RELATIONSHIPS BETWEEN DISSOLVED ORGANIC NITROGEN (DON) AND BIODEGRADABLE DISSOLVED ORGANIC NITROGEN (BDON) TO HALOACETONITRILE FORMATION POTENTIAL IN WATER TREATMENT PLANTS

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ความสัมพันธ์ระหว่างสารละลายอินทรีย์ไนโตรเจนและสารละลายอินทรีย์ไนโตรเจนที่ย่อยสลายได้ทางชีวภาพต่อศักยภาพการเกิดสารฮาโลอะซิโตไนไตรล์ในระบบผลิตน้ำประปา

นายพชรพล อินทุเวศ

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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Thesis Title	RELATIONSHIPS BETWEEN DISSOLVED ORGANIC NITROGEN (DON) AND BIODEGRADABLE DISSOLVED ORGANIC NITROGEN (BDON) TO HALOACETONITRILE FORMATION POTENTIALIN WATER TREATMENT PLANTS
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พชรพล อินทุเวศ : ความสัมพันธ์ระหว่างสารละลายอินทรีย์ไนโตรเจนและสารละลายอินทรีย์ไนโตรเจนที่ย่อยสลายได้ทางชีวภาพต่อศักยภาพการเกิดสารฮาโลอะซิโตไนไตรล์ในระบบผลิตน้ำประปา (RELATIONSHIPS BETWEEN DISSOLVED ORGANIC NITROGEN (DON) AND BIODEGRADABLE DISSOLVED ORGANIC NITROGEN (BDON) TO HALOACETONITRILE FORMATION POTENTIALIN WATER TREATMENT PLANTS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: อ. ดร. ธัญลักษณ์ ราษฎร์ภักดี, อ.ที่ปรึกษาวิทยานิพนธ์ร่วม: รศ. ดร. ปฏิภาณ ปัญญาพลกุล, 114 หน้า.

ในปัจจุบันสารพลอยได้จากสารไนโตรเจนที่เกิดจากการกระบวนการฆ่าเชื้อโรคในน้ำ (N-DBPs) กำลังเป็นประเด็นสำคัญที่ควรตระหนักถึงในระบบผลิตน้ำประปา เนื่องจาก ผลพลอยได้ดังกล่าว มีความเป็นพิษและก่อให้เกิดมะเร็งมากกว่าผลพลอยได้โดยทั่วไป เช่น ไตรฮาโลมีเทน (THMs) สารละลายอินทรีย์ไนโตรเจน (DON) มีบทบาทสำคัญในแหล่งน้ำธรรมชาติ เนื่องจากเป็นสารตั้งต้นที่ทำให้เกิด สารพลอยได้จากไนโตรเจนในกระบวนการฆ่าเชื้อโรคในน้ำ งานวิจัยนี้มีวัตถุประสงค์ที่จะศึกษาการเปลี่ยนแปลงของสารละลายไนโตรเจนทั้งหมดที่ละลายน้ำ (TDN) สารละลายอินทรีย์ไนโตรเจน (DON) และ สารละลายอินทรีย์ไนโตรเจนที่สามารถย่อยสลายได้ทางชีวภาพ (BDON) ในระบบผลิตน้ำประปาของเทศบาลนครขอนแก่น ซึ่งประกอบไปด้วย สถานีผลิตน้ำบ้านโกทา (KWTP) และ สถานีผลิตน้ำท่าพระ (TWTP) และ ระบบผลิตน้ำประปาภายในมหาวิทยาลัยขอนแก่น (KKUWTP) ในงานวิจัยนี้ได้ทำการศึกษาศักยภาพการเกิดสารฮาโลอะซิโตไนไตรล์ (HANFP) จำนวนสี่ ชนิดคือ โมโนคลอโรอะซิโตไนไตรล์ (MCAN) ไตรคลอโรอะซิโตไนไตรล์ (TCAN) ไดคลอโรอะซิโตไนไตรล์ (DCAN) และไดโบรโมอะซิโตไนไตรล์ (DBAN) นอกจากนี้ได้ทำการศึกษาผลกระทบของการเติมโอโซนในตัวอย่างน้ำต่อศักยภาพการเกิดสารฮาโลอะซิโตไนไตรล์ (HANFP) จากการศึกษาพบว่าสารละลายอินทรีย์ไนโตรเจนจากทั้งสามระบบการผลิตน้ำประปามีค่าอยู่ในช่วง 0.44 – 0.66 มิลลิกรัมไนโตรเจนต่อลิตร และพบว่าสารละลายอินทรีย์ไนโตรเจนที่วัดได้ตลอดกระบวนการการผลิตน้ำประปามีแนวโน้มลดลงเล็กน้อย และค่าของสารละลายอินทรีย์ไนโตรเจนที่สามารถย่อยสลายได้ทางชีวภาพ พบว่าคิดเป็นจำนวนประมาณร้อยละ 50 ของสารละลายอินทรีย์ไนโตรเจน ซึ่งปริมาณดังกล่าวมีความสัมพันธ์ต่อศักยภาพการเกิดสารฮาโลอะซิโตไนไตรล์ (R^2 มีค่าระหว่าง 0.34-0.74) ในการเติมโอโซนเพิ่มความเข้มข้นของ BDON มีผลทำให้ศักยภาพภาพเกิดการสารฮาโลอะซิโตไนไตรล์เพิ่มขึ้นอีกด้วย ปริมาณของฮาโลอะซิโตไนไตรล์ทั้งหมดในน้ำหลังได้รับการบำบัดแล้วมีค่าอยู่ในช่วง 4-15 ไมโครกรัมต่อลิตร และ DCAN เป็นชนิดของ HANs ที่พบมากที่สุดคิดเป็นมากกว่าร้อยละ 50 ของฮาโลอะซิโตไนไตรล์ทั้งหมด ผลที่ได้จากการศึกษาในครั้งนี้พบว่า BDON เป็นส่วนสำคัญที่ทำให้เกิด HANs ซึ่งการลดปริมาณของ BDON จะช่วยให้ลดปริมาณของ HANs ลงได้ และผู้ใช้ประโยชน์จากน้ำสามารถนำความรู้ดังกล่าวไปใช้ในการควบคุมการเกิดสารพลอยได้จากไนโตรเจนที่เกิดจากการกระบวนการฆ่าเชื้อโรคในน้ำ (N-DBPs) ในระบบผลิตน้ำประปาได้

สาขาวิชา การจัดการสิ่งแวดล้อม
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KEYWORDS: DISSOLVED ORGANIC NITROGEN / BIODEGRADABLE DISSOLVED ORGANIC NITROGEN / HALOACETONITRILE / CONVENTIONAL TREATMENT PROCESS

PHACHARAPOL INDUVESA: RELATIONSHIPS BETWEEN DISSOLVED ORGANIC NITROGEN (DON) AND BIODEGRADABLE DISSOLVED ORGANIC NITROGEN (BDON) TO HALOACETONITRILE FORMATION POTENTIALIN WATER TREATMENT PLANTS. ADVISOR: THUNYALUX RATPUKDI, Ph.D., CO-ADVISOR: ASSOC. PROF. PATIPARN PUNYAPALAKUL, Ph.D., 114 pp.

Nitrogenous disinfection by-products (N-DBPs) have become an issue of concern in water treatment plant (WTP) since they have more toxicity more than carbonaceous disinfection by-products (C-DBPs) such as trihalomethanes. Dissolved organic nitrogen (DON) in natural water source is known as precursors of nitrogenous disinfection by-products (N-DBPs). This study investigated the fate of total dissolved nitrogen (TDN), dissolved inorganic nitrogen, DON, and biodegradable DON (BDON) along the water treatment trains of Khon Kaen Municipality (Kota WTP (KWTP) and Tapra WTP (TWTP), and Khon Kaen University (KKU Water Treatment plant (KKUWTP)). Occurrence and formation potential of four haloacetonitriles (HANs) including monochloroacetonitrile (MCAN), dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), and dibromoacetonitrile (DBAN) were determined. In addition, the effect of ozonation on HAN formation potential (HANFP) was studied. The result shows that DON concentrations of KWTP, TWTP, and KKUWTP ranged from 0.44 to 0.66 mg-N/L. DON at this level was not effectively removed by conventional water treatment plants. BDON accounted for approximately 50% of DON pool and contributed to HANFP formation based on the formation potential test of three water treatment plants (R^2 of 0.34-0.74). Ozonation increased the BDON and HANFP of water samples. Total HANs concentration in finished waters ranged between 4 to 15 µg/L. Among HANs being measured, DCAN was the most abundant HAN species contributing more than 50% in samples. The finding of this research reveals that BDON was an important organic fraction to the HAN formation. Removal of BDON would also reduce the HAN concentrations. Water utilities might find this information useful for controlling N-BDPs in drinking water.

Field of Study:	Environmental Management	Student's Signature	
Academic Year:	2014	Advisor's Signature	
		Co-Advisor's Signature	

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ABBREVIATIONS

AOM	Algal derived organic matter
BAN	Bromoacetonitrile
BCAN	Bromochloroacetonitrile
BDOC	Biodegradable dissolved organic carbon
BOM	Biodegradable organic matter
CAN	Chloroacetonitrile
CHO	Chiness hamsters overly cells
Da	Dalton
DBA	Dibromoacetic acid
DBAN	Dibromoacetonitrile
DBCAN	Dibromochloroacetonitrile
DBPs	Disinfection by products
DCAN	Dichloroacetonitrile
DHANFP	Dihalogenated acetonitrile formation potential
DIN	Dissolved inorganic nitrogen
DNA	Deoxyribonucleic acid
DOC	Dissolved organic carbon
DOM	Dissolved organic matter
DON	Dissolved organic nitrogen
DON_{bf}	Dissolved organic nitrogen before incubation of blank
DON_{bi}	Dissolved organic nitrogen after incubation of blank
DON_{f}	Dissiolved organic nitrogen before incubation

DON_i	Dissolved organic nitrogen after incubation
DWTP	Drinking water treatment plant
EEM	Fluorescence excitation- emission matrix
EfOM	Effluent organic matter
FA	Fulvic acid
GAC	Granular activated carbon
HA	Humic acid
HAAs	Haloacetic acids
HANFP	Haloacetonitrile formation potential
HANs	Haloacetonitriles
HS	Humic substance
IAN	Iodoacetonitrile
KKUWTP	Khon Kaen university water treatment plant
KWTP	Kota water treatment plant
MCAN	Monochloracetonitrile
MLSS	Mixed liquor suspended solids
MW	Molecular weight
NBDON	Non-biodegradable dissolved organic nitrogen
NOM	Natural organic matter
non-HS	Non-humic substance
PAC	Polyaluminum chloride
R^2	Correlation coefficient
SMP	Soluble microbial product

SUVA	Specific ultraviolet absorbance
TCAA	Trichloroacetic acid
TCAN	Trichloracetonitrile
TDN	Total dissolved nitrogen
THMs	Thihalomethanes
TOC	Total organic carbon
TWTP	Thapra water treatment plant
UV_{254}	Ultraviolet absorbance at 254 nm
WHO	World health organization
WTP	Water treatment plant

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CHAPTER I

INTRODUCTION

1.1 Motivations

Dissolved organic nitrogen (DON) is a major form of organic nitrogen in the natural water and treated water (Wadhawan et al., 2014). DON is a complex mixture of amino acids (composed of 16-50% of DON), amides, protein, peptide, pyrimidine, and heterocyclic nitrogen (Chen et al., 2009). DON may come from allochthonous and autochthonous sources, which include terrestrial runoff, leaching from soil into river, and effluent organic matter(Mash and Westerhoff, 2002; Wantae, 2005)Microbial activities (e.g. nitrification) may act as a source of DON and also increasing of the DON concentration in water body (Chen et al., 2009). Bioavailable dissolved organic nitrogen was reported to be a main portion of DON in freshwater (Halis et al., 2012). The amount of bioavailable DON in water can be quantified as bioavailable dissolved organic nitrogen BDON by batch incubation test using an acclaimed mixed bacterial culture (Halis et al., 2013; Wadhawan et al., 2014). DON and BDON in the water treatment plant has become concerned issue in water reclamation plant and drinking water treatment plant (DWTP) because of its reaction with disinfectants (e.g. chlorine, chloramine) to form nitrogen disinfection by product (N-DBP). For example, haloacetonitriles (HANs), N-nitrosodimethylamine (NDMA), halonitomethane (HNM) which are more carcinogenicity and toxicity than carbonaceous DBPs (C-DBPs)(Bull, 2003; Dotson et al., 2009). From previous researchers, to control DBPs level in drinking water, water treatment utilities need to understand how characteristics of organic precursors and treatment processes play role in DBPs formation. There were many factors that have been considered for predicting and controlling C-DBPs and N-DBPs formation they include , dissolved organic carbon (DOC), dissolved organic nitrogen (DON), ultraviolet absorbance at wavelength 254 nm (UV_{254}), bromide, pH, chlorine dose, temperature, reaction time, and fluorescence properties (Chuang et al., 2013; Yang et al., 2012). Although the fate of DON and BDON in water treatment plants have been monitored in USA and United Kingdom (UK) (Chen et al., 2009; Halis et al., 2013; Leenheer et al., 2007; Simsek, Kasi, et al., 2013; Wadhawan et al., 2014), such data has never been reported for water treatment plants in Thailand. In addition, the role of BDON on the formation of N-DBP has never been investigated. With this information, plant operators or regulatory agencies can use them for improving the water quality of water plant or setting up new standards. This work aims to investigate the fate of DON in the conventional treatment process including raw water, sedimentation, filtration, chlorination, and additional treatment (ozonation process) in Kota Water Treatment Plant (KWTP), Thapra Water Treatment Plant (TWTP) of Khon Kaen Metropolitan, and Khon Kaen University Water Treatment Plant (KKUWTP), Khon Kaen, Thailand. The HAN formation potential (HANFP) in each treatment process was also studied. To assess the role of BDON to HANFP, the water samples from all treatment processes were tested for BDON. The relationship between DON, BDON, and other parameters such as DOC and UV_{254} with HANFP will also be examined.

1.2 Objective

1. To investigate the occurrence and fate of DON and BDON in conventional water treatment processes and ozonation process.

2. To determine the relationship between DON and BDON with specific haloacetonitrile formation potential (HANFP) for conventional water treatment processes and ozonation process.

1.3 Scope of the study

1. Water samples were taken from water treatment plants of Khon Kaen Metropolitan and Khon Kaen University.

2. Four different species of haloacetonitrile including monochloroacetonitrile (MCAN), trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), and dibromoacetonitrile (DBAN) were investigated.

3. Ozonation experiment was conducted only for samples after sedimentation basin.

1.4 Hypotheses

1. The high of DON and BDON concentration in water led to more in the HANs formation during chlorination.

2. The DOC concentration, and SUVA are correlated with HAN formation in water treatment systems.

3. Ozonation increases the BDON concentration.

CHAPTER II

LITERATURE REVIEW

2.1. Natural organic matter (NOM)

2.1.1 Source of NOM

Natural organic matter (NOM) contains a mixture of dissolved organic matter (DOM), nitrogen, oxygen, hydrogen, sulfur, and derived from decomposing living matter (Berman and Bronk, 2003; Xu et al., 2010). The characteristic of NOM depends on its origin. Source of NOM in aquatic system can be attributed to two main sources which are allochthonous and autochthonous NOM source. (Bond et al., 2014; Kornegay, 2000)

2.1.1.1 Allochthonous NOM

Allochthonous NOM (with in a soil profile) is derived from aquatic biota and/or from degradation of terrestrial biomass directly or through soil leaching. The component of allochthonous NOM is a mixture of acidic organic compounds of medium to high molecular weight, originated from the leaching of decaying terrestrial plant and animal material in a catchment and contains more aromatic with high humic acid(Tipping et al., 2010).

2.1.1.2 Autochthonous NOM

Autochthonous NOM (within a water body) comes from the internal aquatic system from excretion or decay product of photosynthesis organism such as microbial product, and algal organic matter (AOM). The discharge of wastewater treatment plant as effluent organic matter (EfOM)is also a source of autochthonous

NOM (Fabris et al., 2008). It is predominantly phenolic and carboxylic in nature, containing amino acids, hydrocarbons, carbohydrates, sterols, and low molecular acids. NOM derived from these sources is typically enriched in aliphatic carbon and organic nitrogen (Boyer et al., 2008).

2.2 The composition of natural organic matter (NOM)

The main composition of NOM are heterotrophic mixture of hydrophobic and hydrophilic organic compound including non-homogenic organic compound such as humic substance, sugar, aliphatic, and aromatic acid.

Natural organic matter (NOM) can be divided into two groups (Figure 2.1) including humic and non-humic substances. Humic substance (HS) is non-polar or hydrophobic character. While non-humic substance (non-HS) is polar or hydrophilic-like compounds (T. Bond et al., 2014)

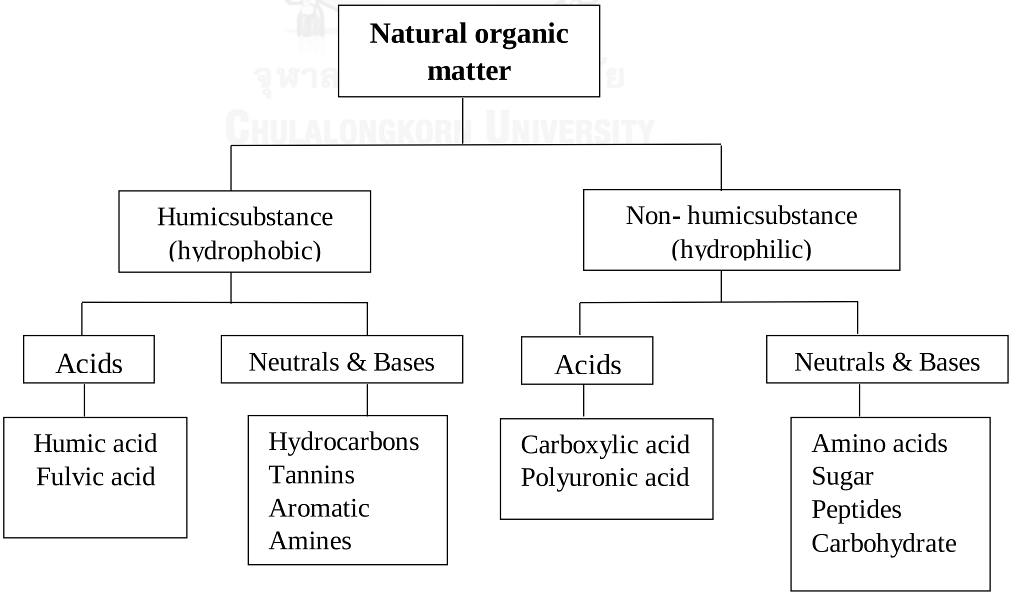


Figure 2.1 Classification of NOM (modified from Leenheer and Croue, 2003)

2.2.1 Humic substance

Humic substance (HS) or hydrophobic compounds are major component of NOM (Westerhoff et al., 2004). Humic substance could divided into 3 groups based on acidity and chemical composition including humic acid (HA), fulvic acid (FA) and humin. In aquatic system, HS contains only HA and FA. HA composes of a mixture of weak aliphatic and aromatic acid which are not soluble in the water under acid condition (Zularisam et al., 2011). FA comprises of polycarboxylates with various degrees of aromaticity and molecular mass. Their abundance in DOC makes fulvic material the largest source of mobile organic carbon on the earth (Filella, 2014; Kim and Yu, 2005)

Humic matter is a precursor of chloroform formed by chlorination of natural waters which can cause harmful to human and biota in aquatic(Frimmel, 2005). HS mainly act as a precursor for the formation of carcinogenic disinfection by products (DBPs) during the chlorination process (Uyguner-Demirel and Bekbolet, 2011). HS are hydrophobic fraction in NOM that are described as heterogeneous polyfunctional polymers formed through the breakdown of plant and animal tissues (Kim and Yu, 2005). Therefore, the molecular structure of HS has play role on the formation of DBP during reaction with disinfection.

2.2.2 Non-humic substance

Non-humic substance (non-HS) or hydrophilic compounds are contain of protein, amino acids, sugar, carbohydrates, hydrophilic acid and polysaccharides (Bin et al., 2011). The dominant of non-HS are biodegradable which often referred as biodegradable organic matter (BOM) (Bond et al., 2014)

2.3 Characterization and quantification parameters of NOM

Identification of NOM characteristics is a tool to understanding the functionality and influences of NOM in an aquatic or engineered system.

The characterization tools can be divided into four types including: preliminary characterization, size characterization, chemical identification, and spectral signature (Peuravuori and Pihlaja, 1997). Preliminary analysis of NOM is usually represented by the measurement of total organic carbon (TOC), DOC, UV_{254}, which does not required sophisticated sample treatment or analytical equipment (Table 2.1). Whereas the complex nature of NOM are required more sophisticated analytical technique which differentiate upon physio-chemical properties. Typical NOM characterization methods are described in the following section.

2.3.1 Total organic carbon (TOC) and dissolved organic carbon (DOC)

Total organic carbon (TOC) is the sum of the particulate and dissolved organic carbon (DOC) (Matilainen et al., 2011). An important of TOC and DOC in water system is used to assess NOM characterization. DOC is used as surrogate parameter to estimate a precursor of DBPs such as THM, HAA, and HANs.

Ultraviolet absorbance at 254 nm (UV_{254} is generally used for quantitative determination of solutions of unsaturated carbon bonds (C=C, C≡C), and aromatic carbon in water samples (Matilainen et al., 2011).

2.3.2 Specific UV-absorbance (SUVA)

Specific UV-absorbance (SUVA) is defined as the UV absorbance of a given sample at 254 nm divided by the DOC concentration (Eq. 2.1) (Ates et al., 2007; Matilainen et al., 2011)

$$\text{SUVA}_{\left(\frac{\text{L}}{\text{mg.m}}\right)} = \frac{\text{UV}\left(\frac{1}{\text{cm}}\right) \times 100\left(\frac{\text{cm}}{\text{m}}\right)}{\text{DOC}\left(\frac{\text{mg}}{\text{L}}\right)} \qquad (2.1)$$

The SUVA value was found to be good representative for hydrophobic, aromatic, humic acid, and fulvic acid. (Fleck et al., 2004). Water with SUVA >4 L/mg.m contains mainly hydrophobic and aromatic material, while the SUVA <2 L/mg.m indicates hydrophilic NOM (Matilainen et al., 2011). In addition, SUVA is a good correlation with trihalomethane (THM) formation potential (Jung and Son, 2008) and other DBPs precursors (Ates et al., 2007)

Table 2.1 Preliminary method (bulk parameter) for NOM characterization.

Method	Detected features	Positive	Negative
TOC	Total organic carbon - content in water	- Easy to use. - Not too expensive. - Can be used as on-line method	Give only information on quantity of NOM
DOC	Dissolved organic carbon in water, after filtration through 0.45 µm filters	- Easy to use - Not too expensive.	
SUVA	High SUVA value > 4 is hydrophobic, <2 is hydrophilic	Easy to determine, analytical equipment Not too sophisticated	High nitrate content in low DOC waters may interfere measurement
UV_{254}	Identified as a potential surrogate measure for DOC		

Source : Adopted from Matilainen et al. (2011)

2.4 The impact of NOM on water treatment plants

The allochthonous NOM contain a humic substance, about 50 % of hydrophobic compounds, which can affect to physical and chemical properties of water body. Especially, the reaction of humic substance on the formation potential of DBPs such as THM and HAA. Therefore, an appropriate technique (e.g. coagulation and granular activated carbon (GAC)) for remaining aromatic compounds in raw water should be applied. Because aromatic fraction can acts as a precursors of DBPs (Chuang et al., 2013).

2.5 Dissolved organic nitrogen (DON)

Dissolved organic nitrogen (DON) is an emerging concerned pollutant for the water treatment plant since it is a precursor of N-DBPs which are more toxic than C-DBPs (THM and HAA) (Lee and Wasterhoff, 2005). Sources of DON in natural water may come from the effluent organic matter (EfOM) from wastewater treatment plant and algal organic matter (AOM). DON is a complex mixture of compounds. The component of DON includes amino acids (16 – 50% of DON), amides, heterocyclic-N (e.g., pyrimidine, imidazole, purine), and characterized compounds (Mash and Westerhoff, 2002; Xu et al., 2010). The dominant isamino acid groups which contain high concentration of protein and tryptophan (Mash and Westerhoff, 2002). Previous research had reported that the median DON concentrations in surface water, shallow and deep ground water were 0.31, 0.24, and 0.18 mg/L as N, respectively (Wantae, 2005).

