Composition changes of dissolved organic matter during drinking water treatment: Investigation based on fluorescence excitation-emission matrix analysis

浄水処理プロセスにおける溶存有機物の組成変化：蛍光励起スペクトル解析による検討

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Abstract

Dissolved organic matter (DOM) is a mixture of organic compounds with different physicochemical properties that affect the overall water treatment effectiveness. The concentration and composition of DOM originated in part from aquatic microorganisms and terrestrially derived substances vary depending on the source of water. DOM is a reservoir for the risk of the potential hazard for the drinking water when it reacts with disinfectant to form disinfection byproducts during the disinfection process in drinking water treatment systems. Moreover, conventional water treatment generates a large amount of drinking water treatment sludge (DWTS) during drinking water production. DWTS is one of the major issues for drinking water treatment plants to deal with. The sludge recycling process is an important pathway to reduce sludge. The recycling process includes the dewatering process of DWTS, where the water is recycled back into the stream of drinking water treatment. However, the main water quality issue associated with the recycling process is the release of DOM from DWTS which can affect the performance of drinking water treatment, such as chlorination. Accordingly, investigating DOM changes during the drinking water treatment associated with the release of DOM from DWTS in a drinking water treatment plant is required to assist the water treatment plant regarding DOM treatability.

Monitoring the DOM composition is essential to warrant the success of a drinking water treatment plant and to achieve the desired quality for intended water use. Conventional monitoring techniques using indexes such as specific ultra-violet absorbance at 254 nm (SUVA), chemical oxygen demand, and DOC have been widely used in drinking water treatment plants to assess the changes and removal efficiency of

DOM. Considering the time consumption, a comparatively simple approach that allows evaluation of the changes in the DOM composition during treatment is expected. Fluorescence excitation-emission matrix (EEM) spectroscopy is used as a rapid and highly sensitive analytical technique to determine the dynamics of DOM and can supply information on DOM quality in various types of water. Since the fluorescence EEM is more sensitive to UV-vis absorbance, it is important to examine the changes of DOM to ensure its reactivity and treatability throughout the drinking water treatment.

The overall water quality parameters were used to evaluate the changes of DOM from source to treated water to assist the effectiveness of fluorescence EEM analysis in monitoring the changes in DOM composition. Raw water feeding the drinking water treatment plants contained high intensity of humic-like substances from terrestrially derived sources. The results showed that humic-like substances in raw water of drinking water treatment plants were removed for 60–86% by coagulation due to their high molecular weight. Chlorination was found to cause the increase and decrease of fluorescent DOM, indicating the desired primary reaction between chlorine and DOM fractions. The extracted single excitation wavelength at 355 nm drew a better relationship between humic-like substances and chlorine consumption than that at 245 nm. The finding suggested that more humic molecules reflected at higher excitation wavelengths were responsible for chlorine consumption. However, plant A had purified water showing the high intensity of humic substances due to the breakdown of aromatic substances into smaller compounds. Chlorine can also react directly with microbes, leading to the generation and elevation of protein-like substances in purified water.

The increase of DOM concentration in purified water is influenced by various factors, such as raw water characteristics, insufficient chlorine dose, temperature, and the

treatment process. In a drinking water treatment plant that applies the sludge recycling process, the issue associated with the release of DOM from DWTS can cause an increase in DOM concentration in purified water. Through treatment of DWTS by varying the oxygen concentration and temperatures, it was made clear that DOM released from DWTS had a higher concentration and complex composition than that of raw water. More DOM was released from non-aerated DWTS than that from the aerated ones, due to enhanced release rate and lowered degradation rate (3.6–6.8 times at 40℃). The fluorescence intensity of humic-like and protein-like substances was found to increase by 45% and 22% respectively at the end of experimental runs without aeration.

The different compositions of DOM released from DWTS can cause different reactivity and treatability for DOM during drinking water treatment. The result of chlorine consumption by DOM demonstrated that tryptophan-like and humic-like substances consumed more chlorine than other substances. DOM released from the sludge was distinctly different between aerated and non-aerated conditions of DWTS in both content and composition, resulting in different consumption rates for chlorine. The chlorine decay rates represented by the first-order rate constant (k) were in the range of 0.7–1.28 h^{-1} and 1.02–1.34 h^{-1} for the water from DWTS stored under aerated and non-aerated conditions, respectively. Compared to those under the aerated condition, the DOM under the non-aerated conditions revealed a better relationship with UV_{260} owing to more chlorine-consumptive substances that were released under non-aerated conditions. Both temperature and oxygen concentration were found to be important factors regarding the storage of DWTS in the thickener tank for sludge in drinking water treatment plants.

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Chapter 1 Introduction

1. Background

Dissolved organic matter (DOM) is a complex mixture of organic compounds that presents in natural water and originates from the decomposition of organic material from plants, algae, and bacteria (Sillanpää, 2015). The presence of DOM in drinking water can cause various problems, such as color, odor, taste, transport of pesticides, transport of heavy metals, and, most importantly, disinfection by-products (DBPs) (Ghernaout, 2020). The production of drinking water is mostly treated by conventional treatment, involving coagulation-flocculation and sedimentation. The changes and removal of DOM in a drinking water treatment plant (DWTP) are dependent on the source water, selected treatment process, and seasonal changes. In most DWTP, coagulation is used to reduce turbidity, color, and another contaminant. However, the removal of DOM via coagulation requires large quantities of the coagulant. This can result in high sludge production and secondary pollution.

During drinking water production, drinking water treatment plants generate large amounts of drinking water treatment sludge (DWTS). As a general waste, DWTS is composed of impurities (e.g., sediments) along with DOM from raw water and Al- and/or Fe-based hydroxides from chemical agents used in treatment processes and is traditionally considered nonhazardous (Wang *et al*., 2022; Ahmad *et al*., 2016a). Environmental restrictions have been placed on disposal methods that require sludge recycling, which is an important pathway for realizing the reduction and reclamation of DWTS from water treatment plants (Zhou *et al*., 2016). DWTS dewatering has become more common, and the ‘recycled water’ is recycled back into the stream of drinking water treatment, achieving zero waste discharge from drinking water treatment plants. However, the main water quality issue associated with the recycling process is the release of DOM from DWTS (Zhou *et al.*, 2015), a release that potentially causes problems for water recycling in drinking water treatment plants, particularly high reduction of disinfectant by DOM.

Disinfection is an integral part of drinking water treatment plants, which inactivates pathogens and mitigates potential risks associated with exposure to waterborne disease as well as reduces and maintains the concentration of DOM in the purified water. Chlorine is widely used for the disinfection of drinking water because of its comparatively low cost, effectiveness in killing bacteria, and chemical stability (Al-Abri *et al.*, 2019). Determining the optimum dose of chlorine during the disinfection process and estimating residual chlorine concentration in the purified water remained a challenge for decades. Factors, including seasonal changes and biogeochemistry of source water, have been reported to influence the quality of purified water and could limit the widespread applications of mathematical approaches (Maqbool *et al.*, 2021). This is because the variations in the relative concentration of natural and anthropogenic concerts of source water with seasonal changes could be linked to the quality of purified water in the drinking water treatment plants.

On the other hand, the presence of extensive DOM from DWTS in drinking water treatment plants that utilize the recycling process could result in a change in the composition of purified water. A study showed the presence of some readily oxidizable substances (such as humic molecules) from DWTS caused the larger reduction of residual chlorine even if its concentration was lower (0.13 to 0.23 mg/L as DOC) (Araya and Sánchez, 2018). The different compositions of DOM also can contribute to a different reactivity with chlorine through the oxidation reactions (i.e., cleaving carbon-carbon double bonds), additional reactions to unsaturated bonds, and electrophilic substitution reactions at nucleophilic sites (Deborde and von Gunten, 2008). The molecular diversity of DOM can influence the overall reaction mechanisms during the disinfection process, which could significantly impact the efficacy of the selected disinfectants. Therefore, efforts are required to study the impact of the variations in the concentration of DOM in source water and water from DWTS on residual chlorine.

Understanding the reactivity and treatability of DOM during the drinking water treatment is crucial to evaluating the performance of DWTP. Traditionally, DOM in water is tested by chemical and biochemical parameters, such as chemical oxygen demand (COD), biological oxygen demand (BOD), dissolved organic carbon (DOC), and total organic carbon (TOC). However, those simple bulk parameters cannot provide information on the chemical composition of DOM and the concentration of different DOM constituents, which are essential for understanding the treatment processes concerning DOM removal (Shi *et al.*, 2021). Furthermore, DOM changes and their removal process and disposal can be expensive, hence there is a need for effective characterization and monitoring of DOM in source water and drinking water treatments, which can provide valuable insight into the variable DOM composition across different water bodies and are effective for tracking the changes of different DOM constituents in a series of the treatment process.

Fluorescence excitation-emission matrix (EEM) spectroscopy has been used as a rapid and highly sensitive analytical technique to determine the dynamics of DOM and can supply information on DOM quality in various types of water. Fluorescence EEM analysis can identify several fluorescence peaks in water and wastewater, including humic-like, tyrosine-like, and tryptophan-like (Rodríguez-Vidal *et al.*, 2021; Baghoth *et* *al*., 2011, Henderson *et al*., 2009). These fluorescence peaks could be associated with the intensity of certain fluorescent components at a certain wavelength and be easily linked with other parameters such as DOC and dissolved organic nitrogen (DON) to predict the capability of online monitoring during drinking water treatment. Since the fluorescence EEM is more sensitive to UV-vis absorbance, (Henderson *et al*., 2009), it is important to examine the changes of DOM to ensure its reactivity and treatability throughout the drinking water treatment. It is reasonable to judge that the treatment process would affect the structural composition of DOM resulting in the increase and decrease of DOM concentration throughout the treatment process. The results suggested that the fluorescence EEM analysis can provide more details on the DOM changes during the treatment in drinking water treatment plants.

2. Research Objectives

This study aims to characterize the DOM and its changes during the drinking water treatment. The research idea on the DOM changes during the drinking water treatment is shown in Fig. 1.1. To achieve the purpose of this study, the specific objectives were set as follows.

- To investigate the changes of DOM during drinking water treatment.
- To characterize the DOM released from DWTS and their changes during storage.
- To investigate the changes of DOM based on its reactivity with chlorine.
- To understand the fluorescence EEM analysis on evaluating the DOM quality and their changes by the treatment process.

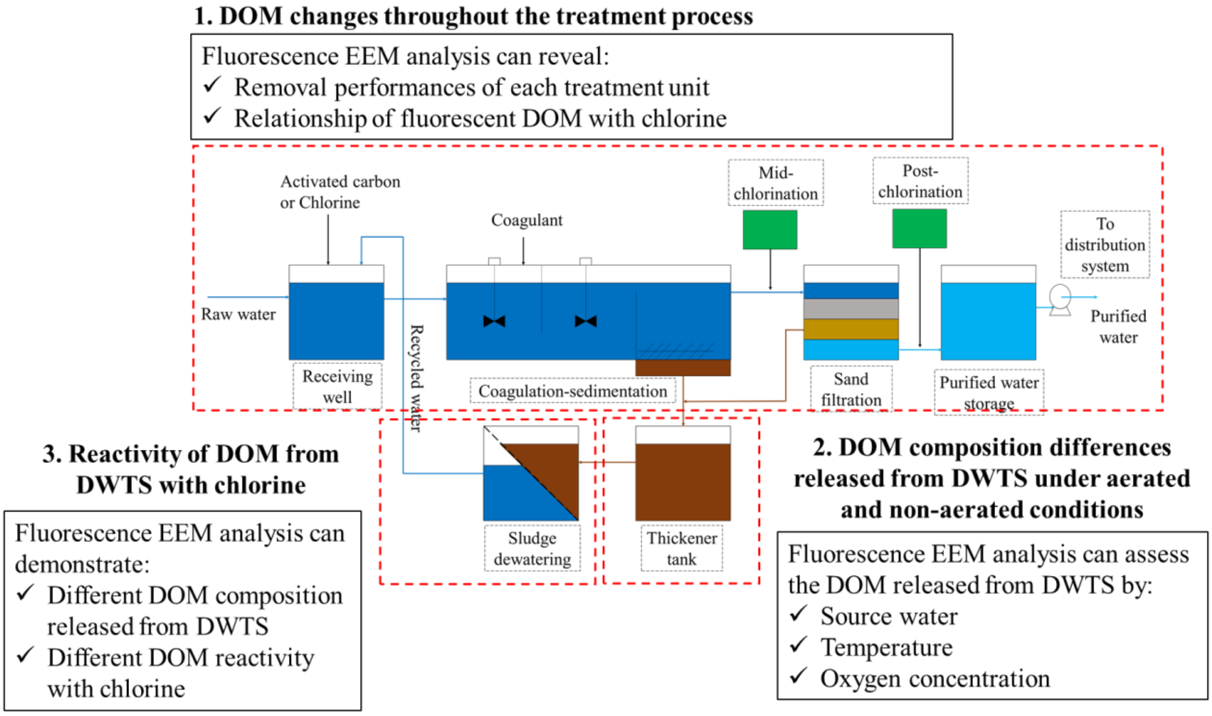

Fig. 1.1. Main study contents and the concerning points in this dissertation.

3. Structure of the Dissertation

The dissertation consists of 6 chapters:

- Chapter 1 presents the overall structure and objective of the study.
- Chapter 2 presents the literature review on basic concepts of the fate and behavior of DOM, fluorescence EEM analysis, drinking water treatment system, and drinking water treatment sludge.
- Chapter 3 presents the changes in DOM contents and compositions during the drinking water treatment.
- Chapter 4 presents the physicochemical properties of DWTS, and the DOM released from DWTS. The influence of storage temperature and oxygen concentration was investigated to know the DOM quality released from DWTS.
- Chapter 5 discusses the chlorine reactivity with DOM released from DWTS.

- Chapter 6 presents the conclusion of this study together with a recommendation for future work.

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Chapter 2 Literature Review

2.1. Dissolved organic matter (DOM)

A wide range of terminology is used to describe dissolved organic matter (DOM) in the environment. DOM is a key component in aquatic environments and presents in aquatic systems, particularly surface waters. As a result of the interactions between the hydrologic cycle and the biosphere and geosphere, the water sources of drinking water generally contain DOM. DOM consists of a wide range of chemical compositions, molecular sizes, and structures. Humic substances are the major constituents of DOM in waters, and are amorphous, dark-colored, acidic in nature, and substituted aromatic rings linked by aliphatic chains (Uyguner-Demirel and Bekbolet 2011). DOM is a type of organic matter that passes through a 0.45 μm filter. A schematic DOM size (μm) and mass (Da) distribution is comparatively different from that of microorganisms and other chemical species in the aquatic system and is shown in Fig. 2.1.

The DOM can be separated into two main groups: hydrophobic and hydrophilic, each of them can be further divided into three next fractions: hydrophobic basic (HoB), hydrophobic acid (HoA), hydrophobic neutral (HoN), hydrophilic base (HiB), hydrophilic acid (HiA) and hydrophilic neutral (HiN). HoB fraction is the carbon in the aliphatic combinations, hydrocarbons, and amines, HoA consists of tannins, polyphenols, and organic complexes of humic substances including humic acid and fulvic acid, HoN contains highly nonpolar connections like humins. The hydrophilic fraction named HiB consists of protein substances, peptides, amino sugars, HiA has highly oxidized organic compounds like humic substances of low atomic mass, HiN is polysaccharides and oligosaccharides of the plant and microbiological origin (Cheftez *et al*., 1998). Table 2.1

provided the properties of HoA described as humic acid and fulvic acid and the hypothetical molecular formula of humic acid is shown in Fig. 2.2.

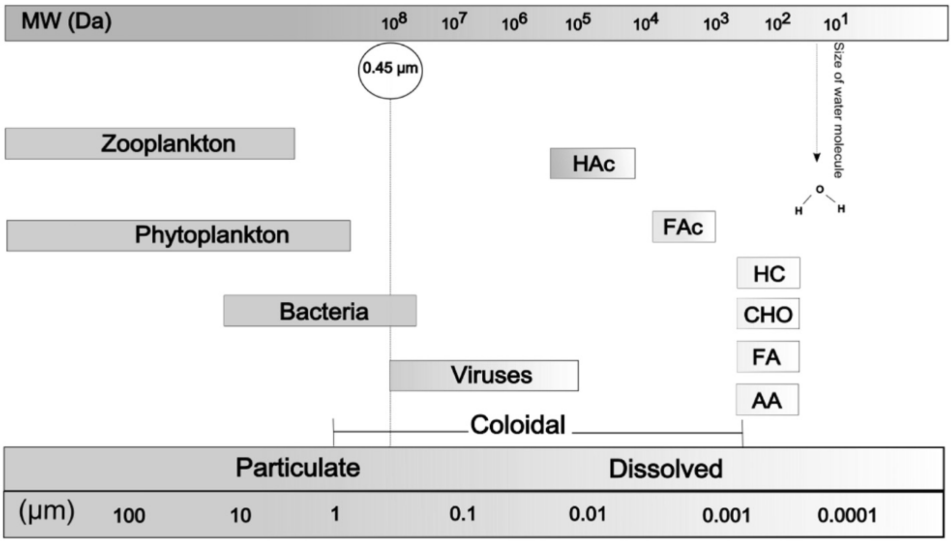

Fig. 2.1. Organic matter size (µm) and mass (Da) distribution of some organisms and chemical molecules in the aquatic system. MW: molecular weight; HAc: humic acid; FAc: fulvic acid; HC: hydrocarbons; CHO: carbohydrates; FA: fatty acids; AA: amino acid. (Thurman, 1985)

DOM has a significant impact on many aspects of water treatment, including the performance of unit processes, the necessity for applications of water treatment chemicals, and the biological stability of the water. As a result, DOM affects potable water quality as a carrier of metals and hydrophobic organic chemicals by contributing to undesirable color, taste, and odor problems. In addition, DOM necessities most of the coagulants and disinfectants used in water treatment. It tends to interfere with the performance of unit operations, such as biofilm growth on media, causing rapid filter clogging and fast saturation of activated carbon beds. DOM is also responsible for the fouling of the membrane and acts as a substrate for bacterial growth in the distribution system (Du *et* *al.*, 2020). Moreover, DOM has been found to be the major contributor to disinfection by-products (DBPs) formation (Tak and Vellanki, 2018). DOM also forms stable complexes with metal ions. Thus, the removal of DOM from water is an emerging issue, and robust and efficient treatment technology is needed to address it.

Table 2.1. Common properties of humic acid and fulvic acid (Snoeyink and Jenkins, 1980)

Property	Humic acid	Fulvic acid
Elemental composition (%w by weight)		
Carbon	50-60	40-50
Hydrogen	4-6	4-6
Oxygen	30-35	44-50
Nitrogen	2-4	<1-3
Sulfur	1-2	0-2
Solubility in strong acid	Not soluble	Soluble
Apparent molecular weight range (atomic mass units)	Few hundred to several million	180-10,000
Functional group distribution (% of oxygen is indicated in functional groups)		
Carboxyl (–COOH)	14-15	58-65
Phenol (–Ph)	10-38	9-19
Alcohol (–R–OH)	13-15	11-16
Carbonyl (–C=O)	4-23	4-11
Methoxyl (–O–CH_3)	1-5	1-2

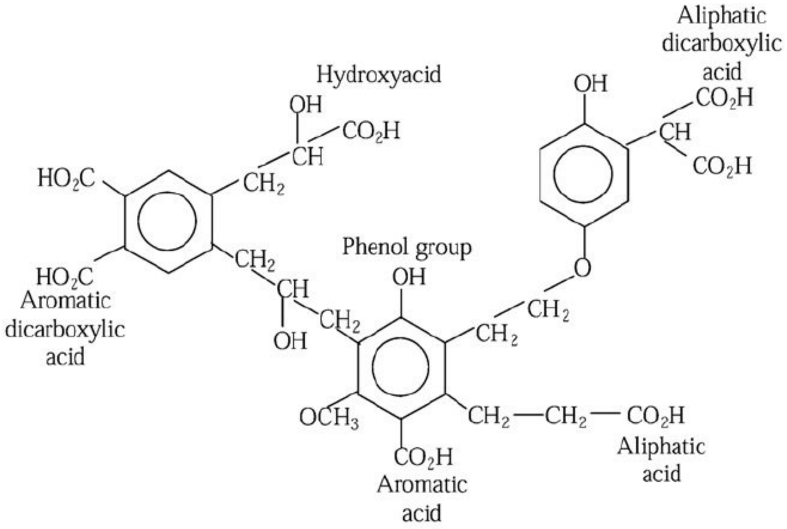

Fig. 2.2. Hypothetical molecular structure of humic acid (Duan and Gregory (2003))

2.2. Fluorescence excitation-emission matrix (EEM) analysis

Fluorescence spectroscopy is considered a suitable technique to detect DOM and to trace its changes and behavior during treatment trains. It is widely reported that compared with that generated from ultraviolet (UV) light, the EEM generated from a constant fluorescence scan contains more dimensional information and has a more sensitive performance in detecting low concentration organic matter. Fig. 2.3 summarizes the recent approaches and applications of 3D fluorescence technology to characterize the DOM in engineering systems.

The peak picking method is the basic method for fluorescence components analysis and other analytical technologies that identify the DOM components by excitation and emission (Ex/Em) pairs, which are the positions of the fluorescence peaks. The differences in structure determine the different intensity responses to excitation and emission, making each type of organic matter have its own unique position in a fluorescence map. The compositions of DOM in drinking water treatment are usually simpler compared to those in wastewater, which is dominated by humic substances and protein-like substances. The variation in peak position could sometimes be seen as a kind of information, which captured the physicochemical properties of the DOM and helped interpret the EEM maps. With regards to the molecular size, a positive relationship was recorded between the molecular weights (MW) and fluorescence emission maxima for humic acids, which could be attributed to the extension of the conjugated system. The increase in molecular weight means accumulation of the substance, which could make the electrons in the delocalized π bond easier to excite, thereby enhancing the Ex/Em wavelength and intensity of fluorescence. For hydrophobicity and hydrophilicity, Lakowicz (2006) presents an early report of the emissions shift to longer wavelengths as the tryptophan residues in proteins become hydrogen-bonded or exposed to water. Baker *et al*. (2008) defines two linear regression models between the peak emission wavelength and hydrophilicity (r = −0.92 and r = −0.76). The influences of molecular weight and hydrophily/hydrophobicity on the peak position are widely acknowledged.

