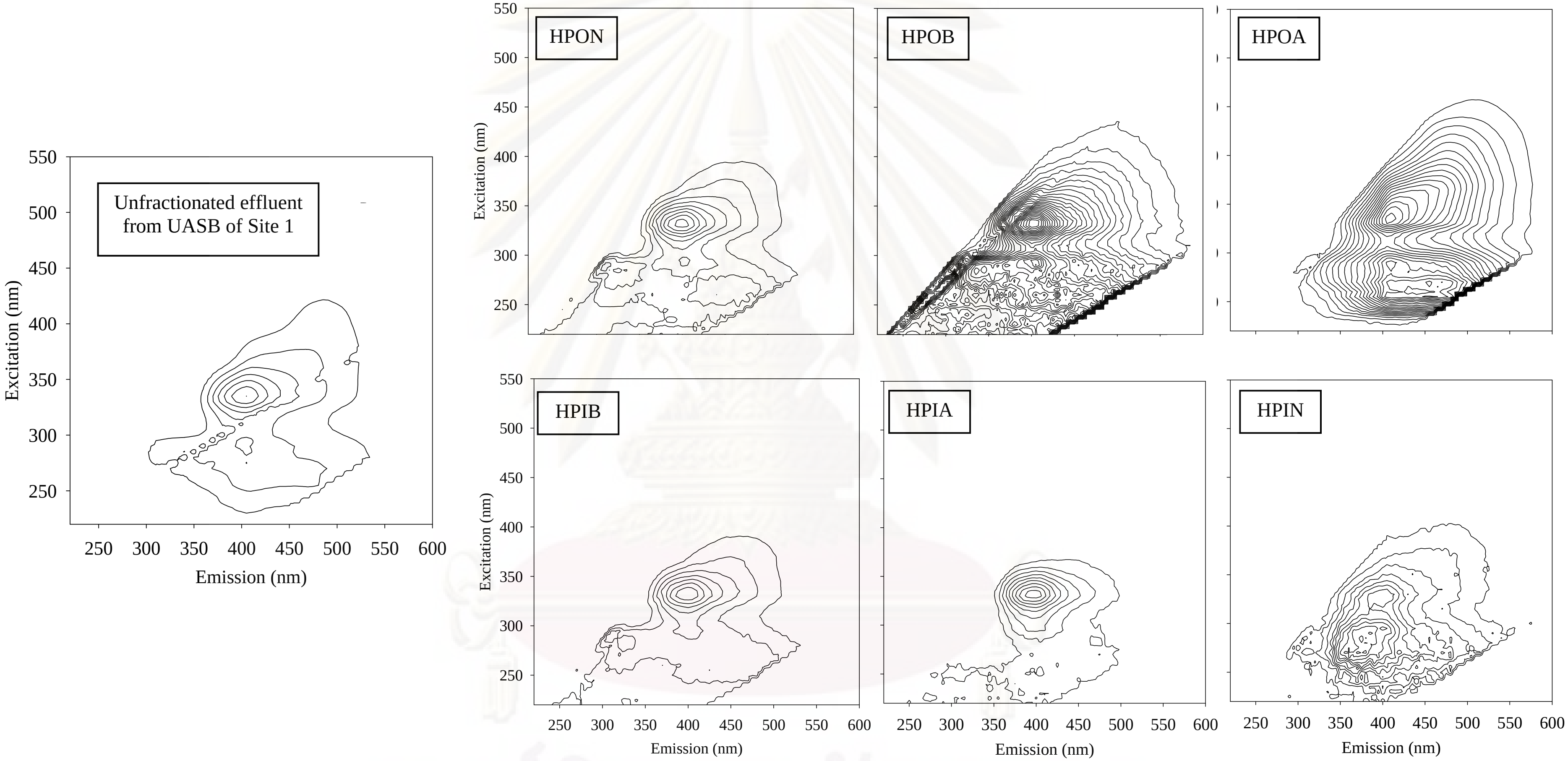

Figure A-2: FEEMs of unfractionated effluent from UASB from Site 1 (30 QSU) and its six DOM fractions (5 QSU)

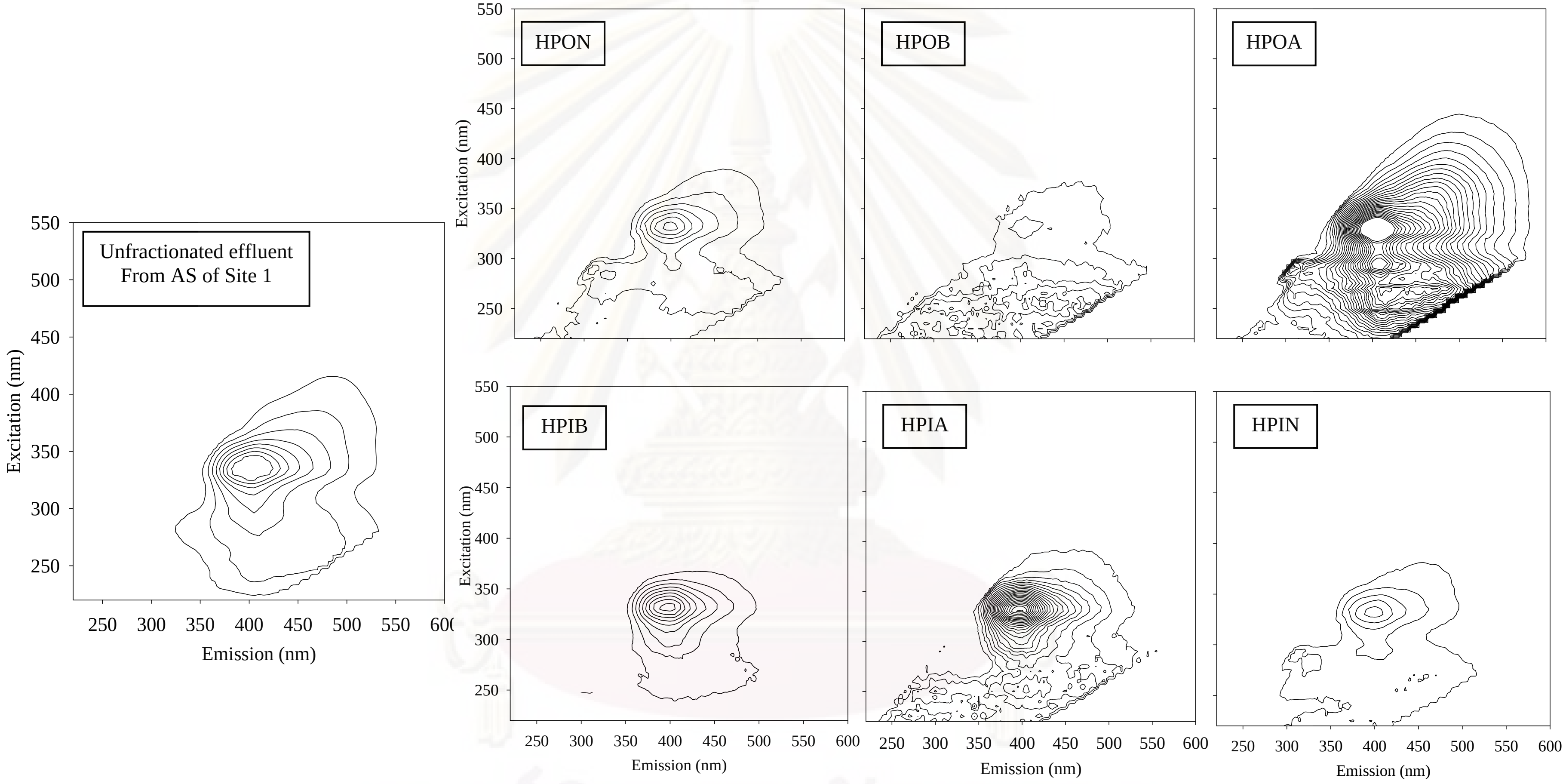

Figure A-3: FEEMs of unfractionated effluent from AS from Site 1 (30 QSU) and its six DOM fractions (5 QSU)