2.5.1 Source of dissolved organic nitrogen (DON)

Sources of DON may come from terrestrial and agricultural runoff, leaching from plant debris and soil into water body, eutrophication and atmospheric decomposition (Berman and Bronk, 2003; Mash and Westerhoff, 2002). Autochthonous source may come from bacteria, algal, zooplankton grazing, cell death, and waste matter. The effluent organic matter (EfOM) from wastewater treatment plant contains the soluble microbial product (SMP). SMP was produced from bacteria growth and released during the lysis and degradation of microorganisms. SMP has organic nitrogen with high concentration of macromolecular protein and amino acids (Mash and Westerhoff, 2002; Wantae, 2005)

2.5.2 Biodegradable dissolved organic nitrogen (BDON)

BDON is a part of DON that can mineralized by an acclimated mixed bacterial culture (Eq. 2.2) (Halis et al., 2012)

$$\text{DON} = \text{BDON} + \text{Non-BDON} \tag{2.2}$$

BDON can serve as a nitrogen source of microbial growth in water system. It may be a precursor of N-DBPs like DON because it is a main part of DON.(Wadhawan et al., 2014). To better understand the role of DON on the formation of N-DBPs, measurement of BDON and Non-BDON (NBDON) are important. The information could be helpful to control N-DBPs precursor and to achieve complete removal of BDON in water treatment plant (Khan et al., 2009)

Method for BDON determination was adopted from Khan and co-workers (2009). The principle was the ability of bacteria to ammonify BDON. BDON was quantified from initial DON concentration (DON_i) subtracting by DON after incubation in the period of incubation time at 20 ^{o}C (DON_f) (Eq. 2.3). The inoculum used was the mixed liquor suspended solids (MLSS).

$$\text{BDON} = (\text{DON}_i - \text{DON}_f) - (\text{DONb}_i - \text{DONb}_f) \tag{2.3}$$

Where,

DON_i and DON_f are DON before and after incubation

DON_{bi} and DON_{bf} are DON before and after incubation of blank

2.5.3 Quantification of dissolved organic nitrogen

Quantification of DON are still challenging for water with high concentration of dissolved inorganic nitrogen (DIN) relative to total dissolved nitrogen (TDN) (Lee and Wasterhoff, 2005). This is because the concentration of DON cannot be measured directly. It is calculated by subtracting the sum of dissolved inorganic nitrogen (DIN) (nitrite, nitrate, and ammonium/ammonia) from total dissolved nitrogen (TDN) (Eq. 2.4 and Eq. 2.5). DIN species can be quantified by several methods as summarized in table 2.2 (Mash and Westerhoff, 2002)

$$\mathrm{DON} = \mathrm{TDN} - \sum \mathrm{DIN} \qquad (2.4)$$

$$\mathrm{DON} = \mathrm{TDN} - [\mathrm{NO_2^-}] - [\mathrm{NO_3^-}] - [\mathrm{NH_4^+}] \qquad (2.5)$$

TDN consists of two main fractions: inorganic fraction (ammonia, nitrate, nitrite) and organic According to (Bronk et al., 2000; Mash and Westerhoff, 2002) fraction (e.g. DON). There are three analytical methods to measure TDN including;

(i) Alkalinepersulfate (peroxodisulphate) oxidation. This method converts all TDN to NO_3^- and then measurement of NO_3^- concentration. There have three options for persulfate oxidation method. First, autoclave digestion under alkaline condition in the presence of $S_2O_8^-$.The limitation of this method is that N=N bonds in urea and some protein are uncleaved, which become problematic. Second, microwave digestion under alkaline condition in the presence of $S_2O_8^-$. The limitation in this option is non-quantifiable of antipyrine. Third, UV digestion under alkaline condition in the presence of $S_2O_8^-$.The limitation of this method is heterocyclic compounds show low recovery.

(ii) High temperature oxidation (HTO). TDN is determined by NO concentration and possibly with NO_2 and N_2 concentration by high temperature oxidation at 680 ^{o}C in the presence of a catalysis (typically Pt, CuO or CoO). There are several limitation of HTO. For example, urea may be recalcitrant, methyl orange, sulfathiazole and antipyrine (N-N) is non-quantify.

(iii) UV oxidation, TDN is converted to NO_3^- by UV-oxidation in the presence of an oxidizing agent ($S_2O_8^-$or H_2O_2) or catalyst (TiO_2 or TiO_2/Pt).

As mentioned previously DON is measured from the difference between TDN and DIN. Therefore, it could add up the error when subtracting several terms. The DON measurement accuracy is depend on DIN:TDN ratio (Lee, 2005). The lower of DIN:TDN ratio is the higher accuracy of DON measurement. Typically, the DIN:TDN ratioshould not exceed 0.60 mg-N/mg-N. (Bronk et al., 2000; Vandenbruwane et al., 2007; Xu et al., 2010). For water samples that have high DIN:TDN ratio, pretreatment such as dialysis is needed to reduce DIN before measurement of DON concentration.

Table 2.2 Analytical methods for inorganic nitrogen

Inorganic species	**Method of analysis**	**Detection limit**
NO_3^-	Ion chromatography	0.1 mg NO_3^-N/L
	Cadmium reduction	Depends upon NO_2^- method
	Second derivative - spectroscopy	< 5 µg NO_3^-N/L
	(VIII) reduction to NO	2-3 µg NO_3^-N/L
	Spongy cadmium reduction	5-1,000 µg NO_3^-N/L
NO_2^-	V(III) reduction to NO	2-3 µg NO_2^-N/L
	Colorimetric determination using sulfanilamide and N-(1-naphthyl)ethylenediamine	1.46-1.89 µg NO_2^- N/L
	Ion chromatography with conductivity detection	0.1 mg NO_2^-N/L
NH_3^+/NH_4^+	Phenate method	0.05-2.0 mg N/L
	Titration (methyl red/methylene blue endpoint)	1 mg N/L
	Ion selective electrode	0.02-0.08 mg N/L

Source : Westerhoff and Mash (2002)

2.5.4 Dissolved organic nitrogen (DON) in water treatment plant and drinking water

DON as a part of dissolved organic matter (DOM) has become important concern in water treatment plant (WTP) and drinking water because of its reaction with disinfectant (e.g. chlorine, chloramine) to form N-DBPs (Bull, 2003; Dotson et al., 2009). The control of DON level cause in the reduction of N-DBPs formation during chlorination process. The concentration of DON was high in treated wastewater (1.1 to 2.1 mg/L as N) (Khan et al, 2009). In secondary treated effluent, the DON level ranged from 1 to 5 mg/L as N (Halis et al., 2012). Summary of DON concentrations in WTP and drinking water treatment plants (DWTP) were presented in table 2.3.

Table 2.3 Average DON concentrations in WTP and DWTP.

Locations	Average DON concentration (mg-N/L)	Reference
Yangshupu DWTP		
- Raw water	0.34	Xu et al., 2011
- Treated water	0.21	
Moorhead WTP		
- Raw water	0.33	Wadhawan et al., 2014
- Treated water	0.23	
Zhejiang WTP		
- Raw water	0.52	Xue et al., 2014
- Treated water	0.38	
28 raw water of DWTP in U.S.	0.19	Lee et al., 2006

2.5.5 The relationship between DON and water quality parameter

Previous studies shown that common water parameters such as DOC/DON ratio and SUVA may serve as indicator for source of DON. Low DOC/DON ratio (range from 4 to 14) indicated that the NOM source comprises of nitrogen-rich compounds (autochthonous DON sources) which are less hydrophobic and more marcromolecule biopolymer produced from microbial activity, eutrophication and photoproductivity. On the other hand, high DOC/DON (range from 15 to 56) ratio represents a high allochthonous DON source (Lee and Wasterhoff, 2005; Mash and Westerhoff, 2002; Nissinen et al., 2001).

SUVA value was found to have positive correlation with DOC/DON ratio. Low SUVA result in low DOC/DON ratio which means water had high level of organic nitrogen.

As mentioned earlier, aromatic amino acid including tryptophan and tyrosine are main components of DON. Since amino acid absorb UV light around 220 nm, UV spectroscopy are difficult to resolved nitro and other salt. Fluorescence spectroscopy has been used to characterize aromatic amino acids in water and may be used as surrogate for DON (Mash and Westerhoff, 2002). In addition, it could be used to identify the different sources of NOM (Andrilli et al., 2013)

2.6. Disinfection process and disinfection by product (DBPs)

Disinfection is a process for destruction of pathogenic microorganism and prevention of water diseases contaminated in drinking water and wastewater treatment plant (Angeloudis et al., 2014). There are several disinfectants used in water treatment such as chlorine, chloramine, chlorine dioxide, and ozone. Among them, chlorine is the most commonly used. During disinfection process, DBPs was formed. Different species of DBPs formation was due to different types of disinfectant used in water treatment process (Table 2.4) (Doederer et al., 2014).

Table 2.4 Identification of DBPs from different type of disinfectants.

Disinfectant	**Significant organo-halogen product**	**Significant inorganic products**	**Significant non-halogenated products**
Chlorine	THMs, HAAs, HANs, chloral hydrate, chloropicrin, chlorophenols, *N*-chloramines, halofuranones	Chlorate (mostly from hypochlorite use)	Aldehydes,cyanoalkanoic acids, alkanoic acids, benzene, carboxylic acids
Chlorine dioxide	-	chlorite, chlorate	unknown
Chloramine	HANs, cyanogen chloride, organic chloramines, chloramino acids,	nitrate, nitrite, chlorate, hydrazine	aldehydes, ketones
Ozone	bromoform, MBA, DBA, DBAC, cyanogen bromide	chlorate, iodate, bromate, hydrogen peroxide	aldehydes, ketoacids, ketones, carboxylic acids

Source : WHO (2000)

2.6.1 Chlorination

Chlorination is a widely used for water disinfection. Chlorine is chemical disinfectant was reacted with organic compounds in water to produce DBPs, which are known to be carcinogenic and/or mutagenic substances. The most frequency found of DBPs during chlorination are THMs and HAAs. Previous study reported that HANs increased during the chlorination with high concentration of DON (Chuang et al., 2013).

2.6.2 Chloramination

Chloramination is an alternative method of disinfection process. Monochloramine (NH_2Cl_2) was used as a disinfectant. Chloramination usually provide lower concentration of DBPs than chlorination (Boorman et al., 1999; Yang et al., 2012). Similar to chlorination, chloramination can cause the formation of THMs, and HAAs (Tchobanoglous et al., 2014). Moreover, it can promote the formation of NDMA, and cyanogen halides. DCAN as HANs species has been reported in chloramination water at the concentration of 0.03 µg/L which lower than the concentration in chlorination process (0.11 µg/l) (Lee and Wasterhoff, 2005).

2.6.3 Disinfection by product (DBPs)

Most of DBPS results from the use of chlorine as disinfectant. The concentration of chlorinated DBPs produced form the reaction of chlorine and natural organic matter is shown in Table 2.5

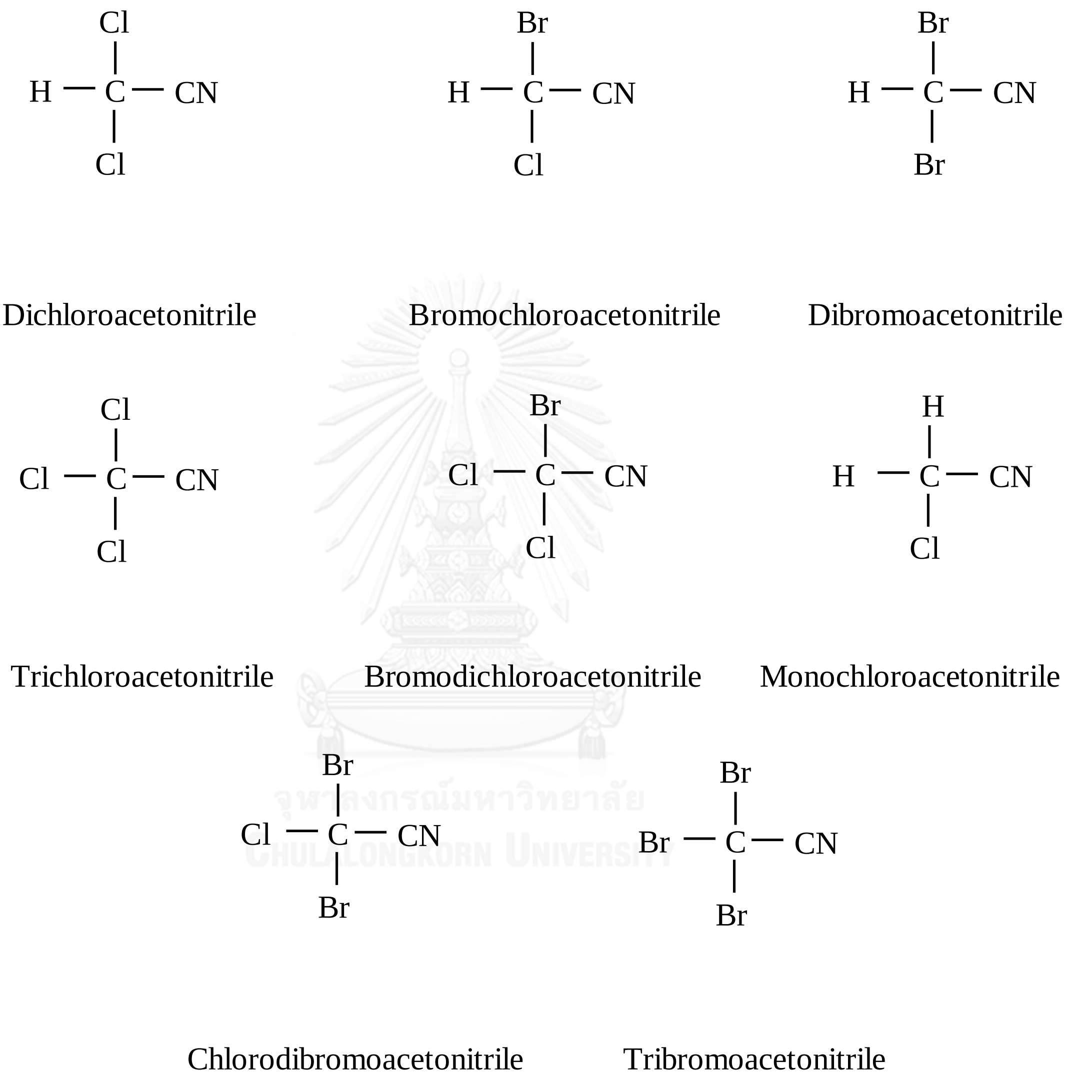
Table 2.5 Summary of chlorinated DBPs concentrations in drinking water from (μg/L)

DBPs	Peters et al (1990)	Krasner et al.(1989)	Nieminski et al. (1983)	Koch et al. (1991)	Reckhow et al. (1990)
THMs	3.1-49.5	30.0-44.0	17.0-51.0	49.0-81.0	201-1280
HAAs	<0.5-14.7	13.0-21.0	5.0-25.0	22.0-32.0	118-1230
HANs	0.04-1.05	2.5-4.0	0.5-5.0	2.0-2.6	3.0-12.0
Haloketones	-	0.9-1.8	0.2-1.6	1.0-2.0	4.8-25.3
Chlorophenols	-	-	0.5-1.0	-	-
Chloralhydrate	-	1.7-3.0	-	-	-
Chloropicrin	-	0.1-0.16	<0.1-0.6	-	-

Source: adopted from WHO (2008)

2.6.3.1 Haloacetonitrile

HANs are nitrogenous disinfection by product (N-DBPs) of drinking water treatment. HANs was produced from the reaction between organic nitrogen compound (such as amino acid) and chorine, chloramines/bromine in the disinfection processes (Ahmed et al., 1991; Prarat, 2011).The composition of HANs concentration with THMs and HAAs was observed. The results found that the mass of HANs typically represent around 10% of the THMs (Prarat et al., 2013). There are several HANs species including chloroacetonitrile (CAN), dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), bromoacetonitrile (BAN), dibromoacetonitrile (DBAN), bromochloroacetonitrile (BCAN), and iodoacetonitrile (IAN)(Muellner et al., 2007). Figure 2.2 shows the chemical structure of HANs species. In drinking water, CAN, BAN, DCAN, BCAN, DBAN, TCAN, and DBCAN were found in US drinking water. Among them, DCAN was the predominant species (Table 2.6) (Templeton et al., 2010).



Dichloroacetonitrile

Bromochloroacetonitrile

Dibromoacetonitrile

Trichloroacetonitrile

Bromodichloroacetonitrile

Monochloroacetonitrile

Chlorodibromoacetonitrile

Tribromoacetonitrile

Figure 2.2 Molecular structure of HAN species

Table 2.6 The concentration of HANs found in drinking water.

Haloacetonitrile	HANs (µg/L)		
	Templeton et al. 2010	**Bougeard et al. 2010**	**Chu et al. 2011**
CAN	0.9	-	N.D.
BAN	0.2	-	-
DCAN	12.0	3.0	8.5
BCAN	3.0	-	N.D.
DBAN	2.0	0.2	N.D.
TCAN	0.4	0.1	N.D.
DBCAN	0.6	-	-

2.6.3.2 Toxicity of HANs

HANshas been reported to be about 5000 times more cytotoxic and genotoxic than C-DBPs such as THMs and HAAs (Huang et al., 2013; Rieder, 2007)

Figure 2.3shows the result of cytotoxicity and genotoxycity of Chinese hamsters overly cells (CHO) for seven HANs. Based on the test of CHO cell density and single cell gel genomic DNA damage, brominated and di- and tri-halogenated HANs were more toxic than chlorinated HANs. The order of genotoxic activity was DBAN > BCAN > TCAN > DCAN > CAN.

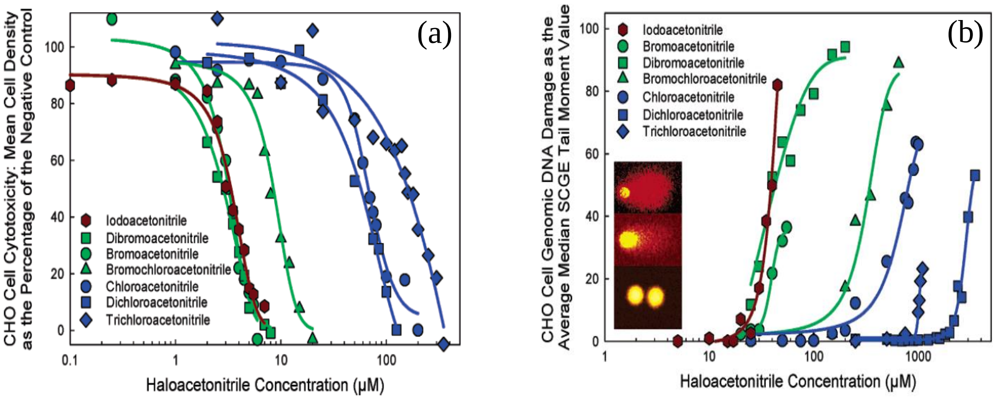


Figure 2.3 (a) Seven HANs analyzed with CHO cell chronic cytotoxicity concentration and (b) SCGE genotoxicity concentrations relative with seven HANs formation (Mueller et al. 2007)

2.6.3.3 Regulation of HANs

Recently, the regulation of HANs contamination in drinking water are not available. However, The World Health Organization (WHO) has published drinking water guidelines for two HANs including a guideline of 70 μg/L for DBAN and 20 μg/L for DCAN based on sub chronic study in rat (WHO, 2008).

2.7. The relationship between water quality parameter and N-DBP precursor

2.7.1 Dissolved organic carbon (DOC) and UV absorbance at 254 nm

The absorbance of the natural water at UV wavelength 254 nm (UV_{254}) could be used to predict the formation of DBPs. Increased DOC and UV_{254} leads to increased of C-DBPs level. (Matilainenetal., 2011; Uyguner-Demirel et al. 2001, Bond et al., 2014). High SUVA values represent the hydrophobicity (less nitrogen content). While low SUVA values indicate more organic nitrogen content (e.g. DON) in water causing the increment of N-DBPs (Uyguner-Demirel et al., 2011). High value of SUVA and UV_{254} mean that the main NOM source was mainly composed of humic substance (hydrophobic), resulting in the formation of C-DBPs during chlorination process.

(Westerhoff et al., 2004). In contrast, the lower value of SUVA can indicated to NOM source was non-humic substance (more nitrogen enriched), causing N-DBPs formation which has more toxicity than C-DBPs. (Dotson et al, 2009).

However UV_{254}, SUVA, and DOC had a correlation with C-DBP, but the relationship with N-DBPs have not been fully investigate (Roccoro et al., 2011). Some previous study reported a weak correlation between UV_{254} and HANFP with $R^2= 0.45$. Some studies found a strong correlation of UV_{254} and dihaloacetonitrile formation potential (DHANFP). The correlation of UV_{254} and HANFP ($R^2 = 0.95$) was depends on properties of water.

2.7.2 Dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) ratio

The DOC/DON ratio has correlation with SUVA trend. The DOC/DON ratio and SUVA value were increased in nitrification process while decreased in denitrification process. The DOC/DON ratio was used to predict the precursor of N-DBPs. Low value of DOC/DON represents N-DBPs precursor. (Westerhoff and Mesh, 2002). However, the basic parameter (e.g. DOC, DON, UV_{254}, and SUVA) could not use to identify the precursor of N-DBPs such as amino acids. Thus, a fluorescence properties was applied as an alternative parameter (Chen, 2007).

2.7.3 Fluorescence spectroscopy

Fluorescence spectrophotometer based on excitation-emission matrix (EEM) DBPs in NOM water. The difference in peak intensity was used to determine the specific precursor profile was shows in table 2.7 (Roccaro et al., 2011).

Table 2.7 Fluorescence peak intensity with vary the Range of excitation and emission (nm)

Peak		**Range of excitation (nm)**	**Range of emission (nm)**
Humic-like	: Peak A	237-260	400-500
Humic-like	: Peak C	300-370	400-500
	Peak C_1	320-340	410-430
	Peak C_2	370-390	460-480
Tyrosine-like	: Peak B_1	225-237	309-321
	Peak B_2	275	310
Tryptophan-like:	Peak T_1	275	340
	Peak T_2	225-237	340-381
Humic (marine):	Peak M	290-310	370-410

The composition of organic matter can be presented as a pattern of fluorescence peak. It can be divided into 2 main part of natural fluorescence including 1) peak A and C (defined as humic and fulvic- like) and 2) peak T and B, which defined as tryptophan and tyrosine like (Bieroza et al., 2009). The model compounds such as tryptophan, aspartic acid were used to study the HANFP since they are potential to be a precursor of HANs. The result from peak intensity show precursor of DCAN was in the peak T, which indicative of amino acid like fraction. (Swietilk and Sikorska, 2004).

Understanding of the impact of treatment process on the fluorescence of the wastewater is require to determine the nature of residual fluorescence signal and used the fluorescence result to predict the N-DBPs and used to monitoring tool of wastewater treatment plants, for instance, the clarification process, has decrease T_1 and T_2 intensity similar to advance treatment process could be decrease of all intensity fluorescence.

As mentioned earlier DON was a precursor of N-DBPs. Some previous studies has been reposted the oxidation of DON to form N-DBPs (Table 2.8). It is could be confirm that DON may a precursor of N-DBPs during chlorination process

Table 2.8 Oxidation of DON on formation of N-DBPs

Nitrogen component	Oxidant	DBPs
Purine and pyrimidines	NaOCl	HANs, HAA
Amino acids, proteins, humic acids	NaOCl	HANs, THMs
Algae, Fulvic acid	NaOCl	DXANs, THMs
Humic and fulvic acid	HOCl	TOX, $CHCl_3$, TCAA, DCAN

2.7.4 Factors influencing the formation of N-DBPs

2.7.4.1 pH

The effect of pH on the formation of DBPs is shown in table 2.9. For example; the concentration of DCAN and CNCl was slightly reduced at pH range from 7.5-9. While a high level of them was observed at pH 5 (Bond et al., 2014)

2.7.4.2 Bromide

Bromide plays an important role in the formation of N-DBPs. (bromide) it can cause DCAN formation up to 95 % in autochthonous source. NOM source can salter the function and structure of N-DBPs For example, the distribution of DHAN was change from DCAN to BCAN. The formation of other bromine-containing DBPs depend on the pH, contact time, and monobromamine or dibromamine dose (Yang et al., 2012).

Table 2.9 Effect of pH on N-DBPs

N-DBPs group	pH effect
Haloacetonitrile	More stable at acidic pH. Hydrolysis at high pH except DCAN.
Haloacetamides	Uncertain but presumably hydrolysed at alkaline pH
Halonitromethanes	Chloropicrin formation decrease with pH
Cyanogen halides	High formation at acidic condition. Unstable in the present of chlorine.
Nitrosamines	Chlorine enhances nitrosation, especially at neutral pH.Nitrosation itself increase with pH but normally lilted by formation of nitrosating agent.