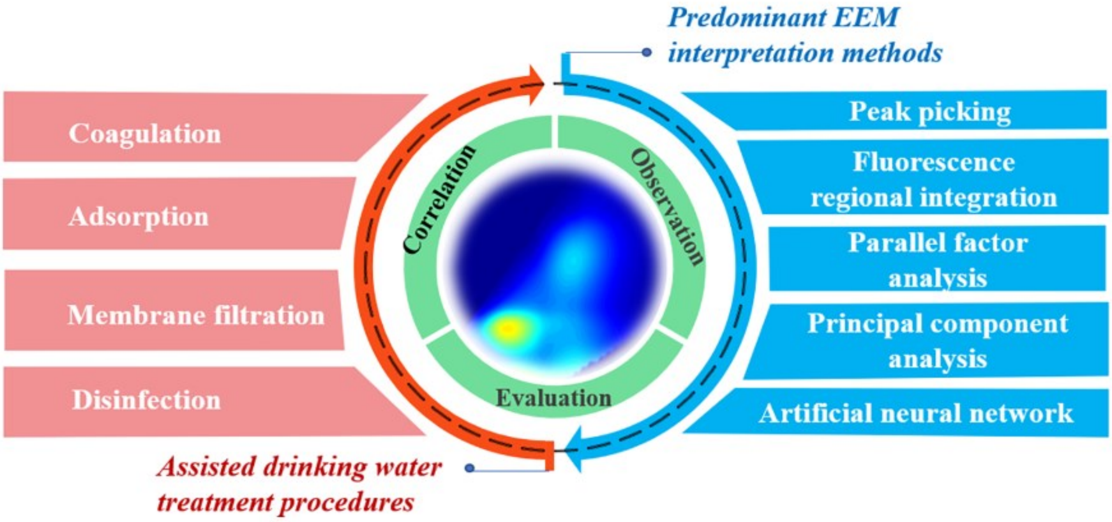

Fig. 2.3. An overview of predominant EEM interpretation methods and major assisted drinking water treatment procedures.

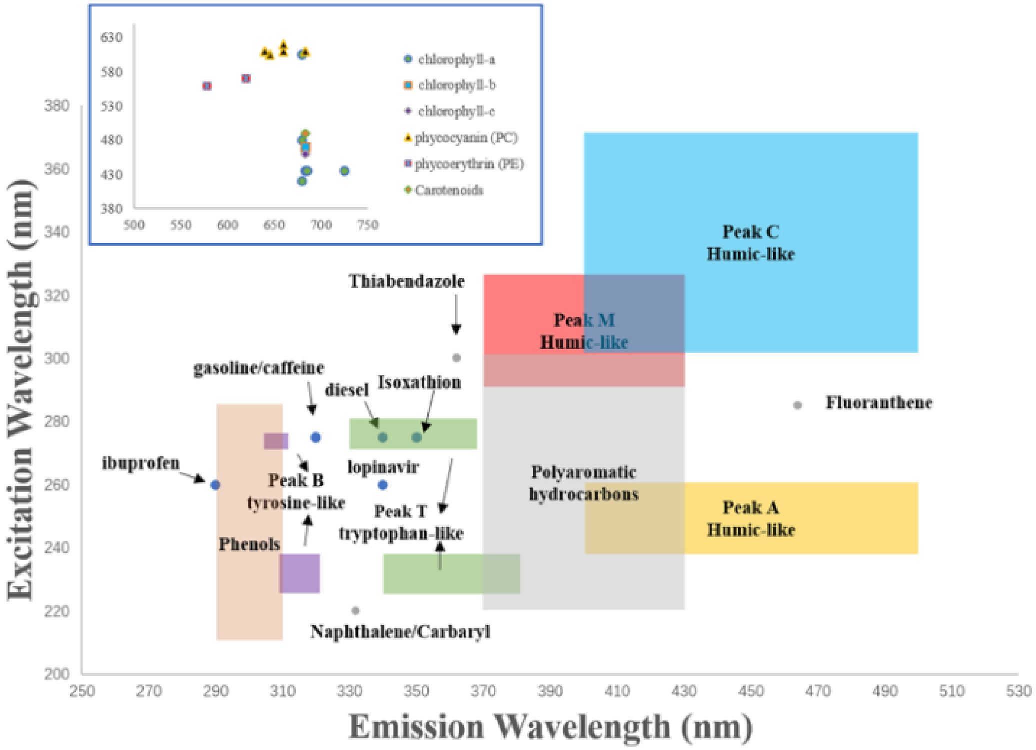

Fig. 2.4. A summary of traditional DOM peaks, representative micropollutant peaks, and algal pigment peaks.

Many peak positions, including protein-like substances and humic substances, have been recorded and summarized systematically. With the popularity of using fluorescence techniques characterizing NOM, peaks of some other types of organic matter have been proposed, represented by micropollutant fluorescence peaks (overlap with NOM peaks evidently) and algae pigment fluorescence peaks (away from NOM peaks). Fig. 2.4 shows a summary of traditional DOM peaks, representative micropollutant peaks, and algae pigment peaks. As fluorescent micropollutants have their own fluorescence peaks, a big impediment in identifying them accurately is overlapping – a kind of interference between DOM fluorescence because the fluorescence spectrum is not simply a point, instead, a scope. Yang *et al*. (2019) investigates the practicability of rapid detection of polycyclic aromatic hydrocarbons and pesticides in surface waters based on peak picking and find that the background noise generated from NOM is non-negligible though with the help of factor analysis algorithm discerning components. In addition, Rodríguez-Vidal *et al.* (2021) summarized some fluorescence peaks in water and wastewater and their respective excitation-emission wavelength range (Fig. 2.5). The fluorescence peaks can be classified into protein-like peaks: Peak 1 (tyrosine-like: Ex/Em: 220–237/305–320), Peak 2 (tryptophan-like: Ex/Em 215–237/340–381), and Peak 4 (tryptophan-like: Ex/Em: 275–285/320–350) and humic-like peaks: Peak 3 (humic-like: Ex/Em: 320–360/420–460) and Peak 5 (humic-like: Ex/Em: 230–260/400–480). Based on the above, direct characterization of micropollutants relying on peak picking seems difficult currently. Instead, indirectly there is a trend using a linear relationship between traditional NOM fluorescence and micropollutant fluorescence to have a prediction (Sgroi *et al.*, 2017).

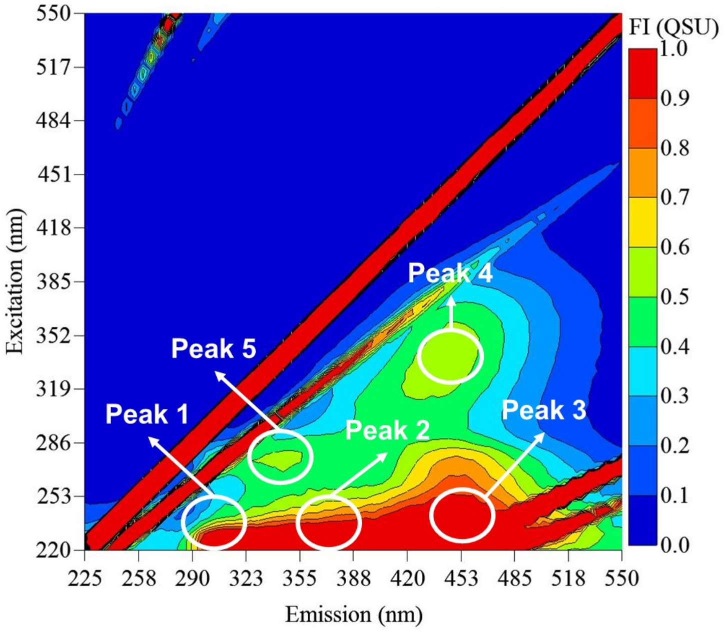

Fig. 2.5. A summary of traditional DOM peaks purposed by Rodríguez-Vidal *et al.* (2021).

Although there are unavoidable uncertainties in the peak locations, peak picking still has advantages for the potential of real-time monitoring, while previous studies have found significant correlations between the peaks and water quality indicators, custom sensors based on fluorescence peak picking have been produced for the detection of BOD, bacteria, and density of algae. Some developed indices from fluorescence EEM, such as humification index (HIX), biological index (BIX), and fluorescence index (FIX) have been applied to characterize the origin and properties of DOM (Huguet *et al.*, 2009). Since the fluorescence EEM is more sensitive to UV-vis absorbance, (Henderson *et al.*, 2009), it is important to examine the changes of DOM to ensure its reactivity and treatability throughout the drinking water treatment.

2.3. Assisted drinking water treatment process

The evaluation system in drinking water treatment is simple by global indicators such as the DOC and COD. The system is effective to a certain extent but also incontestable in that many details are lost. Based on the efficient use of data and the outstanding ability of data visualization, fluorescence spectroscopy has opened new windows into the DOM behavior during water treatment and provides a new tool to evaluate and understand the performance of each process. In addition, the fluorescence technique offers a powerful tool to monitor either the water quality or the performance of water treatment because of its high sensitivity, strong resolving power, and rapid detection.

2.3.1. Coagulation

Coagulation followed by filtration as the main process in conventional water treatment undertakes most of the work, removing the turbidity and color caused by suspended particulate matter and colloidal materials, which are caused by humic substances.

Recently, a few studies investigating coagulation with the assistance of fluorescence techniques have focused on the observation of the removal efficiency and DOM behavior among different coagulants and conditions for its capacity to characterize DOM in detail. Since the removal of DOM is coagulant-dependent, $FeCl_3$, and aluminum sulfate caused the greater removal of humic-like substances than protein-like substances because of the larger molecular size of the former components (Sanchez *et al.*, 2013). However, aluminum chloride exhibited an advantage of adsorbing the organic matter of smaller algae, such as tryptophan-like and amino acid-like substances (Ma *et al.*, 2018). Different types and dosages of coagulant could lead to various results of the DOM structure, reflecting their optical properties. A study by Fan *et al.* (2011) found enhanced fluorescence when a low dosage of $FeCl_3$ was added, which is attributed to the Fe-organic complexation. However, slight changes in the fluorescence were observed when the dosage increased to 5 g/L.

It is still unclear whether coagulation has little effect on the fluorescent DOM or is offset by the fluorescence enhancement because of metal-organic complexation and fluorescence decreased because of the treatment. By comparing the EEM maps of samples treated under different conditions, the optimization of coagulation could be achieved. A study by Gone *et al.* (2009) advised the optimal pH by observing the fluorescence intensity changes during alum coagulation.

2.3.2. Adsorption

The adsorption process aims to remove DOM and micropollutants due to their flexibility, good performance, and low cost. DOM hinders micropollutant removal due to competitive adsorption and pore blockage, making it necessary to characterize its behavior (Li *et al*., 2018). While maybe only a low concentration of refractory DOM remains after treatment before the adsorption process, the fluorescence technology could be seen as an available tool because of its high sensitivity to detect subtle changes in the composition and its excellent resolving power in identifying DOM. The fluorescence technique coupled with the adsorption mechanism could offer insights into DOM behavior. For example, the molecular size presents a negative correlation with the fluorescence index (FIX), which is the ratio of the emission intensity at a wavelength of 470 nm to that at 520 nm, obtained with an excitation of 370 nm (Shimizu *et al*., 2018). Shimabuku *et al*. (2017) finds that the FIX exhibits negative correlations with the parameters representing the ability of adsorption, suggesting that high-FIX, low-MW DOM can access smaller pores, thereby directly competing with micropollutants, while low-FIX, high MW DOM accounts for the pore blockage.

Compared with traditional technologies such as UV absorption, fluorescence indices exhibit more sensitive surrogates in predicting micropollutants during granular activated carbon (GAC) adsorption, which has been concluded by comparing two independent correlation models based on two measurements (Sgroi *et al*., 2018). The preferential adsorption of fluorescent components has also been comprehensively studied by observing the ratios of the peak intensities of different components, and the results can be adsorbent-dependent. It is commonly found that the components located in longer wavelength pairs, such as microbial and terrestrial humic-like components, are more likely to become attached to various adsorbents (GAC, graphene oxide (GO), carbon nanotubes (CNTs), and certain nanoparticles) (Shimabuku *et al*., 2017; Phong *et al*., 2018). However, the opposite phenomenon is observed in a study of the extracellular polymeric substances (EPS) adsorption behavior, showing that protein-like components are more competitive than humic-like components when contacting GO and reduced GO. These differences may be explained by the different hydrophobicity natures and adsorption sites. Preferential adsorption is more evident at a lower pH, as the ratio of components changes to a greater extent, indicating that the fluorescence technique also serves as a tool to observe the process performance. The quantitative and qualitative methods based on 3D fluorescence can provide available approaches to adopt pertinent measures, such as selecting the optimal type of adsorbent in terms of the pore size, hydrophobicity, and pH; improving the performance, especially when dealing with the organic matter with acidic functional groups; and prolonging the operational lives of adsorbents.

2.3.3. Disinfections

Currently, the application of EEM to assist the disinfection process focuses on establishing correlations among the fluorescence parameters, the concentration of DBPs, and their formation potentials and precursors to attempt to find a method to predict, monitor, and control DBPs and to provide a substitute proxy because the present method, laboratory testing, is time-consuming and causes a time lag in guiding the performance of water plants. Compared with traditional surrogates such as DOC, SUVA, and UV absorbance at 260 nm (UV_{260}), the indices generated from EEM that rely on their high sensitivity and solution levels in low concentration detection perform better (e.g., higher R^2) at predicting the formation potentials of DBPs (Watson *et al.*, 2018). In addition to predicting the DBP concentration and formation potential, researchers have also focused on investigating DBP precursors with the help of fluorescence techniques. Chu *et al.* (2010) identify that soluble microbial product-like substances contribute more than humic substances to the formation of dichloroacetamide. In this study, resin separation and fluorescence identification based on peak picking offer a comprehensive specific classification of DOM, and the changes in fluorescence intensity and region integral reveal the underlying relationships from a quantitative view. The correlations mentioned above are valid to unveil the black box, providing deeper insights and showing the potential to be used in DBP precursor online monitoring (Gao *et al.*, 2019).

Slight changes in the EEM maps also indicate changes in the molecular structure during the disinfection process. The shift to shorter wavelengths and decrease in fluorescence intensity is widely reported because the molecular weight decreases as large DOM is degraded. Trueman *et al.* (2016) find that the shift becomes greater with the increase in chlorine dosage during the chlorination process, which seems to correspond with our previous finding. However, the shift increase may also be attributed to the heavy atom effect in which halogen substituents (-Cl, -Br, and -I) with higher relative atomic masses than carbon, hydrogen, and oxygen could result in fluorescence quenching by enhancing the spin-orbit coupling and reducing the energy gap between the singlet and triplet electrons in the excited state. This phenomenon may also contribute to the instability of the quantitative correlations established. Further research is needed to confirm which effect is mainly attributed to the decrease in fluorescence intensity, a blue shift, or a comprehensive effect instead. In addition, the optical changes of DOM are oxidant dependent. Swietlik and Sikorska (2004) report the opposite effect caused by two types of oxidants. Chlorination results in a blue shift of the wavelength in accordance with the abovementioned, while ozonation results in a red shift, which is explained by the change in structure and the release of chromophores. Rodríguez-Vidal *et al.* (2014) undertake a detailed investigation to explore the structural changes during ozonation with the fluorescence technique, thereby finding that the phenomenon differs when the oxidant dosage and DOM change.

2.4. Drinking water treatment sludge (DWTS)

DWTS generated by the conventional treatment process include coagulation solids (sludge) and spent backwash. The spent backwash is often returned to the treatment process to minimize water loss. Sludge may also be recycled to minimize coagulant and coagulant aid doses and improve process performance. Process solids (i.e., coagulation sludge and filtered solids) will contain elevated concentrations of contaminants removed during the treatment process. Depending on the source water concentration of a particular contaminant and any disposal limitations, it may be necessary to evaluate the disposal of process solids with respect to state and local hazardous waste regulations. In some water treatment plants, the sludge is dewatered using various methods to extract the abundant water. The water is recycled and reused as raw water in the production stream, achieving zero discharge of sewage from the drinking water treatment plant (Ahmad *et al*., 2016b). DWTS covers all wastes produced during the treatment of water in a water treatment plant and the properties of the DWTS depend typically on the quality of raw water and the treatment method applied. If the groundwater, generally having stable quality is treated, the quantity and quality of the DWTS fluctuate very little. On the other hand, the treatment of surface water sometimes results in a noticeable change in sludge production in terms of quality and quantity. It may occur due to considerable change in the raw water quality and/or variation in nature as well as the dosage of chemicals used in the treatment processes. The sludge generated in water treatment plants is composed of organic and inorganic matter in the solid, liquid, and gaseous states, whose composition varies in terms of its physical, chemical, and biological characteristics (Sales *et al.*, 2011).

The DWTS contains polydisperse suspension with a wide range of rough disperses or even colloidal particles. The dispersed or colloidal particles present in the raw water are agglomerated and settled down with the aid of chemicals known as coagulants; the chemicals used frequently create a considerable part of the sludge. Commonly used coagulants are aluminum salts ($Al_2(SO_4)_3.18H_2O$), ferric ion salts (e.g., $FeCl_3.6H_2O$), and ferrous iron salts (e.g., $FeCl_2$, $FeSO_4.7H_2O$) (Sales *et al.*, 2011); thus, the DWTS consists of varying concentrations of microorganisms, organic and suspended matter, coagulant products, and chemical elements (Babatunde and Zhao, 2007). The composition of DWTS reported in previous studies is shown in Table 2.2 whereas the separate physicochemical composition of Al-based and Fe-based DWTS (commonly known as alum and ferric sludge respectively). The percentage of different oxides in the sludge may vary because of the quality of raw water, nature of coagulants used, treatment technology involved, and final quality of water produced.

In general, SiO_2 constitutes the major portion of the sludge followed by Al_2O_3 and Fe_2O_3, other oxides such as CaO, MgO, Na_2O, K_2O, P_2O_5, and TiO_2 are also found in a small percentage. The amount of Al_2O_3 or Fe_2O_3 in the WTS is also associated with the coagulant applied (Al or Fe salts) and the concentration of these metals in the raw water. Some heavy metals are also reported in the sludge analyses (Table 2.3). They are carried along with crude water and/or present as impurities in the coagulants which get concentrated into sludge volume during the treatment process. Al and Fe hydroxides of the sludge were found to exhibit amorphous nature.

Table 2.2. Average physicochemical composition of DWTS (Sales *et al.*, 2011; El-Didamony *et al.*, 2014; Ahmad *et al.*, 2016a)

Property		
Physical characteristics of the dry DWTS		
pH	6.82	
Moisture [a] (%)	2.35	
Volatile matter [b] (%)	2.66	
Ash content (%)	89.78	
Loss on ignition [c] (%)	8.96	
Average chemical composition of DWTS (mg.L^{-1})		
	Alum-based	Iron-based
SiO_2	9.3	33.6
Al_2O_3	0.26	13.9
Fe_2O_3	23.3	5.8
CaO	27.2	15.1
MgO	1.31	3.16
SO_3	0.33	0.16
CO_2	18.6	13.9

[a] Heated at 105±5ºC for 24 hours

[b] Combusted at 550±5ºC for 2 hours

[c] Fired at 1000±5ºC for 2 hours

Table 2.3. Average trace metals composition present in the dry DWTS (Sales *et al*., 2011; El Didamony *et al*., 2014; Ahmad *et al*., 2016a)

Element	**ppm**
Ba	749.5
Zr	186.6
Rb	168.2
Ce	152.8
Sr	87.9
Cu	33.0
Pb	32.7
Ni	27.0
Cr	17.6
Ga	15.4
As	15.2
Nb	13.5

Coagulation has been conventionally applied in water treatment to decrease turbidity and color and remove suspended particles and pathogens (Volk *et al*., 2000). In this context, a very important finding reported by many researchers must be highlighted: the optimum operating conditions to remove turbidity or color by coagulation are not necessarily the same conditions for DOM removal (Yan *et al*., 2018). The agglomerated DOM in a floc from indicating that the DWTS form in the sedimentation basin after the coagulation-flocculation process contained mainly inorganic coagulants (alum-based or iron-based) and release to the water phase in forms of the ionic form (Al^{3+} and Fe^{3+}) hydrolyzed and end up forming positively charged complexes highly interactive with the negatively charged colloids (Duan and Gregory, 2003). Further, coagulation has already been reported in the literature that is effective in removing heavier DOM molecules (1000–4000 g/mol), with more affinity towards the hydrophobic fraction, mostly constituted by humic substances (Yee *et al.*, 2009). Since the hydrophobic fraction of DOM has a higher charge density than the hydrophilic fraction, the former is more easily coagulated than the latter (Jarvis *et al.*, 2012, Volk *et al.*, 2000), which necessitates optimizing the coagulation process to improve the NOM removal efficiency. In contrast, based on the removal efficiency of DOM by coagulation, DWTS contains DOM in a larger molecular size and highly hydrophobic fractions constitute with the microorganisms and further released to the water phase after the sludge dewatering. Table 2.4 summarizes the studies on the potential release of organic matter from the flocs formed during the coagulation process under different coagulation conditions.