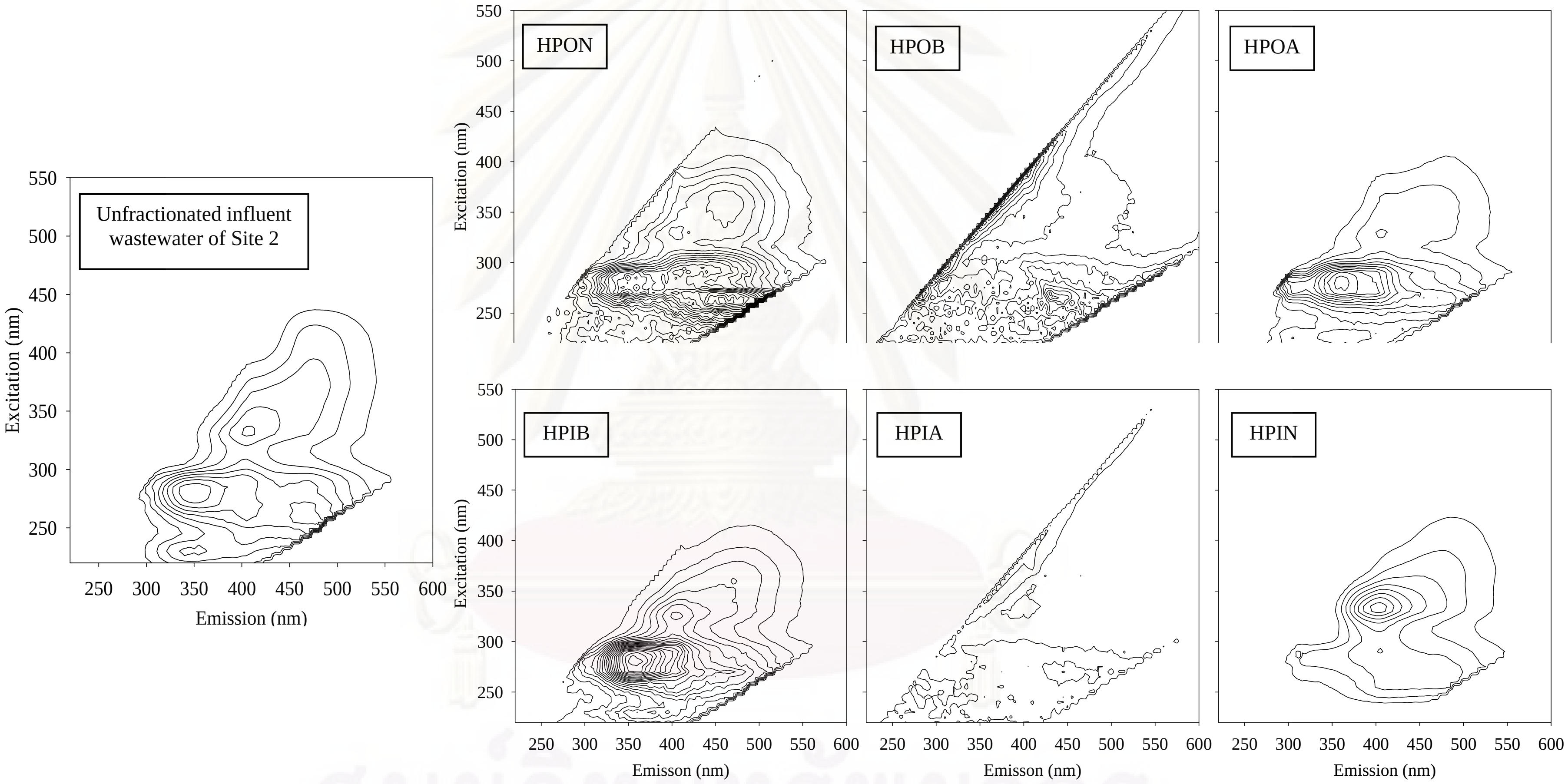

Figure A-4: FEEMs of unfractionated influent wastewater from Site 2 (20 QSU) and its six DOM fractions (5 QSU)

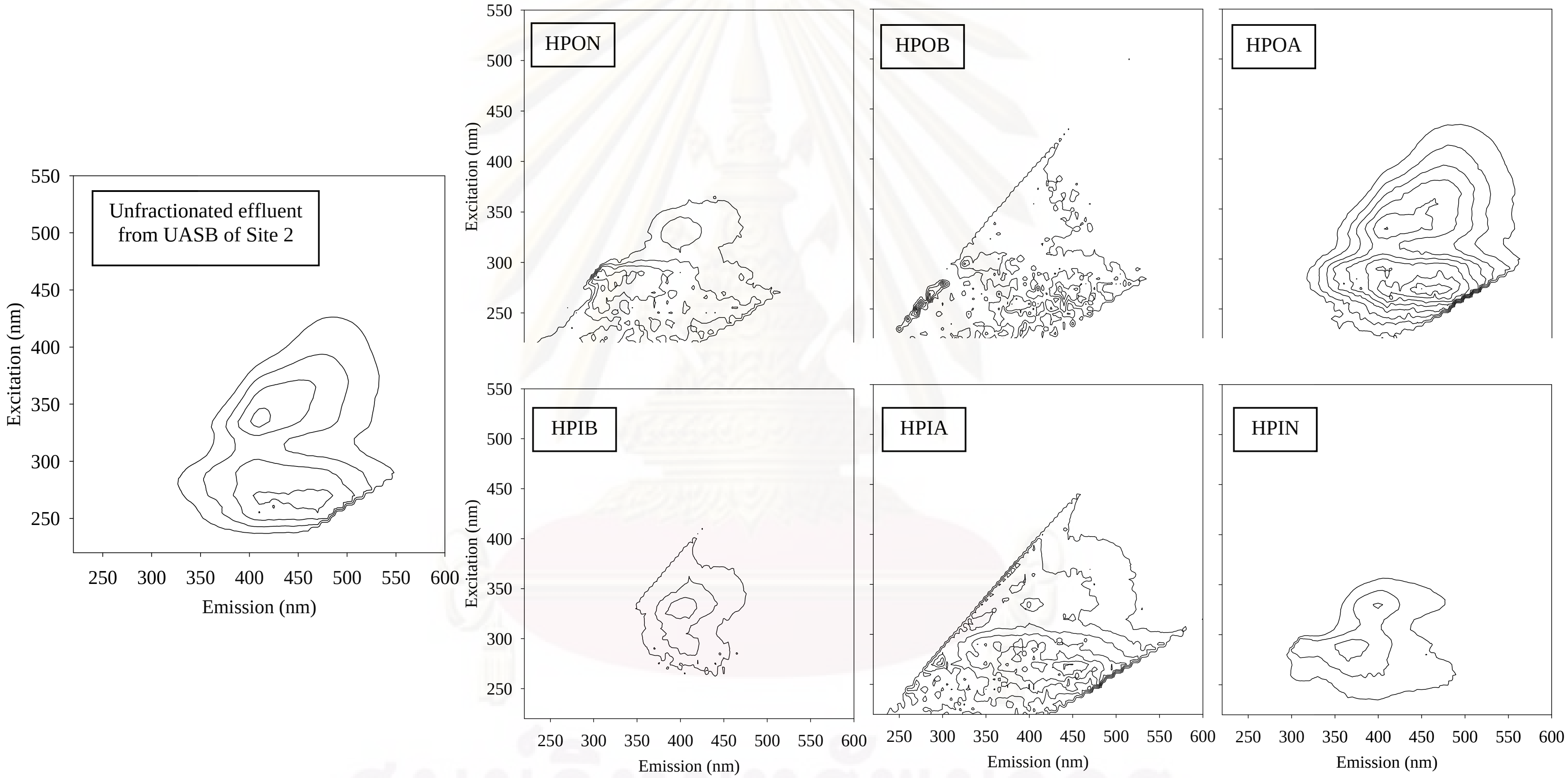

Figure A-5: FEEMs of unfractionated effluent from UASB from Site 2 (20 QSU) and its six DOM fractions (3 QSU)