Source : Bond et al. (2011)

2.7.4.3 The impact of treatment process

The removal of N-DBPs precursor has become important to control N-DBPs formation in wastewater treatment plant and drinking water treatment plant. The most composition of N-DBPs precursors was content nitrogen enrich in NOM source (e.g. DON), which is hydrophilic function (Chang et al., 2013). Conventional treatment process such as coagulation filtration and disinfection has been ineffective to reducing DON concentration (Chu et al., 2011). In addition, the SMP, source of DON requires the biological treatment process to reduce SMP concentration.

The ozonation process was also correlated with the formation of N-DBPs due to an increase in BDON (Wadhawan et al. 2014). A possible explanation is that ozone cleaves larger algal and bacteria soluble into smaller part and increase in BDON concentration (Bond et al. 2011; Chu et al., 2011)

Dotson et al. (2009) isolate NOM fraction from nitrogen rich sources and test formation potential of N-DBPs. the result shows that DCAN was appeared high concentration after chlorination process with highest yields from the most nitrogen rich fraction (hydrophilic). DCAN and other haloacetonitrile are produce form the chlorination of free amino precursor as well (Bond et al., 2012).

In conclusion, conventional treatment process such as coagulation and filtration are ineffective for removing DON concentration and N-DBPs precursors. Therefore, advance treatment process such as membrane, nano-filtration, and biological treatment process are more appropriate to remove DON concentration.

CHAPTER III

MATERIALS AND METHODS

3.1 An experiment framework

The experiment framework in this study is divided into 2 main parts. The first part is the study of the characteristic of raw water and treated water in each process of WTP in order to describe the properties of original water and the relationship with the HANs formation potential. The second part is the investigated of BDON contributing to HANs formation in filtrated water and ozonated water. The framework of this research is shown in Figure 3.1

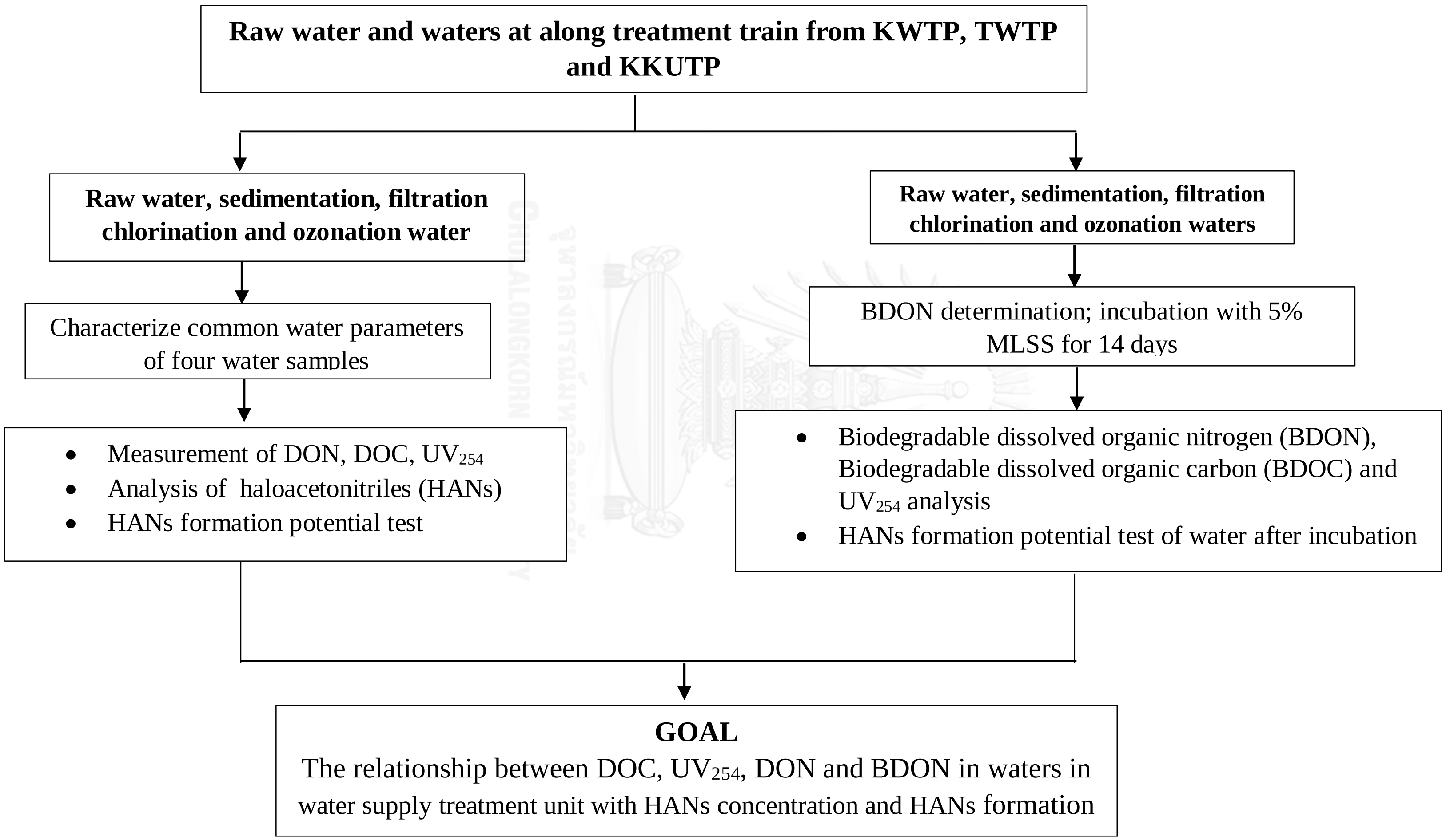


Figure 3.1 An expriment framework

3.2 Glassware

All glassware were washed with detergent, rinsed with tap water, kept in a 10% v/v HCl bath overnight and finally rinsed with de-ionized (DI) water. The washed glassware were dried overnight at 103-105 ^{o}C and then covered with aluminum foil.

3.3 Water treatment processes

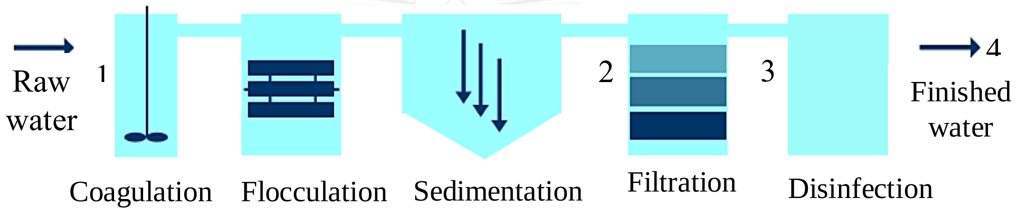
Water samples were obtained from three water treatment plants, which are Kota Water Treatment Plant (KWTP), Thapra Water Treatment Plant (TWTP) and Khon Kaen University water treatment plant (KKUWTP) in Khon Kaen Province. KWTP and TWTP plants produce water supply for Khon Kaen Metropolitan and KKUWTP produces water supply for 50,000 campus population and all facilities in Khon Kaen University. KWTP has a capacity of 139,200 m^{3}day^{-1}. The plants used raw water from Ubolratana dam. TWTP has a capacity of 48,000 m^{3}day^{-1}and used raw water from the Chi River. KKUWTP has a capacity of 8,000m^{3}day^{-1}. All plants have the same treatment process consist of raw water, coagulation and flocculation, sedimentation, sand filtration and disinfection unit. A scheme of treatment process is shown in Figure 3.2.

Polyaluminum chloride (PAC) was used as a coagulant for all plant. Chlorination is applied for KWTP and TWTP while chlorine dioxide was used for KKWUTP.

3.4 Water sample collection

Water samples from three plants were collected from four different processes including 1) raw water, 2) after sedimentation, 3) after filtration, and 4) after chlorination/chlorine dioxide disinfection along the conventional treatment process of

KWTP, TWTP and KKUTP (Figure 3.2). All samples were filtered through a 0.2 µm cellulose acetate membrane within an hour after collection. The water sample has high turbidity, sample was filtered through glass fiber filter (GF/C) before filtering by 0.2 µm membrane flitter. The filtrated water samples were used to determine DIN, DON, and DOC. Sampling period of DOC, TDN, DON were from November 2014 to May 2015 which in dry season. For BDON, HAN and specific HANFP analyses, analytical procedures were successfully developed at the latter stage of the research. Therefore, the water samples were collected from April - May 2015.



Sampling location: 1,2,3,4

Figure 3.2 Conventional water treatment scheme.

3.5 Analytical methods.

3.5.1 DOC, TDN and UV_{254} analyses

Concentration of DOC and TDN were measured using an organic carbon analyzer (TOC multi N/C 2100, Analytic Jena, Germany). UV absorbance at 254 nm was measured with a UV-visible spectrophotometer (DR-6000, HACH, USA).

3.5.2 DIN and DON determination

DON was determined by subtracting TDN concentration with sum of DIN (NH_3-N + NO_2-N + NO_3-N) concentrations as shown in Eq 3.1.

$$\text{DON (mg/L as N)} = \text{TDN} - (NH_3\text{-N} + NO_2\text{-N} + NO_3\text{-N}) \qquad (3.1)$$

(i) Ammonia (NH_3) was measured by phenate method and ammonium chloride was used to prepare standard ammonia solutions (APHA et al., 2005). The procedure was described following;

1) 25 mL of samples were used

2) Add 1 mL of phenol solution follow by 1 mL sodium nitroprusside.

3) Add 2.5 mL alkaline hypochlorite solution to the samples and leave it for 1 hour.

4) Measure UV absorbance at wavelength of 640 nm after 1 hour using spectrophotometer (DR-3000, HACH, USA).

(ii) Nitrite (NO_2^-) in the samples was analyzed by a Standard Method 4500-NO_2,B colorimetric method (APHA et al., 2005)following;

1) 25 mL samples were add in Erlenmeyer flask.

2) Add2 mL color reagent was pipetted into a samples.

3) Incubated in the dark for 10 min.

4) Measure UV absorbance at wavelength of 540 nm after 1 hour using spectrophotometer

5) Sodium nitrite was used for preparation of nitrite standard.

(iii) Nitrate (NO_3^-) was analyzed by spongy cadmium reduction method (Jones, 1984)which modified and use to reduce NO_3-N to NO_2-N. Spongy cadmium was prepared by stand zinc stick (Sigma Aldrich, USA) into a 20% (w/v) solution of cadmium sulfate overnight. The cadmium deposited on the zinc sticks was scrapped and used for nitrate analysis. Spongy cadmium was kept in DI water before used. Potassium nitrate was used as standard. The procedure was following below;

1) 25 mL of sample was added into 50 mL centrifuge tube

2) Add 5 mL of 0.7 M ammonium chloride was added follow by 1 g of wet spongy cadmium.

3) The mixture was shaken at 200 rpm for 90 min at room temperature.

4) Pipetted samples 10 mL and add 2.5 mL of color reagent, incubated in the dark for 10 min.

5) Measure UV absorbance at wavelength of 540 nm after 1 hour using spectrophotometer

The value obtained in this step was the nitrite concentration (reduced from nitrate plus original nitrite). The concentration of nitrate was subtracted with original nitrite concentration that was determined separately.

Biodegradable dissolved organic nitrogen (BDON) was developed from Khan et al. (2009).BDON is calculated from the difference between initial DON (DON_I) and final DON (DON_f) after incubation Eq. 3.2.

$$BDON = (DON_i - DON_f) - (DON_{bi} - DON_{bf}) \qquad (3.2)$$

Where, DON_i and DON_f are DON before and after incubation

DON_{bi} and DON_{bf} are DON_{bf} before and after incubation of blank

Sample for BDON was prepared by filtrating through 0.2 μm pore size cellulose acetate. Two hundred milliliters of each filtrated were inoculated with 2 ml of 5% mixed liquor suspended solids (MLSS) obtain from WWTP. The mixture was incubated at 20^{o}C in dark amber bottle 14 day after incubation were used to determined DON final (DON_T) during incubation periods (Figure 3.3), the solution in bottle was shaken to aerate at least once a day to maintain aerobic conditions (Halis et al., 2012)

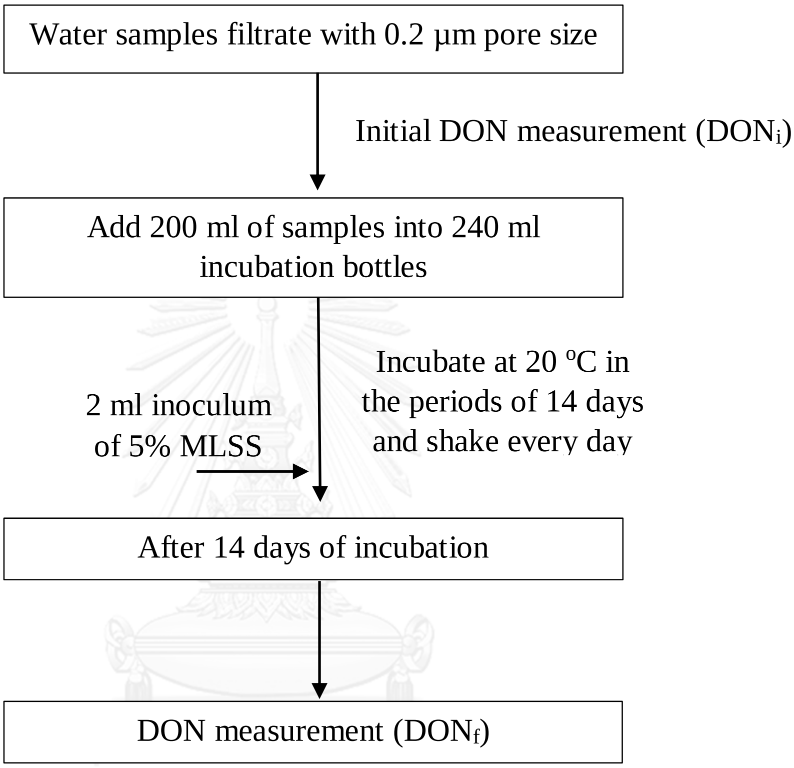


Figure 3.3 BDON experiment procedure

3.6 Ozonation experiments

Ozone was generated from self-mode ozone generator based on the principles of the photolysis of oxygen by UV at wavelength 185 nm. Ozonation was applied to water samples after sedimentation processes. The location of water samples was chosen based on practical application of ozone in water treatment plant that always between after sedimentation basin and before filtration. Ozonation helps in removal of taste and odor compounds and also increases the biodegradability of organics which later will be removed in biologically active filter. Ozone dose 0.6 mgO_3/ DOC was applied to 2 L of sample through glass diffuser. After ozone dose was transfers in water samples, ozonated samples were stored at 4 °C for no more than 24 hours before analysis.

3.7 HANs formation potential

The HANFP experiments were conducted under an excess of chlorine dosage. during reaction time of 24 hours, 25 °C at pH 7.0 (Figure 3.4) The water sample were buffered using phosphate buffer. The reason why the formation potential test conducted at 24 hours in this study. It was because the distribution systems in the real situation that contributed the samples to consumers was about 1 days (24 hours).

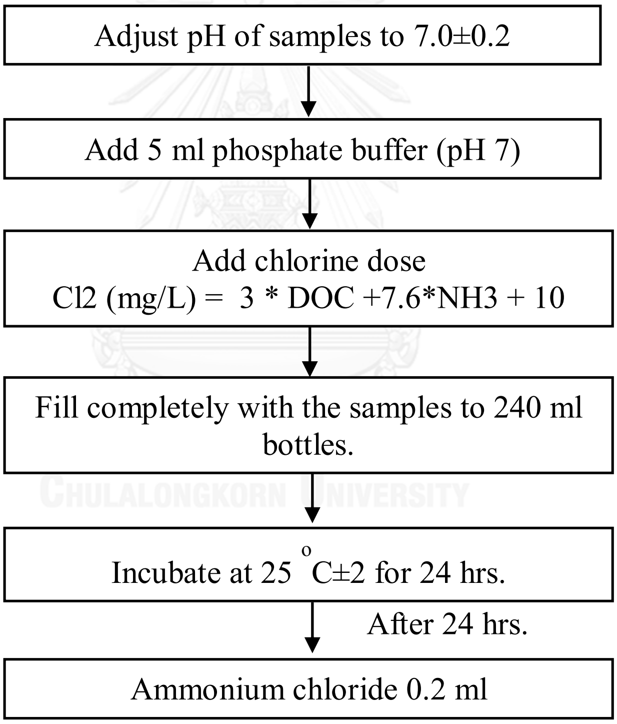


Figure 3.4 The formation potential test diagram

The chlorine dose added to samples was based on the DOC and ammonia concentration plus 10 mg/L extra chlorine. This was to ensure that the final residual chlorine of 3-5 mg/L remained in the samples after incubation periods of 24 hours (Chen and Westerhoff, 2010) as show in the following equation 3.3:

$$\text{Chlorine dose (mg/L)} = (3 \times \text{DOC}) + (7.6 \times \text{NH}_3\text{-N}) + 10 \qquad (3.3)$$

The chlorine dose was used in this study base on the DOC and NH_3 only one water samples of raw water from KWTP and used the same chlorine dose to the formation potential test which the chlorine dose of 25 mg/L. After incubation 24 hours (similar to typical hydraulic retention time in distribution system), the samples were quenched with ammonium chloride (NH_4Cl). Chlorine residue was tested with DPD Ferrous Titrimetric method (4500-Cl^- F, APHA, 2005). In this study chlorine residue of the water samples range from 4.25 to 4.60 mg/L.

3.8 HANs analysis

The water samples were extracted using a liquid/liquid extraction method and analyzed by a gas chromatograph (GC) equipped with an electron capture detector (GC-ECD) system (Agilent 4890 D). The GC column used was a SPB-608 fused silica capillary column (30m x 0.53 mm x 0.5 µm). Helium was a carrier gas (EPA 551.1). The temperature program was started at 40 ^{o}C for 2.5 min, and then running up to 240 ^{o}C for 1 min at the rate 40 ^{o}C/min. Injection volume was 1.0 µL. The detection limit of three HAN (TCAN, MCAN, DCAN) was 0.25 µg/L and DBAN was 0.1 µg/L. the retention time for TCAN, MCAN, DCAN, and DBAN was 1.3, 1.8, 2.0, and 4.5 minutes. The HANFP was calculated from HAN divided by DON which defined as specific HANFP (µg/mg).

CHAPTER IV

RESULTS AND DISCUSSIONS

4.1 Water quality characteristics

4.1.1 Source water quality parameters.

The results of water quality parameters in raw water samples collected from three water treatment plants of Khon Kaen Municipality including Kota water treatment plants (KWTP), Thapra water treatment plants (TWTP) and Khon Kaen University water treatment plants (KKUWTP) were presented in Table 4.1.

Table 4.1 Characteristics of raw water at KWTP, TWTP and KKUWTP

Parameters	**Units**	**KWTP**	**TWTP**	**KKUWTP**	**n**
Temperature	^{o}C	32.3±0.82	31.8±1.60	32.1±1.38	10
pH	-	7.67±0.82	7.72±0.35	7.69±0.30	10
Alkalinity	mg/L as $CaCO_3$	92±12.27	98±5.96	93±7.96	10
Hardness	mg/L as $CaCO_3$	84±4.34	93±10.68	85±9.82	10
DOC	mg-C/L	5.60±0.76	5.36±0.83	6.20±0.74	10
BDOC	mg-C/L	2.23±0.23	1.78±0.09	1.40±0.37	4
UV_{254}	cm^{-1}	0.111±0.01	0.094±0.28	0.121±0.01	10
SUVA	L/mg.m	2.01±0.32	1.80±0.42	2.04±0.28	10
TDN	mg-N/L	0.94±0.1	0.72±0.1	0.84±0.1	10
DIN	mg-N/L	0.36±0.10	0.124±0.05	0.34±0.13	10
DON	mg-N/L	0.58±0.11	0.57±0.13	0.52±0.21	10
BDON	mg-N/L	0.27±0.19	0.36±0.04	0.21±0.06	4
DOC/DON	mg/mg	10.72±3.6	10.05±2.53	12.44±2.91	10

Average value ± standard deviation, n = number of sample

The surrogate water parameter such as dissolved organic carbon (DOC), dissolved organic nitrogen (DON), UV_{254} and SUVA were used to categorize the natural organic matter (NOM) properties. There surrogates were able to predict a precursor of DBPs in water treatment plants. DOC represents the amount of organic carbon content in water. High level of DOC could lead to more formation of DBPs during disinfection process. Typically, the concentration of DOC in surface water such as rivers and lakes ranged from 2 to 15 mg/L (Degens, 1982). DOC concentrations of raw water from these three water treatment plants were from river and ranged between 5-6 mg/L (Table 4.1). This level is considered to be moderate. When comparing of average DOC concentrations of raw water of US and China (3.44 and 4.95 mg-C/L) (Lee, 2006; Xue et al., 2014), the values of DOC from this study were little bit higher.

In this research, the UV_{254} and SUVA were in the range of 0.094-0.121 cm^{-1}, and 1.80-2.04 L/mg.m, respectively. UV_{254} indicates the unsaturated carbon structure including double carbon bond and aromatic as well as hydrophobicity. SUVA represents the term of UV_{254} normalized with DOC of water sample. This is to be able to compare the aromaticity of the water from different sources. The high SUVA (2-4) indicated that the water sample contains humics substances and mixture of hydrophobic and hydrophilic organic compounds (Edzwald and Tobiason, 1999). For this study, the SUVA values were about 2 or less. The low SUVA values (<2) mean that organic content is mainly consist of non-humics, low hydrophobicity, and low molecular weight compounds (Edzward and Tobiason, 1999).

DON concentrations of three raw waters were in the ranged of 0.52-0.58 mg-N/L. These values were higher than an average DON concentration reported in US. (0.186 mg-N/L) and China 0.34 mg-N/L)(Lee, 2006; Xue et al., 2014).DOC/DON ratios of KWTP, TWTP and KKUWTP were 10.72, 10.05, and 12.44 mg/mg, respectively.DOC/DON ratio serves as indicators of nitrogen content in water sample. The United State Geological Survey’s database reported that water with the high ratio of DOC/DON (15-56) has low nitrogen content. It implied that this kind of water source has more hydrophobic content, which derived from plant, soil contribute to NOM (allochthonous NOM source). However, low DOC/DON (4-14) ratio means water is rich in nitrogen. The organic content with low DOC/DON water is derived from algae or bacteria aquatic NOM (autochthonous) (Mash and Westerhoff, 2002; Xu et al., 2010; Xue et al., 2014).The result of DOC and DON concentration in Khon Kaen water treatment plants could implies that there are a significant amount of organic nitrogen and organic carbon carried over to finish water and possible to form C-DBPs and N-DBPs such as THMs, HAA or HANs during chlorination process, thereby increasing the number of health risk effect.

Although the seasonal variation could affect the composition of NOM in the water system, the effect of seasonal may be minimum due to the sampling time during in the study was the dry season which from November 2014 to May 2015. It might not significantly change the effect of NOM properties such as DOC and DON concentration in the water samples.

4.2. Fate of dissolved organic carbon (DOC) and SUVA along treatment processes

4.2.1 Dissolved organic carbon along treatment processes

Figure 4.1 (a-c) shows the average DOC concentration profiles of ten water samples of raw water, after sedimentation, after filtration, and after chlorination of KWTP, TWTP and KKUWTP, respectively. It was noticed that the reduction of DOC concentrations were quite small in each step of water treatment process. Overall removal efficiencies of DOC in finished water were 12.52%, 16.57% and 19.00% in KWTP, TWTP and KKUWTP, respectively. These three plants used polyaluminium chloride (PAC) as coagulant. Although, PAC is an effective and common coagulant used in water treatment, low DOC removal efficiency could happen like in this study. There are several factors influencing the DOC removal efficiency by coagulation process. For example, PAC has been reported to be more effective at low temperature of 10-15 °C (Minear and Any, 1995). In this work, the temperate of water was about 30-32 °C. Another important factor is the characteristic of NOM in water itself. Based on the DOC concentrations and SUVA values (<2 L/mg.m), the organic content in water was mainly non humics, hydrophilics, low molecular weight organic compounds. This type of organic was reported to have poor removal by coagulation process. Edzwald and Tobiason (1999) reported that less than 25% removal of DOC can be achieved by alum for this type of water. Sand filtration also took part in DOC removal. The DOC removal in sand filter might be due to the removal of colloidal organic or biodegradable organic carbon. Again, the efficiency of sand filter was very minimum.