Table 2.4 Selected research study on the DOM removal from waters by coagulation using alum-based and iron-based coagulant, indicated the release of DOM from sludge after sludge disposal

Targeted organic compounds	Water source and characteristics	Main operating conditions	Monitored parameters	References
Natural organic matter	Natural water from a reservoir (Northern UK) Turbidity: 3.5 NTU DOC: 12.9 mg/L Specific UV absorbance (SUVA): 4.8 L/mg m.	Coagulant: $Al_2(SO_4)_3$ Dosage: 5-15 mg/L pH: 4-8 Reaction time: Around 30 min Stirring rates: 30-200 rpm.	DOC and turbidity reduction Floc formation and size	Jarvis *et al.*, 2012
Algal organic matter and humic substances	Synthetic solutions including bovine serum albumin, peptides/proteins of *M.*	Coagulant: $Al_2(SO_4)_3$ Optimum dosage: 0.2–10 mg/L Reaction time: around 15 min	pH, DOC, UV_{245}, and residual Al	Pivokonsky *et al.*, 2015

	aeruginosa, and peat HS DOC: 8–13 mg/L, depending on the ratios of the components.	Mixing shear rates: 50–200 s^{-1}.		
Humic acid	HA-kaolin synthetic water Turbidity: 15 NTU UV$_{254}$: 0.43 cm^{-1} DOC: 4.38 mg/L pH: 8.2	Coagulant: $Al_2(SO_4)_3$ Dosage: 1–6 mg L^{-1} pH: 4–9 Reaction time: 40 min Stirring rates: 40–200 rpm	Turbidity, UV$_{254}$, and DOC Floc formation, size, and strength	Zhao *et al*., 2011
Humic acid	Runoff water from peat extraction site (Vihanti, Finland) pH: 4.5 DOC: 76.2 mg/L SUVA: 3.8 L/mg m Turbidity: 6.9 NTU	Coagulant: ferric sulfate [$Fe_2(SO_4)_3$] Dosage; 0–100 mg/L pH: 4.5 and 6.5 Reaction time: around 45 min Stirring rate: 50–300 rpm.	DOC, SUVA, and some elemental analysis	Heiderscheidt *et al*., 2016
Algal organic matter	Algal turbid water Turbidity: 20 NTU pH: 8.7 Zeta potential: -19.7 mV Optical density: 0.29 at 750 nm	Coagulant: $FeCl_3$ Dosage: 0.03–0.2 mmol/L pH: 5–9 Reaction time: around 40 min Stirring rate: 40–200 rpm	Turbidity and zeta potential Floc formation and size	Chekli *et al*., 2017

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Chapter 3 Contents and compositions of dissolved organic matter from source to treated water

3.1 Introduction

Dissolved organic matter (DOM) is a mixture of organic compounds with different physicochemical properties that make up concerns related to the effectiveness of water treatment processes. The concentration and composition of DOM vary among natural waters depending on the source, climate, and land use (Xenopoulos *et al*., 2021). In surface water, DOM can originate from aquatic algae which comprises a relatively large nitrogen content and low aromatic carbon and phenolic contents, and/or terrestrially derived substances which have low nitrogen but large amounts of aromatic carbon and phenolic contents (Wang *et al*., 2020). DOM could increase the coagulant dose and be considered as a reservoir for the risk of the potential hazard to the drinking water when it reacts with disinfectant to form disinfection byproducts (DBPs) during the disinfection process in drinking water treatment systems (Maqbool *et al*., 2020). Conventional monitoring techniques, such as specific ultra-violet absorbance at 254 nm (SUVA), chemical oxygen demand, and dissolved organic carbon (DOC) have been widely used in many drinking water treatment plants to assess the changes and the removal efficiency of DOM during drinking water treatment (Li *et al*., 2020, Moyo *et al*., 2019). However, these parameters are not capable to reflect the composition of DOM that are complex and have a wide range of molecular structure, size distribution, hydrophobicity, and aromaticity (Zhang *et al*., 2020, Vera, *et al*., 2017). Therefore, sensitive analytical approaches are required to provide more detail on the reactivity and treatability of DOM.

Fluorescence excitation-emission matrix (EEM) spectroscopy has been used as a rapid and highly sensitive analytical technique to determine the dynamics of DOM and can supply information on DOM quality in various types of water. It has been applied to monitor the DOM removal in water treatment processes, predict the formation of DBPs, and evaluate the performance of membrane technology associated with membrane fouling (Wang *et al*., 2020; Maqbool *et al*., 2020; Yu *et al*., 2020). Fluorescence EEM analysis can identify several fluorescence peaks in water and wastewater, including humic-like, tyrosine-like, and tryptophan-like (Hudori *et al*., 2021; Rodríguez-Vidal *et al*., 2021; Wassawa *et al*., 2019). These fluorescence peaks could be associated with the intensity of certain fluorescent components at a certain wavelength and be easily linked with other parameters such as DOC and dissolved organic nitrogen (DON) to evaluate the treatment process. Some developed indices from fluorescence EEM, such as humification index (HIX), biological index (BIX), and fluorescence index (FI) have been applied to characterize the origin and properties of DOM (Lidén *et al*., 2017). Since the fluorescence EEM is more sensitive to UV-vis absorbance (Rinot *et al*., 2021), it is important to examine the changes of DOM to ensure its reactivity and treatability throughout the drinking water treatment.

Previous studies have reported the application of fluorescence analysis for the assessment of drinking water treatment processes. Maqbool *et al*. (2020) demonstrated the changes in the relative intensity of fluorescent DOM in full-scale drinking water treatment plants. The study employed the fluorescent ratio approach to evaluate the performance of drinking water treatment plants in China. A study by Vera *et al*. (2017) demonstrated the capability of fluorescence EEM analysis to characterize the fate, occurrence, and removal of natural organic matter during the water treatment process. The study showed that the differences in DOM composition due to seasonal variations along the treatment trains point out the suitability of using fluorescence measurements in monitoring and optimizing the operation condition. Moreover, the composition of DOM fractions in recycled water from drinking water treatment sludge analyzed by fluorescence EEM behaved differently against the chlorination, with humic-like substances consuming more chlorine than other DOM fractions (Rosadi *et al*., 2021). The study revealed that fluorescence EEM analysis can predict the reactivity and treatability of DOM. The relationship between fluorescent DOM and other water quality parameters, such as DOC, DON, and total bacteria number have also been assessed in the water source and different water treatment units (Lidén *et al*., 2017).

Although the application of the fluorescence EEM in the full-scale drinking water treatment in Japan has already been reported, it is noteworthy that the water source, temperature, and rainfall largely govern the chemical composition and concentration of DOM in the influent and the treated water, which can assist in determining the efficiency of the treatment process. To generate more information for a better understanding of the changes of DOM using fluorescence EEM analysis, this study investigated the changes of DOM from source to the treated water of drinking water treatment plants for elucidating the changes of DOM compositions in different physicochemical processes of drinking water treatment plants. The observed fluorescence parameters, represented by the fluorescence peak of humic-like and protein-like substances were analyzed using fluorescence EEM. Based on the ratio emission wavelengths at a certain excitation wavelength of fluorescence EEM data, the fluorescence indices were established and discussed to better understand the characteristics of DOM in the source water and during the treatment process. Moreover, using the bulk DOM parameter in terms of DOC, the removal efficiency of each treatment unit in treatment plants was observed to demonstrate the efficacy of the treatment process. Principal component analysis (PCA) was performed for a better understanding of the correlation between the fluorescence parameters and basic water quality indices in raw water and purified water.

3.2 Materials and methods

3.2.1 Configuration of drinking water treatment plants and sample collection

Water samples from two representative drinking water treatment plants were collected monthly from July 2020 to December 2020 in Aichi prefecture, Japan. Plant A and plant B have a design capacity of 87,500 m^3/day and 76,500 m^3/day, respectively. The characteristics of raw water feeding plant A and plant B are shown in Table 3.1. The raw water for plant A originates from the open reservoir and plant B from river water. Both plants use polyaluminum chloride for coagulation with a dose is around 25 mg/L. 10 mg/L of activated carbon is added in plants A and B. Pre-chlorination using 5 mg/L sodium hypochlorite (NaClO) is performed in plants A and B in July and August. Both plants adopted a mid-chlorination process and NaClO (0.5–1.2 mg/L) is injected.

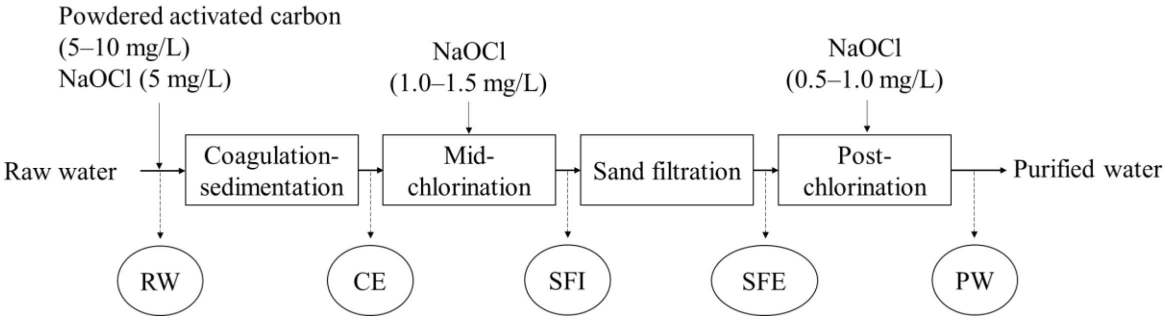

Fig. 3.2. Flowchart of the treatment process in two selected drinking water treatment plants. The circle icons represent the sampling points from each treatment unit. RW: raw water; CE: coagulation effluent; SFI: filtration influent; SFE: filtration effluent; PW: purified water.

The samples were collected from the inlet and outlet of each unit process (Fig. 3.2). Samples were collected in 2 L pre-washed and cleaned glass bottles and were transferred to the laboratory. pH, electrical conductivity (EC), oxidation-reduction potential (ORP), and dissolved oxygen (DO) were measured for the collected water samples. Sodium thiosulfate was added to water samples containing residual chlorine to discontinue the oxidation of DOM by chlorine.

Table 3.1. Water quality of raw water from two drinking water treatment plants. The results are presented as mean. The values in the parentheses indicate the minimum and the maximum. The different letters (a and b) indicate that the observed differences are statistically significant at $p < 0.05$.

Parameters	Plant A (n = 12)	Plant B (n = 6)
pH	7.07 (6.60–7.52) [a]	7.02 (6.74–7.12) [a]
EC (mS/m)	5.88 (4.0–9.49) [a]	7.64 (6.14–6.92) [b]
DO (mg/L)	8.52 (6.13–10.4) [a]	8.90 (6.84–10.5) [a]
ORP (mV)	378 (346–521) [a]	412 (325–584) [a]
Turbidity (NTU)	2.32 (0.28–7.14) [a]	1.99 (1.14–2.73) [b]
DOC (mg/L)	1.84 (1.22–3.67) [a]	0.95 (0.70–1.26) [b]
UV_{260} (m^{-1})	4.03 (1.90–6.87) [a]	2.49 (2.16–2.72) [b]
SUVA (L/ mg m)	2.29 (1.20–4.36) [a]	2.83 (1.80–3.64) [b]
NO_3^--N (mg/L)	0.11 (0.08 – 0.18) [a]	0.18 (0.07–0.23) [a]
TN (mg/L)	0.33 (0.24–0.39) [a]	0.23–0.31) [a]

3.2.2 Water quality analysis

Water samples were filtered through a 0.2-μm cellulose acetate membrane filter (Advantec, Japan) using vacuum filtration apparatus. Filtered samples were analyzed for DOC using a TOC-V_{wet} analyzer (Shimadzu, Japan). UV_{260} was recorded using a UV-1600 spectrophotometer (Shimadzu, Japan). SUVA was calculated as a ratio of UV_{260} to DOC. UV_{260} was widely used to reflect the content of humic substances in natural water and its value is less than 5% higher than UV_{254} (Li *et al.*, 2003). Other parameters such as nitrate-nitrogen (NO_3^--N) and ammonium-nitrogen (NH_4^+-N) were analyzed using an ion chromatography system (LC-20AD SP, Shimadzu, Japan) and total nitrogen (TN) was measured with the procedures described in the APHA standard methods. DO was measured using a DO meter (HQ40D, Hach, Japan), pH, EC, and ORP were measured using a multi-water quality meter (MM-60R, TOA DKK, Japan).

Filtered water was analyzed for EEM spectra using an RF-5300 spectrofluorometer (Shimadzu, Japan). The excitation and emission scans showed wavelengths between 220 nm and 550 nm at 5 nm increments. The obtained fluorescence intensities of the samples were normalized using the quinone sulfate unit (QSU) by dividing the fluorescence intensity values of all samples by that of 10 ppb quinone sulfate (in a 0.05 M H_2SO_4 solution) at the designated excitation wavelength of 350 nm and the emission wavelength of 450 nm. The peak-picking method was used in this study to describe the obtained fluorescence peaks. The fluorescence peaks found in this study can be classified into protein-like peaks: Peak 1 (tyrosine-like: Ex/Em: 220–237/305–320), Peak 2 (tryptophan-like: Ex/Em 215–237/340–381), and Peak 4 (tryptophan-like: Ex/Em: 275–285/320–350) and humic-like peaks: Peak 3 (humic-like: Ex/Em: 320–360/420–460) and Peak 5 (humic-like: Ex/Em: 230–260/400–480) (Rodríguez-Vidal *et al.*, 2021).

The humification index (HIX) indicates the degree of DOM humification and was calculated as the area under the emission spectra of 435 to 480 nm divided by the sum of the emission spectra of 300 to 345 nm and 435 to 480 nm, at an excitation wavelength of 254 nm (Ohno, 2002). A high HIX value (10–16) indicates strongly humified organic matter from the terrestrial origin, while a low HIX (<4) indicates autochthonous organic matter (Yan *et al.*, 2018). The fluorescence index (FIX) indicates the microbial or terrestrial source of DOM and was calculated as the fluorescence intensity ratio of the emission wavelengths of 470 nm and 520 nm, at an excitation wavelength of 370 nm (McKnight *et al.*, 2001). FIX < 1.4

indicates terrestrial and soil sources, and FIX > 1.9 indicates aquatic and microbial sources. A high BIX value (>1) indicates an autochthonous biological activity in water freshly released DOM, while a low BIX value (0.6–0.7) indicates low DOM production in natural water. BIX was calculated as the ratio of the emission wavelength of 380 nm to that of 430 nm using an excitation wavelength of 310 nm. The freshness index (β:α) indicates the age or extent of decomposition, and a high value indicates freshly produced DOM. β:α was calculated as the fluorescence ratio of emission wavelengths of 380 nm and 420–435 nm, at an excitation wavelength of 310 nm (Lidén *et al*., 2017).

3.3 Results and discussion

3.3.1 Raw water characteristics

Fig. 3.3 shows the DOC, UV_{260}, and fluorescence intensity in raw water feeding plants A and B. DOC concentration of plants A and B in the raw water varied from 1.22 to 3.67 and 0.70 to 1.26 mg/L, respectively. The results demonstrate that a significant difference in basic water quality parameters of the two water treatment plants exists. The low concentrations of DOC with high UV_{260} values in plant A could attribute to the high concentration of aromatic tryptophan substances which are recognized with less organic carbon than humic compounds. UV_{260} in the raw water feeding plant A was higher compared to that in plant B, suggesting that aromatic DOM such as humic substances with organic fractions ranging from low to high molecular weights (Edzwald and Tobiason, 2010). Low UV_{260} values in raw water feeding plant B suggest the low contribution of terrestrial DOM. More aromatic substances might transform into non-aromatic substances through the biogeochemical process (Pisani *et al*., 2011) in raw water of plant B.

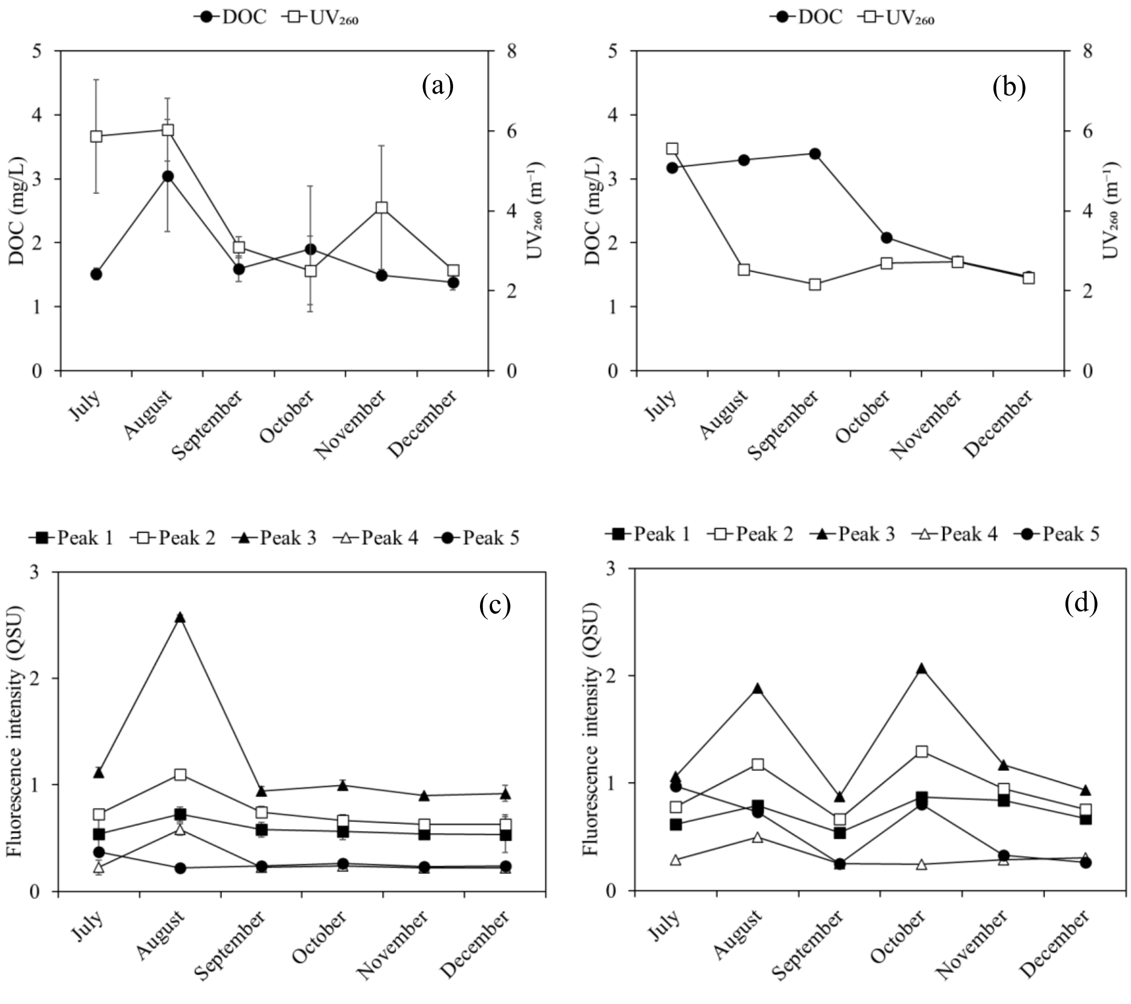

Fig. 3.3. DOC, UV$_{260}$, and fluorescent DOM in raw waters feeding (a and c) plant and (b and d) plant B during the investigation. The error bars represent the standard deviation from averaged data obtained two times for one month. Peak 1: tyrosine-like; Peak 2: tryptophan-like; Peak 3 and 4: humic-like substances from fluorescence EEM.

Five fluorescence peaks shown in Fig. 3.4 featured the composition of DOM found in plants A and B. The fluorescence EEM spectra of DOM in the raw water samples from the two plants showed high intensities of Peak 3, indicating the presence of large amounts of humic-like substances. Peaks 3 and 5 are located beyond the emission of 380 nm and are assigned to humic-like substances, and they are believed to originate from terrestrial humic substances and/or microbial humification (Li *et al*., 2014; Maqbool *et al*., 2020). Peaks 1, 2, and 4 are located in the emission of <380 nm that are assigned to different protein-like substances. These fluorescence signatures of protein-like substances are primarily derived from tryptophan- and tyrosine-like which were mainly associated with microbes and plankton in water (Yamashita *et al*., 2010; Baghoth *et al*., 2011).

The variability in fluorescence intensity was observed in raw water feeding plants A and B (Fig. 3.3). The high proportion of Peak 3 in plants A (56%) and B (34%) may attribute to high precipitation in July and September that enhances the release of humic materials from the watershed. Temperature and the size of colloids also affect the fluorescence intensity, thus rising temperature will increase the fluorescence intensity by about 1% (Nebbioso and Piccolo, 2013; Zaitseva *et al*., 2018). Because raw water in plant A was stored in an open reservoir, the water stagnation received more ultraviolet that supported photodegradation and microbial activity, thus increasing the intensity of DOM. However, the intensity of Peak 5 in the raw water of plant A was higher compared to that of plant B, despite the raw water of plant B having higher DOC levels. This finding demonstrates that the DOM that existed in the raw water of plant B is complex and was less microbially impacted at the source (FIX =

1.46), suggesting the supply of DOC in the raw water of plant B was perhaps made up of biopolymers, which are non-fluorescent and not easily taken up by microorganisms.

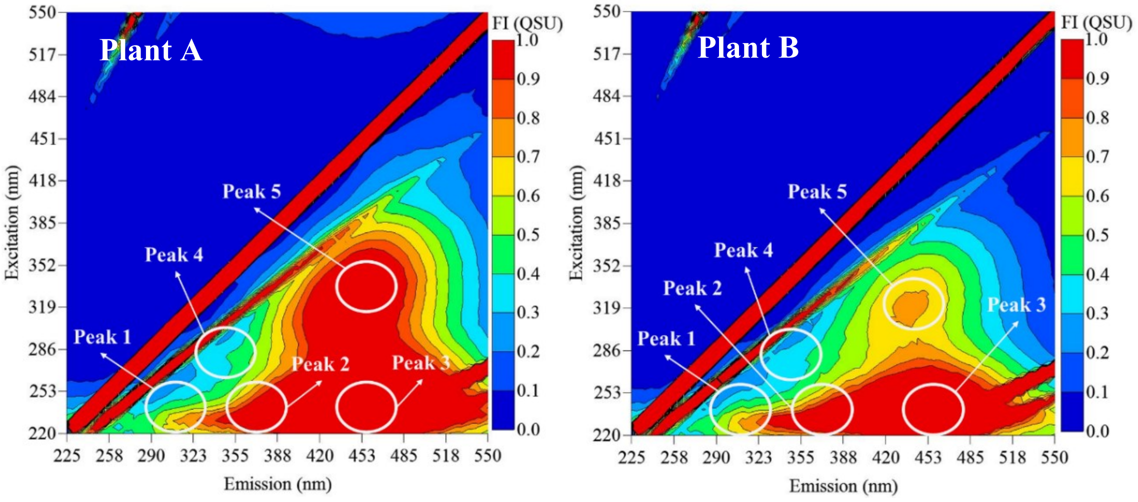

Fig. 3.4. Fluorescence spectra of raw water of plant A and plant B. FI: fluorescence intensity; Peak 1: tyrosine-like; Peak 2: tryptophan-like; Peak 3 and 4: humic-like substances from fluorescence EEM.