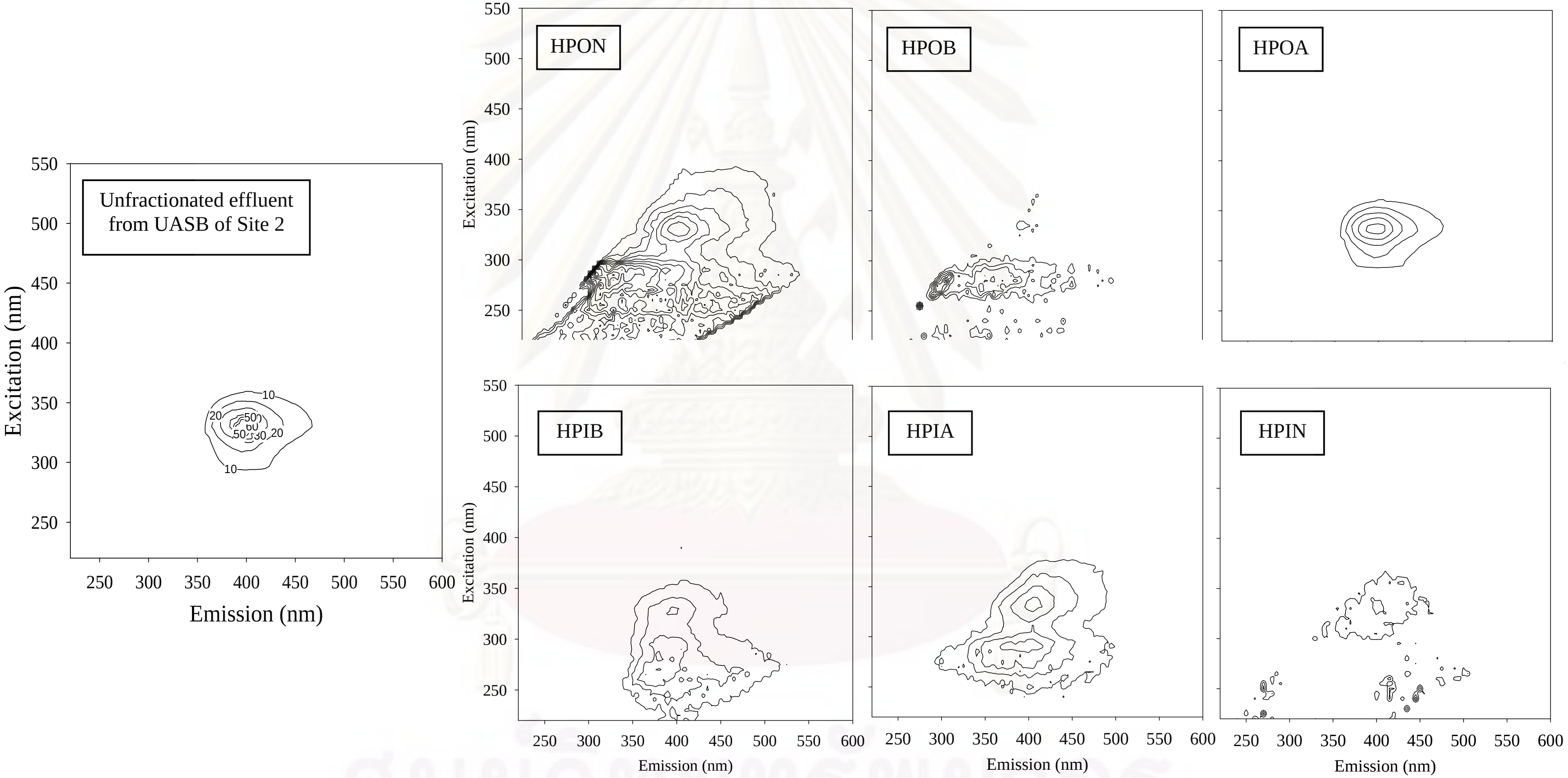

Figure A-6: FEEMs of unfractionated effluent from AS from Site 2 (10 QSU) and its six DOM fractions (2 QSU)