4.2.2 Specific UV-absorbance (SUVA) along water treatment processes

The values of SUVA was found to be good representative for hydrophobic, aromatic acid and aromatic carbon (Czerwionka et al., 2012; Fleck et al., 2004). were shown in Figure 4.2(a-c), respectively. Removal efficiencies of SUVA from raw water to finished water of three plants were higher than DOC reduction (34.34% for KWTP, 26.43% for TWTP and 22.55% for KKUWTP). Note that substantial reduction of SUVA occurred in coagulation and sedimentation steps. This suggested that the unsaturated or aromatic carbon substances (e.g. primary UV absorbing compound) were favorable to be removed by coagulation. Figure 4.2a, the large reduction of SUVA was found in sample after chlorination of KWTP. This could imply that organic content compose of SUVA was reactive to oxidant/disinfectant such as chlorine.

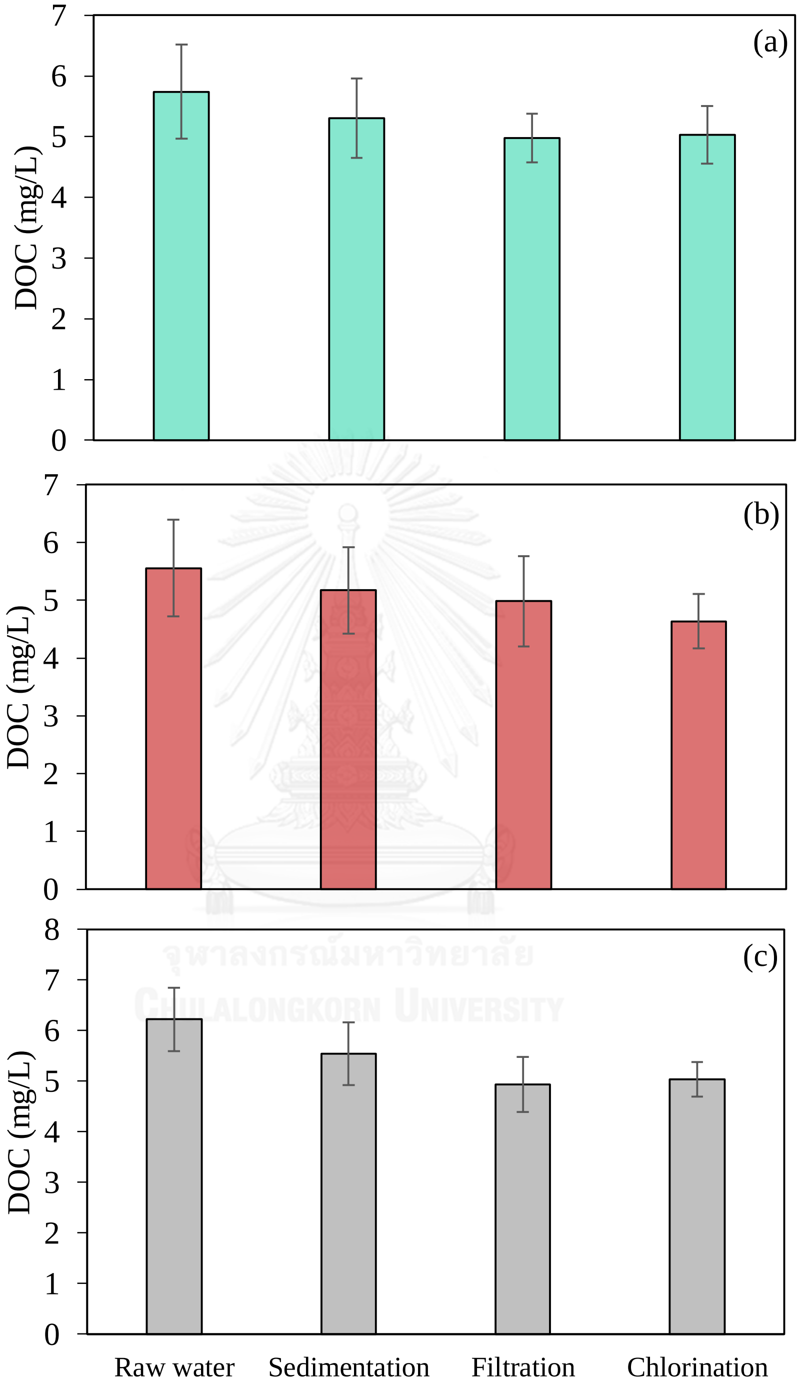


Figure 4.1 Concentration of DOC in different treatment process in (a) KWTP (n =10), (b) TWTP (n =10) and (c) KKUWTP (n = 8)

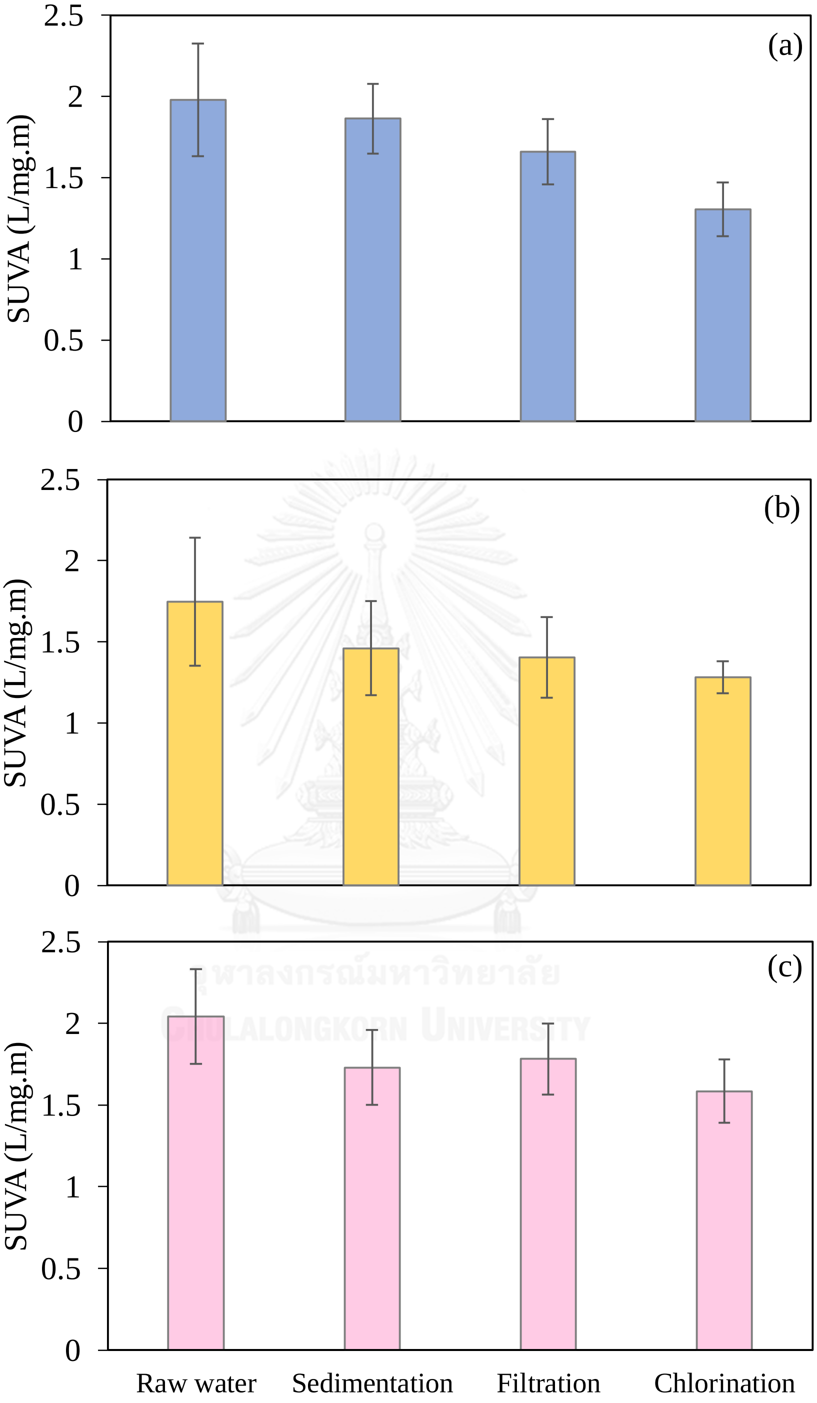


Figure 4.2 SUVA values in different treatment process in (a) KWTP (n =10), (b) TWTP (n =10) and (c) KKUWTP (n =10)

4.3 Fate of inorganic nitrogen species (DIN), total dissolved nitrogen (TDN) and dissolved organic nitrogen (DON) along treatment processes

4.3.1 Dissolved inorganic nitrogen (DIN) and TDN concentrations.

Figure 4.3, 4.4, 4.5 shows the fate of DIN and TDN along treatment train of KWTP, TWTP, and KKUWTP, respectively. For KWTP, TWTP, and KKUWTP, the DIN ranged from 0.23-0.36 mg-N/L, 0.09-0.19 mg-N/L, 0.15 - 0.35 mg-N/L, respectively. The amount of DIN in KWTP, TWTP, and KKUWTP accounted for 15-30%, 13-25%, and 17-29% of TDN, respectively. Dissolved inorganic nitrogen is made of ammonia, nitrite and nitrate. From all three water plants, the concentrations of ammonia, nitrite, and nitrate were in the ranges of 0.01-0.07, 0.001-0.01, 0.04-0.33 mg-N/L, respectively. It was found that nitrate was the major component of DIN.

When considering the concentration of DIN species, it was observed that concentration of ammonia decreased along the treatment train (Figure 4.4-4.5 (a)). For example, Ammonia concentrations of KWTP in raw water, samples after sedimentation, filtration and effluent water averaged 0.014, 0.01, 0.007 and 0.001 mg-N/L, respectively. It was noticed that about 92% of ammonia removal occurred during coagulation and sedimentation. Similarly, TWTP and KKUWTP also were found to have majority of ammonia removal (> 60%) in coagulation and sedimentation. The removal of ammonia could be explained by nitrification process occurred in coagulation and sedimentation basins. Some small change of ammonia concentrations was also found after filtration and chlorination. The loss of ammonia could be from assimilation by biomass attached to the filter medium.(W. Lee and Westerhoff, 2006). The reduction of ammonia after chlorination could be from the reaction with chlorine used in disinfection process as described in Eq. 4.1.

$$NH_4^+ + 4HOCl \rightarrow 6H^+ + NO_3^- + 4Cl^- + 3H_2O \qquad (4.1)$$

Nitrate concentrations along the treatment train of three water plants exhibited the interesting trends. Nitrate concentrations for KWTP and KKUWTP appeared to be decreased substantially after coagulation and sedimentation by 33%, and 50%, respectively (Figure 4.3b, and 4.5b). Since PAC was used as a coagulant, the removal of nitrate resulted from the adsorption to the metal- hydroxide precipitates (Lacasa, et al, 2011). However, TWTP, the nitrate concentration was relatively unchanged (Figure 4.4a). This might due to very low concentration of nitrate of raw water to be able to sorbet by PAC floc. Small nitrate increased after filtration could be from nitrification in the filter. However, it was interesting that nitrate concentrations increased after chlorination. The increase of nitrate could not be from nitrification nor oxidation of ammonia since the initial ammonia concentrations were much lower than nitrate formed. Rather, it could be from the oxidation of DON by chlorine in which finally yielded nitrate as an end product. Nitrite concentrations were very minimum and remained quite stable along the treatment train. For TDN (Figure 4.3b-4.5b), there was not much change of TDN concentration profile along the water treatment train. The reduction of TDN of raw water comparing to finished water were 12%, 20%, and 16% for KWTP, TWTP, and KKUWTP, respectively. Slight increase of TDN was found for KWTP and TWTP after filtration. This was probably duo to the release of nitrogen compound from biomass attached to the filter medium. For the fate of DIN, TDN and DON the average concentration of ten times water sampling was determined.

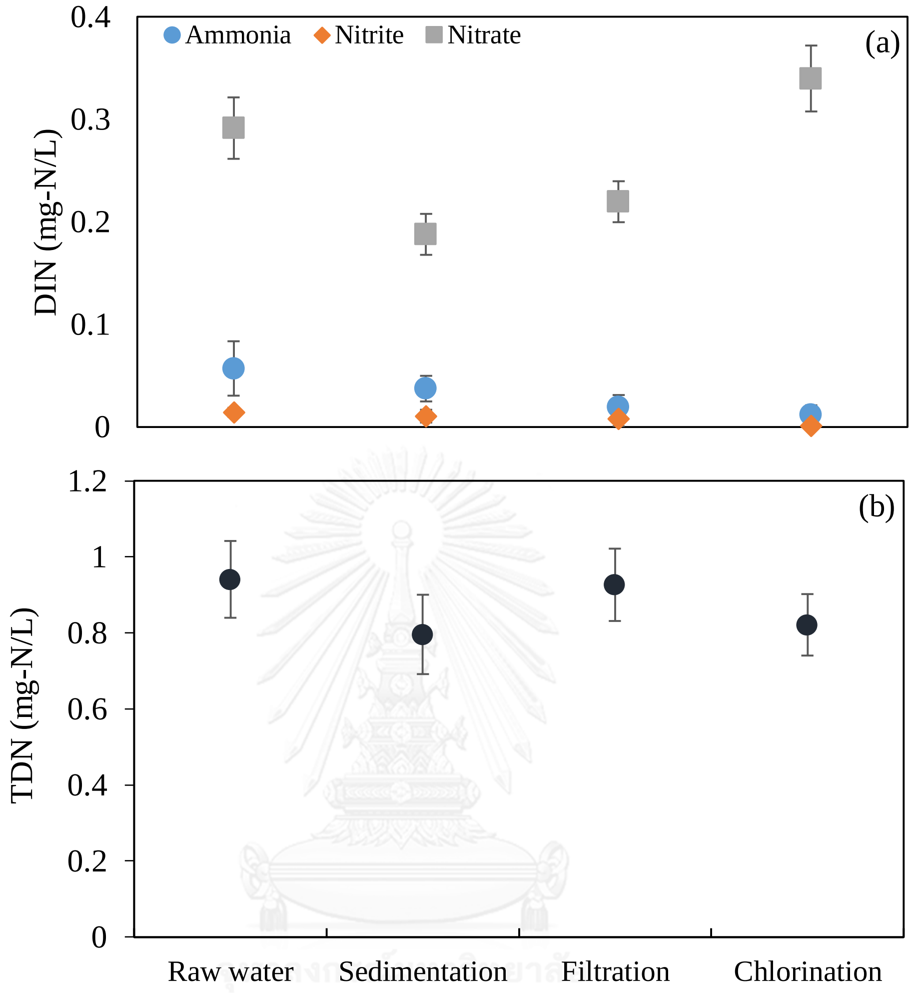


Figure 4.3(a) concentration of DIN and (b) TDN along treatment process trains of KWTP (n=10).

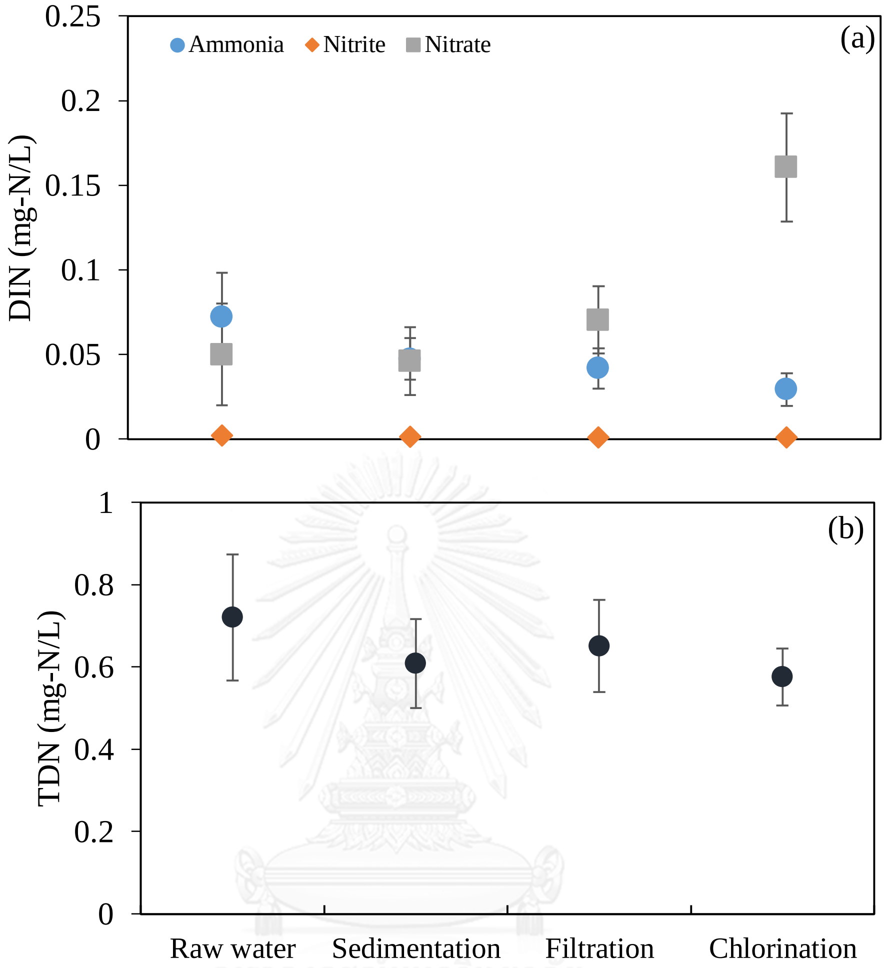


Figure 4.4(a) concentration of DIN and (b) TDN along treatment process trains of TWTP (n=10)

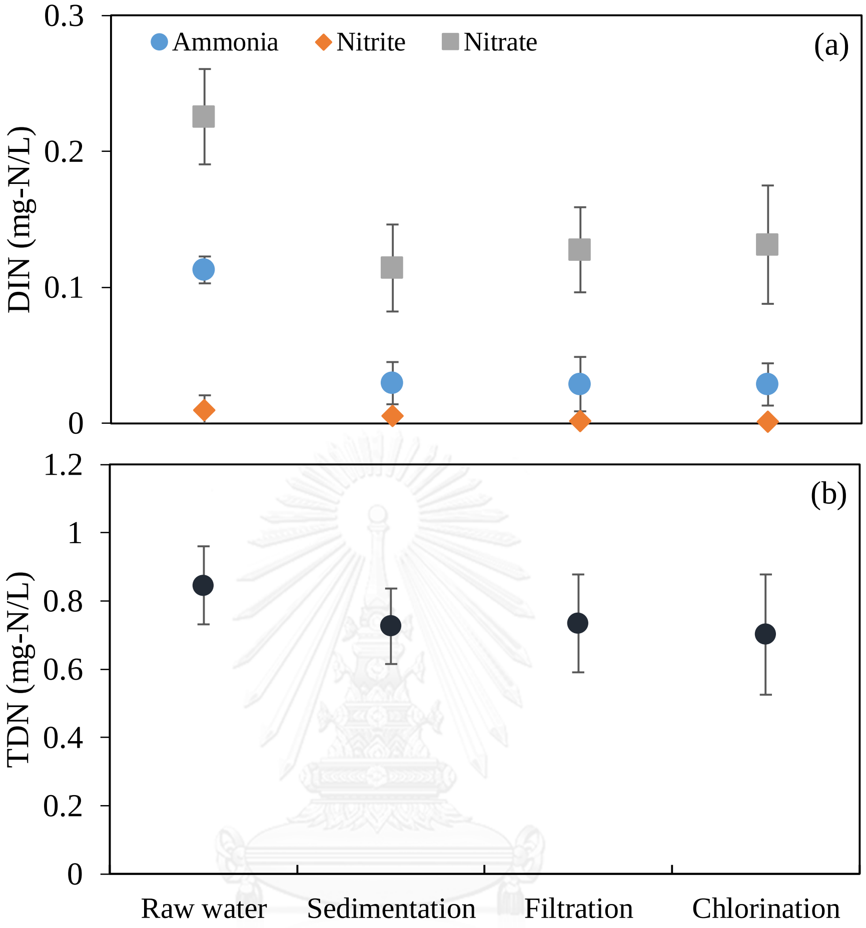


Figure 4.5 (a) concentration of DIN and (b) TDN along treatment process trains of KKUWTP (n=8)

4.3.2 Dissolved organic nitrogen (DON) concentrations.

Typically, concentration of DON in water cannot be determined directly. DON was calculated by TDN –ΣDIN. Therefore, it might collect systematic errors from TDN and all DIN analyses, particularly at low concentration of DON and high concentration of DIN. To improve the accuracy for DON determination, DIN/TDN ratio was recommended not to exceed 0.6 mg/mg (Xu et al., 2010). In this work, the accuracy checked was performed. For KWTP, the DIN/TDN ratios in raw water, sedimentation, filtration and chlorination were 0.38, 0.29, 0.26, and 0.42, respectively. Also the DIN/TDN ratios of TWTP and KKUWTP along treatment train were in the range of 0.15-0.33 and 0.21-0.41, respectively. This indicated good accuracy of DON determination and reliable DON data because DIN/TDN ratios were less than 0.6 mg/mg.

Figure 4.6 (a-c) shows the fate of DON along treatment trains from KWTP, TWTP and KKUWTP. Overall, the profile of DON of three plants generally decreased. For example, average DON concentrations of raw water and the effluent of sedimentation, filtration and chlorination process at KWTP (were 0.58, 0.54, 0.66 and 0.44 mg-N/L, respectively (Figure 4.6 a). The removal efficiency of DON in comparing between raw water and finished water of KWTP, TWTP, and KKUWTP were 24.1%, 31.5%, and 3.84%, respectively. Low removal of DON concentrations was observed for all plants for coagulation and sedimentation processes. The coagulant used in both plants was polyaluminum chloride (PACl). The result suggested that this type of coagulant and/or coagulation plus sedimentation processes may not be effective for removing organic nitrogen(Chu et al., 2011). It was noticed that after filtration process of KWTP, TWTP, KKUWTP, there was small increase of DON concentrations. The explanation could be from microbial activities in the filter that produce soluble microbial products which is a source of DON (Leenher and Croue 2003). After chlorination, some reduction was observed. This could be from oxidation of DON by chlorine which led to nitrate formation. The decreasing of DON concentration in Figure 4.6a of KWTP was approximately the same with the nitrate concentration formed (Figure 4.3a). When comparing of median DON concentration of treated water (0.184 mg/L-N in US) (Lee, 2006) with treated from those three plant, the result showed the comparable values of DON concentrations. These levels of DON suggested that there were certain amount of organic nitrogen presented in finished waters and possible to form N-DBPs such as HANs during chlorination process. Consequently, it increases the health risk effect of consumers.