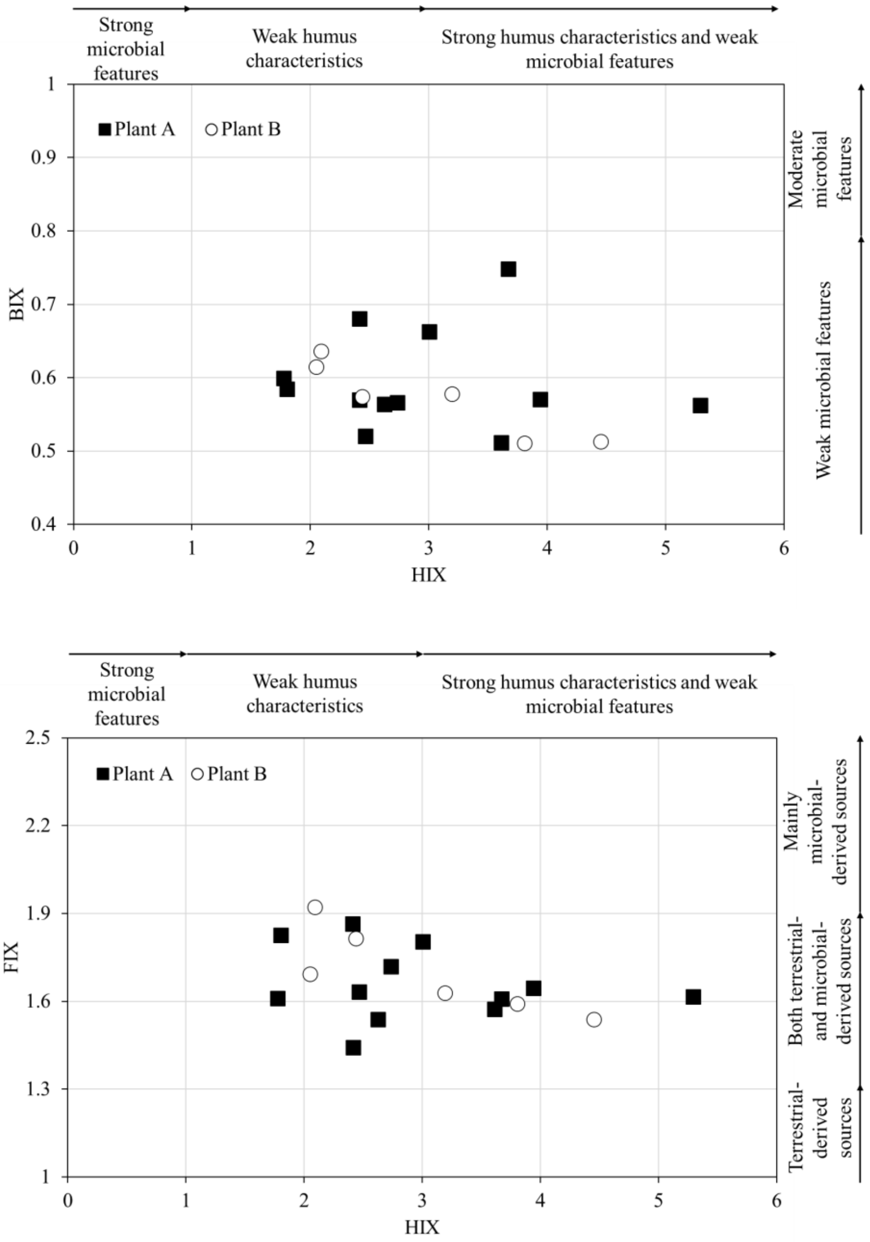

Fig. 3.5. Variation values of FIX, BIX, and HIX in raw water during the investigation.

The FIX for the raw water feeding plant A and B was less than 1.9 and higher than 1.3, indicating a mixture of microbial and terrestrially derived DOM (Fig. 3.5). A study by Birdwell and Engel (2010) demonstrated that FIX was negatively correlated with the aromaticity of DOM. However, the autogenous characteristics were stronger as FIX was higher. The values of FIX in raw water of plant A were in a range of 1.53–1.96 and that of plant B were 1.44–1.97. This indicates that half of DOM in raw water feeding plants A and B has a similar composition of humus and autogenic characteristics, while the other is derived from plankton and microorganisms' degradation. The BIX values observed in this study were ranging from 0.50–0.64 and 0.50–0.66 for plants A and B, respectively. Therefore, the DOM in the raw water feeding both plants was external sources (i.e., microbial metabolism), showing weaker authigenic components. The values of HIX in plant A were in the range of 1.89–4.44 and 1.89–2.43, and in that of plant B, the values of HIX were 1.81–5.29. These showed that DOM had both the characteristics of humus and autogenic features. Compared to plant A, plant B had more DOM with a high degree of humification in raw water.

3.3.2 DOM compositions in different treatment units

As shown in Fig. 3.6, raw water feeding plants A and B is characterized by the presence of humic substances: an intense Peak 3. Coagulation caused a decrease in fluorescence intensity, showing a better removal of humic-like substances than tyrosine-like and tryptophan-like substances. High DOC concentration relates to the higher contribution of humic substances, preferentially removed by coagulation due to their high molecular weight (Bieroza *et al*., 2010). In addition, this could be because of the transformation occurring from DOC to particulate organic matter as DOM agglomerates into flocs (Yang *et al*., 2017). The highest removal of Peak 3 was 58% and 36% in plant A and plant B, respectively. The fluorescence intensity was found to increase in sedimentation effluent of plant B with an overall enhancement of 17%. At this stage, water is retained for a long enough residence time for microorganisms to acclimatize to the environment and produce enzymes necessary to assimilate the available DOM in the water (Krzeminski *et al*., 2019). Our findings coincide with the previous study which demonstrated that tryptophan-like concentrations increase with each treatment step due to chemical changes, temperature, and pH (Kurajica *et al*., 2021). Therefore, the increase of fluorescence intensity after the sedimentation process in plant B could potentially be due to the preference of microorganisms to assimilate low molecular weight DOM fractions from the water, yielding high molecular weight biomolecules as metabolic byproducts.

The fluorescence intensity decreased in the filtration influent due to the addition of chlorine in the mid-chlorination stage. Conjugated double bonds and activated aromatic rings of DOM are disrupted by chlorine, resulting in the production of smaller and hydrophilic organic substances (Tak and Vellanki, 2018). Filtration successfully removed all DOM fractions for both plants. The protein-like substances (Peak 1 and Peak 2) were the least removed from both plants, where the removal of humic-like substances Peak 5 was 38% and 24% for plants A and B, respectively. Overall, plant A removed 48% of fluorescent DOM higher than that of plant B. The low removal rate of fluorescent DOM after the sand filtration process in plant B could be caused by the clogging of the filter due to backwash, raw water characteristics, residence time, and temperature, which changes the composition and concentration of DOM.

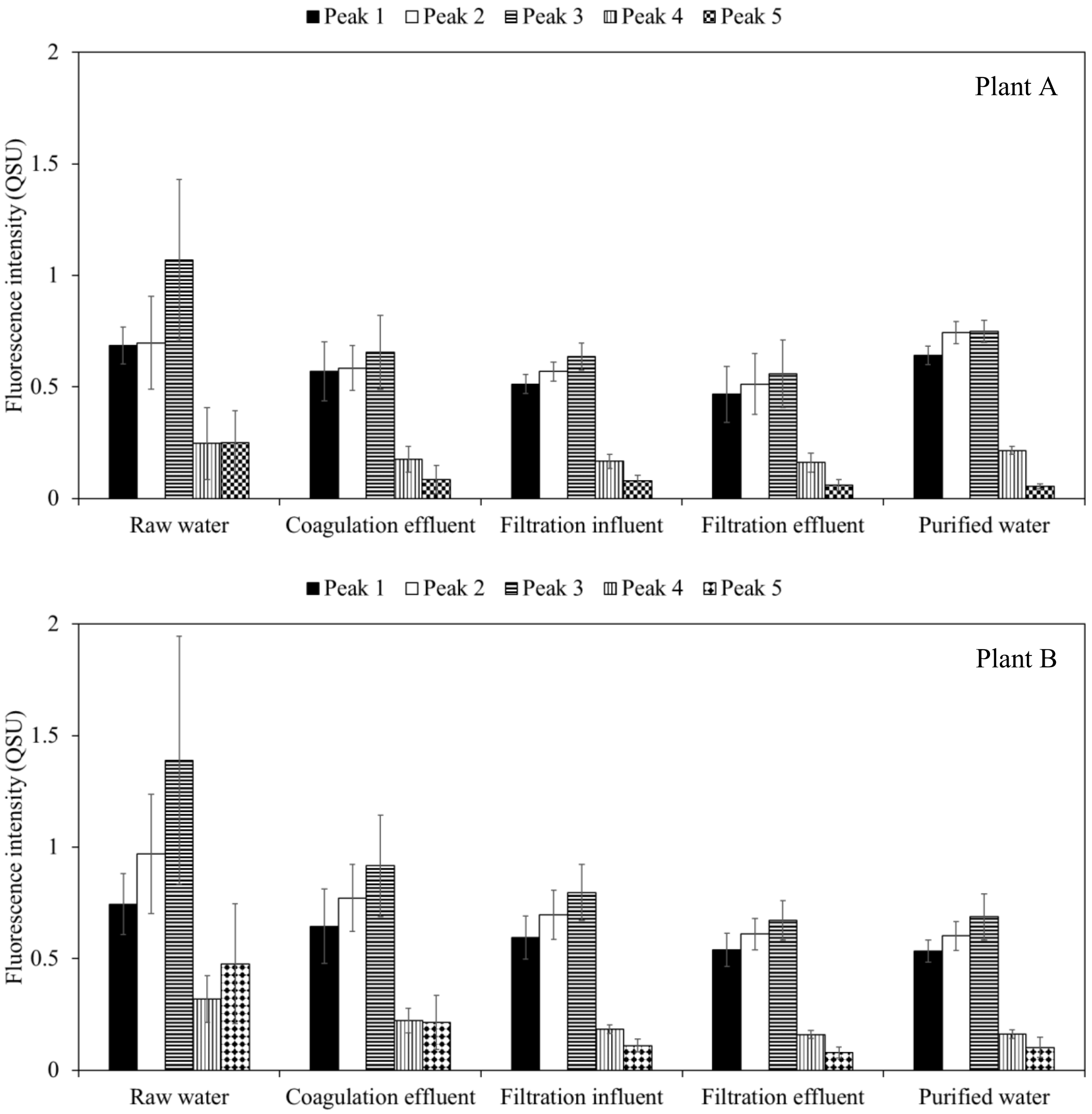

Fig. 3.6. Changes of DOM composition during treatment process in plant A (n = 12) and B (n = 6). Peak 1: tyrosine-like; Peak 2 and Peak 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM.

The increase of all DOM fractions in plant A after post-chlorination was probably attributed to extracellular material excreted by heterotrophic bacteria to digest the DOM exsitu and cell death where the bacteria had outgrown the available nutrients due to the low capability of chlorine to oxidize the DOM and bacteria, in particularly Peak 1 and Peak 2 (Terry & Summers, 2018). The increase of Peak 3 could be due to the heterotrophic bacteria community preferentially utilizing a non-fluorescent signature. The increase and decrease of fluorescence intensity during post-chlorination indicate the desired primary reaction between chlorine and DOM fractions.

The higher fluorescence intensity for PW can be explained by the increase of tryptophan-like Peak 2 and humic-like Peak 3 intensity due to the breakdown of aromatic structures in humic molecules into smaller compounds. The depletion of residual chlorine during the storing of PW enhances the microbial activity and resulted in the higher amounts of autochthonous DOM ascribed to tryptophan-like substances (Bieroza *et al*., 2010). Overall, the quantity of fluorescent DOM upon chlorination depends on the quantity and quality of DOM, chlorine dosage, and contact time (Dong *et al*., 2014). Therefore, monitoring humic fractions at both plants is necessary to curtail the concertation of DOM.

3.3.3 Selective removal of fluorescent DOM at each treatment stage

Fig. 3.7 shows that the removal of bulk DOM (in terms of DOC) and humic-like substances (Peak 3 and 5) by coagulation in plants A and B was generally higher compared to other fluorescent DOM. Higher DOC concentration link to the high contribution of humic substances, preferentially removed by coagulation due to their high molecular weight (Bieroza *et al*., 2010). On the contrary, the sand filtration and chlorination process are more effective to eliminate fluorescent DOM than DOC. Biofilm formation could influence the DOC level and fluorescent DOM (protein-like substances) in the sand filtration unit, resulting in the increase of DOC, Peak 1 and Peak 4 in the sand filtration effluent of plant B. Chlorination could increase DOC concentration by the hydrolysis of particulate organic matter and degradation of chlorine-killed bacteria (Yang *et al.*, 2017), resulting in the negative removal value. As for the fluorescent DOM, Peak 5 was more highly removed by chlorination than other components through the oxidation of unsaturated and conjugated groups, leading to the differential removal among the fluorescent DOM.

As shown in Fig. 3.7, DOC and Peak 5 were highly removed in the selective treatment stage, and a low removal rate was observed for other fluorescent DOM. However, Plant A and B were observed with a negative removal rate of fluorescent DOM in the chlorination process, resulting in an increase in fluorescent DOM intensity in PW. This suggests both plants are less effective in removing fluorescent DOM in the chlorination process. The raw water quality might influence the composition and structure of fluorescent DOM and their changes throughout the treatment process. Fluorescence analysis can rapidly and sensitively detect the fluorescent DOM during the drinking water treatment process and understanding the dynamics of fluorescent DOM is necessary to monitor and control the water quality since the overall removal of DOM is strongly correlated to its fluorescent components (Maqbool *et al.*, 2020; Moyo *et al.*, 2019).

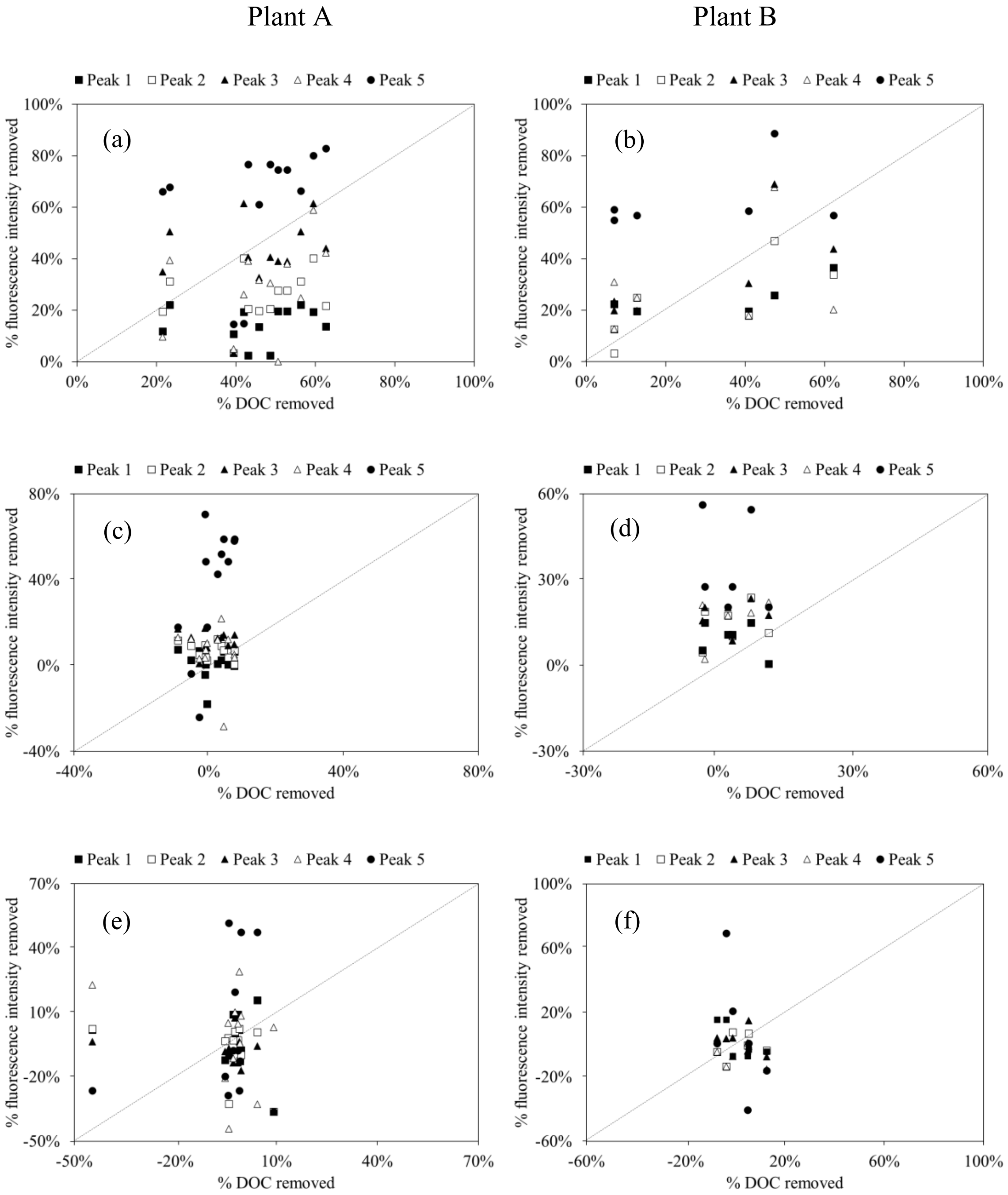

Fig. 3.7. Relationship between the removal of DOC and fluorescence intensity of DOM after (a–b) coagulation, (c–d) sand filtration and (e–f) post chlorination in plant A (n = 12) and B (n = 6). Peak 1: tyrosine-like; Peak 2 and Peak 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM.

3.3.4 Relationship among the fluorescence indices

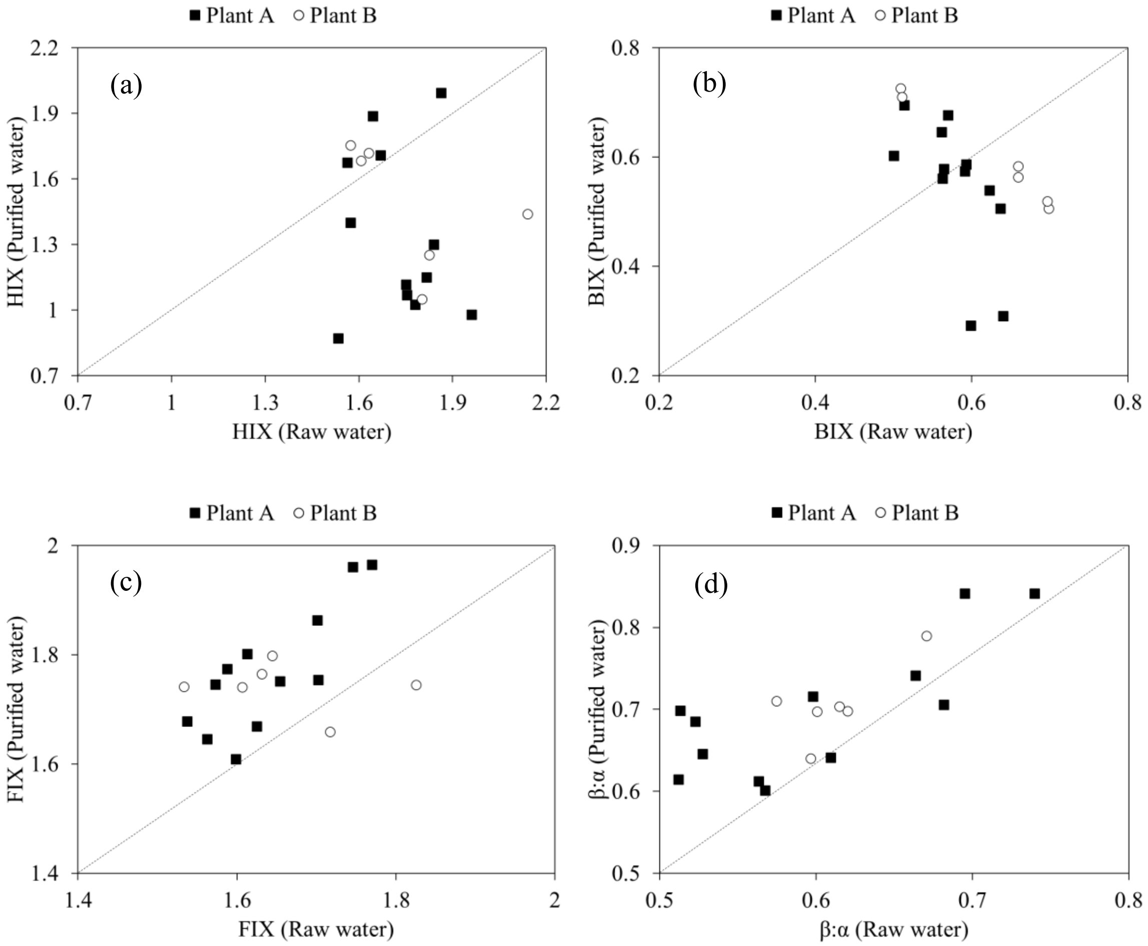

Fig. 3.8. Changes of (a) HIX, (b) BIX, (c) FIX and (d) β:α from raw water to purified water of plant A (n = 12) and B (n = 6).