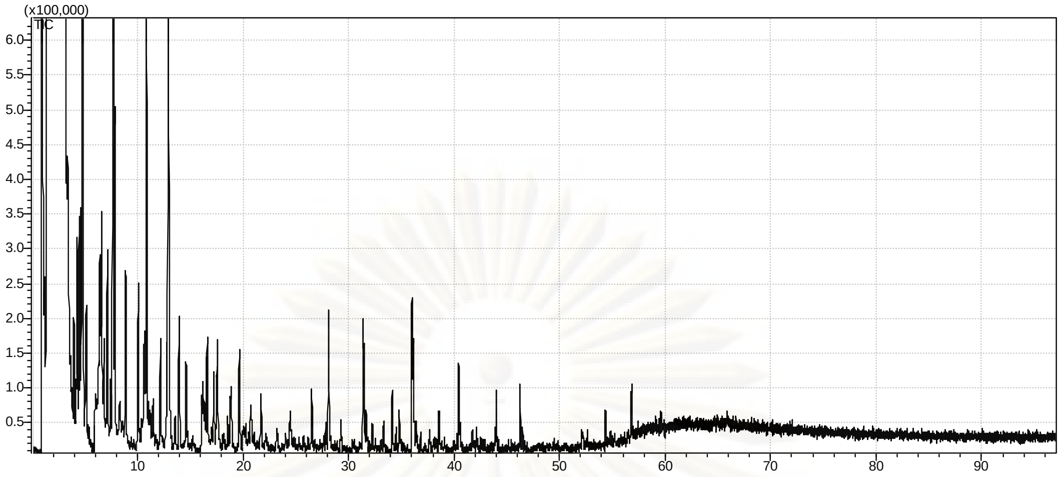

Figure A-7: Pyrogram of influent wastewater from Site 1

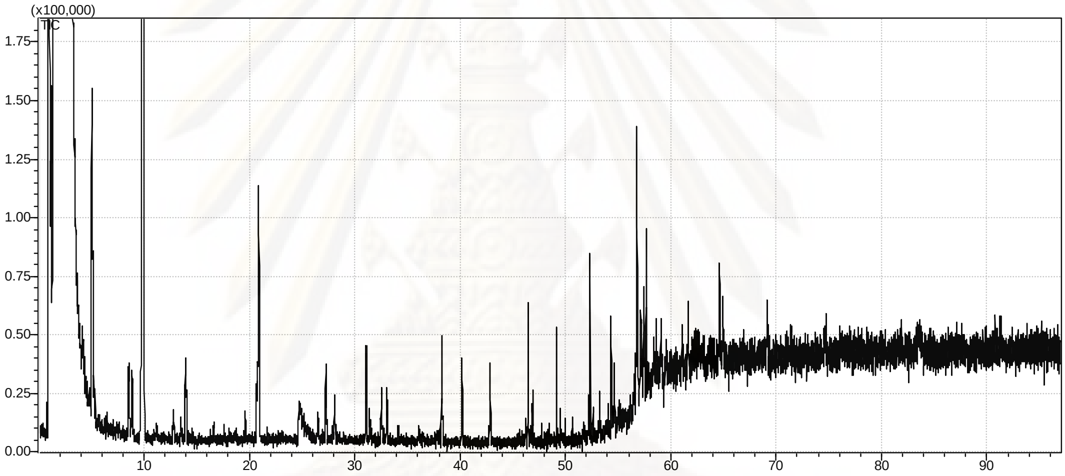

Figure A-8: Pyrogram of effluent from UASB from Site 1

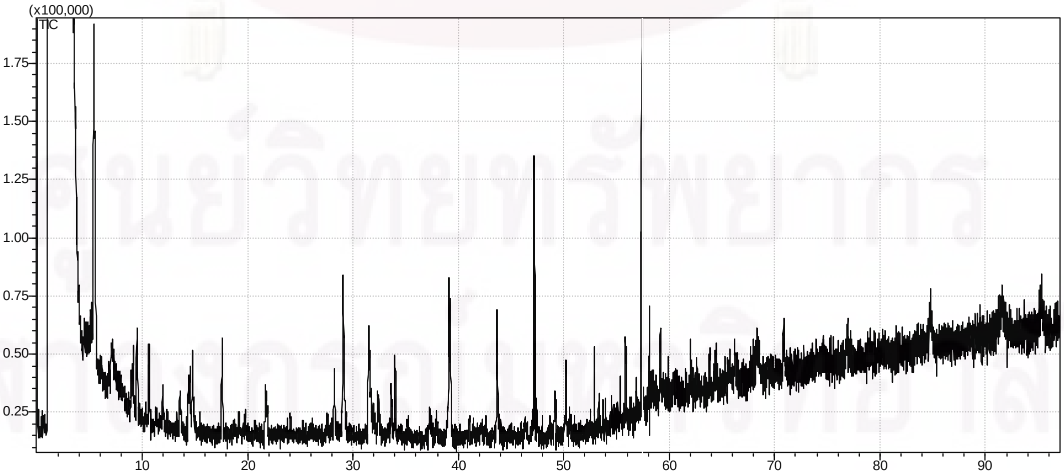

Figure A-9: Pyrogram of effluent from AS from Site 1

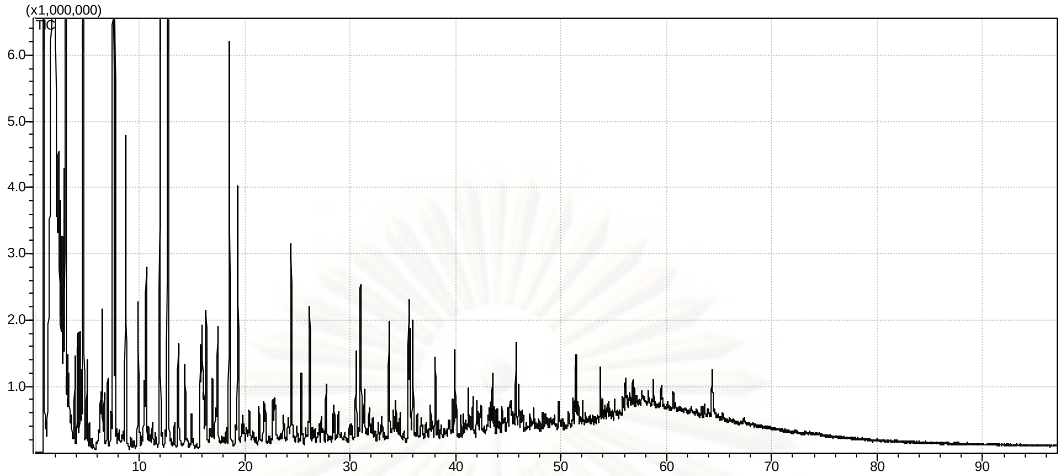

Figure A-10: Pyrogram of influent wastewater from Site 2

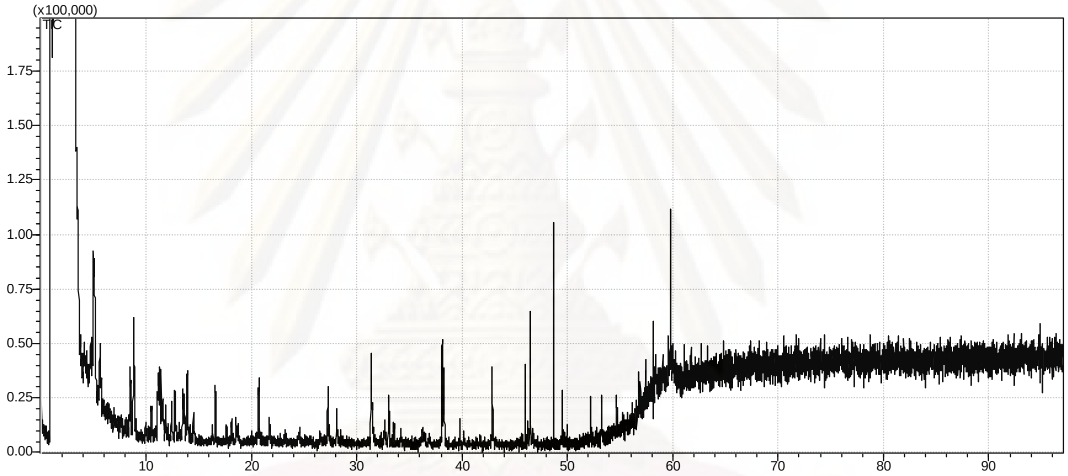

Figure A-11: Pyrogram of effluent from UASB from Site 2

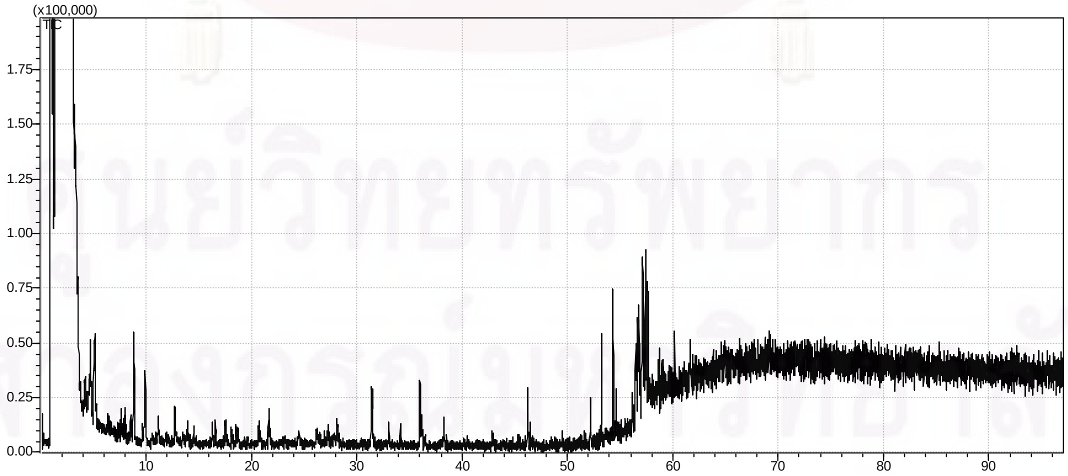

Figure A-12: Pyrogram of effluent from AS from Site 2

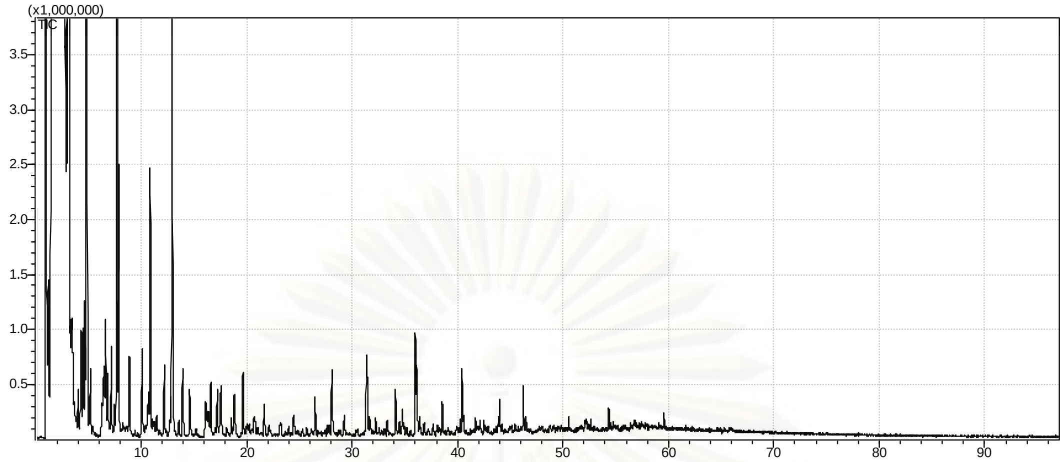