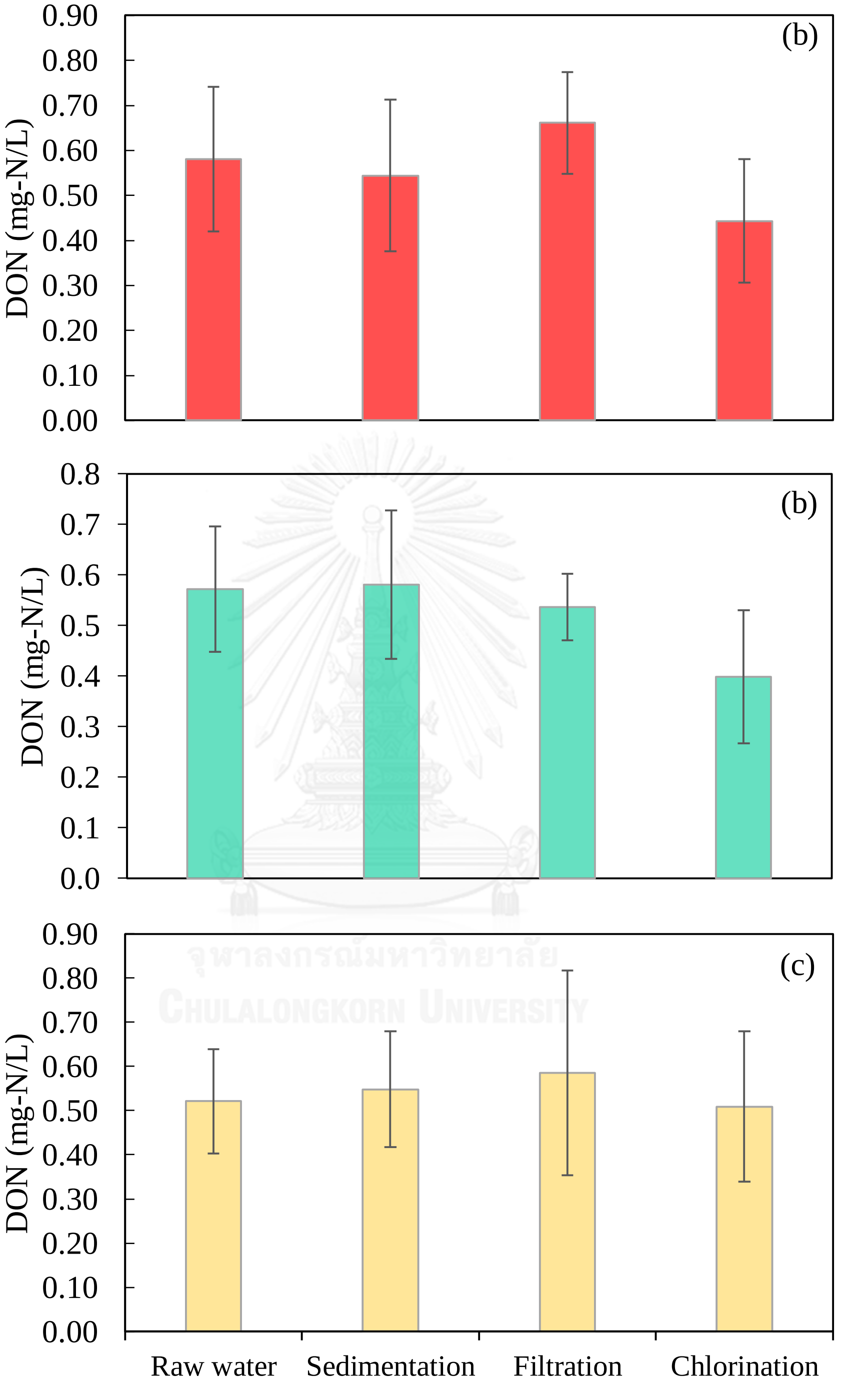


Figure 4.6 Concentration of DON in different treatment process in (a) KWTP (n=10), (b) TWTP (n =10) and (c) KKUWTP (n =8)

4.3.3 DON and TDN correlation

Figures 4.7 (a-c) show the ratio of DON/TDN of water samples along the treatment train of KWTP, TWTP, and KKUWTP, respectively. Overall, the percentage of DON ranged from 53% to 84% of TDN in water samples. This indicated that DON was considered large portion of TDN pool in drinking water. As mentioned earlier, DON is calculated based on the difference between TDN and sum of DIN. This means there are several analyses to be performed to obtain DON value. Therefore, it increase the sum of error associated with analytical methods. High percentage of DON in TDN suggested that there might be a possibility to determine just TDN and used it to estimate DON in drinking water. In addition, measurement of TDN is quite simple and reliable using TOC/TN analyzer. In order to achieve this objective, linear regression between DON and TDN concentrations were determined for the samples along the treatment train (Table 4.2, Appendix B).The results showed that there were variations of correlation coefficients (R^2) among water samples from different stages of water treatment plant. High correlation was found in water samples that had less DIN (Table 4.2). This suggested that the correlation of DON and TDN are depending on type of water samples and water characteristics.

Table 4.2 Correlation coefficient (R^2) values for linear relationship between DON and TDN of all water samples in KWTP, TWTP, and KKUWTP.

Samples	Raw water	Sedimentation	Filtration	Chlorination
KWTP	0.43	0.52	0.34	0.23
TWTP	0.77	0.78	0.26	0.53
KWTP	0.55	0.43	0.53	0.84

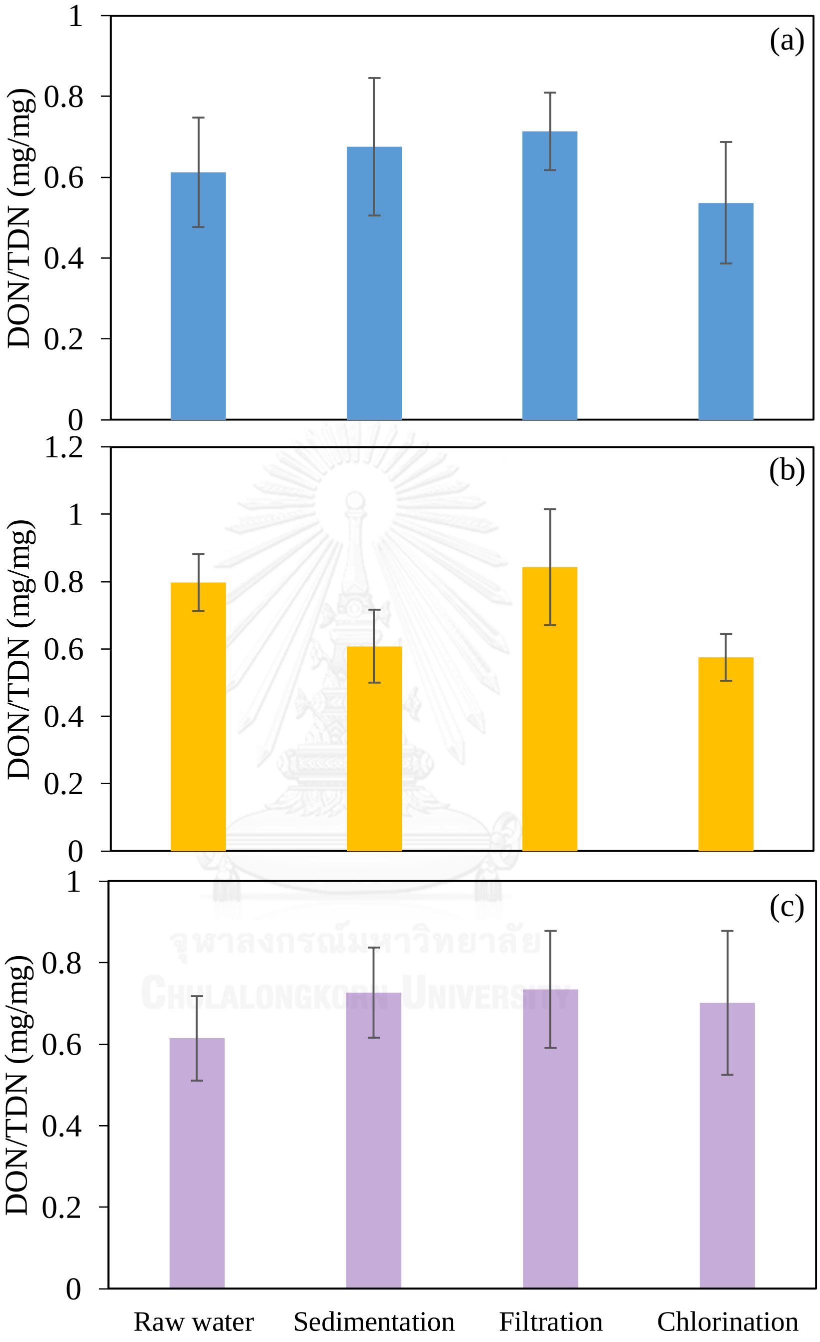


Figure 4.7 DON/TDN values of (a) KWTP (n=10), (b) TWTP (n=10), and (c) KKUWTP (n=8)

4.4 Biodegradable dissolved organic nitrogen (BDON) along water treatment plants

Dissolved organic nitrogen in water samples composed of biodegradable DON and non-Biodegradable DON (NBDON)(Sattayatewa et al., 2009; Simsek, Wadhawan, et al., 2013; Wadhawan et al., 2014). Huo et al. (2013) also reported that about 28-70% of effluent DON was bioavalible or biodegradable. To determine the concentration of BDON and NBDON in the DON profiles,incubation with inoculum of 5% MLSS were used. The concentration of DON before and after incubation was determined. The DON level after incubation was referred as NBDON. BDON was calculated by subtracting of DON before incubation with DON after incubation (NBDON) (Khan et al., 2009). For the control of BDON test, glycine, dominant species of free amino acid (Wadhawan et al., 2014), was used to determine bioavailability of DON. The bioavailability of DON in this study was 78% of biodegradable, which is in a good agreement with the previous study (Khan et al., 2009)

Figure 4.8 (a) shows the average of four water samples of BDON profiles from KWTP along treatment trains. The BDON profile had a similar trend as that of DON profile. Average BDON in raw water and three of water after sedimentation, filtration, and chlorination were 0.27, 0.21, 0.31, and 0.19 mg-N/L, respectively. The removal efficiency of BDON in finished water was 29% with BDON increased by 14% in filtration process. The explanation, was the same for DON concentration increased in filtration process due to the release of soluble microbial products from the filter. In KWTP most portion of DON were biodegradable (about 53% in raw water, 56% in sedimentation, 55% in filtration, and 51% in chlorination). This result had similar trend with previous studies that BDON are main dominant of DON in water samples (Chen et al., 2011). The compound made up for BDON may contain of low molecular fraction of DON such as aliphatic amino acid (e.g. glycine; MW = 57.05 Da, alanine; MW = 89.09, aspartic acid; MW = 133 Da). Approximately, another half of DON in KWTP was NBDON. NBDON consists of unidentified DON or non-biodegradable organic nitrogen that considered to be mainly in the unidentified high molecular weight organic fraction or humic compounds. It is note that the non-bioavailable may also came from the specific type of humic compounds or other type of aromatic amino acid and possibly other high molecular weight nitrogen compounds(Dotson and Westerhoff, 2009; Tang et al., 2012; Templeton et al., 2012; X. Yang et al., 2010).

Figure 4.8 (b) illustrated the BDON profile along treatment process of TWTP. The BDON concentration of raw water and effluents samples from sedimentation, filtration, and chlorination were 0.36, 0.27, 0.14, and 0.22 mg-N/L corresponding to 38% removal in finished water. Substantial reduction of BDON in water samples after filtration suggested that there were biological activities in the filter of TWTP or BDON fractions of TWTP was ready bioavailable compare to other water plants. Slight increase of BDON after chlorination could be due to partial oxidation of DON by chlorine to make DON become more biodegradable

In KKUWTP, average BDON in raw water and three of effluent from sedimentation, filtration, and chlorination were 0.21, 0.31, 0.24, and 0.15 mg-N/L, respectively (Figure 4.8 (c)). The removal efficiency of BDON in finished water comparing to raw water was 28%. The possible explain why non-biodegradable were high portion of DON was that the raw water may contain aromatic nitrogen than aliphatic nitrogen. The key factors that appeared to affect bioavailability of DON by bacteria and algae or increase non-biodegradable organic nitrogen may come from two possible reasons: 1) the effect of pH and salinity in water receiving DON, which increase nitrogen containing humic substance (contain aromaticity) and 2) effect of physical and chemical interactions of nitrogen species due to water chemistry (Stensel, 2008)

Overall, most of DON in water treatment plants are biodegradable range from 35-60%, which similar with previous study that reported the BDON accounted for 40-60% (Halis et al., 2012; Khan et al., 2009; Wadhawan et al., 2014). Some water plants had NBDON portion more than BDON. This depended on water characteristics. The remaining of DON portion in water system in WTP may be oxidized in chlorination process to form nitrogenous disinfection by product (N-DBP) such as HANs, which are more toxic and carcinogenic than regulated DBP (Chen, 2007)

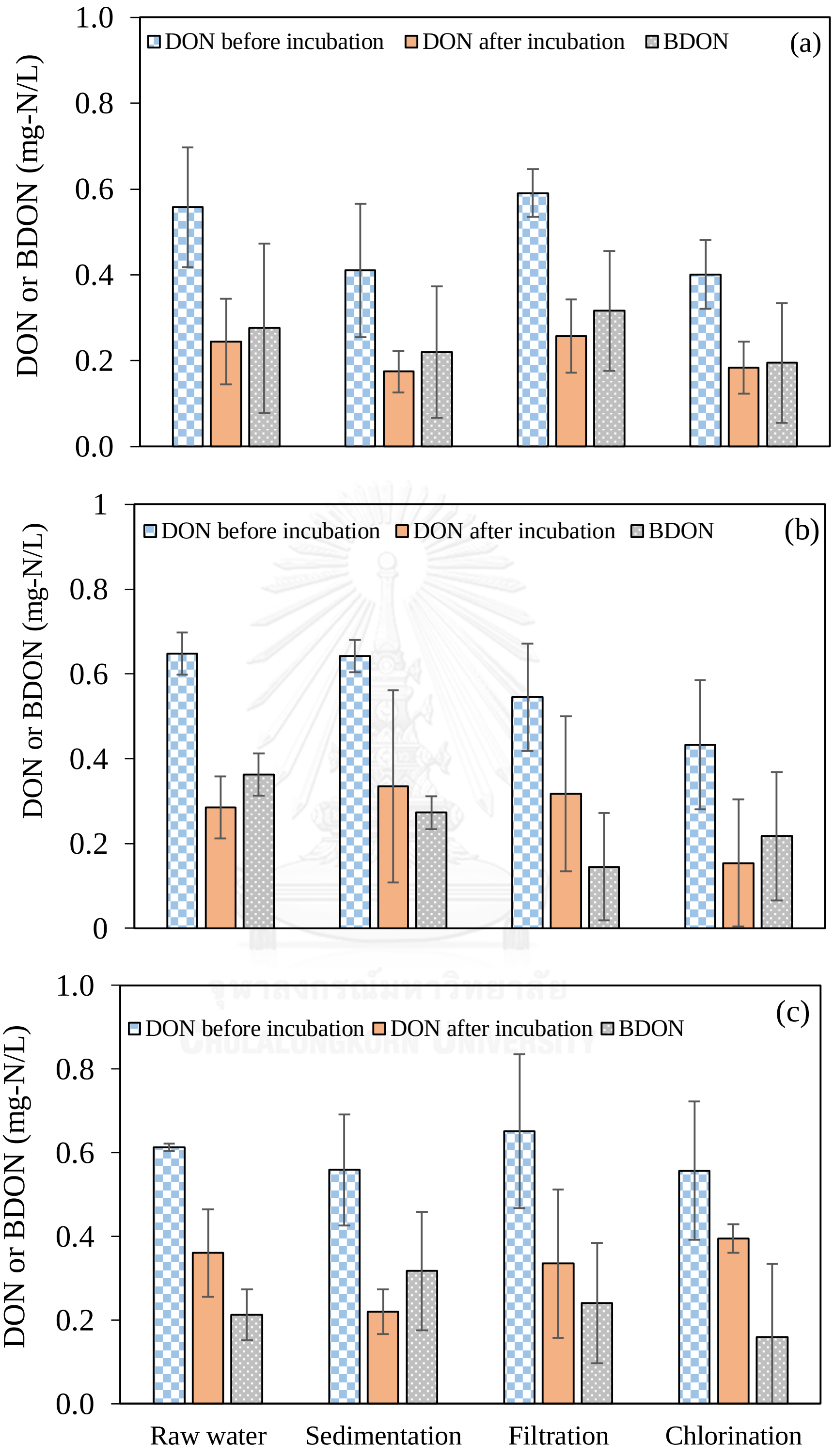


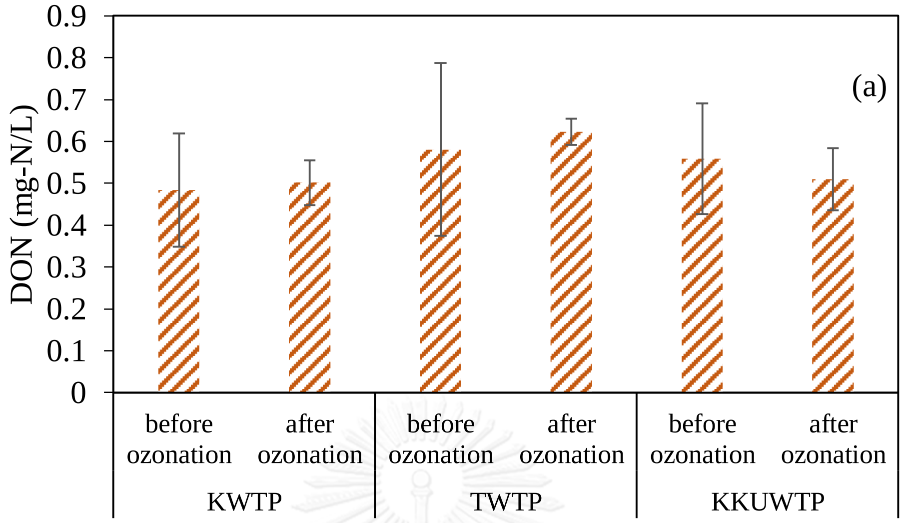
Figure 4.8 DON before and after incubation and BDON concentration along treatment process of (a) KWTP (n=4), (b) TWTP (n=4), and (c) KKUWTP (n=4)

4.5. Effect of ozone on DON and BDON

Ozonation is usually practiced either at the headwork of a conventional treatment plants or after chemical coagulation and sedimentation (Minear and Any, 1995). In this study, ozone was applied to water samples after sedimentation process for KWTP, TWTP and KKUWTP in order to evaluate the change of DON and BDON. Ozone was generated from self-made ozone generator based on the principle of the photolysis of oxygen by UV at wavelength 185 nm. The average concentration of DON and BDON was from four water samples. The applied ozone dosage was 0.6 mgO_3/mg DOC which was in the typical range of ozone dosage for drinking water plant (0.6 – 1.0 mgO_3/mg TOC) (Collins and Vaughan, 1996). Figure 4.9 a shows the DON concentration of water samples before and after ozonation. The results showed that ozonation of settled waters increased, the average DON concentration in KWTP and TWTP by 4.16 % and 3.63%, respectively. However, DON concentration of KKUWTP decreased from 0.59 to 0.55 mg-N/L (6.77%) after ozonation. (Bin et al., 2011) found that average DON concentration increased 15% after the ozonation process. In contrast, Wadhawan et al. (2014) reported that the average DON concentrations before and after ozonation were relatively unchanged. The results suggested that DON from different location may have different susceptibility to ozone. Increasing of DON concentration in KWTP and TWTP could be explained that ozone breaks down the organic nitrogen associated with particles such as bacteria and algae to become dissolved constituent. On the other hand, the decrease of DON in KKUWTP after ozonation might be due to the composition of DON of KKUWTP was easily oxidized by ozone to become inorganic nitrogen.

For BDON concentration, ozonation increased BDON of KWTP and TWTP by 47% and 8.0%, respectively (Figure 4.9b). However, the BDON concentration of ozonated KKUWTP decreased by 9.6%. Another study also reported the BDON increased 147% in ozonation process (Wadhawan et al., 2014). The different train was observed in KKUWTP, the BDON concentration was decreased by 9.6%.

Increasing of BDON in KWTP and TWTP by ozonation was because of the conversion of aromatic DON into aliphatic DON. Aromatic compound breaks down to aliphatic compound via oxidation reaction of ozone. The product compounds are believed to be more readily biodegradable, which may increase the BDON concentration (Hua and Reckhow, 2013; Tchobanoglous et al., 2014; Wadhawan et al., 2014; Wert and Rosario-Ortiz, 2011). It is noticed that ozone could modify organic structure and characteristic significantly. However, it could not reduce the amount of NOM significantly (Collins and Vaughan, 1996). For KKUWTP, the BDON concentration decreased. It might be suggest that water samples in KKUWTP are contain DON compounds that both bioavailable and readily oxidized by ozone.



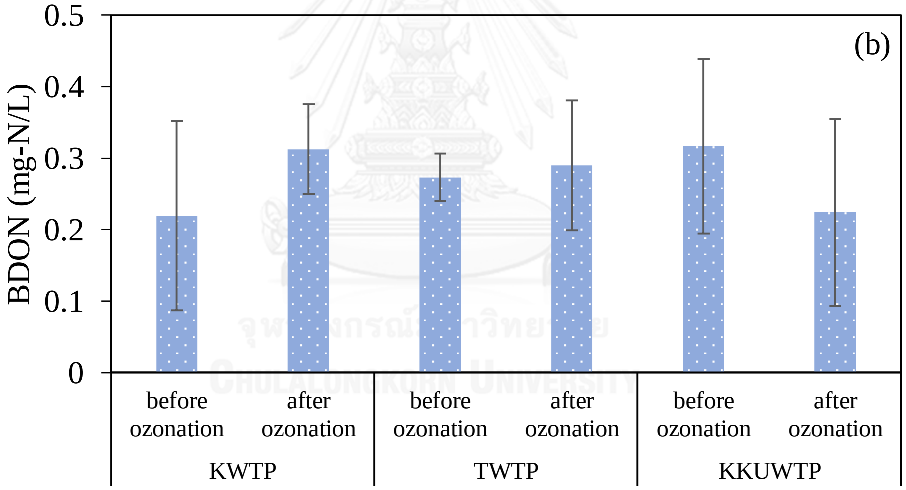


Figure 4.9 Concentration of (a) DON and (b) BDON before and after ozonation of coagulated-settled water from KWTP (n =4), TWTP (n=4), and KKUWTP (n=4)

4.6 Haloacetonitrile (HANs) profile and specific haloacetonitrile formation potential (HANFP) along treatment process

4.6.1 HANs profile

In natural water resources, the organic in water was mainly from allochothonous and autochotounous sources. The organic precursors may produce by-products after the disinfection by chlorine or chloramines, which increased effect to human health and toxicity in treated water. Disinfection by-products in water treatment plants composed of regulated disinfection by product (DBP) such as thihalomethanes (THMs) and haloacetic acid (HAAs) and non-regulated DBPs such as N-DBPs (e.g. haloacetonitriles; HANs). Nowadays the non-regulated DBP (N-DBPs) had become emerging contaminants of concern in water treatment plants because they have more toxicity and carcinogenic than regulated DBPs(Wadhawan et al., 2014)

In this study, four HANs species including monochloacetonitrile (MCAN), dichloroacetonitrile (DCAN), trichloroacetonitrile (TCAN), and,dibromoacetonitrile (DBAN) were measured. HANs profiles in water treatment plants were presented in Figure 4.10 (a-c). Note that the concentration of each species was average values of four sampling periods.

The results showed that in raw waters, HANs were also present at relatively low concentration. The total HAN concentrations in raw water of KWTP, TWTP, and KKUWTP were 1.21, 1.2, and 0.5 µg/L, respectively. As water pass along the treatment process, the concentrations of HANs increased Figure 4.10 (a-c). After chlorination, the HAN concentrations increased dramatically. The sum of four HAN concentrations of KWTP, TWTP, and KKUWTP were 7.67, 14.7, and, 4.93 µg/L. This is not surprised since reaction of chlorine and DON is known to produce HAN. Among three plants, TWTP had the highest total HANs concentrations. This could be explained by several reasons including characteristics of NOM, pH, and disinfectant (chlorine/chlorine dioxide dosage. At the time of study, all parameters of raw water for three plants seem to be comparable (Table 4.1). The only two different characteristics of TWTP from other plants are the SUVA and BDON. It was noticed that raw water of TWTP has lowest SUVA and highest BDON values. This suggested that the organic compounds in TWTP were more hydrophilic and readily reactive with chlorine to form HANs. Low HANs concentration for KKUWTP could be from different disinfectants used. At KKUWTP chlorine dioxide was applied. Since chlorine dioxide has electrochemical oxidation potential (E^o = 0.84 V) less than free chlorine (E^o = 1.48 V) (Tang et al., 2012), therefore this could yield less HANs concentration. Interesting trend of HAN concentrations in raw water and water after filtration process which found the HAN concentration. It was from the pre-chlorination of raw water before adding the coagulants in TWTP leading to increase HANs concentration. Another increase of HAN after filtration process was because chlorinated water was used in backwash process of three plants. This chlorinated water used to backwash may contain the chlorine residue from disinfection process and possible to react with the organic nitrogen in the filter to form HANs. For HAN speciation, DCAN was the highest of HAN species being analyzed and accounted for about 50% of chlorinated samples. Except that KKUTWP that MCAN become the highest fraction in HANs being analyzed. Again, this could be from either characteristic of NOM or type of disinfectant that was chlorine dioxide.

Based on previous studies of HAN concentrations, there were a variation of HANs found in chlorinated water. In US, it was reported that the median and maximum of sum of HANs species including dichloroacetonitrile (DCAN) , bromochloroacetonitrile (BCAN), trichloroacetonitrile (TCAN), and dibromoacetonitrile (DBAN) was about 4.0 and 14.0 µg/L, respectively (Kranser et al., 2007). . In Australia high HANs level of 36 µg/L was detected while low concentration was observed in Scotland with median concentration at 1 µg/L (Bond et al., 2011). In Khon Kaen, Thailand, The average of total of four HANs species after disinfection process in water treatment plants of Khon Kaen Municipality and Khon Kaen Univerisity ranged from 4 to 15 µg/L. This range of HANs was relatively high comparing to the HAN fount in US and Scotland. Although the sum of HANs concentration in this study seem to be high, the values were below recommend guidelineof single HAN compound for drinking water. For example, the guideline for DCAN and DBAN were 20, and 70 µg/L, respectively (WHO, 2000).