HIX can be translated to the presence of humic-like substances and their presence is highly observed in the PW of plants A and B, reflecting the higher HIX (Fig. 3.8). Although the removal of humic-like substances was higher by the coagulation process, the high intensity of humic-like substances still can be observed in the PW of plants. The reason could be due to the raw water characteristics, residence time, and temperature that influence the compositions, abundance, or activity of the bacterial community (Prest *et al*., 2016). The long residence times after chlorination and during the storing in the PW tank can affect the HIX. The new-produced humic-like substances can be acted as a substrate for microorganisms to regrowth during the storing of PW in the plant, due to insufficient residual chlorine concentration, thus leading to the low HIX. The remaining small particles in the water after the chlorination process in plant A could be associated with fluorescent DOM-attached particles that continue to be transported to the PW, resulting in the high intensity of fluorescent DOM. However, the observed high HIX value in this study could be explained by the humification process that occurs by the remaining humic-like substances in the chlorinated water and coincides with the decay of the residual chlorine.

The relationship between HIX and DOC reduction further explained that the high HIX value after treatment revealed a less removal efficiency in plants A and B (Fig. 3.9). High HIX means that DOM contains a high proportion of humic substances that can easily be removed by the conventional treatment process. Thus, low HIX should be observed in the water after treatment. However, a contrarian finding was observed in this study, where a high HIX value was observed in PW. The raw water and purified water BIX in plants A and B have no significant correlation. This suggests that the biological and microbial DOM could be more resistant to removal by conventional treatment, resulting in no changes of BIX along the treatment process in both plants.

High FIX in the PW of plants A and B indicates that most of the terrestrially derived DOM were removed along with the treatment. It is known that biopolymers and humic substances have a relatively high removal during the conventional treatment, thus explaining the increasing FIX. The low β:α after treatment in plants A and B could be explained by the successive removal of more DOM with low aromaticity and low molecular weight. The high β:α value in PW of both plants indicated that the degraded DOM transformed into humic-like substances through condensation reactions or structure rearrangements during the chemical process in both plants (Parlanti *et al*., 2000).

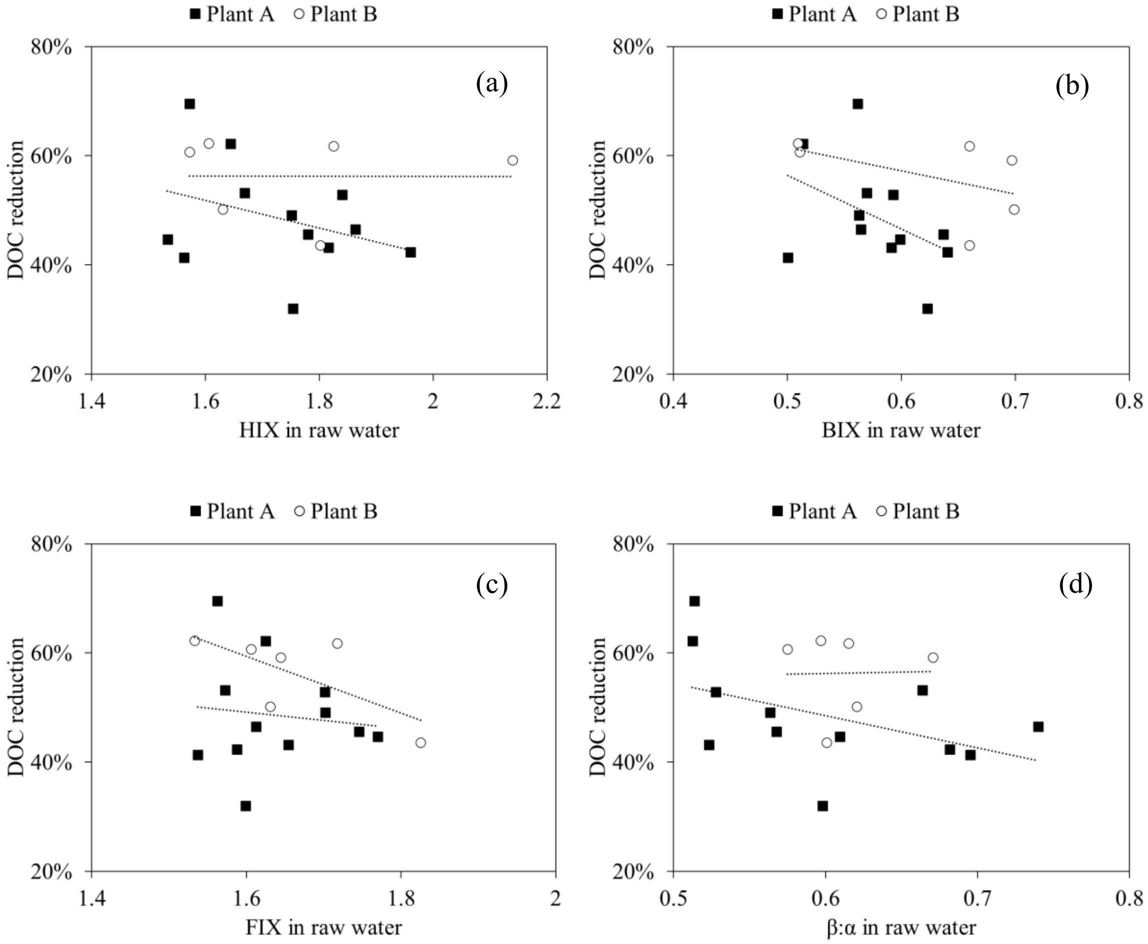

Fig. 3.9. Correlation of DOC reduction and (a) HIX, (b) BIX, (c) FIX, and (d) β:α for the raw water.

The relationship between FIX and β:α and DOC reduction follows a similar trend (Fig 3.9). This could be because they are both influenced by microbial-derived DOM, either by source (FIX) or degree of degradation (β:α). The significant correlations of fluorescence indices in the RW and PW were observed in this study, supported by the significant correlation of reduction of DOC and fluorescence indices (Fig. 3.9). This shows that fluorescence indices are more sensitive than DOC in monitoring the changes of DOM throughout the treatment process, and the related results might not be universal. A significant correlation between fluorescence indices and DOC reduction was also observed in the previous studies to monitor the changes of DOM during the treatment of drinking water (Moyo *et al*., 2019; Lidén *et al*., 2017). Thus, the potential for fluorescence indices for online monitoring can be used for process adaptation to the drinking water quality.

3.3.5 Relationship between fluorescent DOM and water quality indices

Principal component analysis (PCA) was used to explain the relationship between fluorescent DOM and water quality indices in the whole process of drinking water treatment plants. A PCA revealed that the two PCA axes for plant A explained 73.6% of the total variance, with PCA 1 and PCA 2 accounting for 48.3% and 25.3% of the dataset, respectively (Fig. 3.10a–b). Meanwhile, PCA axes for plant B explained 78% of the total variance, with PCA 1 and PCA 2 accounting for 44.6% and 33.4% of the dataset, respectively (Fig. 3.10c–d). The scatter plot of the PCA scores for plant A (Fig. 3.10b) for each treatment unit indicated that the PCA 1 scores ranged from -2.15–2.26, and the PCA 2 scores for plant A ranged from -2.14–1.96. PCA scores for plant B for each treatment unit indicated that PCA 1 scores ranged from -1.16–1.38, and the PCA 2 scores for plant B ranged from -1.69–1.61.

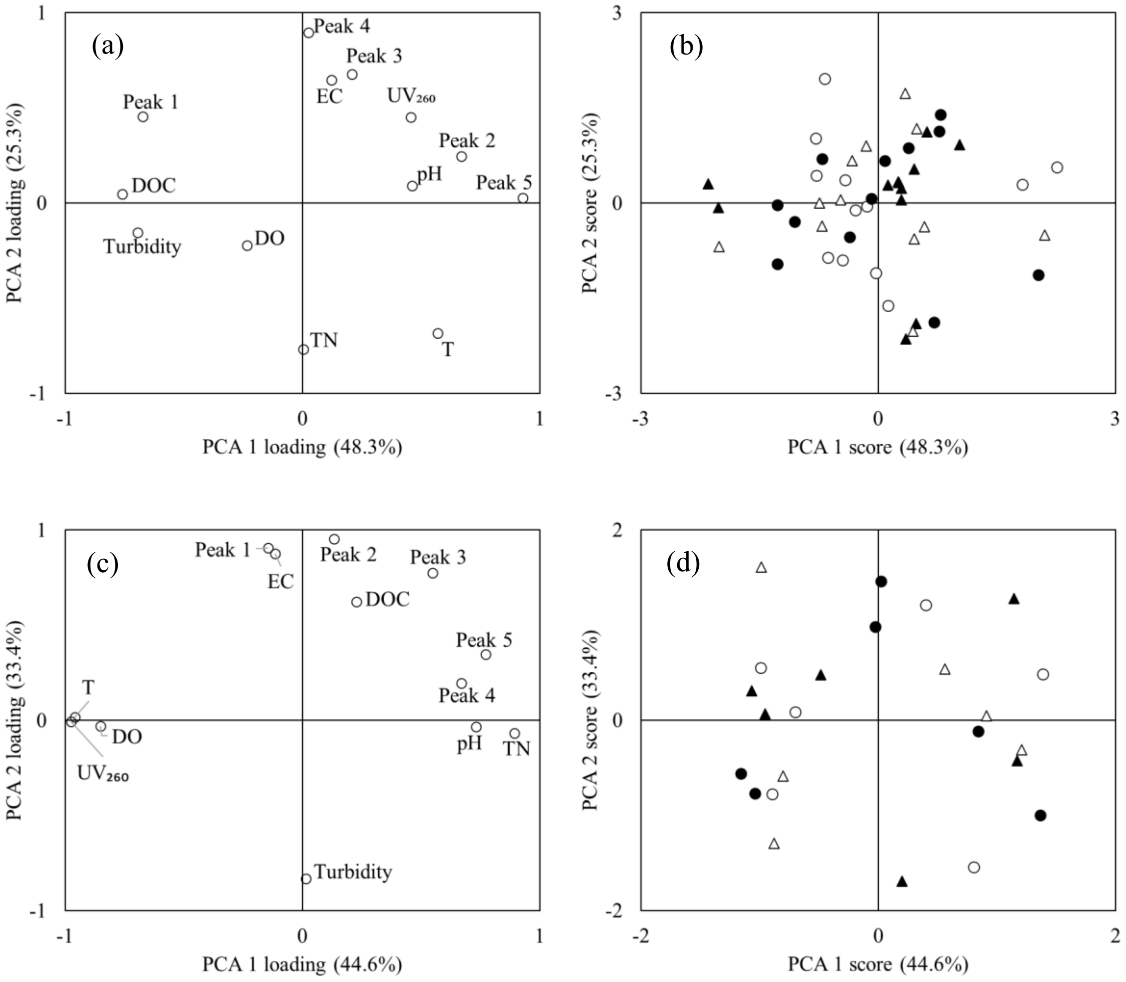

Fig. 3.10. PCA factor loadings of water quality indices and PCA factor scores using all observed data during the whole process of drinking water treatment in plants A (a–b) and plant B (c–d). The black and white circle and triangle represent the sample collected after the coagulation-sedimentation process (white circle), mid-chlorination (black circle), sand filtration (black triangle), and post-chlorination (white triangle).

The PCA 1 loading for plant A (Fig. 3.10a) showed a positive correlation with UV_{260} and all fluorescent DOM except Peak 1. UV_{260}, Peak 2, Peak 3, Peak 4, and Peak 5 clustered along with PCA 1 in the PCA for plant A (Fig. 3.10a), indicating those parameters were closely related and had a common source. Additionally, the fluorescent DOM seemed to be closer to UV_{260} relative to DOC, and it indicated decreasing the UV_{260} was a better way to monitor the fluorescent DOM in plant A. However, Peak 1 and DOC showed a different removal pattern, and the coordinates of Peak 1 and DOC were accordingly found in the opposite direction in the PCA plot. The result indicates the less removal of humic-like substances Peak 1 and DOC, resulting in the increase of humic molecules after treatment in plant A. Fig. 3.10b showed that the PCA score for sand filtration did not change obviously, suggesting the less removal of DOM in plant A.

The PCA 1 loading for plant B (Fig. 3.10c) showed a strong positive correlation with Peak 1 (tyrosine-like) and Peak 2 (tryptophan-like). The bulk DOM (DOC) assembled along with PCA 1, indicating the fluorescent DOM and DOC are relevant and their removal patterns are similar, while UV_{260} was found in the opposite direction with fluorescent DOM in the PCA plot of plant B. This result is contrary to the result from plant A, while UV_{260} is considered as the bulk DOM associated with the fluorescent DOM, and their removal was significantly associated. The reason could be due to the characteristics of source water in plant B (river water), and more organic matter with higher humic molecules presented even after treatment in plant B. Combination of the loading results with the corresponding score plots indicated that fluorescent DOM significantly changed along with the treatment unit in plant B. The coagulation-sedimentation process caused the high removal of fluorescent DOM, while the post-chlorination increased the intensity of fluorescent DOM.

3.3.6 Relationship between fluorescent DOM and chlorine reduction

The correlation between chlorine reduction and fluorescent DOM during mid-chlorination and post-chlorination is presented in Fig. 3.11. Predicting and controlling the residual chlorine concentration in purified water remain a challenge. The relationship highlighted that the humic-like fluorescence component could serve as an indicator to determine the chlorine consumption in the drinking water treatment plant; the higher humic-like fluorescence in the purified water indicated the quicker depletion of residual chlorine. However, no significant correlation was found between Peak 1, 3, and 5 with chlorine reduction in the post-chlorination. Principally, an increasing fluorescence intensity could not be an indicator; the rising concentration of any organic content could not be linked with depletion of chlorine consumption.

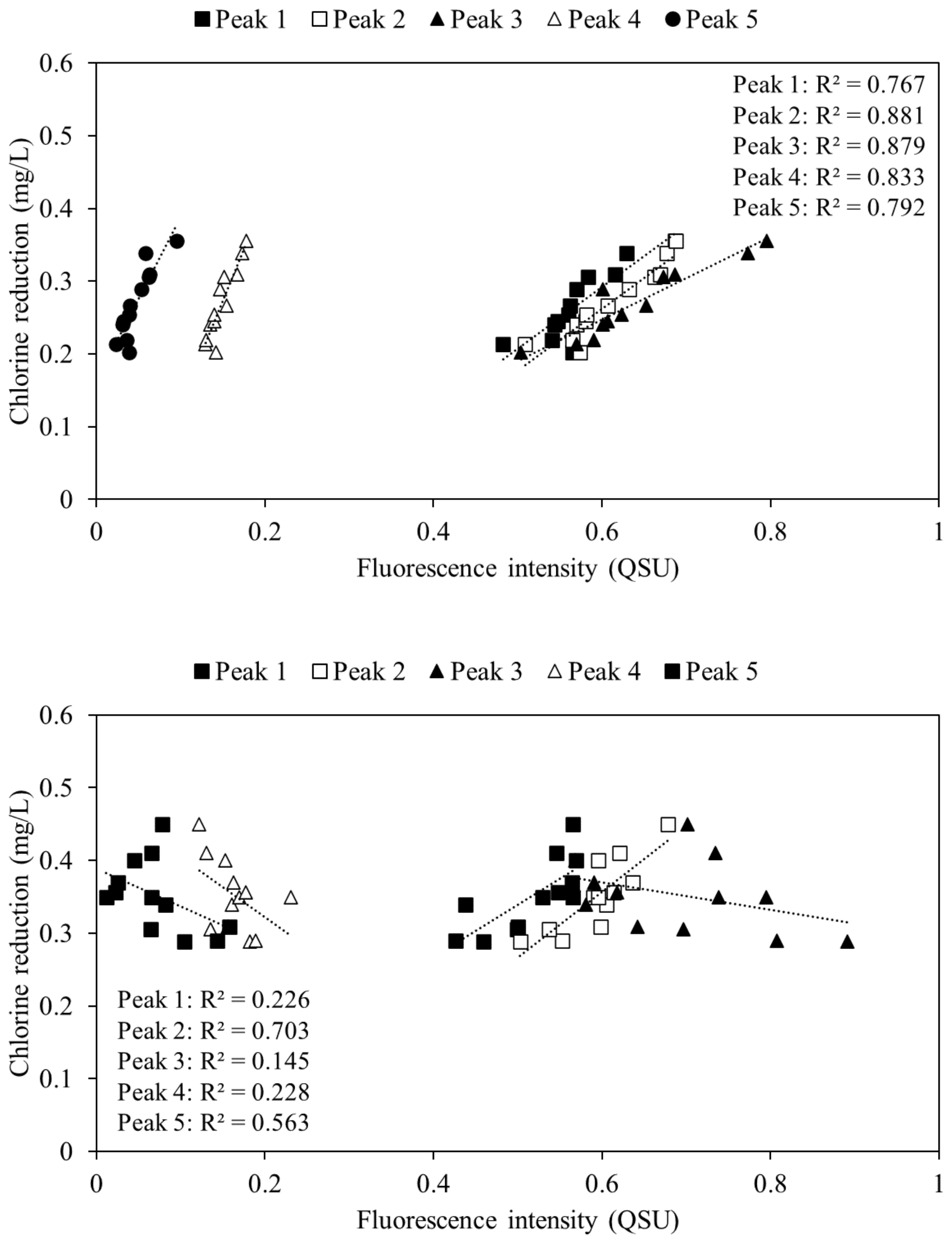

Fig. 3.11 Relationship between fluorescent DOM and chlorine reduction during mid- and post-chlorination in plant A. Peak 1: tyrosine-like; Peak 2 and Peak 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM.

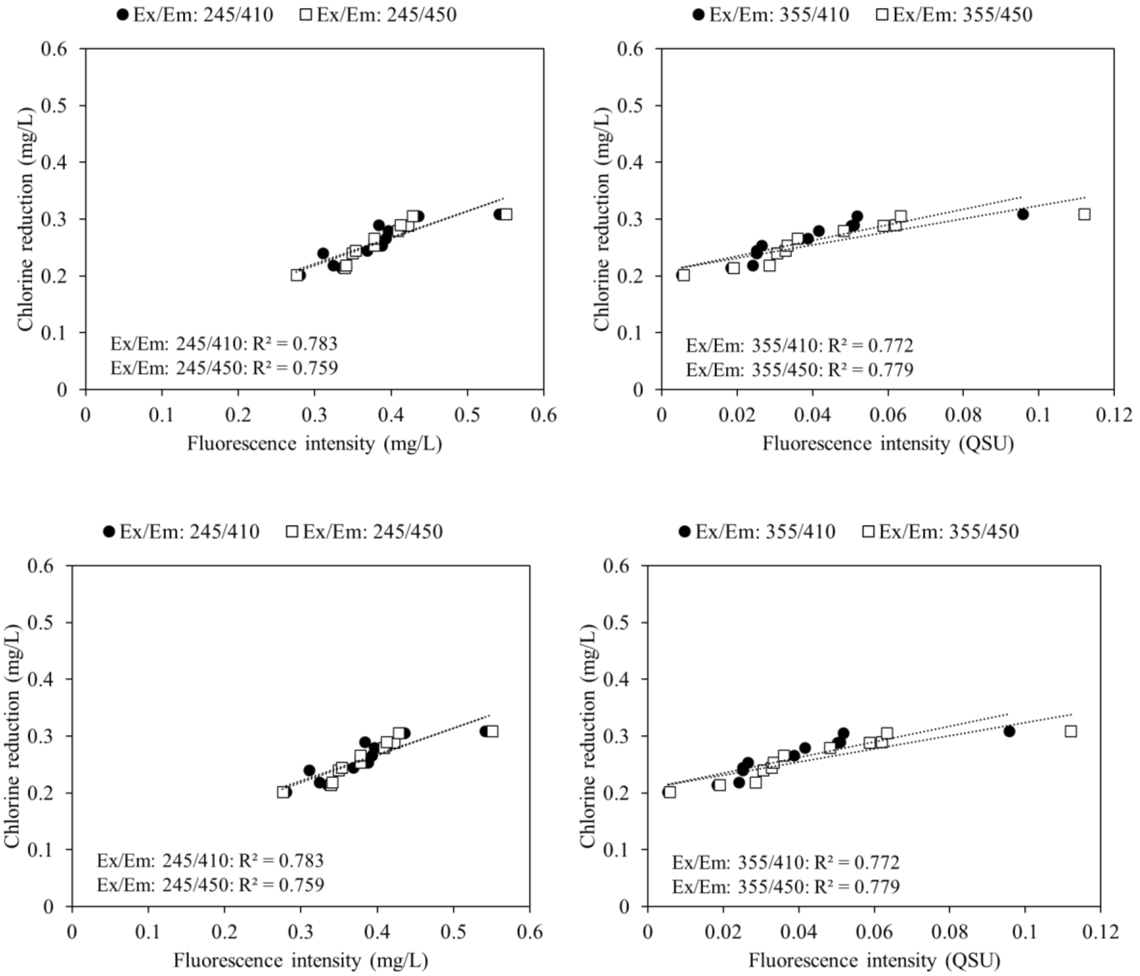

Fig. 3.12. Relationship between chlorine reduction and the single excitation peaks of humic-like substances at 245 and 355 nm from fluorescence EEM during (a–b) mid-chlorination and (c–d) post-chlorination in plant A. Ex/Em: excitation/emission wavelength.

Based on the selected fluorescent component (humic-like substances), the suitability of four peaks; $I_{Ex/Em: 245/410}$, $I_{Ex/Em: 335/410}$, $I_{Ex/Em: 245/450}$, and $I_{Ex/Em: 335/450}$ with the intensity at excitation of 245 and 335 nm, respectively having a common emission wavelength of 410 and 450 nm against chlorine consumption has also been tested and presented in Fig. 3.12. These selected peaks directly represent humic-like substances in the treatment train (raw and purified water). These extracted fluorescence peaks sufficiently explained the behavior of chlorine consumption during mid- and post-chlorination concerning DOM available in the purified water as shown in Fig. 3.12. Compared to $I_{Ex/Em:\ 245/410}$, the $I_{Ex/Em:\ 335/410}$ better explained the chlorine reduction. This is probably due to the abundance of the desired species of humic-like substances reacted with chlorine which contained carbon double bonds in aromatic molecules and halogen substitution reactions (Gonsior *et al*., 2014; Larson and Weber, 1994).