Figure A-13: Pyrogram of influent wastewater from Site 3

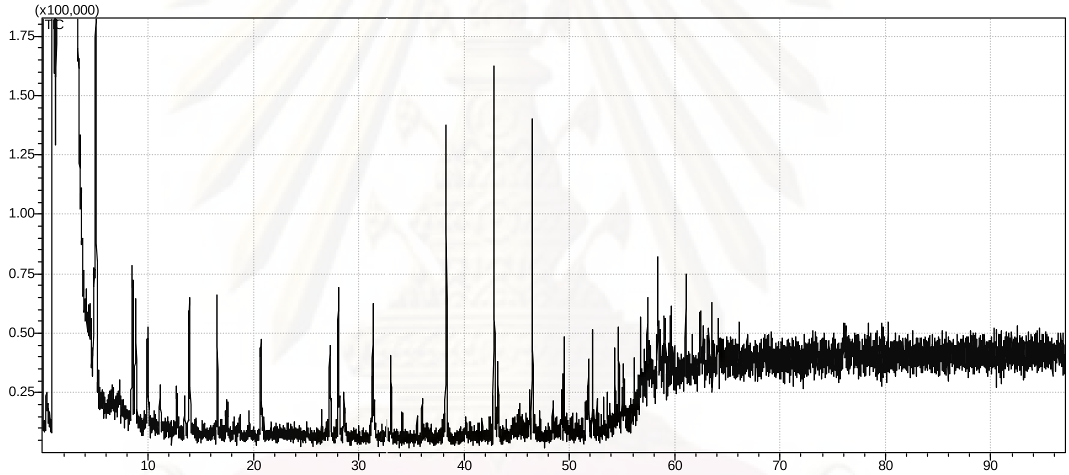

Figure A-14: Pyrogram of effluent from UASB from Site 3

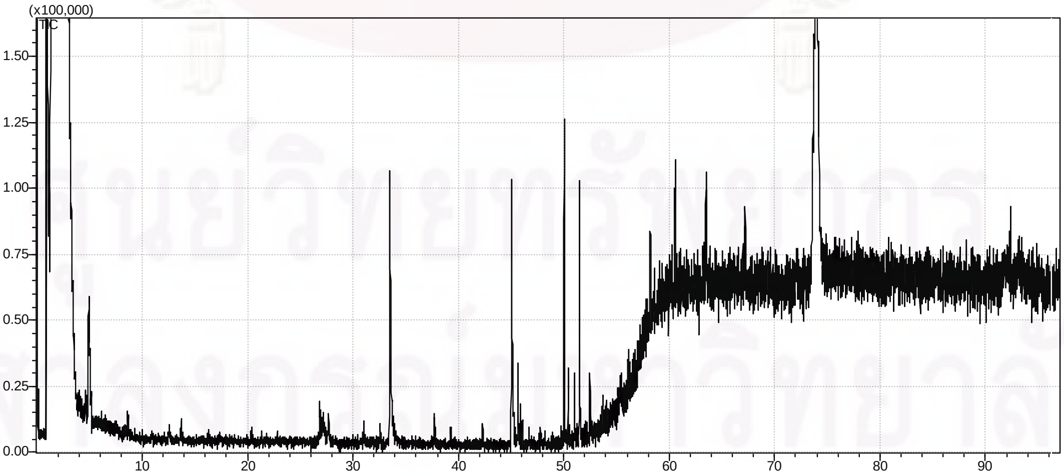

Figure A-15: Pyrogram of effluent from AS from Site 3

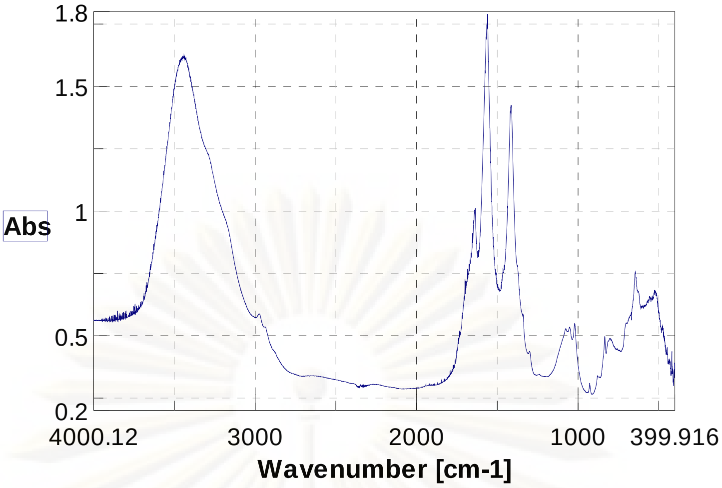

Figure A-16: FTIR of influent wastewater from Site 1

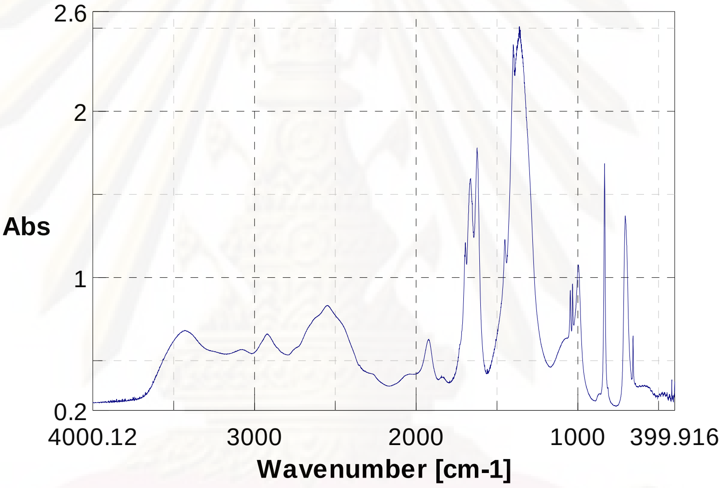

Figure A-17: FTIR of effluent from UASB from Site 1

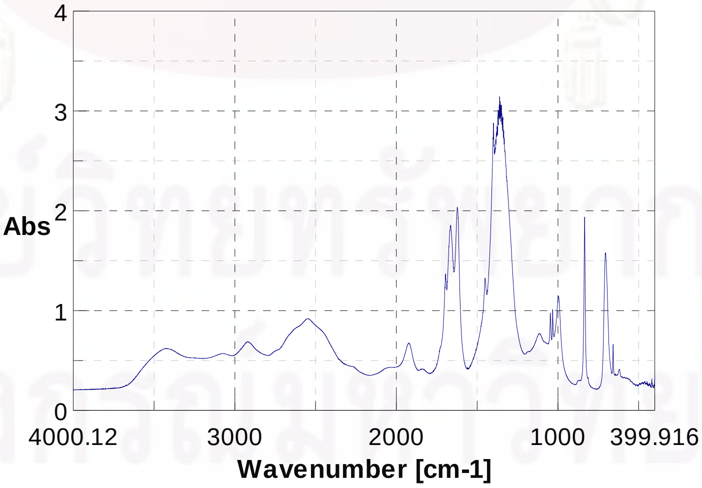

Figure A-18: FTIR of effluent from AS from Site 1

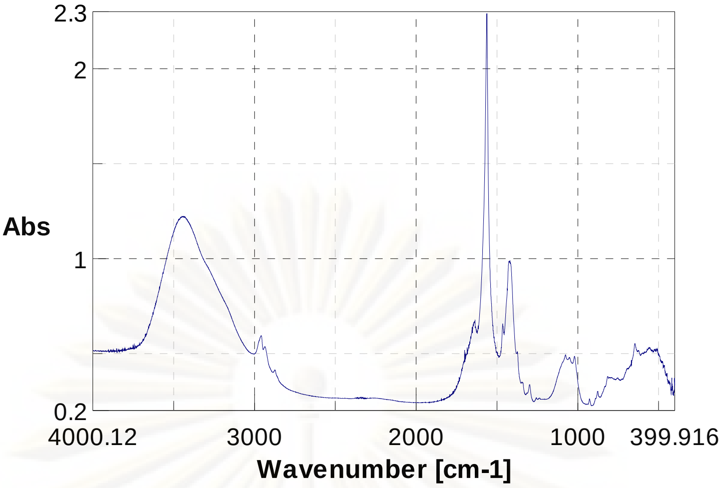