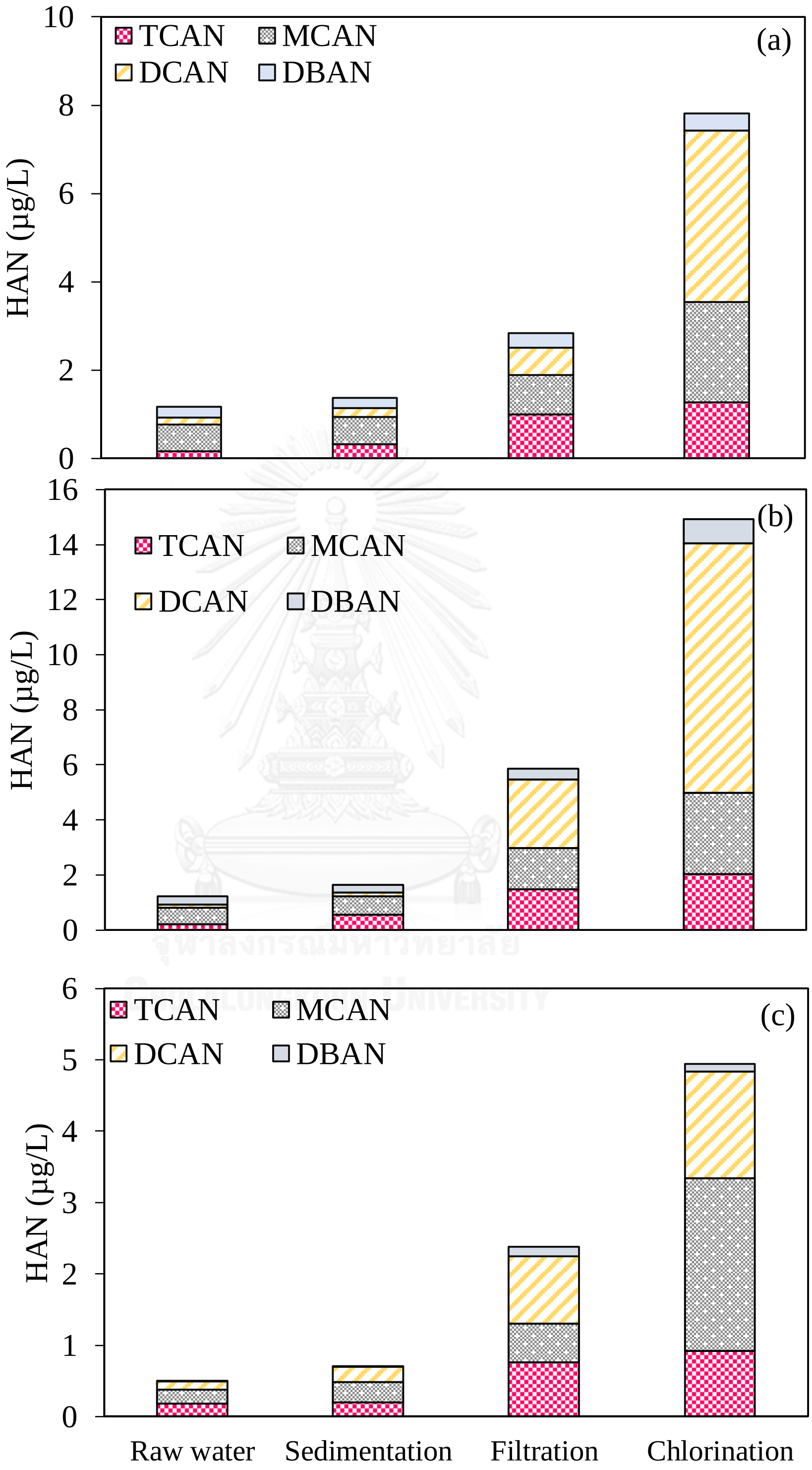


Figure 4.10 HANs profile in raw water and water treatment train of (a) KWTP (n=4), (b) TWTP (n=4) and (c) KKUWTP (n=4)

4.6.2 Specific HANFP along treatment process before and after incubation

As water pass through treatment plant, water has undergone different unit operations to remove constituents from water. In this study, specific HANFP at different stage of water treatment was determined. This was to evaluate whether or not such a treatment unit could remove precursor of HANs. Also the biodegradation experiment was performed with the samples by incubating with MLSS to determine the effect of biodegradable organic fraction associated with the formation of HANs.

Figure 4.11, 4.12, and 4.13 illustrated the individual specific HANFP species of water samples along the treatment train before and after incubation for KWTP, TWTP, KKUWTP, respectively. Also Figure 4.14 presents the sum of four specific HANFP of water samples. Specific HANFP was calculated from HAN divided by DON. The increasing of specific HANFP after a treatment process implied that such unit process could generate HANs or precursor of HANs. For example, after chlorination, all samples from three plants had an increase of specific HANFP substantially. This was because HAN was already formed by chlorination in the water plant. Also some of organic was oxidized and reacted with chlorine again during the formation potential test. Another example of increase of specific HANFP was filtration. Water sample after filtration of TWTP had large increase in the formation potential of MCAN, DCAN, and DBAN. This could be from a release of soluble microbial products (SMPs) from biofilm in the filter. This SMPs was reported to be a precursor of N-DBPs (Liu et al., 2014).

When comparing the specific HANFP between before DON incubation and after incubation, the result showed the decrease of all specific HANFP species after incubation. For example, 63%, 73.5%, 62% reduction of specific DCANFP was observed in water after sedimentation of KWTP, TWTP, and KKUWTP, respectively.

This elucidated that some part of HAN precursors had been biodegraded during the incubation period of 14 days. This finding suggested that biodegradation could be the treatment unit for removing the precursor of HAN.

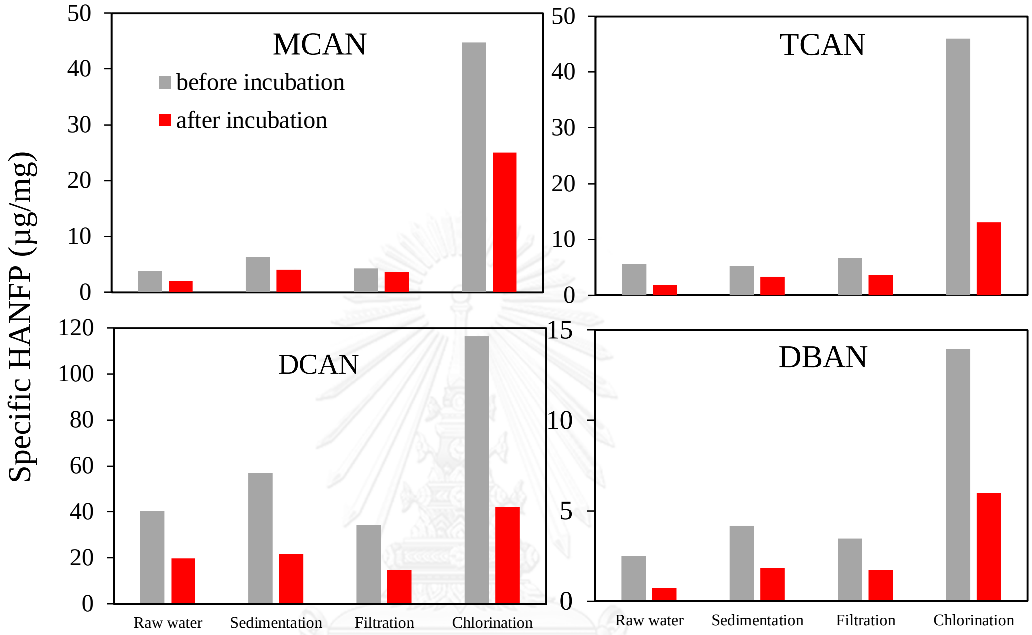


Figure 4.11 Formation potential of individual HAN in samples before and after incubation along treatment process of KWTP

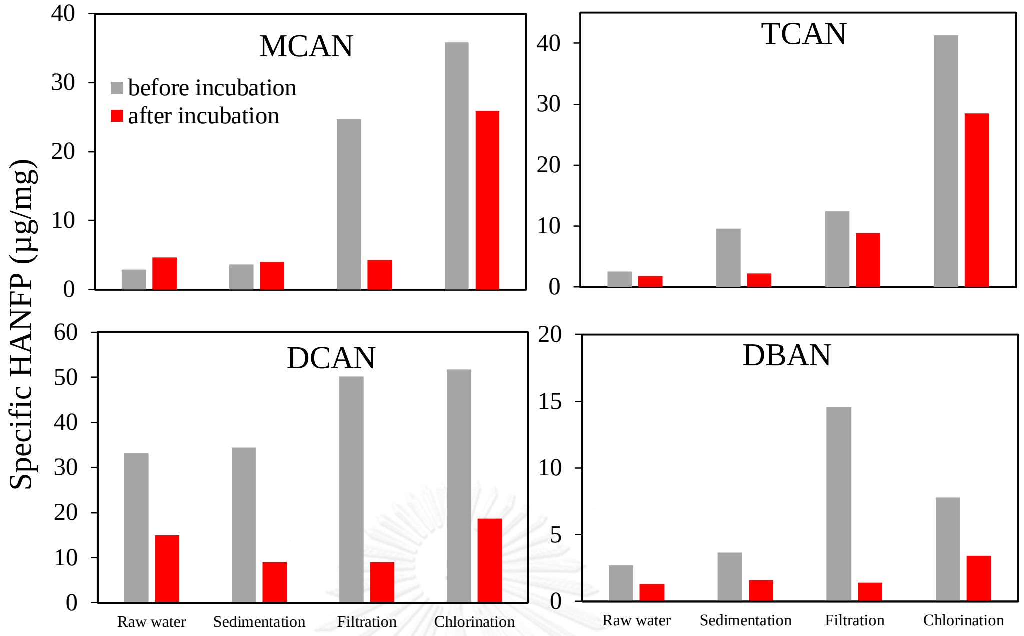


Figure 4.12 Formation potential of individual HAN in samples before and after incubation along treatment process of TWTP

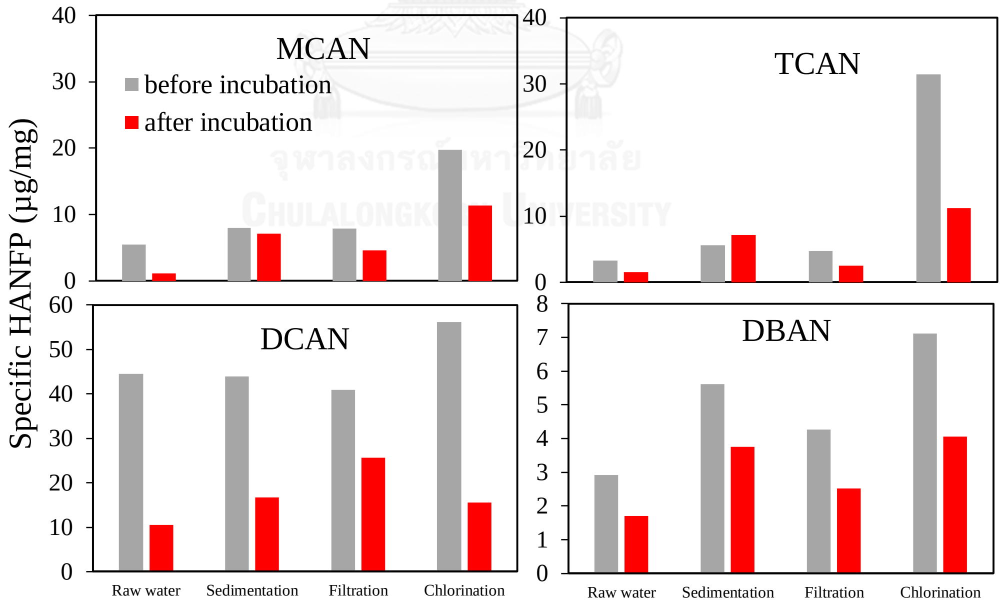


Figure 4.13 Formation potential of individual HAN in samples before and after incubation along treatment process of KKUWTP

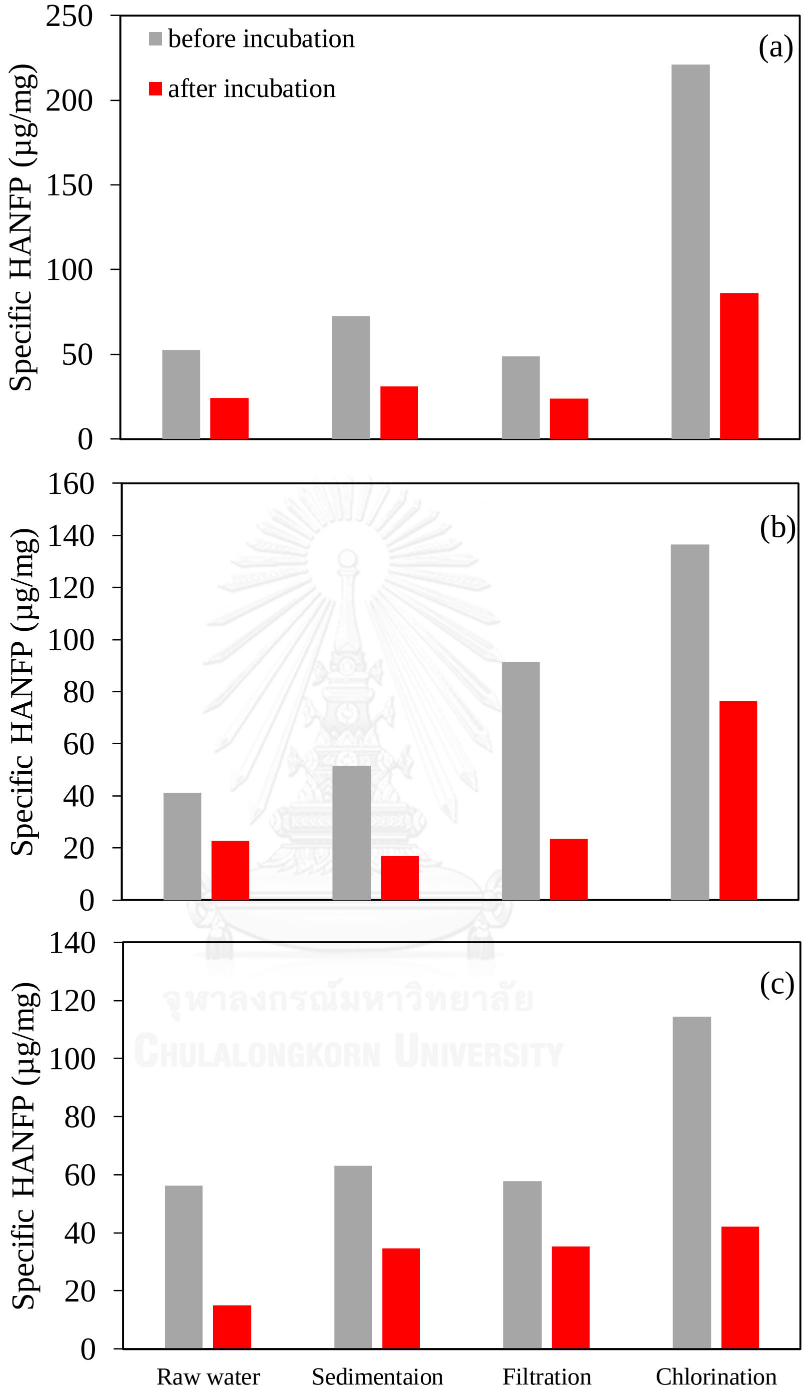


Figure 4.14 Formation of total HANs in before and after incubation from (a) KWTP, (b) TWTP, and (c) KKUWTP

4.6.3 Correlation between DON concentrations or biodegradability of DON (BDON/DON) and total specific HANFP.

The correlation between DON concentrations and DON biodegradability (BDON/DON) to specific HANFP in separate water samples of all treatment plants was shows in Figure 4.15 (a), and (b), respectively. There were moderate correlation between DON concentration and raw water ($R^2 = 0.69$), sedimentation ($R^2 = 0.61$), and chlorination ($R^2 = 0.73$) but there was poor correlation between DON and effluent from filtration process ($R^2 = 0.34$). Based on previous research, the relationship between HAN and DON were varied depending upon the source of waters. (Hohner, 2009) found good correlation of HAN and total organic nitrogen ($R^2 = 0.83$), which indicated organic nitrogen moieties as precursor of N-DBPs. In contrast, (Kransner et al., 2012) has reported no correlation between DON and HAN concentration ($R^2= 0.24$). The good correlation between DON and specific HANFP could be explained that the portion of DON contained high portion of biodegradable DON, which consist of low molecular weight DON such as low MW of amino acids. Previous study reported low MW amino acid such as aspartic acid, alanine can form the dihalogenated HAN during chlorination and chloramination process (Bond et al., 2014; X. Yang et al., 2010). HAN could be formed though amine in their amino groups during chlorination process (Xu et al., 2010).The relationship between specific HANFP on the biodegradability were shown in Figure 4.15 (b). There were moderate correlation between biodegradability and HANFP in raw water ($R^2 = 0.55$), sedimentation ($R^2 = 0.64$), and chlorination ($R^2 = 0.73$) effluents of three water treatment plants and after filtration process was low correlation ($R^2 = 0.15$). This suggested that the biodegradable of DON led to formation of HANs, due to the increase in the N- containing biodegradable during the formation potential test. This result could be confirm that the BDON or biodegradable portion could be increase in the formation of HANs. (Templeton et al., 2010).

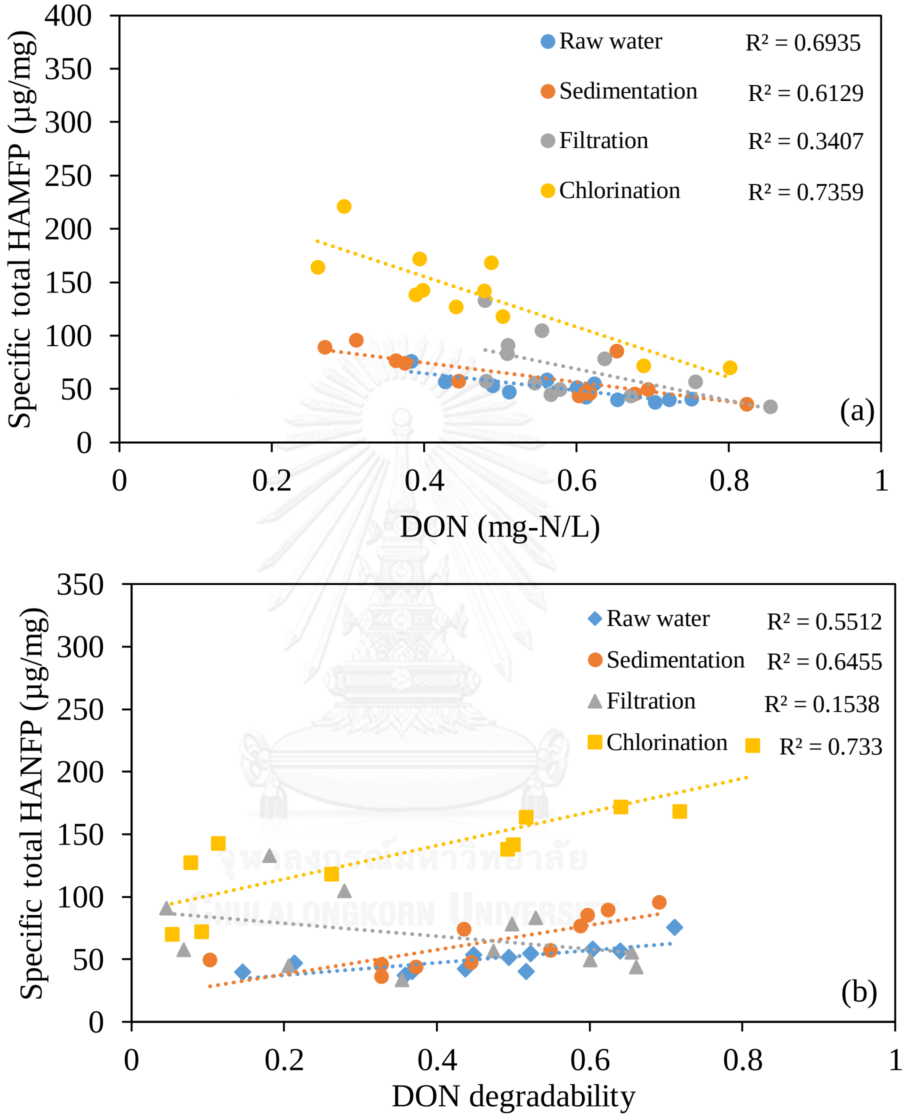


Figure 4.15 (a) Correlation between DON and specific total HANFP, (b) corrlation between DON biodegradability (BDON/DON) and specific total HANFP in all treatment plants.

4.6.4 Effect of ozone to specific HANFP.

Figure 4.16 (a-c) present the effect of ozonation on the formation potential of total HANs. The results compared three formation of HAN including specific HANFP in samples before ozonation, after ozonation, and samples of ozonation after incubation. It was found that specific HANFP increased after ozonation and decrease to approximately the same level as before ozonation after incubation (biodegradation) except for KKUWTP. For KWTP, specific HANFP of three water samples were 75, 144, and 83 µg/mg, respectively (Figure 4.16 (a). The sample of TWTP also had similar trend. Similar finding was reported the increase of the HAN concentration of six water treatment plants in UK (Templeton et al., 2012). It might be due to ozone can oxidize some of hydrophobic NOM to become more hydrophilic NOM. Also ozone attacks double bonds and amino groups to small aliphatic compounds, which may increase the N-DBP precursors and enhance the reactivity of NOM with chlorine (Qin et al., 2015). Another studies found that ozone increased the formation of DBPs on hydrophilic fraction than hydrophobic fraction (Xu et al., 2007). Difference trend was presented in KKUWTP (Figure 4.16 (c)). Ozonation reduced the specific HANFP from 63 µg/mg to 50 µg/mg, and 42 µg/mg for after ozonation, and 42 µg/mg, respectively. This result suggested that the ability of ozone to destroy HAN precursors depended on the precursors properties and water qualities (Hua and Reckhow, 2013).

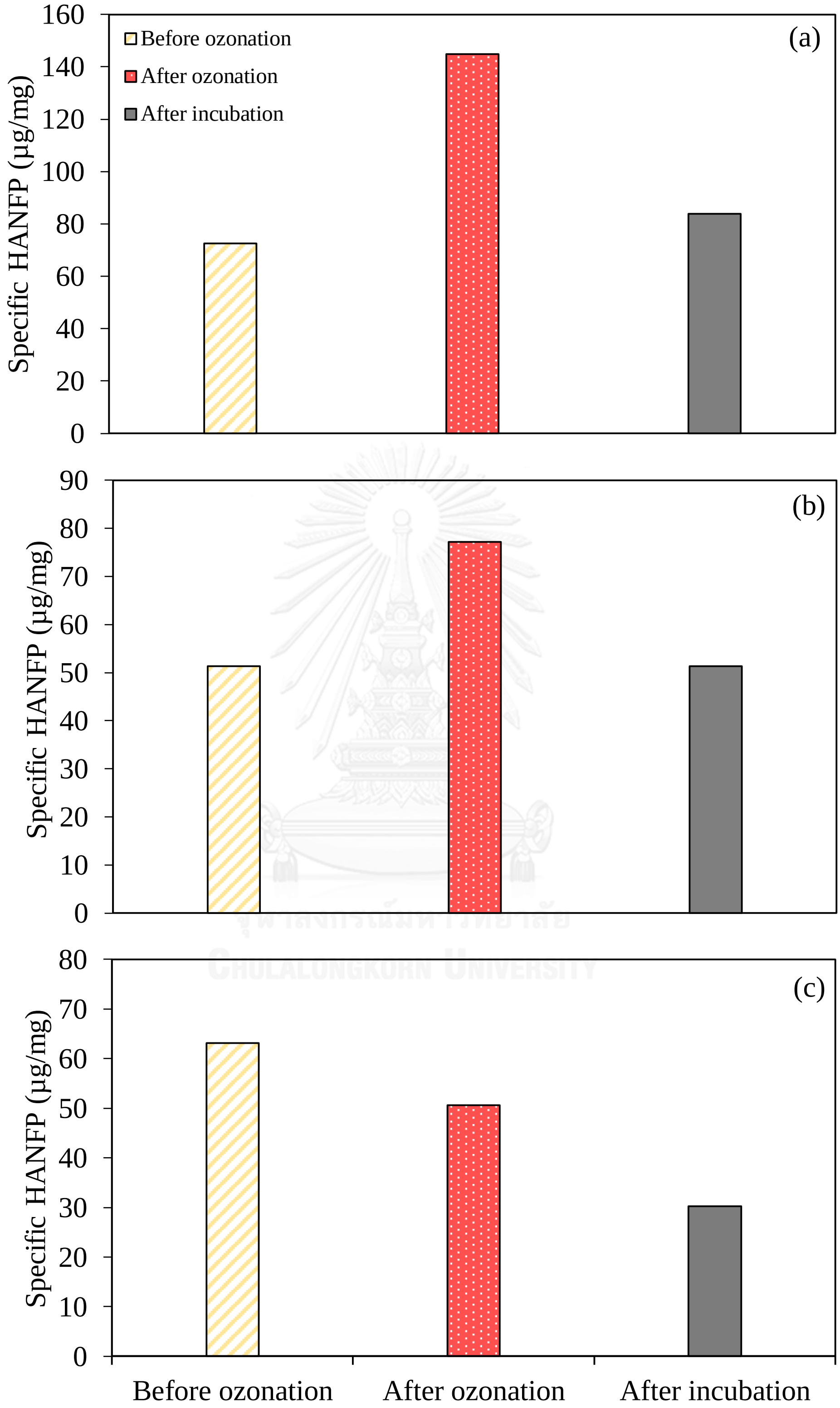


Figure 4.16 Effect of ozonation in HANFP of (a) KWTP (n=4), (b) TWTP (n=4), and (c) KKUWTP (n=4).