Additionally, the shorter emission wavelength at 410 nm is better explained the correlation between humic-like substances and residual chlorine. The longest emission wavelength can result in a shift of absorption and emission maxima due to the changing environment of the molecule emitted in the longest wavelength. The emitted photons have lower energy because of losses in intermolecular relaxation processes (Stokes shift) (Michalet and Weiss, 2005), resulting in only a small amount of DOM molecule existing in the longest wavelength that corresponded to the reduction of chlorine. This approach of extracting relevant peaks with the help of the peak picking method could help in designing online and portable sensors for water quality monitoring as well as estimating the chlorine dose required to guarantee the moderate concentration of residual chlorine in the consumer’s tap.

3.4. Summary

This study presented the application of fluorescence EEM analysis to investigate and monitor water quality from the source and throughout the drinking water treatment. Fluorescence EEM analysis provided the appearance of fluorescence peaks (Peak 1, 2, 3, 4, and 5) associated with humic-like and protein-like substances. The observed five peaks in the raw water were found to be common in plants A and B. The fluorescence intensity of DOM revealed the effect of the source water of the plants, associated with the origin of fluorescent DOM. Both plants showed a decrease in fluorescent DOM, particularly after coagulation and the mid-chlorination process. However, the removal rate was lower than bulk DOM (in terms of DOC), suggesting a more efficient removal of non-fluorescent DOM. The increase and decrease of fluorescence intensity during post-chlorination indicate the desired primary reaction between chlorine and DOM fractions. Fluorescence indices verified that purified water in plants A and B contained and generated new-produced organic matter during the storing. The representative fluorescence peaks, $I_{\mathrm{Ex/Em:\ 245/410}}$ and the $I_{\mathrm{Ex/Em:\ 335/410}}$, extracted from fluorescence EEM analysis could help in designing a fluorescence tool for relating DOM with chlorine consumption.

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Chapter 4 Contents and compositions of dissolved organic matter from drinking water treatment sludge

4.1. Introduction

A drinking water treatment plant generates large amounts of drinking water treatment sludge (DWTS) as a by-product of drinking water. DWTS is primarily composed of amorphous Fe/Al hydroxides and is produced during flocculation-sedimentation or floatation, as Fe- and Al-based coagulants are commonly used (Zhou *et al.*, 2016). Large volumes of DWTS are generated during the production of drinking water, equivalent to 4-7% of the total drinking water produced (Sun *et al.*, 2015). DWTS also contains organic fractions that can be attributed to the presence of bacteria, humic-like materials derived from the decay of plants, and small quantities of extracellular polymeric substances (EPS) produced by bacteria (Zhou *et al.*, 2018). The properties of DWTS can vary according to the quality of raw water and the treatment method applied. Groundwater tends to be stable in quality, and the DWTS that forms during the treatment of groundwater fluctuates very little in quantity or quality. In contrast, the treatment of surface water sometimes results in noticeable changes in sludge quality and quantity (Ahmad *et al.*, 2016b).

Increasing urbanization and industrialization have resulted in the dramatic growth of drinking water volumes generated, which has led to large amounts of DWTS being generated by drinking water treatment plants. Also, environmental restrictions have been placed on disposal methods that require sludge recycling, which is an important pathway for realizing the reduction and reclamation of total waste residues (Zhou *et al.*, 2016). In recent years, DWTS dewatering has become more common, and the extracted water is recycled back into the stream of drinking water treatment, achieving zero waste discharge from drinking water treatment plants. However, the main water quality issue associated with the recycling process is the release of dissolved organic matter (DOM) from extracellular or intracellular organics that originate from DWTS (Zhou *et al*., 2015), a release that potentially causes problems for water recycling in drinking water treatment plants.

In some drinking water treatment plants in Japan that rely on rapid sand filtration, sludge from the sedimentation basin is discharged to the thickener tank. The sludge is usually dewatered using various methods, and in some plants, the water that is extracted in dewatering along with other wastewater, including backwash water, is pumped back to the raw water receiving well. In a water supply system located in Central Japan, water extracted from DWTS was found to contain many substances, including DOM, that may affect the quality of the purified water and may result in a rapid decrease in the residual chlorine concentration of the purified water at some supply points.

Various factors such as temperature can affect DWTS when it is settling in the thickener tank, and these factors can lead to cumulative increases in levels of organic matter and other substances such as ammonia. Many studies have indicated that temperature substantially increased the accumulation of dissolved organic carbon (DOC) and dissolved organic nitrogen (DON), and the microbial abundance in the wastewater activated sludge from aerobic and anaerobic processes (Komatsu *et al*., 2020; Du and Li, 2017; Jin *et al*., 2016; Shao *et al*., 2013). However, little information is available on how the storage condition influences the transformation of DOM at different temperatures since the temperature and retention time of DWTS in the thickener tank are the dominant factors affecting the transformation of DOM in DWTS. Our study found that, after DWTS was stored under different temperature conditions, the characteristics of DOM released in water extracted from DWTS were distinct from those of freshwater extracted from DWTS and those of raw water. The main objectives of this study were as follows: 1) to characterize the DOM in extracted water obtained after the dewatering of DWTS, and 2) to investigate how different storage conditions influenced the water quality. The characteristics of DOM in water extracted from DWTS can guide the selection of treatment processes and establish grounds for the assessment of quality risks associated with water extracted from DWTS during drinking water production at drinking water treatment plants.

4.2. Materials and methods

4.2.1. Drinking water treatment sludge (DWTS)

DWTS was sampled from the thickener tank of a drinking water treatment plant which has a treatment capacity of 200,000 m^3/day (Fig. 4.1). The plant uses a conventional sand filtration system, including coagulation, flocculation, sedimentation, sand filtration, and disinfection. Poly-aluminum chloride is used as the coagulant. The sludge in the sedimentation basin is discharged to the thickener tank. The sampled DWTS was transferred immediately to the laboratory for use. The obtained DWTS was measured for volatile solids (VS) and total solids (TS). Initial extracted water was obtained by centrifuging the DWTS at 2500 rpm for 15 min, and the supernatant was filtered through a 0.2-µm membrane filter for the measurement of pH, electric conductivity (EC), UV absorbance at 260 nm (UV_{260}), DOC, DON, dissolved inorganic nitrogen (DIN), fluorescence excitation-emission matrix (EEM), and molecular weight distribution in the initial extracted water.

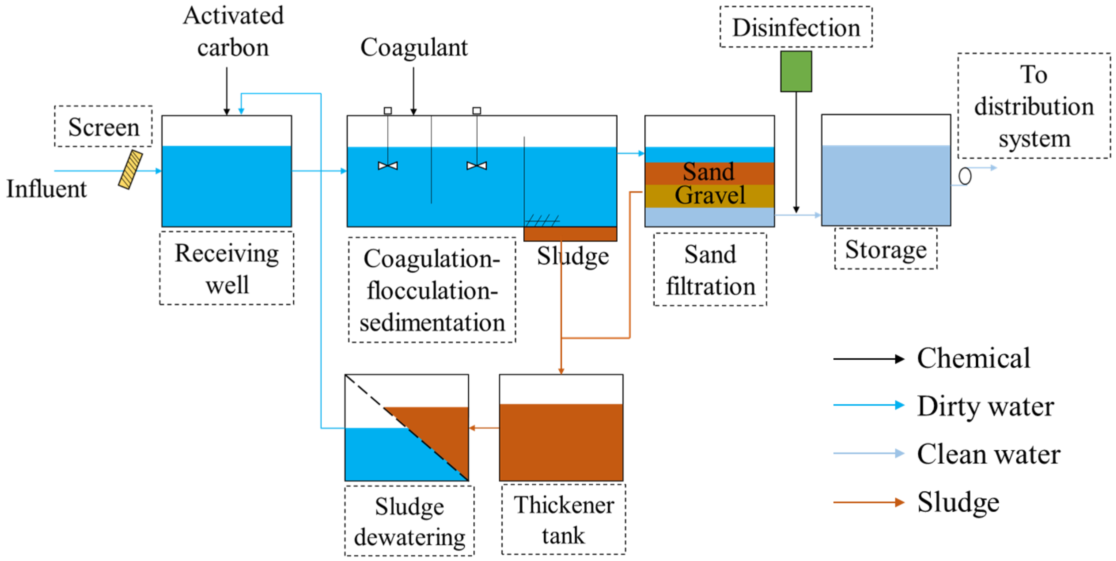

Fig. 4.1. Configuration of a drinking water treatment plant that recycles the water from DWTS.

4.2.2. Storage experiment

Six parallel storage systems, each with a volume of 3 L, were used for the experiment. Storage was performed at different storage temperatures: 5ºC, 20ºC, and 40ºC. Air pumps were used to supply the air at a flow rate of 2.5 L/min for the aerated condition. The non-aerated condition was performed in a tightly sealed reactor. During the storage experiment, samples were collected from each reactor at designated time points (7, 14, and 21 days). After filtration through a 0.2-μm membrane filter, the filtrates were subjected to quality analysis for DOM. This analysis mainly focused on DOC, UV_{260}, fluorescence EEM, and molecular weight distribution, and the details of each are described below. In addition to these measurements, dissolved oxygen (DO), pH, and EC inside all the reactors were monitored, and DIN (NO_2^--N, NO_3^--N, and NH_4^+-N) was analyzed using the filtrates of all samples with an ion chromatography system.

4.2.3. Water quality analysis

DOC was quantified with a TOC analyser (TOC-V_{wet}, Shimadzu, Japan). UV_{260} was measured by a UV-vis spectrophotometer (UV-1600, Shimadzu, Japan). The calculation ratio of UV_{260} to DOC was defined as the SUVA. UV_{260} was also widely used to reflect the content of humic substances in natural water and its value is less than 5% higher than UV_{254} (Li *et al.*, 2003). Other parameters such as nitrate-nitrogen (NO_3^--N) and ammonium-nitrogen (NH_4^+-N) were analyzed using ion chromatography system (LC-20AD SP, Shimadzu, Japan) and total nitrogen (TN) was measured with the procedures described in the APHA standard methods. DO was measured using a DO meter (HQ40D, Hach, Japan), pH, EC, and ORP were measured using a multi-water quality meter (MM-60R, TOA DKK, Japan).

The fluorescence EEM spectra of the chlorinated water were measured by spectrofluorometer (RF-5300, Shimadzu, Japan). After the temperature of the samples reached room temperature (25°C), samples were poured into a 1 cm cuvette. The high-sensitivity cell holder was used to trap twice efficiency compared to the standard cell holder. The pure water was measured prior to the 10 ppb quinone sulfate and samples to confirm the neatness of the cuvette. The excitation and emission scans showed wavelengths between 220 nm and 550 nm at 5-nm increments. The obtained fluorescence intensities of the samples were normalized using the quinine sulfate unit (QSU) by dividing the fluorescence intensity values of all chlorinated water by that of 10 ppb quinine sulfate (in a 0.05 M sulfuric acid solution) at the designated excitation wavelength (Ex) of 350 nm and the emission wavelength (Em) of 450 nm. The peak-picking method was used in this study to describe the obtained fluorescence peaks. The fluorescence peaks found in this study can be classified into protein-like peaks: Peak 1 (tyrosine-like: Ex/Em: 220–237/305–320), Peak 2 (tryptophan-like: Ex/Em 215–237/340–381), and Peak 4 (tryptophan-like: Ex/Em: 275–285/320–350) and humic-like peaks: Peak 3 (humic-like: Ex/Em: 320–360/420–460) and Peak 5 (humic-like: Ex/Em: 230–260/400–480) (Rodríguez-Vidal *et al*., 2020).

The humification index (HIX) indicates the degree of DOM humification and was calculated as the area under the emission spectra of 435 to 480 nm divided by the sum of the emission spectra of 300 to 345 nm and 435 to 480 nm, at an excitation wavelength of 254 nm (Ohno, 2002). A high HIX value (10–16) indicates strongly humified organic matter from the terrestrial origin, while low HIX (<4) indicates autochthonous organic matter (Yan *et al*., 2018). The fluorescence index (FIX) indicates the microbial or terrestrial source of DOM and was calculated as the fluorescence intensity ratio of the emission wavelengths of 470 nm and 520 nm, at an excitation wavelength of 370 nm (McKnight *et al*., 2001). FIX < 1.4 indicates a terrestrial and soil source, and FIX > 1.9 indicates aquatic and microbial sources. A high BIX value (>1) indicates an autochthonous biological activity in water freshly released DOM, while a low BIX value (0.6–0.7) indicates low DOM production in natural water. BIX was calculated as the ratio of the emission wavelength of 380 nm to that of 430 nm using an excitation wavelength of 310 nm. The freshness index (β:α) indicates the age or extent of decomposition, and a high value indicates freshly produced DOM. β:α was calculated as the fluorescence ratio of emission wavelengths of 380 nm and 420–435 nm, at an excitation wavelength of 310 nm (Líden *et al*., 2017).

The molecular weight characteristics of DOM were evaluated at a wavelength of 260 nm using a high-pressure size-exclusion chromatography (HPSEC) system that consisted of a silica chromatographic column (GL-W250-X, 10.7 x 450 nm, Hitachi) and a UV detector (LC-10AV, Shimadzu). Pure water containing 0.02 M of Na_2HPO_4 and 0.02 M of KH_2PO_4 was used as the eluent and was introduced to the column at a constant flow rate of 0.5 mL/m. Calibration was made with a standard solution composed of polystyrene sulfonate (PSS) with three different molecular weights of 1430, 4950, and 6530 g/mol. Weight-averaged molecular weight (M_w) and number-averaged molecular weight (M_n) were calculated according to the following equations (Karanfil *et al*., 1996; Li *et al*., 2003):

$$M_w = \sum_{i=1}^{N} MW_i(t) h_i(t)\,\Delta t \Big/ \sum_{i=1}^{N} h_i(t)\Delta t$$

$$M_n = \sum_{i=1}^{N} h_i(t)\,\Delta t \Big/ \left(\sum_{i=1}^{N} h_i(t)\Delta t / MW_i \right)$$

where, $MW_i(t)$ is the molecular weight as a function of the eluent time t, $h_i(t)$ is the detector response, and Δt is the time interval. Polydispersity index, a parameter defined as the ratio of M_w/M_n, was adopted to evaluate the heterogeneity of DOM and the changes in DOM molecular weight distribution that occurred during sludge storage (Karanfil *et al*., 1996; Li *et al*., 2003).

4.2.4. Data Analysis

The significant differences between the mean values of the observed parameters of the treatment for DWTS before and after storage and the chlorine consumption were analyzed by two-way analysis of variance (ANOVA) with a 95% confidence level (p = 0.05). Pearson's correlation analysis was performed to investigate the relation between water quality parameters and chlorine consumption. The statistical analysis was conducted by using IBM SPSS Statistics (version 24) software program.

4.3. Results and discussion

4.3.1. Physicochemical properties of DWTS

DO concentrations are constantly affected by diffusion and aeration, photosynthesis, respiration, and decomposition and fluctuate with temperature. As DO concentration is shown in Table 4.1, lower DO under non-aerated storing conditions can affect the sludge disintegration and release rate of DOM from sludge. High temperature can decrease DO concentration at the same time increasing metabolic rates that affect biological oxygen demand (BOD) decay, nitrification, and decomposition. The pH of DWTS during storage was in the range of 6.1 to 7.2, and the ORP of the sludge was -132 to 169 mV. The EC value of DWTS was during storage in the range of 6.42–45.1 mS/m.

Table 4.1. The property changes of DWTS after storage. The values for each experiment are given as mean and standard deviation (n = 3). The different letters (a–f) indicate that the observed differences are statistically significant at $p < 0.05$.

Parameter	Initial	Aerated			Non-aerated		
		5°C	20°C	40°C	5°C	20°C	40°C
pH	6.01 ± 0.25 ^{a}	6.24 ± 0.14 ^{b}	6.65 ± 0.12 ^{b}	7.01 ± 0.02 c	6.58 ± 0.09 ^{b}	6.61 ± 0.21 ^{b}	6.59 ± 0.09 ^{b}
DO (mg/L)	1.12 ± 0.06 ^{a}	11.0 ± 1.00 ^{e}	9.12 ± 0.09 ^{e}	6.81 ± 0.24 ^{d}	4.12 ± 0.17 ^{c}	2.98 ± 0.08 ^{b}	1.03 ± 0.04 ^{a}
EC (mS/m)	36.1 ± 2.45 ^{e}	14.5 ± 0.11 ^{c}	24.0 ± 0.05 ^{d}	41.0 ± 0.06 ^{f}	10.6 ± 0.04 ^{b}	7.85 ± 0.04 ^{a}	38.2 ± 0.02 ^{e}
ORP (mV)	142 ± 4.20 ^{d}	101 ± 0.69 ^{c}	113 ± 1.17 ^{c}	151 ± 2.01 ^{d}	-74.2 ± 1.63 ^{b}	-84.1 ± 2.10 ^{b}	-130 ± 2.16 ^{a}
VS (g/L)	5.14 ± 1.02 ^{a}	7.25 ± 1.20 ^{c}	8.12 ± 0.10 ^{d}	8.51 ± 0.12 ^{d}	6.12 ± 1.21 ^{b}	6.02 ± 0.12 ^{b}	5.73 ± 0.12 ^{b}
TS (g/L)	47.2 ± 2.14 ^{a}	50.1 ± 0.69 ^{a}	54.1 ± 1.35 ^{c}	53.4 ± 2.41 ^{b}	54.2 ± 1.02 ^{c}	52.4 ± 0.45 ^{b}	50.3 ± 1.21 ^{a}

4.3.2. Contents of DOM from DWTS

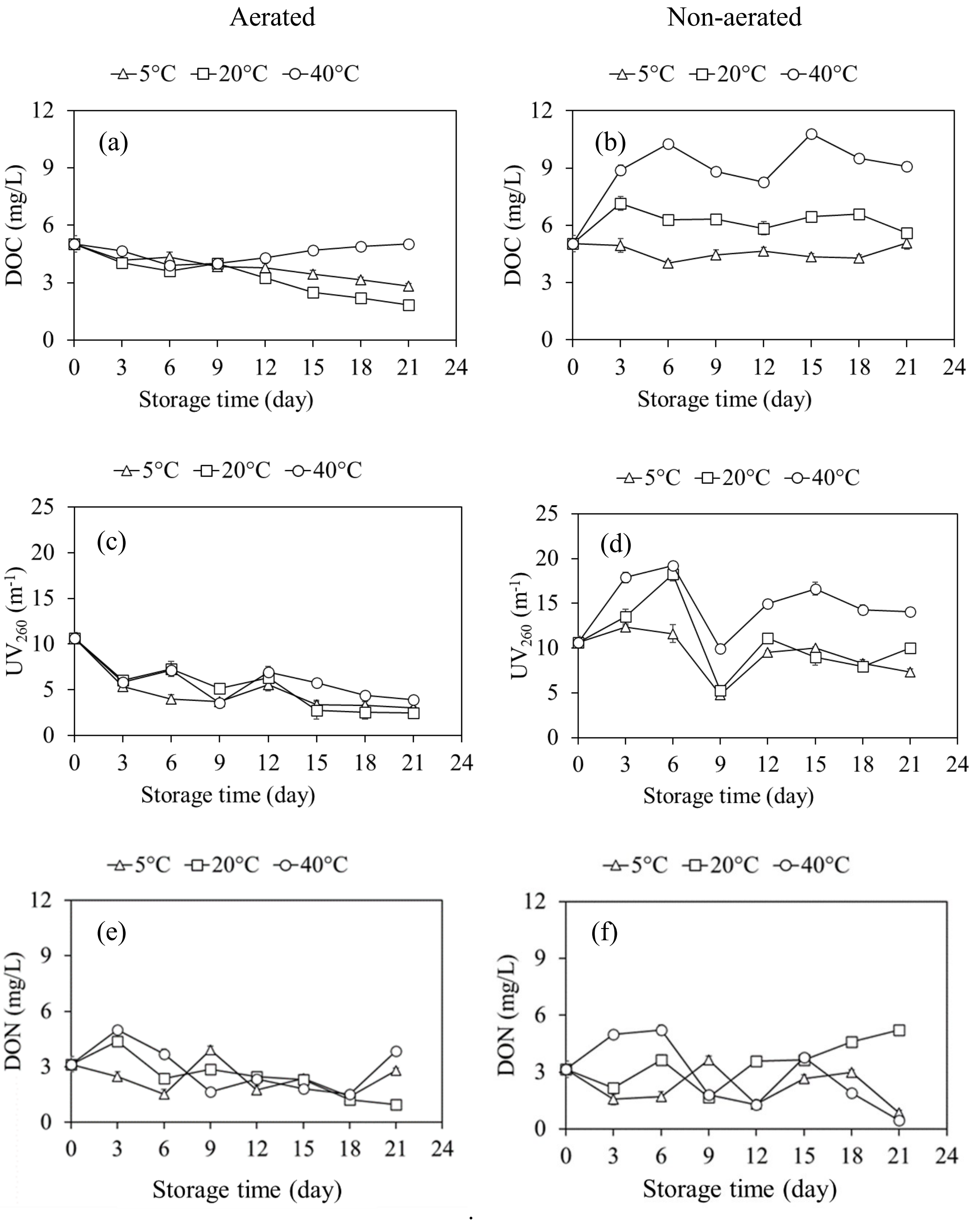

Fig. 4.2. Changes of (a–b) DOC, (c–d) UV_{260}, and (e–f) DON in the water from DWTS under aerated and non-aerated conditions.

The trend of DOC during the 21-day storage period varied among the three storage temperatures under the aerated and non-aerated conditions (Fig. 4.2a–b). The average DOC concentrations in water from DWTS during the storage period at 21 days for aerated and non-aerated were 3.74 mg/L and 6.75 mg/L, respectively. The decrease in DOC concentration from the initial concentration (5.03 mg/L) to the range of 1.84 to 5.02 mg/L at the end of the storage period for each aerated condition was probably due to the degradation of DOM, and some organic compounds were oxidized to carbon dioxide (He *et al.*, 2011). The higher DOC concentration under non-aerated conditions reflected the higher release rate and lower degradation rate of DOM. The DOC concentration increased under non-aerated conditions after day 6 at temperatures of 5 and 40 ºC. The results indicated that low and high temperatures of non-aerated conditions promoted the release of DOM and remained during the storage.