Figure A-19: FTIR of influent wastewater from Site 2

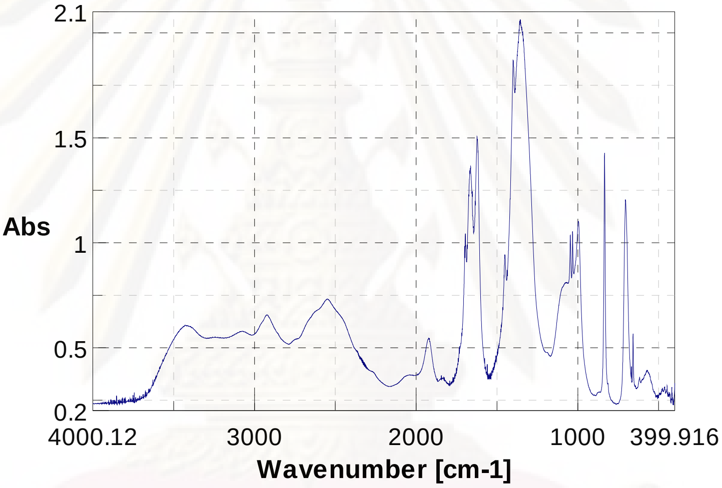

Figure A-20: FTIR of effluent from UASB from Site 2

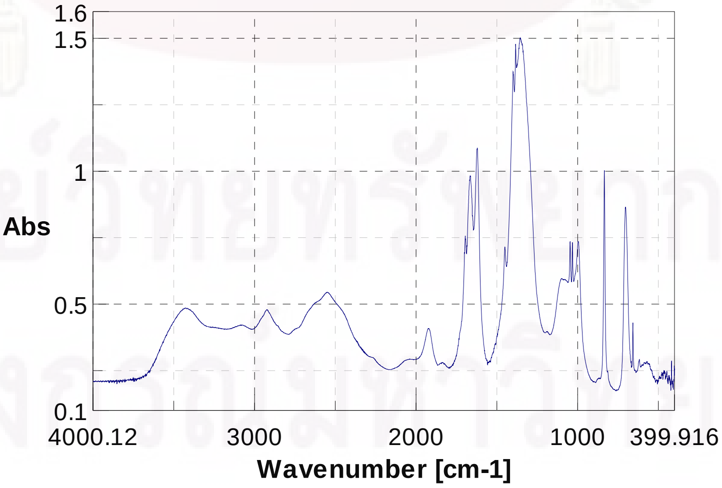

Figure A-21: FTIR of effluent from AS from Site 2

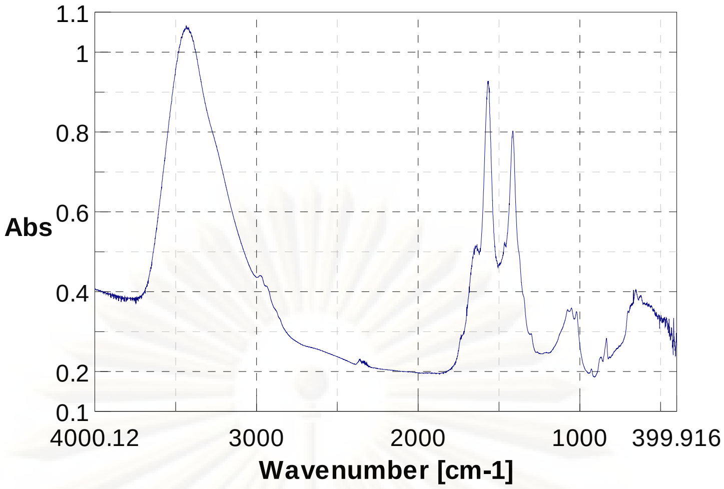

Figure A-22: FTIR of influent wastewater from Site 3

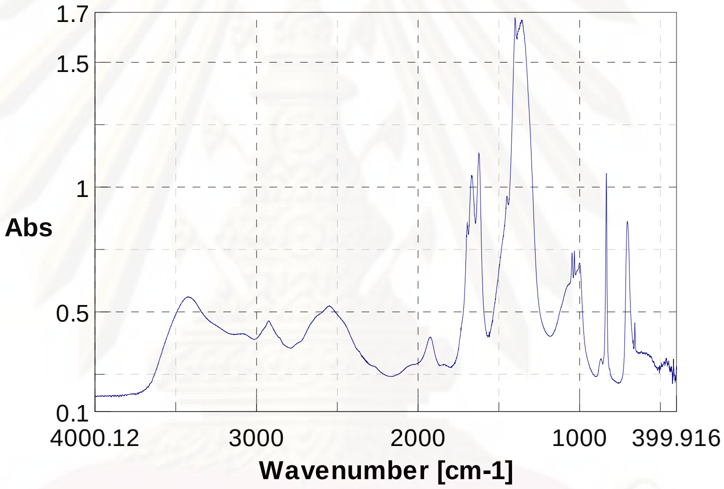

Figure A-23: FTIR of effluent from UASB from Site 3

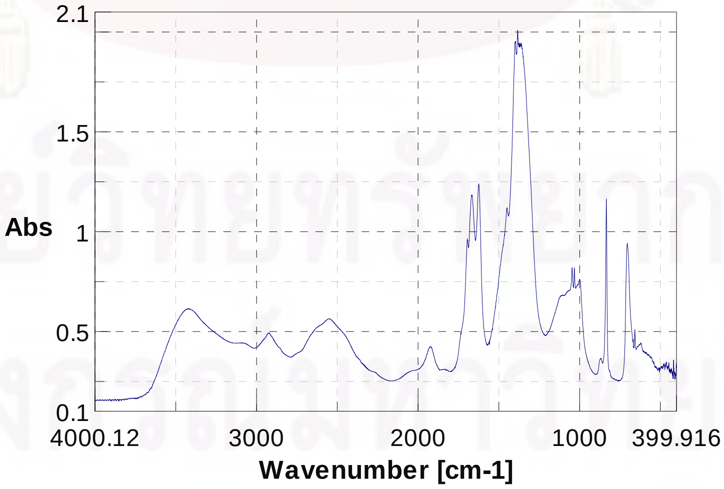

Figure A-24: FTIR of effluent from AS from Site 3

Table A-5: THM species of DOM in wastewater and treated wastewater from UASB and AS treatments