4.7 Correlation between specific HANFP and DOC or SUVA

DOC and SUVA are two common parameters used in drinking water treatment. In the past, DOC and SUVA was successfully used to predict the formation of other C-DBP such as THM (Sadiq and Rodriquez, 2004). This section presents the correlation between specific HANFP and DOC or SUVA of all water samples in different plants Figures 4.17 (a-c) and 4.18 (a-c) show the plot of DOC versus specific HANFP and SUVA versus specific HANFP of KWTP, TWTP, and KKUWTP, respectively. It was noticed that HANs had the no correlation between DOC and specific HANFP of all water samples from three plants (R^2 range from 0.09 to 0.30) and also not found the correlation with SUVA (R^2 range from 0.03 to 0.41). No correlation of DOC or SUVA with HANFP were not surprising because the DOC and SUVA were used as a hydrophobic organic compound indicator while the precursors of HAN are more hydrophilic than hydrophobic organic compounds (Bin et al., 2011; Chuang et al., 2013; Xue et al., 2014). Thus, DOC and SUVA might not be used as a surrogate for estimated HANs formation potential.

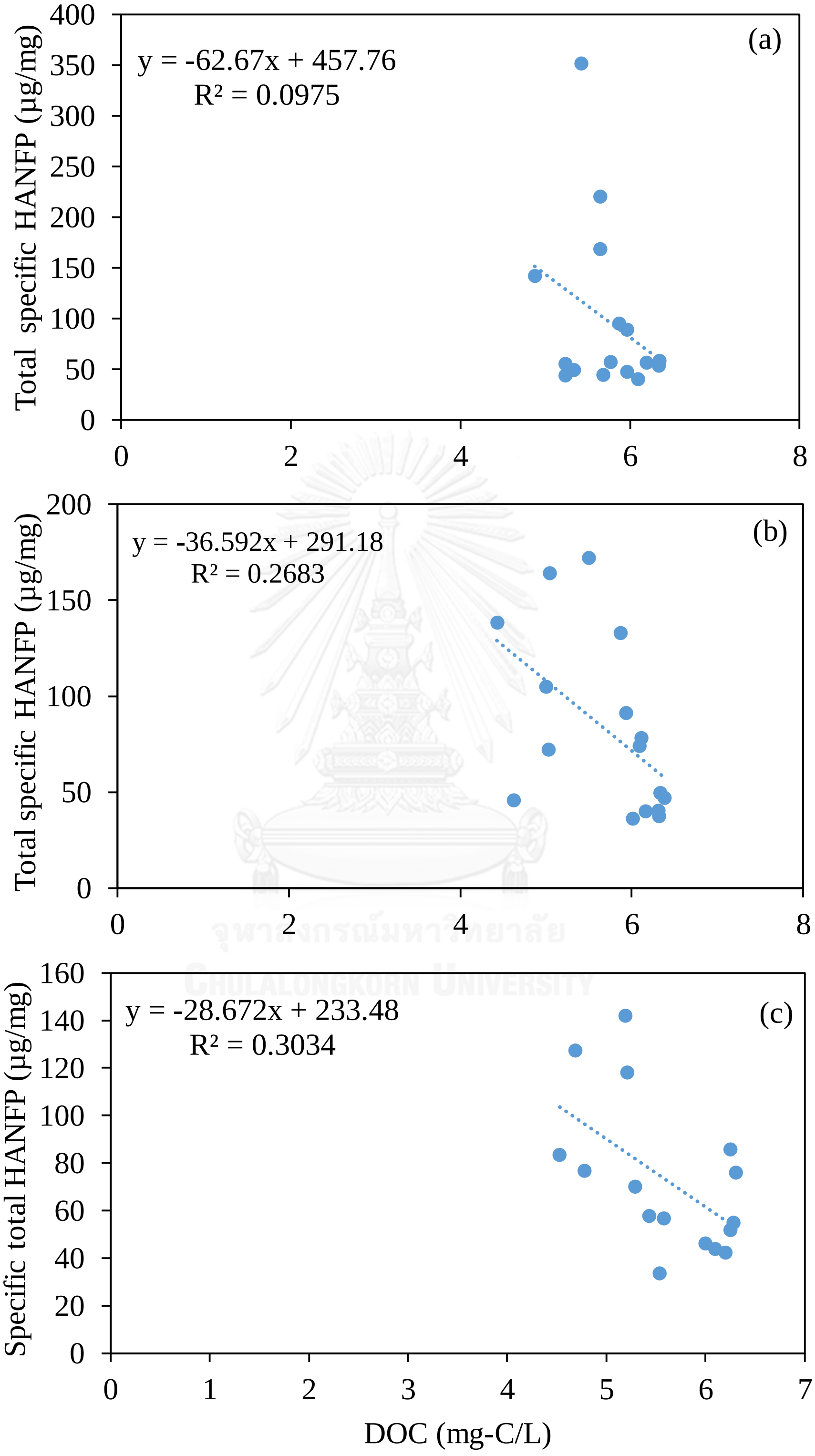


Figure 4.17 Correlation between DOC concentrations and specific HANFP of all water samples from (a) KWTP, (b) TWTP, and (c) KKUWTP.

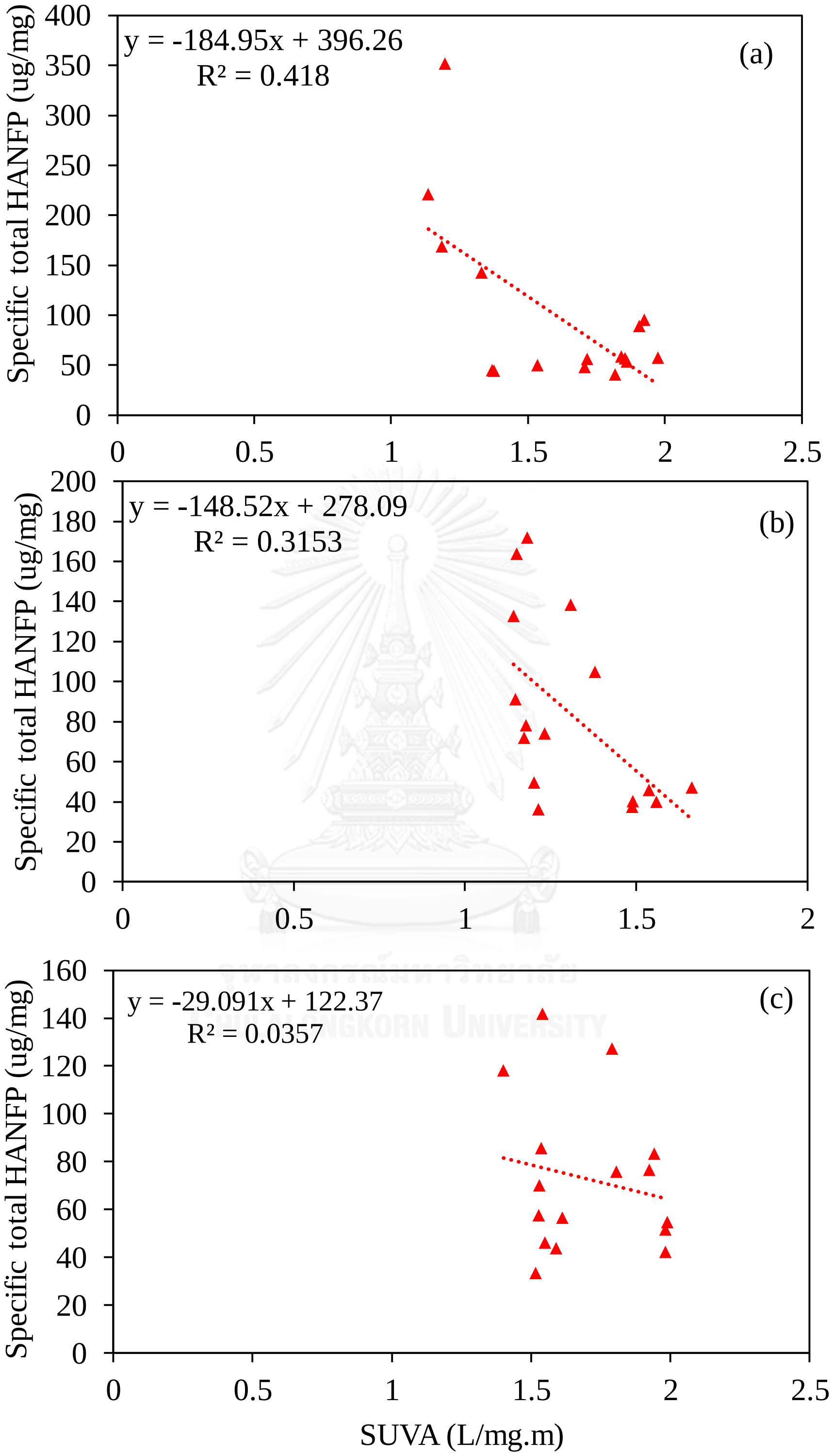


Figure 4.18 Correlation between SUVA values and specific HANFP of all water sample from (a) KWTP, (b) TWTP, and (c) KKUWTP.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

5.1 Conclusions

This study investigated the water quality parameters along the water treatment plants of Khon Kaen Municipality and Khon Kaen University, Thailand. It is for the first time the concentration of HANs, which are the emerging unregulated carcinogenic N-DBPs, has been reported in Thailand. Also relationship of water quality parameters to the formation of fours HANs (MCAN, TCAN, DCAN, and DBAN) was determined. Thus, the following conclusions were presented.

5.1.1 Water qualities along treatment process

1) Raw water characteristics of KWTP, TWTP, and KKUWTP indicated the NOM sources contain high amount of organic nitrogen (SUVA less than 2 and low DOC/DON ratio < 15). High contain of organic nitrogen should be effect to form N-DBPs during chlorination process

2) DOC and UV_{254}, representing organic compounds in water treatment plants, were not well to remove by conventional treatment processes including coagulation, sedimentation, and filtration. This got carried over to disinfection process and would lead to formation of HANs.

3) DON and BDON along treatment process were presented high concentration when compare with previous studies (raw water 0.34 mg-N/L and treated water 0.184 mg-N/L). The composition of DON could be divided in to two part: 1)

biodegradable DON (BDON) and 2) non-biodegradable DON. The result from KWTP and TWTP show dominant portion of DON was BDON, which contain amount of 53% and 56% in treated water of KWTP and TWTP, respectively. While the BDON was lower than non-biodegradable in KKUWTP.

5.1.2 HAN profiles and HAN formation potential

HAN profiles along three water plants show an increase of HAN concentrations along the treatment train. The range of HAN concentrations was between 4-15 μg/L which below the recommended HANs levels for drinking water (WHO). DCAN was the most abundant and accounted for more 50% of HAN species. Formation of HAN depends on NOM characteristics and type of disinfectants. Chlorine dioxide was found to produce less HANs comparing to free chlorine. The specific HANFP of water samples in before and after incubation indicated that some precursor of HANs were biodegradable. .

5.1.3 Effect of ozone in DON, BDON and specific HANFP

1) Increasing of DON and BDON after ozonation present in KWTP and TWTP. This indicated that ozone can convert aromatic DON into aliphatic DON. The resulting compounds are believed to be more readily biodegradable, which may increase the BDON concentration. While KKUWTP DON and BDON were reduce. The water samples in KKUWTP are contain higher aromatic or large organic compounds than those of two plants, which are not biodegradable compound

2) Formation potential of HAN after ozonation in DON before ozonation, which may indicated as biodegradable was higher than samples after

incubation. The result confirms with previous section that the biodegradable DON may increase the HAN formation.

5.1.4 Correlation of DON, and common water parameters with specific HANFP

1) Fairly high correlation were presented in DON before incubation and HANFP (R^2= 0.73 in treated water) but very low correlation was presented in DON after incubation (R^2 = 0.01). The result may concluded that the formation of HAN produced from the biodegradable DON, which are the main portion of DON

2) Low correlation of DOC or SUVA with HANFP were observed. Therefore, DOC and SUVA might not be appropriate to predict the formation of HANs.

5.2 Recommendations for future work

1) The composition DON in before and after incubation should be determined such as type amino acid and protein, which might be main component of DON.

2) Biodegradable DON influences the formation of HAN. More study on biodegradation process in drinking water for removal of HANs or other N-DBPs precursor should be investigated

3) Effect of disinfectant concentration and contact of HAN formation should be investigated and

4) Effect of seasonal variation should be studies.

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APPENDIX

APPENDIX A

Chemical analysis

1. Haloacetonitrile analysis

1.1 Haloacetonitrile preparation

A stock solution of MCAN, TCAN, DCAN, and DBAN were prepare from initial concentration of 10,000 mg/L. this solution was dilute in MTBE for 10 ml of mix HANs solution. The stock solution was dilute to 1, 5, 25, 50, 75, and 100 mg/L in distillation water. The area and HANs peak detected from GC-ECD were shown in table A.1. The standard curve of four HAN species were presented in Figure A.1

Table A.1 Peak area of HANs species.

HANs (μg/L)	**MCAN**	**TCAN**	**DCAN**	**DBAN**
	Area	**Area**	**Area**	**Area**
1	51.99	54.06	120.08	108.88
5	101.25	197.82	290.32	308.272
25	672.31	804.32	1108.93	1109.2
50	1154.72	1401.43	1987.67	2697.43
75	1695.99	2200.982	2985.349	4011
100	2176.119	2619.14	4218.26	4894.154

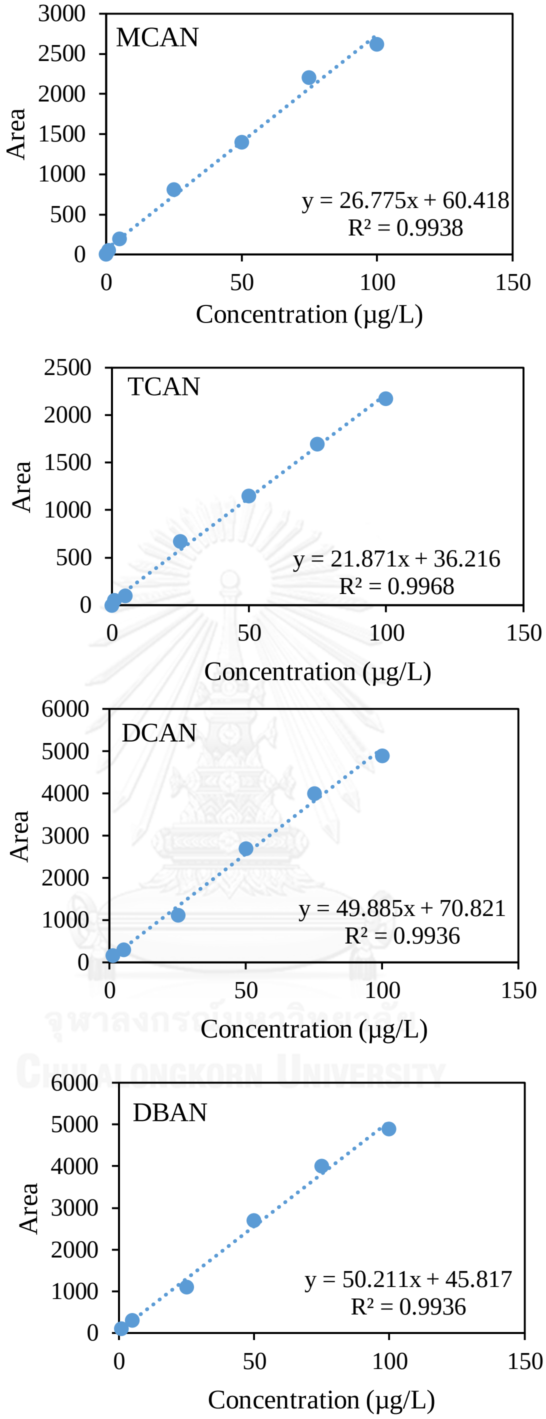

Figure A.1 Standard curve of four HANs species

APPENDIX B

Linear regression between DON and TDN

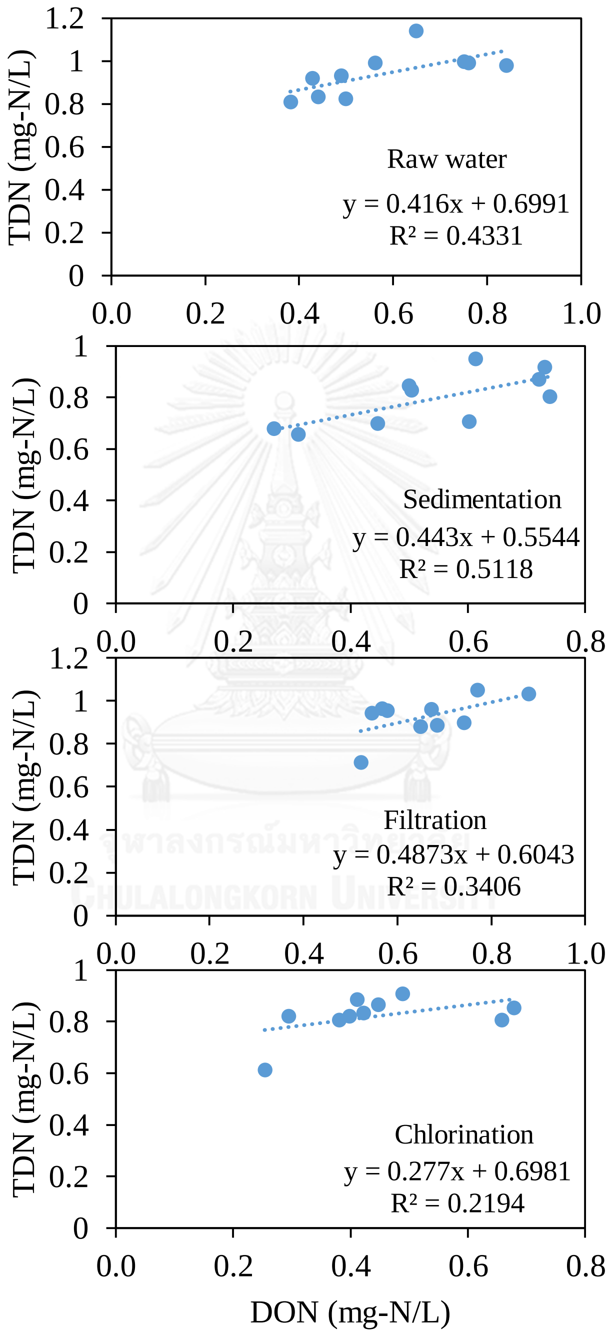

Figure B.1 linear regression between DON and TDN of KWTP

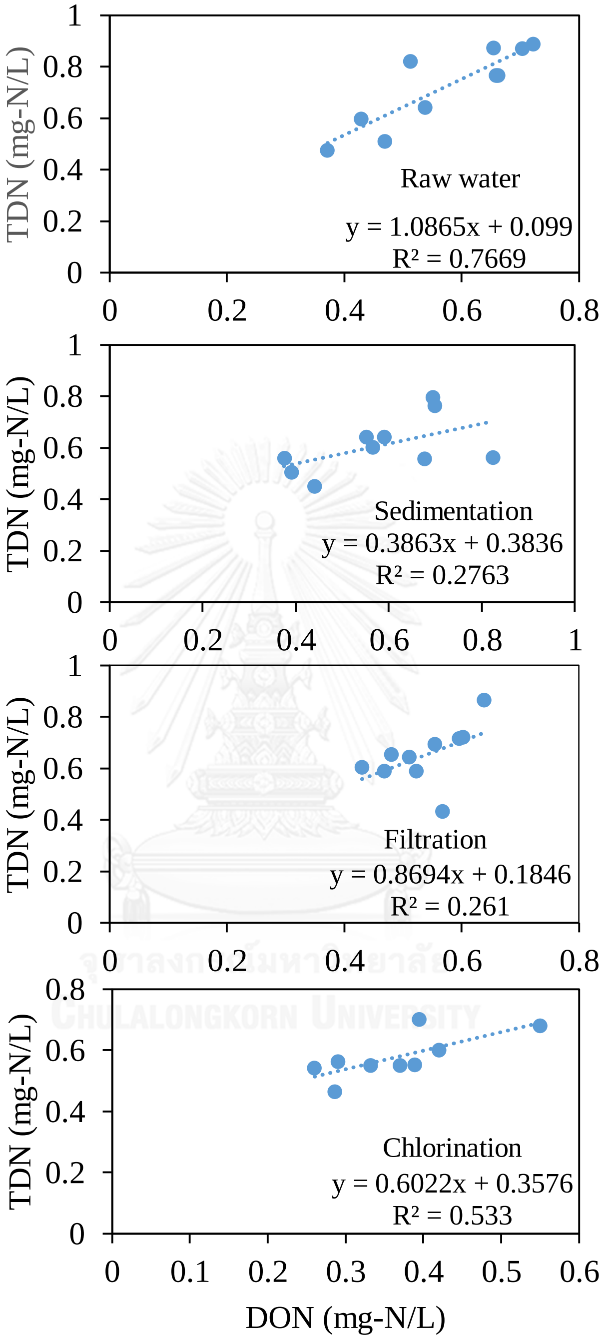

Figure B.2 linear regression between DON and TDN of TWTP

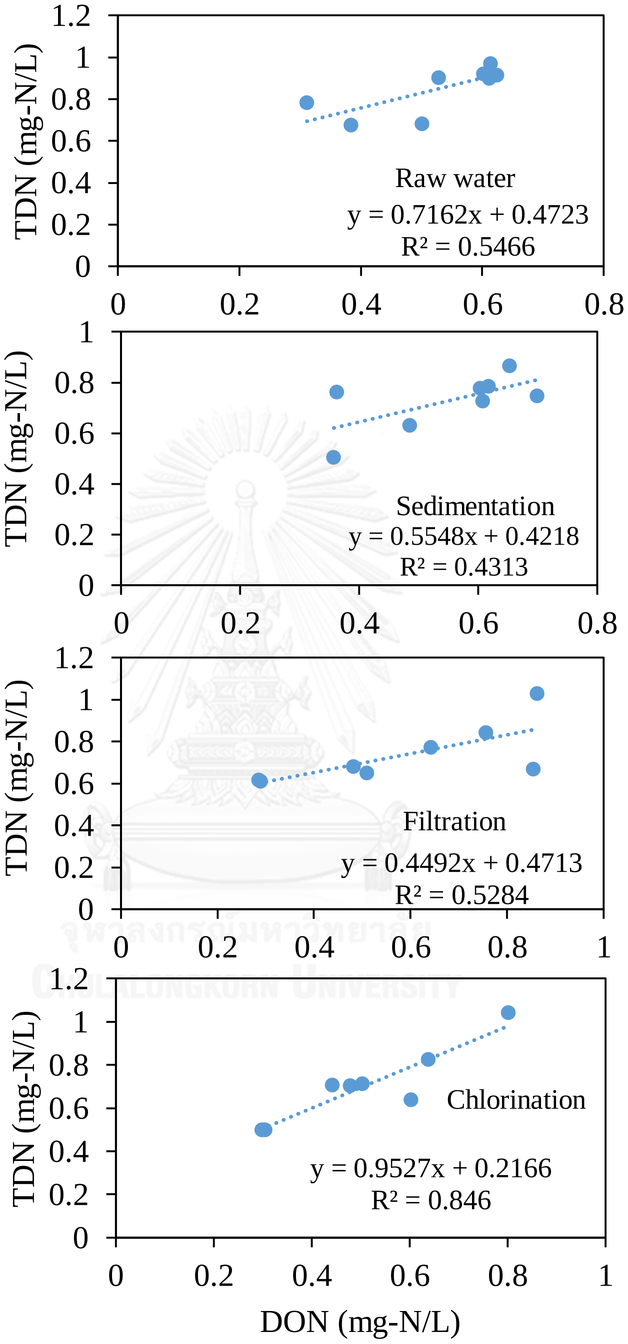

Figure B.3 linear regression between DON and TDN of KKUWTP

APPENDIX C

Characteristics of raw water.