UV_{260} is a good parameter for understanding aromatic content and the humic fraction of DOM (Hua *et al.*, 2015). Fig. 4.2c–d show the increase of UV_{260} after 3-days in all non-aerated condition except that under aerated one. This may be due to its association with the transformation of non-aromatic compounds, which led to an apparent enrichment in aromatics. Furthermore, the UV_{260} for water from DWTS stored under non-aerated conditions was higher than under aerated conditions, suggesting that the water was high in aromatic compounds. UV_{260} values were significantly higher under the non-aerated condition at 40ºC than under the other conditions, suggesting that greater amounts of aromatic substances formed and remained under non-aerated conditions. In the latter period of storage, the decrease of UV_{260} may be attributed to the degradation of aromatic compounds in the stored DWTS, which further transform aromatic substances into non-aromatic ones (Hua *et al*., 2015). UV_{260} value was higher at 20 and 40ºC than at 5ºC. The high storage temperature could have caused DOM with high aromaticity to be released during the non-aerated condition through biodegradation under prolonged storage. The high UV_{260} value under 40ºC storage is consistent with the findings of fluorophore intensity assessed by fluorescence EEM. Based on the FIX results, which found that DOM mainly originated from the extracellular release by microorganisms, the storage treatment employed for non-aerated DWTS should release a higher UV_{260} value than that of aerated DWTS. The UV_{260} values in all stored DWTS exhibited a common relationship: non-aerated UV_{260} > aerated UV_{260}.

The changes of DON in the water from DWTS after storage treatment are shown in Fig. 4.2e–f. The average DON concentrations in the water after aerated and non-aerated conditions were 2.59 mg/L and 3.06 mg/L, respectively. During storage at a high temperature, abundant nitrogen is released into the supernatant due to the degradation of protein in the extracellular polymeric substances, resulting in an increase of DON on day 3. The increase of DON at the end of the non-aerated storage period at 20 and 40 ºC may be due to the mineralization of DON accompanied by increases in temperature and pH (Chan *et al*., 2016). The concentration of DON was decreased after 3 days of aerated condition.

4.3.3. Compositions of DOM from DWTS by fluorescence EEM

The EEM spectra of the DOM before storage and after 3 days of storage are shown in Fig. 4.3 and Fig. 4.4, respectively. The EEM spectra of initial water (Fig. 4.3) show an apparent peak of humic-like substances (Peak 3). The presence of this peak indicates that humic-like substances were the major DOM fraction found in the water from the DWTS. The DOM fractions in the initial water were mainly produced from the extracellular substances by bacteria during the agglomeration of flocs after coagulation-flocculation. Additionally, the presence of Peak 3 arose from raw water that showed humic-like substances as the major DOM fractions. Peaks 3 and 5 were present in all the samples under aerated conditions, coinciding with peaks typical of humic-like substances. The presence of these peaks indicates that humic-like substances that are non-biodegradable or that have low biodegradability primarily formed from the hydrolysis of the sludge (Pang *et al*., 2014) and remained in the liquids after storage probably because of the slower degradation.

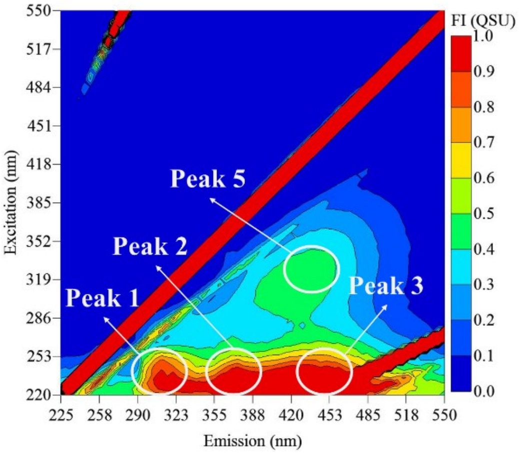

Fig. 4.3. EEM contour plot for water from DWTS before storage. FI: fluorescence intensity; Peak 1: tyrosine-like substances; Peak 2 and 4: tryptophan-like substances; Peak 3 and 5: humic-like substances from fluorescence EEM.

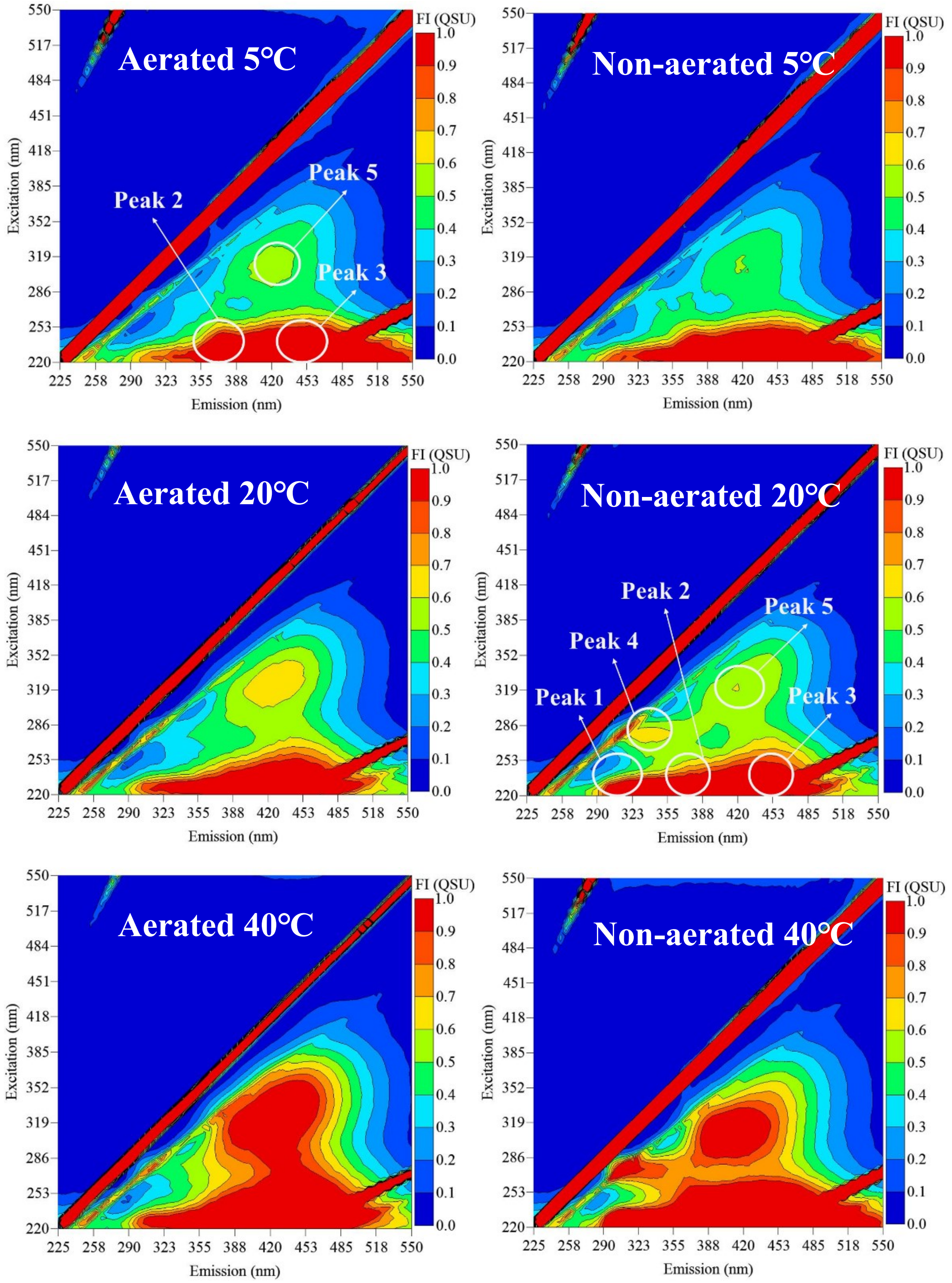

Fig. 4.4. EEM contour plot for water from DWTS at 3 days of aerated and non-aerated conditions. FI: fluorescence intensity; Peak 1: tyrosine-like substances; Peak 2 and 4: tryptophan-like substances; Peak 3 and 5: humic-like substances from fluorescence EEM.

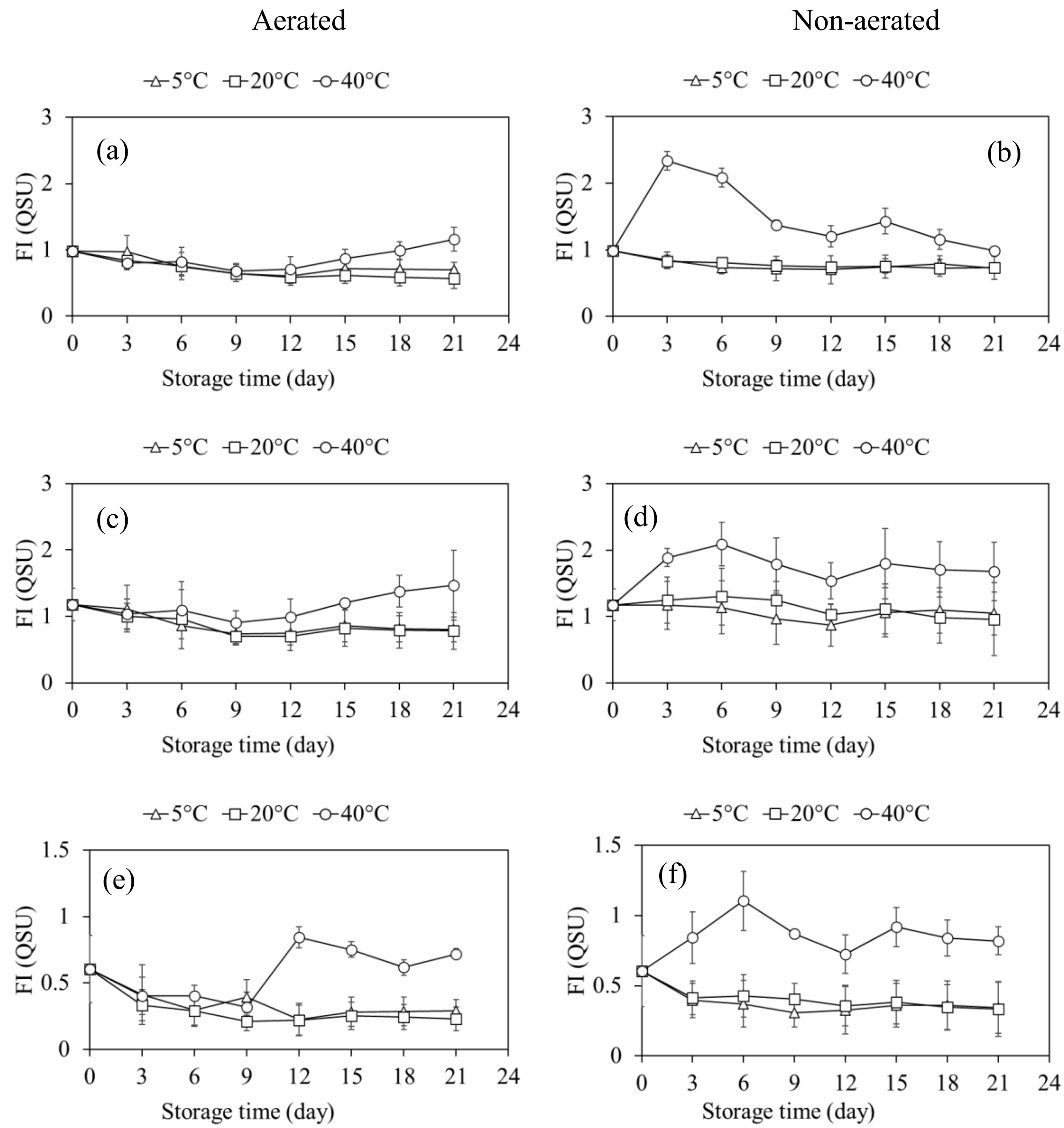

Fig. 4.5. Changes of DOM compositions in water from DWTS under aerated and non-aerated conditions. FI: fluorescence intensity; (a–b) Peak 1: tyrosine-like substances; (c–d) Peak 2 and (e–f) 4: tryptophan-like substances from fluorescence EEM.

Peaks 1, 2, and 4 were observed in the water after a non-aerated condition at 40ºC. These three peaks can be attributed to aromatic protein-like substances in the DOM fraction, such as tryptophan-like substances and tyrosine-like substances. Peak 4 may have arisen from the presence of phenol-like materials that originated from lignin degradation. The presence of peaks 1, 2, and 4 suggested that the sludge from the aerated condition might consist of substantial amounts of aromatic proteinaceous material and small amounts in the aerobic condition that can be bonding with, or physical encapsulation within, the humified centers of DOM (Hassouna *et al*., 2010). Based on the above analysis, the majority of DOM is considered to be consisted of humic-like materials and protein-like substances presented in the samples. The relatively high fluorophore intensity of Peak 2 under the non-aerated conditions at all temperature ranges was mainly attributed to the abundance of aromatic substances produced during the storage of DWTS. The high fluorophore intensity of Peak 2 is consistent with the high UV_{260} value under non-aerated conditions.

The variations in the levels of all components in the water from DWTS during the 21-day storage period were characterized by fluorescence intensity values (Fig. 4.5–4.6). Peak 1, described as tyrosine-like substances DOM, might be an indication of some activities of microbial DOM during DWTS storage and remained in the extracted water (Baghoth *et al*., 2011). The lower intensity of Peak 1 under 5ºC and 20ºC indicated that the DOM was easy to be degraded by bacteria under low-temperature conditions compared to that under 40ºC (Fig. 4.5(b)). Meanwhile, Peak 2 and Peak 3 have higher fluorescence intensity than the other three components in the water, indicating that tryptophan-like substances and humic-like substances were completely non-biodegradable and the major contributors to the fluorescent

DOM during sludge storage and were more likely to be accumulated and remained in the water. The variations in Peak 2 averaged 0.97 QSU and 1.30 QSU in aerated and non-aerated conditions respectively, and Peak 3 averaged 1.13 QSU and 1.49 QSU in aerated and non-aerated conditions, respectively.

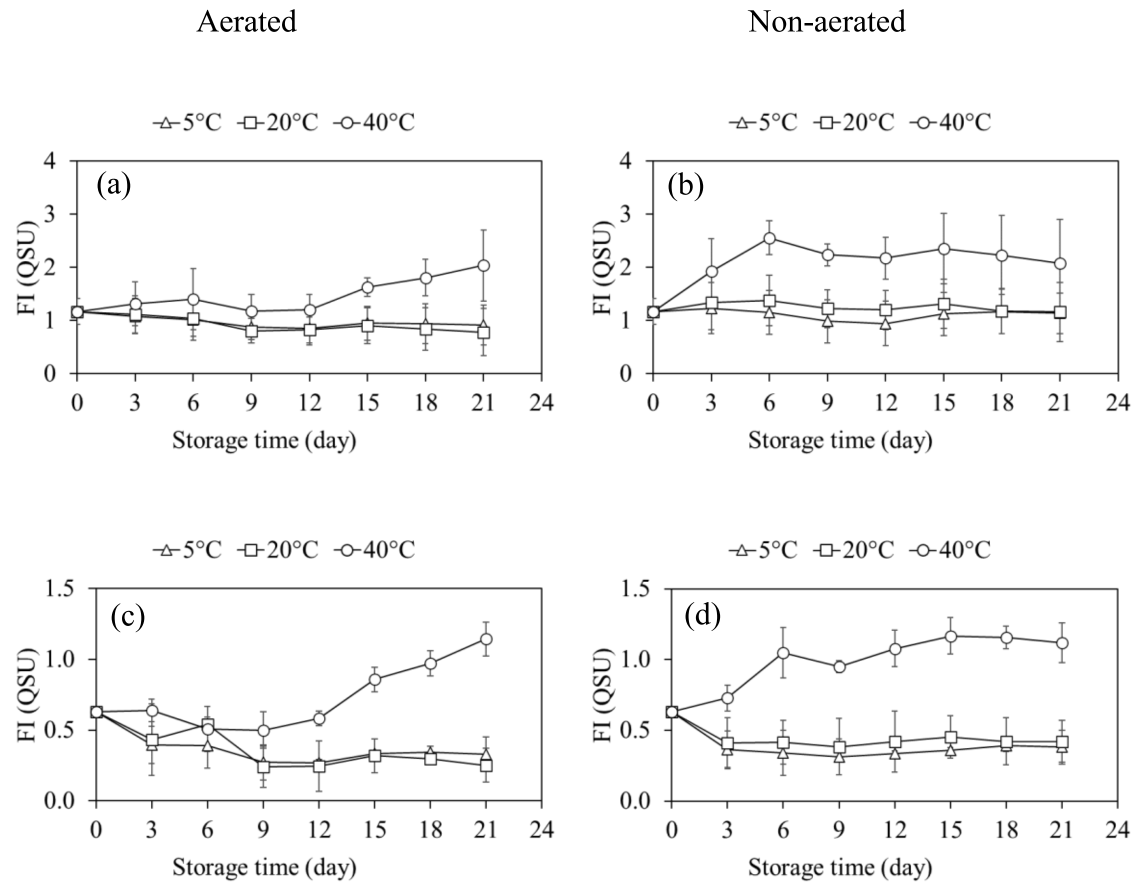

Fig. 4.6. Changes of DOM compositions in water from DWTS aerated and non-aerated conditions. FI: fluorescence intensity; (a–b) Peak 3 and (c–d) 5: humic-like substances from fluorescence EEM.

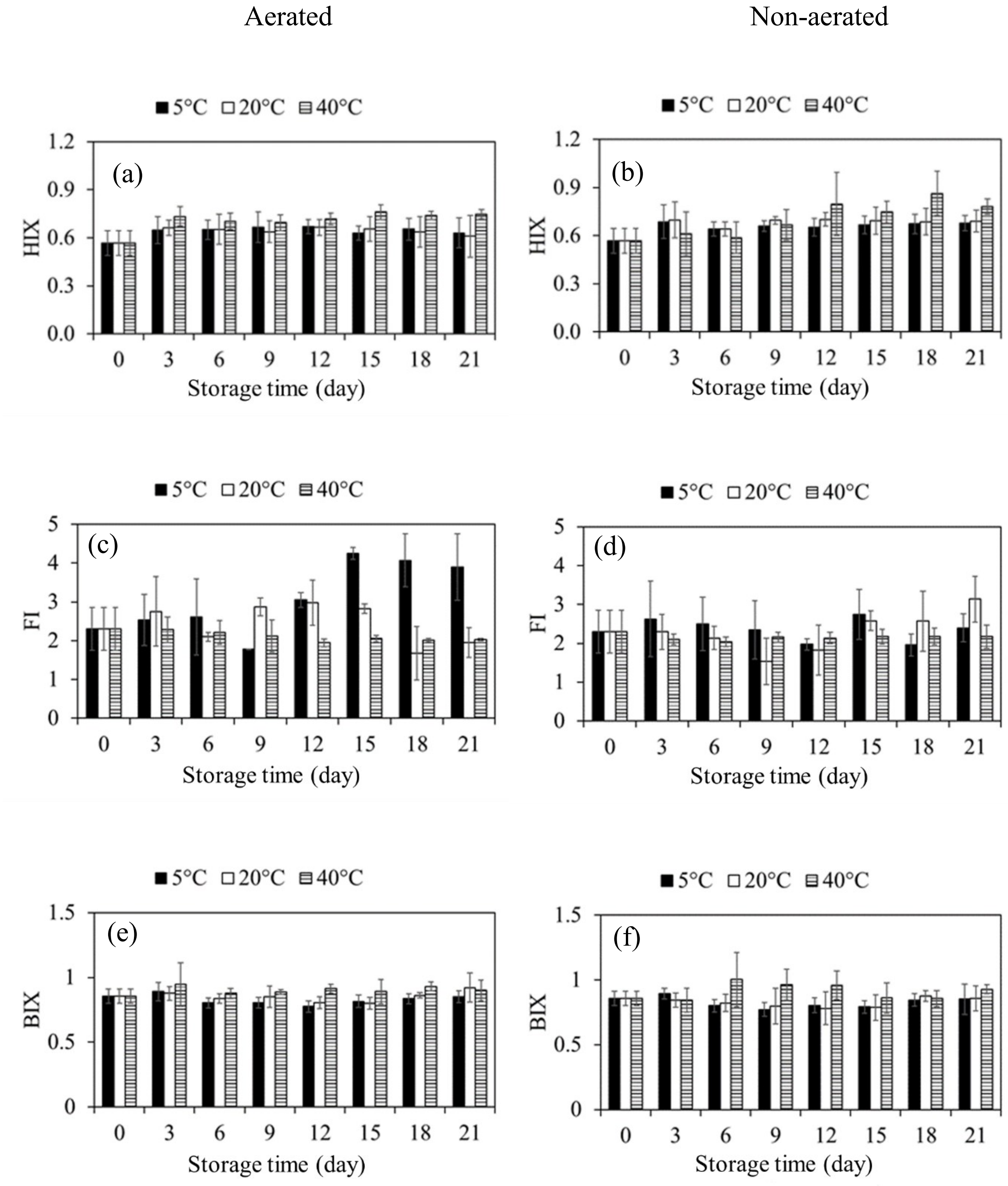

Fig. 4.7. (a–b) HIX, (c–d) FIX, and (e–f) BIX for water from DWTS under aerated and non-aerated conditions.

The changes in HIX, FIX, and BIX for the six systems during the experiment are shown in Fig. 4.7. The HIX values ranged from 0.46 to 1.02 in the storage system. HIX values typically indicate the extent of humification, with higher values corresponding to greater humification (Hansen *et al*., 2016). HIX values in water from DWTS under the non-aerated condition at 40°C were <0.8, indicative of low humic levels. The average HIX after storage was higher for the non-aerated conditions than for aerated conditions, which indicates greater humification under non-aerated conditions.