	Water sources	THMFP (µg/L)				
		$CHCl_3$	$CHCl_2Br$	$CHClBr_2$	$CHBr_3$	**Total THMFP**
Site 1	Influent wastewater	2877.9	301.7	99.8	1.8	3281.2
	Effluent from UASB	936.0	229.0	14.5	4.2	1183.6
	Effluent from AS	775.7	177.0	6.1	1.7	960.5
Site 2	Influent wastewater	2257.1	237.5	145.3	6.3	2646.2
	Effluent from UASB	370.0	95.0	5.3	2.5	472.8
	Effluent from AS	202.1	53.5	1.5	0.0	257.1
Site 3	Influent wastewater	4771.8	410.2	131.5	2.3	5315.8
	Effluent from UASB	3016.3	729.9	15.4	1.2	3762.9
	Effluent from AS	932.8	203.2	5.2	1.0	1142.1

APPENDIX B
DETAILS OF THREE BREWERIES

Three local breweries in Thailand namely Sites 1, 2 and 3, were selected as a model system in this study. The studied Sites 1 and 3 produce lager beer, whereas, Site 2 produces the light beer. Diagram of Brewing process of these three breweries is demonstrated in Figure C-1. Although the brewing process for both lager beer and light beer is similar, the operating conditions of brewing are different. Lager is the English name for cool fermenting beers of Central European origin. The name *lager* comes from the German *lagern* for "to store". Lager yeast is a cool bottom-fermenting yeast (*Saccharomyces pastorianus*) and typically undergoes primary fermentation at 7–12 °C (the fermentation phase), and then is given a long secondary fermentation at 0–4 °C (the lagering phase). During the secondary stage, the lager clears and mellows. The cooler conditions also inhibit the natural production of esters and other byproducts, resulting in a "cleaner"-tasting beer. In case of light beer, Light beer is beer that is reduced in alcohol content or in calories, compared to normal beer. The Light beer production is operated at higher fermentation temperatures tend to cut down on alcohol content.

Site 1

Product

: Lager beer

Raw materials for brewing

:100% barley malt with strong hop characters

: groundwater and supplied water

: yeast

Beer Production capacity

: 1,600 m^3/d

Water consumption

: 520 m^3/d

Wastewater flowrate

: 4,100 m^3/d

Wastewater characteristics

: COD ~ 10,000 mg/L

: BOD ~ 5,000 mg/L

<u>Site 2</u>

Product

: Light beer

Raw materials for brewing

: barley malt and hop

: supplied water

: yeast

Beer Production capacity

: 700 m^3/d

Water consumption

: 320 m^3/d

Wastewater flowrate

: 3,000 m^3/d

Wastewater characteristics

: COD ~ 6,000 mg/L

: BOD ~ 2,800 mg/L

Site 3

Product

: Lager beer

Raw materials for brewing

: barley malt and hop

: groundwater and supplied water

: yeast

Beer Production capacity

: 2,000 m^3/d

Water consumption

: 650 m^3/d

Wastewater flowrate

: 4,700 m^3/d

Wastewater characteristics

: COD ~ 12,000 mg/L

: BOD ~ 7,000 mg/L

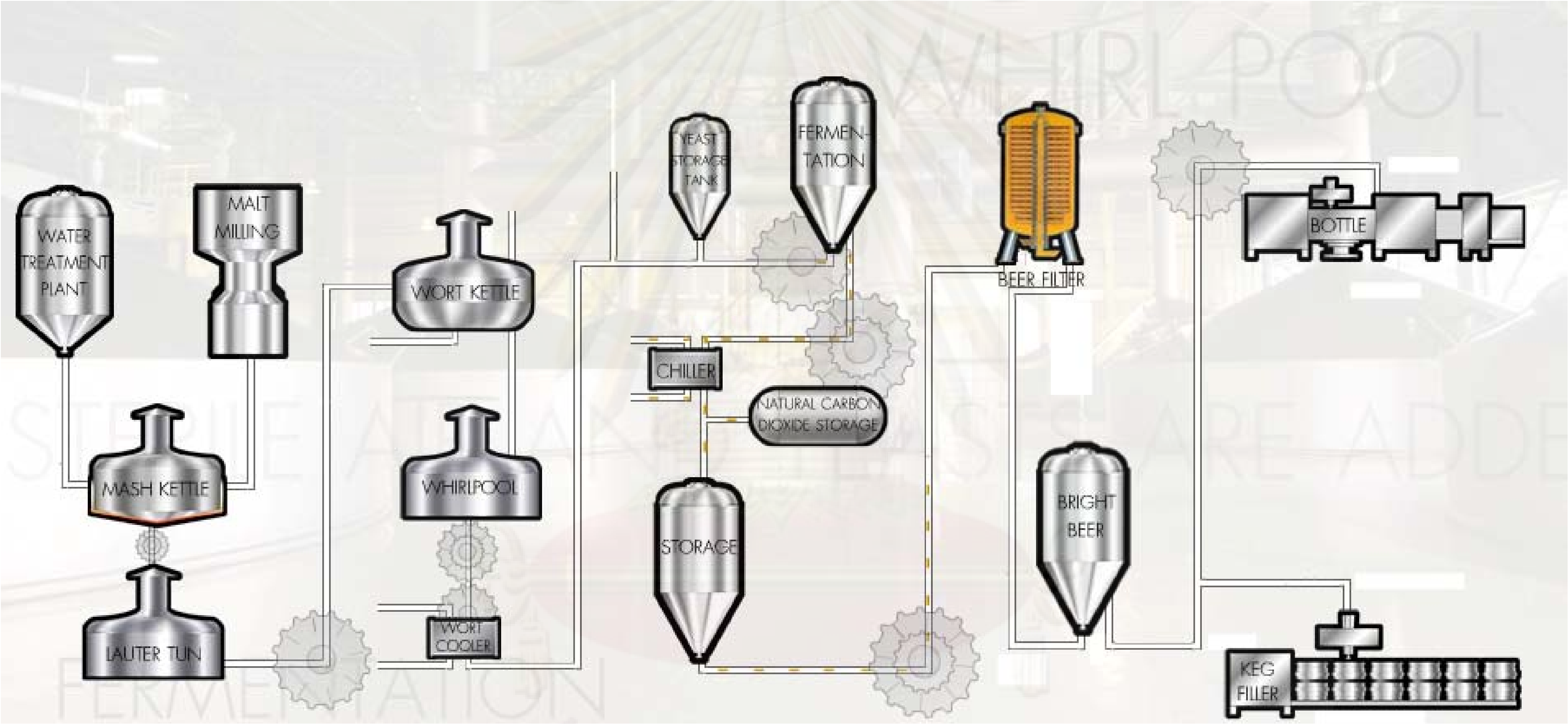

Figure B-1: Diagram of Brewing process for all three breweries

APPENDIX C
TREATMENTS OF DOM FRACTIONS

There are other processes that enable to remove DOM from water sources, such as adsorption, ion exchange, membrane filtration, and advanced oxidation processes. The AWWA (1998) examined the capability of granular activated carbon (GAC) to adsorb DBPs precursors from several source waters. Water samples were collected from six utilities including the Cincinnati Waterworks (source water: Ohio River, ORW), South Central Connecticut Regional Water Authority (Lake Gaillard, LGW), Jefferson Parish Water Department (Mississippi River, MRW), Passaic Valley Water Commission (Passaic River, PRW), City of Phoenix (Salt River Project, SRPW), and Florida Cities Water Company (groundwater, FGW). It was found that the early GAC effluent samples were composed of nonadsorbable NOM, which were found to be almost entire nonhumic and aliphatic and composed of small molecular size fractions. Samples later in the breakthrough curve gradually demonstrated the appearance of humic and aromatic fractions and larger molecular size fractions. Pretreatment with coagulation almost equally had an effect on the humic and nonhumic fractions. Larger and humic material was preferentially removed by ozonation and biofiltration over smaller and nonhumic material. Optimizing coagulation pretreatment could result in longer GAC life.