Table C. 1 Raw water of KWTP

Samples ID	Temp °C	Turbidity NTU	pH -	Alkalinity mg/Las $CaCO_3$	Hardness mg/Las $CaCO_3$	DOC mg-C/L	BDOC mg-C/L	SUVA L/mg.m	TDN mg-N/L	DIN mg-N/L	DON mg-N/L	BDON mg-N/L	DOC/DON mg/mg
13/11/14	33	12.3	6.5	90	88	4.24	-	2.73	0.99	0.24	0.76	-	5.57
18/11/14	33	13.2	8,1	116	86	5.21	-	1.51	0.83	0.41	0.44	-	11.83
09/12/14	32	14.7	7.8	107	77	5.14	-	2.21	0.98	0.16	0.84	-	6.11
09/01/15	33	12.1	6.9	90	90	6.57	-	1.81	0.81	0.45	0.38	-	17.21
06/06/15	31	15.3	8.2	85	85	5.02	-	2.31	0.82	0.34	0.50	-	10.05
27/02/15	33	14.6	7.7	86	86	6.23	-	1.82	1.14	0.51	0.65	-	9.59
29/04/15	31	12.8	7.7	79	79	6.10	1.94	1.81	1.00	0.35	0.75	0.53	8.12
08/05/15	33	13.5	8.1	80	80	6.35	2.43	1.90	0.99	0.35	0.56	0.29	11.31
10/05/15	33	14.6	8.0	78	75	6.20	2.14	1.85	0.92	0.44	0.43	0.06	14.48
25/05/15	32	13,3	8.1	94	80	6.34	2.32	1.86	0.93	0.39	0.49	0.21	12.94
Average	**32.3**	**13.6**	**7.7**	**90.50**	**82.60**	**5.61**	**2.24**	**2.01**	**0.94**	**0.36**	**0.58**	**0.28**	**10.72**
S.D.	**0.78**	**1.05**	**0.5**	**11.77**	**4.78**	**0.74**	**0.24**	**0.33**	**0.10**	**0.10**	**0.15**	**0.20**	**3.69**

Table C.2 Raw water of TWTP

Samples ID	Temperature	Turbidity	pH	Alkalinity	Hardness	DOC	BDOC	SUVA	TDN	DIN	DON	BDON	DOC/DON
	ºC	NTU	-	mg/Las	mg/Las	mg-C/L	mg-C/L	L/mg.m	mg-N/L	mg-N/L	mg-N/L	mg-N/L	mg/mg
13/11/14	30	4.7	7.50	98	110	3.71	-	2.56	0.64	0.11	0.54	-	6.90
18/11/14	30	4.6	7.89	106	82	5.21	-	2.21	0.48	0.11	0.37	-	14.03
09/12/14	30	5.0	8.11	90	90	5.14	-	1.51	0.76	0.11	0.66	-	7.76
09/01/15	30	4.8	7.12	97	89	5.87	-	1.58	0.76	0.11	0.66	-	8.91
06/06/15	33	4.3	7.67	96	86	5.04	-	2.06	0.51	0.05	0.47	-	10.74
27/02/15	33	4.9	7.40	90	87	5.41	-	1.34	0.60	0.17	0.43	-	12.63
29/04/15	33	5.1	8.09	104	109	6.38	1.68	1.66	0.82	0.25	0.51	0.33	12.46
08/05/15	33	4.3	7.98	102	88	6.16	1.78	1.50	0.87	0.13	0.65	0.34	9.42
10/05/15	33	4.8	7.76	101	89	6.32	1.90	1.49	0.87	0.11	0.70	0.35	8.99
25/05/15	33	5.0	7.52	99	95	6.31	1.77	1.49	0.89	0.11	0.72	0.44	8.74
Average	**32**	**4.75**	**7.70**	**98**	**93**	**5.37**	**1.78**	**1.80**	**0.72**	**0.12**	**0.57**	**0.36**	**10.06**
S.D.	**1.55**	**0.28**	**0.32**	**5.36**	**9.54**	**0.83**	**0.09**	**0.43**	**0.15**	**0.05**	**0.11**	**0.05**	**2.53**

Table C.3 Raw water of KKUWTP

Samples ID	15.5Temperature	Turbidity	pH	Alkalinity	Hardness	DOC	BDOC	SUVA	TDN	DIN	DON	BDON	DOC/DON
	ºC	NTU	-	mg/Las	mg/Las	mg-C/L	mg-C/L	L/mg.m	mg-N/L	mg-N/L	mg-N/L	mg-N/L	mg/mg
09/12/14	30	16.7	8.02	89	80	6.84	-	1.81	0.68	0.59	0.50	-	13.68
09/01/15	31	15.2	7.87	87	84	5.68	-	2.16	0.79	0.50	0.31	-	18.25
06/06/15	33	13.3	7.94	94	89	5.08	-	2.69	0.68	0.31	0.38	-	13.26
27/02/15	33	15.4	7.34	79	70	7.11	-	1.88	0.90	0.38	0.53	-	13.48
29/04/15	33	14.1	7.18	98	85	6.31	1.02	1.80	0.97	0.30	0.61	0.27	10.30
08/05/15	33	16.2	7.92	89	86	6.20	1.72	1.94	0.92	0.23	0.60	0.13	10.31
10/05/15	34	15.2	8.02	87	103	6.25	1.74	1.98	0.92	0.24	0.62	0.22	10.03
25/05/15	33	16.2	7.59	92	97	6.28	1.15	1.99	0.90	0.24	0.61	0.22	10.27
Average	**32.50**	**15.30**	**7.74**	**89.38**	**86.75**	**6.20**	**1.41**	**2.05**	**0.85**	**0.35**	**0.52**	**0.21**	**12.45**
S.D.	**1.31**	**1.13**	**0.33**	**5.63**	**10.08**	**0.74**	**0.38**	**0.34**	**0.11**	**0.13**	**0.12**	**0.06**	**2.92**

APPENDIX D

Dissolved organic carbon (DOC) and SUVA values along treatment processes.

Table D.1 DOC and SUVA of KWTP

Samples ID	DOC (mg-C/L)				SUVA (l/mg.m)			
	RW	SW	FW	CW	RW	SW	FW	CW
13/11/14	4.24	4.03	4.60	5.01	2.74	2.16	1.74	1.26
18/11/14	5.21	5.32	4.88	4.63	2.22	1.89	1.69	1.39
09/12/14	5.14	4.76	4.72	4.38	1.52	1.62	1.78	1.38
09/01/15	6.57	5.62	4.90	5.22	1.81	1.53	1.63	1.23
06/02/15	5.02	4.73	4.36	4.34	2.31	2.18	2.06	1.71
27/02/15	6.23	5.04	4.81	5.10	1.83	1.75	1.68	1.24
29/04/15	6.10	5.97	5.24	5.45	1.82	1.71	1.72	1.19
08/05/15	6.35	5.77	5.34	4.88	1.84	1.98	1.54	1.33
10/05/15	6.20	5.97	5.24	5.65	1.85	1.91	1.38	1.14
25/05/15	6.34	5.87	5.69	5.43	1.86	1.93	1.37	1.20
Average	**5.74**	**5.31**	**4.98**	**5.03**	**1.93**	**1.86**	**1.66**	**1.31**
S.D.	**0.78**	**0.65**	**0.40**	**0.48**	**0.35**	**0.21**	**0.20**	**0.16**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

Table D.2 DOC and SUVA of TWTP

Samples ID	**DOC (mg-C/L)**				**SUVA (l/mg.m)**			
	RW	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**
13/11/14	3.71	4.03	3.80	4.17	2.56	1.98	1.63	1.41
18/11/14	5.21	5.32	4.88	4.63	1.52	1.62	1.78	1.38
09/12/14	5.14	4.76	4.72	4.38	2.22	1.89	1.69	1.39
09/01/15	5.87	4.84	4.30	4.15	1.58	1.34	1.40	1.28
06/02/15	5.04	4.72	4.22	4.11	2.06	1.44	1.54	1.34
27/02/15	5.41	4.99	5.01	4.92	1.35	1.16	1.14	1.20
29/04/15	6.38	6.33	6.11	5.50	1.66	1.20	1.18	1.18
08/05/15	6.16	4.62	5.00	4.43	1.56	1.54	1.38	1.31
10/05/15	6.32	6.01	5.93	5.03	1.49	1.21	1.15	1.17
25/05/15	6.31	6.09	5.87	5.04	1.49	1.23	1.14	1.15
Average	**5.56**	**5.17**	**4.98**	**4.64**	**1.75**	**1.46**	**1.40**	**1.28**
S.D.	**0.84**	**0.75**	**0.78**	**0.47**	**0.39**	**0.29**	**0.25**	**0.10**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

Table D.3 DOC and SUVA of KKUWTP

Samples ID	DOC (mg-C/L)				SUVA (l/mg.m)			
	RW	SW	FW	CW	RW	SW	FW	CW
13/11/14	6.84	5.05	4.47	4.97	1.81	2.02	1.92	1.69
18/11/14	5.68	4.67	4.13	4.43	2.17	2.03	2.03	1.42
09/12/14	5.08	5.58	4.82	5.02	2.70	1.72	2.01	1.91
09/01/15	7.11	6.25	4.94	5.47	1.88	1.47	1.68	1.39
06/02/15	6.31	4.78	5.58	5.29	1.81	1.54	1.61	1.53
27/02/15	6.20	6.00	4.53	4.69	1.98	1.92	1.94	1.79
29/04/15	6.25	6.10	5.54	5.19	1.98	1.55	1.52	1.54
08/05/15	6.28	5.54	5.43	5.21	1.99	1.59	1.53	1.40
Average	**6.84**	**5.05**	**4.93**	**5.03**	**2.04**	**1.73**	**1.78**	**1.58**
S.D.	**0.68**	**0.62**	**0.54**	**0.34**	**0.29**	**0.23**	**0.22**	**0.19**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

APPENDIX E

Fate of inorganic nitrogen species (DIN), total dissolved nitrogen (TDN), and dissolved organic nitrogen (DON) along treatment process

Table E.1 Fate of DIN, TDN, and DON of KWTP

Samples ID	DIN (mg-N/L)				TDN (mg-N/L)				DON (mg-N/L)			
	RW	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**
13/11/14	0.24	0.20	0.15	0.18	0.99	0.92	1.03	0.85	0.76	0.73	0.88	0.68
18/11/14	0.41	0.34	0.20	0.42	0.83	0.83	0.88	0.86	0.44	0.50	0.68	0.45
09/12/14	0.16	0.17	0.28	0.15	0.98	0.87	1.05	0.81	0.84	0.72	0.77	0.66
09/01/15	0.45	0.08	0.16	0.42	0.81	0.80	0.90	0.81	0.38	0.74	0.74	0.38
06/02/15	0.34	0.12	0.20	0.36	0.82	0.71	0.71	0.61	0.50	0.60	0.52	0.25
27/02/15	0.51	0.36	0.23	0.47	1.14	0.85	0.88	0.89	0.65	0.50	0.65	0.41
29/04/15	0.35	0.28	0.33	0.36	1.00	0.95	0.94	0.91	0.75	0.61	0.55	0.49
08/05/15	0.35	0.17	0.30	0.33	0.99	0.70	0.95	0.82	0.56	0.45	0.58	0.40
10/05/15	0.44	0.35	0.25	0.47	0.92	0.68	0.96	0.82	0.43	0.27	0.67	0.30
25/05/15	0.39	0.29	0.36	0.36	0.93	0.66	0.96	0.83	0.40	0.31	0.57	0.42
Average	**0.36**	**0.24**	**0.25**	**0.35**	**0.94**	**0.80**	**0.93**	**0.82**	**0.58**	**0.54**	**0.66**	**0.44**
S.D.	**0.10**	**0.10**	**0.07**	**0.11**	**0.10**	**0.10**	**0.09**	**0.08**	**0.16**	**0.17**	**0.11**	**0.14**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

Table E.2 Fate of DIN, TDN and DON of TWTP

Samples ID	**DIN (mg-N/L)**				**TDN (mg-N/L)**				**DON (mg-N/L)**			
	RW	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**
13/11/14	0.109	0.09	0.07	0.18	0.64	0.64	0.59	0.60	0.54	0.55	0.52	0.42
18/11/14	0.108	0.12	0.18	0.17	0.48	0.50	0.60	0.55	0.37	0.39	0.43	0.37
09/12/14	0.105	0.05	0.12	0.18	0.76	0.64	0.59	0.46	0.66	0.59	0.47	0.29
09/01/15	0.108	0.07	0.12	0.13	0.76	0.76	0.72	0.68	0.66	0.70	0.60	0.55
06/02/15	0.05	0.03	0.02	0.19	0.51	0.45	0.43	0.56	0.47	0.44	0.57	0.29
27/02/15	0.17	0.04	0.12	0.22	0.60	0.60	0.72	0.55	0.43	0.57	0.60	0.33
29/04/15	0.25	0.22	0.17	0.24	0.82	0.80	0.86	0.70	0.51	0.63	0.64	0.39
08/05/15	0.13	0.10	0.14	0.19	0.87	0.56	0.69	0.55	0.65	0.68	0.55	0.39
10/05/15	0.11	0.11	0.08	0.17	0.87	0.56	0.65	0.55	0.70	0.82	0.51	0.69
25/05/15	0.11	0.13	0.12	0.23	0.89	0.56	0.65	0.54	0.72	0.37	0.48	0.26
Average	**0.12**	**0.09**	**0.11**	**0.19**	**0.72**	**0.61**	**0.65**	**0.58**	**0.57**	**0.58**	**0.54**	**0.40**
S.D.	**0.05**	**0.06**	**0.05**	**0.03**	**0.15**	**0.11**	**0.11**	**0.07**	**0.12**	**0.15**	**0.07**	**0.13**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

Table E.3 Fate of DIN, TDN and DON of KKUWTP

Samples ID	DIN (mg-N/L)				TDN (mg-N/L)				DON (mg-N/L)			
	RW	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**
09/12/14	0.59	0.16	0.17	0.20	0.68	0.51	0.61	0.50	0.50	0.36	0.29	0.30
09/01/15	0.50	0.15	0.17	0.19	0.79	0.63	0.62	0.50	0.31	0.48	0.29	0.31
06/02/15	0.31	0.05	0.17	0.03	0.68	0.75	1.03	0.64	0.38	0.70	0.86	0.60
27/02/15	0.38	0.12	0.13	0.19	0.90	0.73	0.77	0.82	0.53	0.61	0.64	0.64
29/04/15	0.30	0.15	0.15	0.18	0.97	0.87	0.84	1.04	0.61	0.65	0.76	0.80
08/05/15	0.23	0.32	0.17	0.18	0.92	0.76	0.65	0.71	0.60	0.36	0.51	0.44
10/05/15	0.24	0.11	0.14	0.17	0.92	0.79	0.67	0.70	0.62	0.62	0.85	0.48
25/05/15	0.24	0.12	0.14	0.15	0.90	0.78	0.68	0.71	0.61	0.60	0.48	0.50
Average	**0.35**	**0.15**	**0.16**	**0.16**	**0.85**	**0.73**	**0.73**	**0.70**	**0.52**	**0.55**	**0.59**	**0.51**
S.D.	**0.13**	**0.08**	**0.02**	**0.05**	**0.11**	**0.11**	**0.14**	**0.18**	**0.12**	**0.13**	**0.23**	**0.17**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

APPENDIX F

Biodegradable dissolved organic nitrogen (BDON) along treatment process

Table F.1 BDON data of KWTP

Samples ID	DON before incubation (mg-N/L)				DON after incubation (mg-N/L)				BDON (mg-N/L)			
	RW	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**
29/04/15	0.75	0.61	0.55	0.49	0.22	0.18	0.19	0.14	0.53	0.43	0.36	0.35
08/05/15	0.56	0.45	0.58	0.40	0.27	0.22	0.23	0.14	0.29	0.22	0.35	0.26
10/05/15	0.43	0.27	0.67	0.30	0.37	0.19	0.23	0.27	0.06	0.08	0.44	0.03
25/05/15	0.49	0.31	0.57	0.42	0.13	0.11	0.38	0.19	0.21	0.14	0.12	0.15
Average	**0.56**	**0.41**	**0.59**	**0.40**	**0.24**	**0.17**	**0.26**	**0.18**	**0.28**	**0.22**	**0.32**	**0.19**
S.D.	**0.14**	**0.15**	**0.06**	**0.08**	**0.10**	**0.05**	**0.09**	**0.06**	**0.20**	**0.15**	**0.14**	**0.14**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

Table F.2 BDON data of TWTP

Samples ID	**DON before incubation (mg-N/L)**				**DON after incubation (mg-N/L)**				**BDON (mg-N/L)**			
	RW	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**
29/04/15	0.51	0.69	0.64	0.39	0.18	0.39	0.32	0.07	0.33	0.30	0.32	0.32
08/05/15	0.65	0.68	0.55	0.39	0.32	0.38	0.40	0.20	0.34	0.30	0.15	0.19
10/05/15	0.70	0.82	0.51	0.69	0.36	0.55	0.49	0.34	0.35	0.27	0.02	0.34
25/05/15	0.72	0.37	0.48	0.26	0.28	0.02	0.06	0.01	0.44	0.22	0.09	0.01
Average	**0.65**	**0.64**	**0.55**	**0.43**	**0.29**	**0.33**	**0.32**	**0.15**	**0.36**	**0.27**	**0.15**	**0.22**
S.D.	**0.09**	**0.19**	**0.07**	**0.18**	**0.07**	**0.23**	**0.18**	**0.15**	**0.05**	**0.04**	**0.13**	**0.15**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

Table F.3 BDON data of KKUWTP

Samples ID	DON before incubation (mg-N/L)				DON after incubation (mg-N/L)				BDON (mg-N/L)			
	RW	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**
29/04/15	0.61	0.65	0.76	0.80	0.34	0.20	0.40	0.39	0.27	0.45	0.36	0.41
08/05/15	0.60	0.36	0.51	0.44	0.47	0.24	0.24	0.39	0.13	0.12	0.27	0.05
10/05/15	0.62	0.62	0.85	0.48	0.40	0.28	0.55	0.44	0.22	0.34	0.30	0.04
25/05/15	0.61	0.60	0.48	0.50	0.23	0.16	0.15	0.36	0.22	0.36	0.03	0.13
Average	**0.61**	**0.56**	**0.65**	**0.56**	**0.36**	**0.22**	**0.34**	**0.39**	**0.21**	**0.32**	**0.24**	**0.16**
S.D.	**0.01**	**0.13**	**0.18**	**0.17**	**0.10**	**0.05**	**0.18**	**0.03**	**0.06**	**0.14**	**0.14**	**0.18**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

APPENDIX G

Total HANs profile, specific HANFP of DON before and after incubation.

Table G.1 HAN profile of KWTP, TWTP, and KKUWTP

Species (µg/L)	**KWTP**				**TWTP**				**KKUWTP**			
	RW	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**
MCAN	0.17	0.31	0.99	1.27	0.20	0.55	1.48	2.04	0.18	0.20	0.76	0.92
TCAN	0.60	0.62	0.90	2.27	0.61	0.69	1.49	2.93	0.20	0.28	0.54	2.42
DCAN	0.16	0.20	0.61	3.89	0.11	0.13	2.50	9.08	0.11	0.21	0.95	1.50
DBAN	0.24	0.23	0.34	0.38	0.31	0.28	0.38	0.87	N/D	N/D	0.13	0.11
Total HANs	**1.16**	**1.37**	**2.84**	**7.82**	**1.23**	**1.64**	**5.86**	**14.93**	**0.49**	**0.69**	**2.38**	**4.95**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

Table G.2 Total specific HANFP before incubation of KWTP, TWTP, and KKUWTP

Samples ID	**KWTP**				**TWTP**				**KKUWTP**			
	RW	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**
29/04/15	40.4	47.8	55.9	168.5	47.0	49.5	78.2	172.0	75.8	85.6	56.7	70.0
08/05/15	58.4	57.3	49.7	142.6	40.1	45.7	104.9	183.4	42.3	76.3	83.4	127.3
10/05/15	57.0	89.3	43.9	220.8	37.6	36.1	91.2	72.0	51.7	46.2	33.6	141.9
25/05/15	53.5	95.5	45.0	351.9	40.3	74.2	132.8	164.0	54.9	43.8	57.7	118.2
Average	**52.3**	**72.5**	**48.6**	**220.9**	**41.2**	**51.4**	**101.8**	**136.6**	**56.2**	**63.1**	**57.8**	**114.3**
S.D.	**8.19**	**23.49**	**5.46**	**18.40**	**4.03**	**16.19**	**23.40**	**45.37**	**14.19**	**21.24**	**20.33**	**31.11**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

Table G.3 Total specific HANFP after DON incubation of KWTP, TWTP, and KKUWTP

Samples ID	**KWTP**				**TWTP**				**KKUWTP**			
	RW	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**	**RW**	**SW**	**FW**	**CW**
29/04/15	37.19	42.30	35.56	95.44	27.87	19.53	17.69	152.8	19.53	77.06	37.31	76.05
08/05/15	26.38	25.04	27.32	80.25	23.68	20.64	29.71	69.56	10.92	19.45	81.24	26.25
10/05/15	5.50	10.81	14.17	41.51	12.33	9.12	17.20	28.54	7,42	15.22	8.03	36.99
25/05/15	27.97	45.86	17.70	127.1	26.92	18.20	29.51	54.44	21.97	26.87	14.28	29.36
Average	**24.26**	**31.00**	**23.69**	**86.06**	**22.70**	**16.87**	**23.53**	**76.36**	**14.96**	**34.65**	**35.21**	**42.16**
S.D.	**13.38**	**16.25**	**9.67**	**35.53**	**7.14**	**5.26**	**7.03**	**53.76**	**6.91**	**28.68**	**33.17**	**23.04**

RW = Raw water, SW = Sedimentation water, FW =Filtration water, CW = Chlorination water

APPENDIX H

Effect of ozone to DON, BDON and specific HANFP.

Table H.1 Effect of ozone to DON, BDON and specific HANFP before and after incubation of KWTP

Samples ID	KWTP			
	DON	**BDON**	**HANFP before incubation**	**HANFP after incubation**
29/04/15	0.54	0.42	179.88	147.65
08/05/15	0.55	0.28	104.53	58.74
10/05/15	0.48	0.27	142.93	30.42
25/05/15	0.44	0.28	152.10	98.50
Average	**0.50**	**0.31**	**144.86**	**83.83**
S.D.	**0.05**	**0.06**	**31.14**	**34.20**

Table H.2 Effect of ozone to DON, BDON and specific HANFP before and after incubation of TWTP

Samples ID	**TWTP**			
	DON	**BDON**	**HANFP before incubation**	**HANFP after incubation**
29/04/15	0.61	0.39	74.55	96.52
08/05/15	0.61	0.15	109.94	42.61
10/05/15	0.67	0.27	57.01	24.61
25/05/15	0.60	0.35	67.44	41.71
Average	**0.62**	**0.29**	**77.23**	**51.36**
S.D.	**0.03**	**0.09**	**22.96**	**31.22**

Table H.3 Effect of ozone to DON, BDON and specific HANFP before and after incubation of KKUWTP

Samples ID	**TWTP**			
	DON	**BDON**	**HANFP before incubation**	**HANFP after incubation**
29/04/15	0.42	0.42	62.70	68.98
08/05/15	0.49	0.24	44.86	13.72
10/05/15	0.53	0.05	45.76	7.05
25/05/15	0.60	0.18	49.19	31.13
Average	**0.51**	**0.22**	**50.63**	**30.22**
S.D.	**0.07**	**0.13**	**8.26**	**27.76**

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Phacharapol Induvesa, Patiparn Punyapalakul and Thunyalux Ratpukdi. DISSOLVED ORGANIC NITROGEN AND HALOACETONITRILES FORMATION POTENTIAL IN WATER TREATMENT PLANTS, KHON KAEN MUNICIPALITY, THAILAND. The proceeding of 4th International Conference on Environmental Engineering, Science and Management May 27-29, 2015 at Lotus Hotel Pang Suan Kaew, Chingmai, Thailand, Organized by Environmental Engineering Association of Thailand.