Korshin et al. (1997) studied the adsorption of NOM on hydrous iron oxide. The water sources were the influents to the water treatment plants in Everett, WA and Mt Veron, WA. It was found that the surface of iron oxide considerably interacted with HPON, HPOB, HPOA, HPIB, and HPIA in the influent, and not HPIN. HPIA and HPOA interact most strongly with the iron oxide surface. Bolto et al. (2002) studied the removal of natural organic matter by ion exchange. Four fractions of water samples were fractioned into very hydrophobic acids (VHS), slightly hydrophobic acids (SHA), charged hydrophilic compounds and neutral hydrophilic compound. The resins tested were received from Rohm and Hass, Bayer, ResinTech and Purolite. Anion exchangers of open structure and high water content were observed as the best resin type for the very efficient removal of hydrophobic and hydrophilic organic matter.

Membrane filtration has been used to remove DOM. Microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) membranes have been utilized to remove DOM from water. Many studies focused on the fouling of the UF, NF and RO by DOM, because it could provide a basis for the appropriate selection and operation of membrane technology for drinking water treatment. Fan et al. (2001) ordered potential foulants: hydrophilic neutrals > hydrophobic acids > transphilic acids. Lee et al. (2004) evaluated fouling in low-pressure membrane (MF/UF) filtration by NOM. Two MF and UF membranes possessing hydrophilic and hydrophobic properties were used. Four French surface waters, Marne River, Cazau Lake, La Bultiere Reservoir and Yffiniac River, were selected as the water samples and fractionated into hydrophobic, transphilic and hydrophilic fractions. Source water that contained a high HPI fraction content of NOM resulted in a significant flux decline. A difference in the flux decline between hydrophobic and hydrophilic membranes was not founded. The shape and size of molecules and roughness of membrane were found to be important influential factors that affected flux decline. Membrane fouling mechanisms were not only a function of membrane type but also depended upon feed water characteristics. Kennedy et al. (2005) evaluated the NOM fouling of ultrafiltration membranes. Water samples were collected from Ijssel Lake (Andijk, North Holland) and fractioned into three NOM fractions: hydrophobic, hydrophilic and transphilic. Hollow fiber UFC M5 membranes from X-Flow were used for the UF made of a hydrophilic PES/PVP blend (MWCO 150-200 KDa). The filtration of three NOM fractions suggested that the fouling potential ordered from high to low was as follows: hydrophilic > hydrophobic > transphilic.

Hu et al. (2003) studied the treatability of organic fractions derived from secondary effluent by reverse osmosis (RO) membrane. The water sample was treated secondary effluent from a local water reclamation plant. The experimental procedure was conducted in three phases. In the first phase, the secondary effluent was filtered through microfiltration and fractionated using resin fractionation into seven fractions including HPON, HPOB, humic acid (HA), fulvic acid (FA) (HA + FA = HPOA), HPIB, HPIA and HPIN. In the second phase, each fraction was subjected to treatment by the RO process to study the treatability of organic fractions using the RO system. In the third phase, the same batch of secondary treated effluent was filtered through microfiltration prior to being feed into the RO process. The RO feed, RO concentrate and RO permeate were subsequently fractioned into six fractions. The RO system was obtained from Nimbus^{TM} (NIMBUS^{TM} H-400) using a thin film polyamide membrane. In the case of the treatability of organic fractions by the RO process (first and second phases), it was found that the RO treatment had a better performance in removing hydrophobic fractions than hydrophilic fractions (except for the based fractions). The highest DOC removal was obtained from HPOA, whereas in the case of HPIA, it was not readily rejected and tended to permeate through the membrane. When compared among the hydrophobic fractions or hydrophilic fractions, the removal efficiencies from high to low were ordered as follows: Acid > Neutral > Base (except for HPIN). For the treatment efficiency of the RO process with respect to each DOM fraction (third phase), the percentage composition of the hydrophobic fractions in the permeate decreased, while the percentage composition of the hydrophilic fractions increased. The RO process could effectively reduce HPOA.

The advanced oxidation processes (AOP) has been reported to have the potential to remove NOM from water sources. Parsons and Murray (2004) utilized Fenton's reagent, photo-Fenton's reagent and titanium dioxide photocatalysis to remove NOM from water from the inlet to the Albert Water Treatment Works, England. In comparison to conventional coagulation/flocculation processes, these three processes had higher removal efficiencies in terms of both DOC and UV-254 absorbance. Under the optimum conditions all three processes could remove DOC and UV-254 over 80% and 90% respectively. Goslan et al. (2006) investigated reservoir NOM reduction by UV photolysis and AOP. They utilized four treatment technologies, including UV-C photolysis, UV/H_2O_2, Fenton's reagent (FR) and photo-Fenton's reagent (PFR), to remove NOM in moorland reservoir water from the Gorple (lower) Reservoir, one of the sources for the Albert WTW, England. It was found that the reduction of UV-254 required very high UV-C doses, in which UV-C irradiation did not result in DOC removal at doses up to 1100 J cm^{-2}. H_2O_2 treatment combined with UV-C light could increase the reduction of UV-254 compared with UV-light alone. In terms of UV-254 reduction, PFR did not show remarkably good treatment efficiency at the optimum condition compared with FR, however, in terms of DOC removal, PFR was the most efficient process.

From past previous researches on the removal of DOM fractions, it can be seen that hydrophobic organic fractions, especially HPOA, could be successfully removed using coagulation/flocculation, GAC and membrane processes, whereas these processes were considerably unsuccessful to remove hydrophilic fractions. However, different water sources may lead to different water characteristics, therefore, the performance capabilities of treatment processes to remove DOM could be different. A recommendation for the removal of HPOA and HPIA from treated wastewater could be drawn: enhanced coagulation practices may be an appropriate technique for removing HPOA from the treated wastewater. The GAC and membrane filtration processed could be used after coagulation to enhance the reduction of HPIA, however, the effects of the membrane properties such as roughness, hydrophobicitty and hydrophilicity, and surface charge on removing HPIA should be investigated in order to provide an appropriate selection and operation of membrane technology for reclamation plants.

APPENDIX D

PUBLICATIONS

Peer Reviewed International Journal/Book

1. Janhom, T., Wattanachira, S., and Pavasant, P. (2008). Characterization of brewery wastewater with spectrofluorometry analysis. Journal of Environmental Management. 90: 1184–1190.

International Symposium / Conference Proceedings

1. Janhom, T., Wattanachira, S., and Pavasant, P. (2006). Reduction of Trihalomethane Created from Six Fractions of Dissolved Organic Matter in Raw Water Supply by Alum Coagulation. The Proceedings of the International Conference on Hazardous Waste Management for a Sustainable Future. January 10-12, Bangkok, Thailand.
2. Janhom, T., Wattanachira, S., and Pavasant, P. (2007). Characterization of Brewery Wastewater by FEEM and Pyrolysis GC/MS Wastewater Treatment. The Proceeding of the Fifth International Symposium on Southeast Asian Water Environment. pp. 154-157, November 7-9, Chiang Mai, Thailand.

National Symposium / Conference Proceedings

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