During the 21-day storage, aromatic protein-like substances were present in all samples under non-aerated conditions. The non-aerated conditions may promote and accelerate the production of protein materials derived from extracellular lysis and lignin degradation. Greater humification is associated with more complex, condensed aromatic structures and/or more conjugation in aliphatic chains, which are resistant to degradation. The increase of HIX during an aerated condition at 40ºC may have been caused by the degradation and accumulation of recalcitrant DOM. On the other hand, non-aerated conditions led to a more readily oxidation process than under non-aerated conditions at temperatures of 5ºC and 20ºC. The presence of humic substances in non-aerated conditions can be utilized for microbial respiration and oxidizing DOM in the systems (Shao *et al*., 2013).

FIX is also an indicator of DOM source, with higher values (~1.8) indicating DOM from the extracellular release and leachate from bacteria and algae, and lower values (~1.2) indicating terrestrial DOM sources (McKnight *et al*., 2001). The high FIX values in all six storage systems suggested that DOM was mainly produced from the extracellular release of microorganisms as shown in Fig. 4.7(c–d). FIX values that are greater than the microbial end-member range of 1.7 to 2.0 (McKnight *et al*., 2001) can be employed for characterizing humic and fulvic acids. The BIX values observed during storage of DWTS were ranging from 0.73–1.13 and 0.64–1.24 for aerated and non-aerated conditions, respectively. Therefore, certain fractions of DOM released from DWTS was probably contained inside the microbes.

4.3.4. The molecular weight distribution of DOM

The molecular weight distribution of DOM in the water from DWTS was measured by HPSEC and is given in terms of UV absorbance at 260 nm (Fig. 4.8). The DOM for non-aerated conditions shows a large molecular weight shown in a narrower distribution. The aerated condition resulted in a broader distribution which is positioned on the left side of the molecular weight distribution chromatogram, reflecting small molecular weight (Fig. 48(a)). The molecular weights are lower for water from DWTS under aerated conditions than in non-aerated conditions, indicating the presence of humic-like substances. The distribution of molecular weight in water from non-aerated DWTS at a temperature of 40ºC is distinct from that for the same storage under two other temperature conditions (5ºC and 20ºC). Under those two conditions, protein-like substances with high molecular weights are associated with high UV_{260} values.

Table 4.2 shows that M_w is greater for the DOM that formed and remained after the non-aerated conditions. The large weight-averaged molecular weight seen under the non-aerated condition at 20ºC indicates that large protein-like substances were produced during storage. This result is consistent with the fluorescence EEM under those conditions at 3 days of storage, where the protein-like fraction is the main substance in the water from DWTS under non-aerated conditions. The polydispersity index also shows that the DOM which formed and remained after the aerated condition is more heterogeneous than that which formed after the non-aerated conditions. The large fraction of DOM assessed by molecular weight distribution observed in the non-aerated condition of DWTS is consistent with the results assessed by fluorescence EEM, suggesting that more protein-like substances with relatively high fluorophore intensities formed under non-aerated conditions than under aerated conditions.

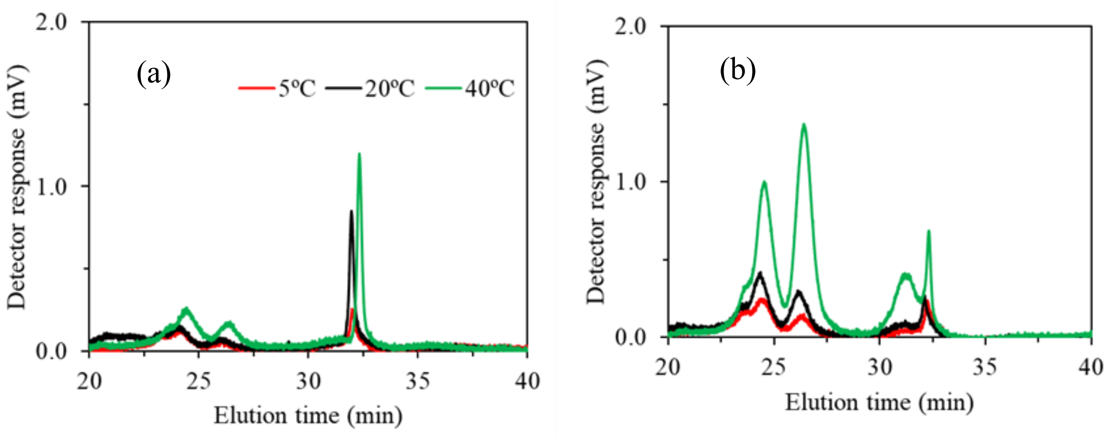

Fig. 4.8. The molecular weight distributions for water from DWTS at 3 days of (a) aerated and (b) non-aerated conditions.

The M_w of the DOM in the water from DWTS was found to be high under a non-aerated condition at 20ºC and it probably consisted mainly of protein-like substances with a high degree of aromaticity. In this study, a non-aerated condition at a moderate temperature (20ºC) could release DOM with high molecular weights. DOM formed under a non-aerated condition at a temperature of 5ºC had a higher polydispersity than those at 20ºC and 40ºC.

The high temperature of storage could present less disperse DOM under the non-aerated condition than that under the aerated condition.

Table 4.2. Molecular weight and polydispersity of initial water from DWTS and after 3 days storage period.

Sample name	M_w (g/mol as PSS)	M_n (g/mol as PSS)	Polydispersity (–)
Initial	5079	4767	1.06
Aerated 5ºC	2349	4751	0.49
Aerated 20ºC	6073	4279	1.42
Aerated 40ºC	5461	4892	1.12
Non-aerated 5ºC	6232	4534	1.37
Non-aerated 20ºC	6915	5831	1.18
Non-aerated 40ºC	5785	5674	1.02

4.4. Summary

Prolonged aerated and non-aerated storage of DWTS (21 days) at different temperatures (5ºC, 20ºC, 40ºC) and DOM transformation in sludge were investigated. Non-aerated condition at high temperatures was found to promote high DOC concentrations and UV_{260} values, which indicates that aromatic DOM formed during storage. Compositional analysis by fluorescence EEM indicated that more humic-like substances formed during aerated than non-aerated conditions and that more protein-like substances formed during non-aerated than aerated conditions. With increases in DOM, high-temperature storage was able to accelerate the humification process for aerated conditions, suggesting that the bulk DOM was more humified under those conditions. Moreover, compositional analysis based on the molecular weight distribution found that the UV-absorbing DOM constituents that formed in non-aerated conditions had higher molecular weights at high temperatures than the molecular weights seen in the aerated conditions.

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Chapter 5 Reactivity of dissolved organic matter from drinking water treatment sludge with chlorine and its composition changes

5.1. Introduction

A rapid sand filtration system is widely used for drinking water production. All impurities and health concerned substances (including pathogenic microbial agents) that can be captured into the coagulated flocs are removed through sedimentation and sand filtration following coagulation using aluminum or ferric coagulants. When potable water is produced from source water, drinking water treatment sludge (DWTS) is generated. DWTS contains humic-like substances, bacteria, and small quantities of extracellular polymeric substances (such as carbohydrates and proteins) (Zhou *et al*., 2018; Liu *et al*., 2010). With a higher water content (>80 wt%), the DWTS is dewatered, and the water is then recycled as raw water in many treatment plants for drinking water production (Ahmad *et al*., 2016a). However, the use of recycled water has been found to increase turbidity, dissolved organic carbon (DOC), ammonium-nitrogen (NH_4^+-N), aluminum, and others in the plant influent (Liu *et al*., 2017). Their removal efficiency during the treatment process may affect chlorine consumption in the water distribution system (Jamwal *et al*., 2016; Araya and Sánchez, 2018). In our previous studies, the water quality in the final treated water and the water at the designated monitoring points in the distribution lines were analyzed (Hudori *et al*., 2020). The results showed obvious decreases of residual chlorine during summer in the monitored water supply points from the plant, and the composition analysis further indicated that the decreases were caused in part by the organic matter from the sludge which had distinct composition compared with dissolved organic matter (DOM) in the source water (Hudori *et al*., 2020; Rosadi *et al*., 2020). The release of organic matter from DWTS is a result of the combined involvement of physicochemical reactions and some biological reactions by bacteria in the sludge, the extent of which may differ greatly depending on temperature and oxygen concentration.

Chlorine is widely used for the disinfection of drinking water because of its comparatively low cost, effectiveness in killing bacteria, and chemical stability (Reichert and Young, 1997; Abdullah *et al*., 2009). The kinetics of chlorine decay is determined by the type and amount of organic and inorganic impurities (such as humic substances and NH_4^+-N) present in water (Jamwal *et al*., 2016). Therefore, given the different characteristics and components present in water, the organic matter that consumes chlorine can be divided into rapid and slow reacting fractions (Gallard and von Gunten, 2002). Aliphatic hydrocarbons and aromatic hydrocarbons are the possible fast and slow reacting components of organic matter in different types of water, respectively (Jamwal *et al*., 2016). In drinking water treatment plants that utilize the water from DWTS, a larger reduction of residual chlorine was shown to be caused by the presence of some readily oxidizable substances (such as humic molecules) even if its concentration was lower (0.13 to 0.23 mg/L as DOC) (Araya and Sánchez, 2018; Gallard and von Gunten, 2002). The DOM released from DWTS may also have different compositions (i.e., phenols, aromatic amino acids) that can contribute to the different chlorine consumption. The different compositions of DOM can contribute to a different reactivity with chlorine through the oxidation reactions (i.e., cleaving carbon-carbon double bonds), additional reactions to unsaturated bonds and electrophilic substitution reactions at nucleophilic sites (Deborde and von Gunten, 2008; Criquet *et al*., 2015; Zhang *et al*., 2016).

A study has recently observed the effect of the recycling process of sedimentation sludge water in a drinking water treatment plant (Hu *et al*., 2021). It was found that aromatic protein-like compounds with low molecular weight DOM released from sedimentation sludge water were more reactive with chlorine, which increased the risk of disinfection by-products generations (Hu *et al*., 2021). Sharma *et al*. (2021) studied the reactivity of DOM in drinking water and wastewater effluents. The hydrophobic acid and neutral fractions of DOM that existed in the secondary treated effluent are the most reactive fractions of DOM with chlorine. However, little information is available on how the storing condition influences the release of DOM from DWTS at different temperatures and oxygen concentrations. Our previous study showed that DOM varied in concentration and compositions released from DWTS under aerated and non-aerated conditions at different temperatures (Rosadi *et al*., 2020). The DOM released from DWTS may have different properties of fluorescent components with different molecular weights which may contribute to the different chlorine consumption.

Because different components of DOM released from ‘incubated DWTS’ may consume and react with chlorine differently, quantitative and qualitative clarification of their consumption and reactivity is central for better operation and management of the drinking water treatment plants that recycle water from DWTS. The information on chlorine consumptive DOM in water from DWTS is still not clear, so is the impact of the DOM composition under different storage conditions for the DWTS. Therefore, the main objective of this study was to investigate the consumption of chlorine by DOM in the water from

DWTS under different storage conditions. For this purpose, an incubation experiment was conducted using DWTS from a treatment plant in reactors supplied with and without air (referred hereafter as aerated and non-aerated, respectively) under three different temperatures (5, 20, 40°C), and the chlorine consumption was conducted by chlorination experiment and data analysis with the first-order reaction model. DOM released from the DWTS during storage was analyzed using fluorescence excitation-emission matrix (EEM) in addition to the well-used overall water quality indexes of total organic carbon and ultra-violet absorbance at 260 nm (UV_{260}).

5.2. Materials and methods

5.2.1. Sample collection and preparation of water containing DOM from DWTS based on storage experiment

DWTS was sampled from the thickener tank of a drinking water treatment plant which has a treatment capacity of 200,000 m^3/day. The plant uses a conventional sand filtration system, including coagulation, flocculation, sedimentation, sand filtration, and disinfection. Poly-aluminum chloride is used as the coagulant. The sludge in the sedimentation basin is discharged to the thickener tank. The sampled DWTS was transferred immediately to the laboratory for use. The volatile solids (VS) in the DWTS were 0.35 ± 0.01 g/L and the total solids (TS) were 3.01 ± 0.05 g/L. The VS/TS ratio of 0.116 indicated that about 12% of the sludge was made up of organic matter (including humic acid, bacteria, and other types of particulate organic matter). Other measured parameter values for the sampled sludge were pH 6.86 ± 0.08, dissolved oxygen (DO) 2.01 ± 0.54 mg/L, oxidation-reduction potential (ORP) 137 ± 1.21 mV and electric conductivity (EC) 41.3 ± 0.06 mS/m.

A set of storage experiments were conducted under aerated and non-aerated conditions for three different temperatures: 5ºC, 20ºC, and 40ºC for 3 days following the procedures described previously in Chapter 4. At the end of storage, each sample of DWTS was subjected to centrifuge at 2500 rpm and the supernatant was filtered through 0.2-µm membrane filters. The obtained filtrates under all storage conditions were diluted to the same DOC concentration (2 mg/L) and were used as the water for the followed experiment of DOM consumption for chlorine.

5.2.2. The experiment of DOM consumption for chlorine

The experiment on DOM consumption for chlorine was conducted at a chlorine dose of 5 mg/L using sodium hypochlorite (NaClO). In the treatment plant where the samples were taken, the chlorine dose was in the range of 3–5 mg/L. Samples were poured into the prepared test bottles and dosed with NaClO and aliquot samples were taken at various time intervals for chlorine residual determinations. Sodium thiosulfate was added to quench the residual chlorine at the end of the chlorination period. The chlorine concentration was measured by the N,N-diethyl-p-phenylenediamine colorimetric method using the Chlorine Checker (CRP-1000, Suido Kiko, Japan). The chlorinated samples were measured for DOC, UV_{260}, specific ultra-violet absorbance (SUVA), and fluorescence (EEM).

5.2.3. Water quality analysis

DOC was quantified with a TOC analyzer (TOC-V_{wet}, Shimadzu, Japan). UV_{260} was measured by a UV-vis spectrophotometer (UV-1600, Shimadzu, Japan). The calculation ratio of UV_{260} to DOC was defined as the SUVA. UV_{260} was also widely used to reflect the content of humic substances in natural water and its value is less than 5% higher than UV_{254} (Li *et al*., 2003). Other parameters such as nitrate-nitrogen (NO_3^--N) and ammonium-nitrogen (NH_4^+-N) were analyzed using an ion chromatography system (LC-20AD SP, Shimadzu, Japan) and total nitrogen (TN) was measured with the procedures described in the APHA standard methods. DO was measured using a DO meter (HQ40D, Hach, Japan), pH, EC, and ORP were measured using a multi-water quality meter (MM-60R, TOA DKK, Japan).

The fluorescence EEM spectra of the chlorinated water were measured by spectrofluorometer (RF-5300, Shimadzu, Japan). After the temperature of the samples reached room temperature (25°C), samples were poured into a 1 cm cuvette. The high-sensitivity cell holder was used to trap twice efficiently compared to the standard cell holder. The pure water was measured before the 10 ppb quinone sulfate and samples to confirm the neatness of the cuvette. The excitation and emission scans showed wavelengths between 220 nm and 550 nm at 5-nm increments. The obtained fluorescence intensities of the samples were normalized using the quinine sulfate unit (QSU) by dividing the fluorescence intensity values of all chlorinated water by that of 10 ppb quinine sulfate (in a 0.05 M sulfuric acid solution) at the designated excitation wavelength (Ex) of 350 nm and the emission wavelength (Em) of 450 nm. The peak-picking method was used in this study to describe the obtained fluorescence peaks. The fluorescence peaks found in this study can be classified into protein-like peaks: Peak 1 (tyrosine-like: Ex/Em: 220–237/305–320), Peak 2 (tryptophan-like: Ex/Em 215–237/340–381), and Peak 4 (tryptophan-like: Ex/Em: 275–285/320–350) and humic-like peaks: Peak 3 (humic-like: Ex/Em: 320–360/420–460) and Peak 5 (humic-like: Ex/Em: 230–260/400–480) (Rodríguez-Vidal et al. 2020).

5.2.4. Data Analysis

The significant differences between the mean values of the observed parameters of the treatment for DWTS before and after storage and the chlorine consumption were analyzed by two-way analysis of variance (ANOVA) with a 95% confidence level (p = 0.05). Pearson's correlation analysis was performed to investigate the relation between water quality parameters and chlorine consumption. The statistical analysis was conducted by using IBM SPSS Statistics (version 24) software program.

5.3. Results and discussion

5.3.1. Chlorine decay behavior

Fig. 5.1 shows the chlorine decay curve of water from stored DWTS under different conditions. To compare chlorine decay kinetics for the water from DWTS, the first-order rate constant is estimated by fitting the observed chlorine decay curve with the following first-order reaction model.

$$C_t = C_0 e^{-kt}$$

where k = first-order rate constant (h^{-1}); C_t = residual chlorine after a given contact time; C_0 = initial concentration of chlorine at t = 0 min and t = contact time.

The chlorine decay curves varied in the different water from DWTS, reflecting the presence of different compositions and proportions of DOM. Chlorine in water from aerated DWTS at all different temperatures decayed slowly compared to non-aerated DWTS in the first 1 hour of chlorination (Fig. 5.1). This result might be caused by the lower availability of

DOM released from aerated conditions compared to non-aerated conditions. The non-aerated condition with a high temperature can accelerate the disintegration of sludge flocs and enhance the release of DOM, resulting in higher DOM in non-aerated conditions than in aerated conditions. The water from aerated and non-aerated DWTS at 40°C observed a higher chlorine consumption compared to others. Peak 2 and Peak 3 consumed chlorine faster in the first 12 h in water from non-aerated DWTS (Fig. 5.2). This finding suggested that the composition of DOM in that water might be rich in a high proportion of conjugated and substituted aromatic structures (humic-like substances) that is more susceptible to chlorine attack (Wenk *et al*., 2013) which formed during storage at high temperature. As also reported by others, chlorination could reduce the maximum emission band of humic-like substances in water samples containing hydrophobic acids, reflecting the destruction of aromatic structures and the breakdown of the humic molecules.

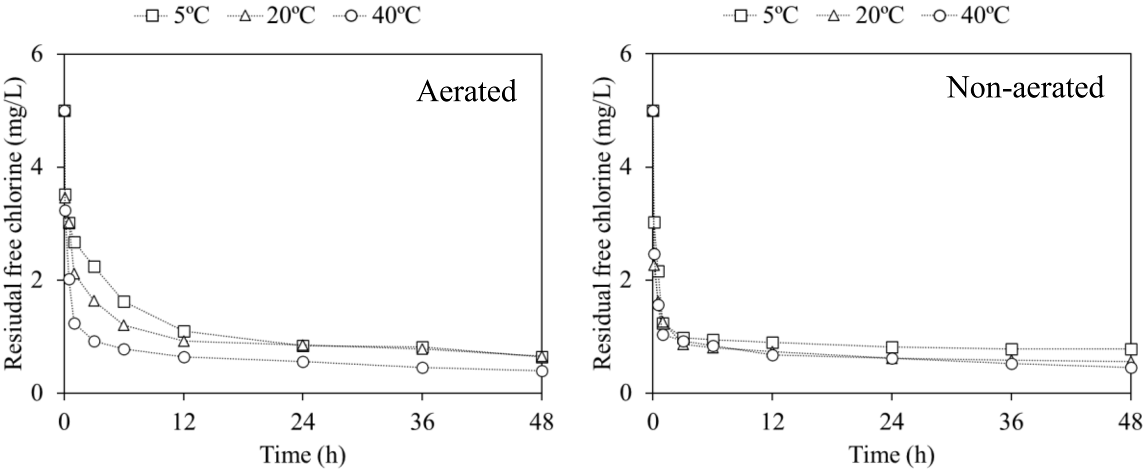

Fig. 5.1. Chlorine decay curves of water samples obtained from DWTS after storage under different conditions. The initial DOC concentration in all water samples was adjusted to the same level of 2 mg/L.

Fig. 5.3 shows the first-order rate constants for each water sample when the DOC concentration was normalized to 2 mg/L. The first-order kinetic of the data for the fast consumption rate (1 h) is presented; rate constants are indicated as the slope of the linear regression through data in Fig. 5.3. The value of *k* was ranging from 0.41 to 1.86 h^{-1} and 1.08 to 1.96 h^{-1} in water from aerated and non-aerated DWTS, respectively. Chlorine consumption during the fast stage was greater for the water from non-aerated DWTS than aerated ones. Since DOC was normalized to the same level, the fast decrease of chlorine in the initial stage was not considered a function of DOC concentration. The high UV_{260} value in the water of non-aerated DWTS was hypothesized to be responsible to cause the fast decrease of chlorine in the initial stage as well as the different DOM compositions that might consist of aromatic structures.

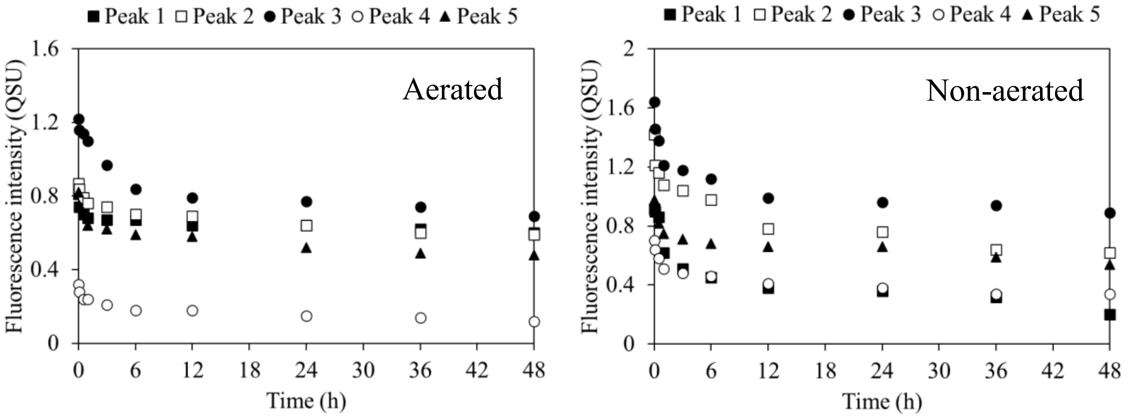

Fig. 5.2. Fluorescence intensity of water from the aerated and non-aerated conditions of DWTS under the temperature of 40°C during chlorination. Peak 1: tyrosine-like; Peak 2 and 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM.

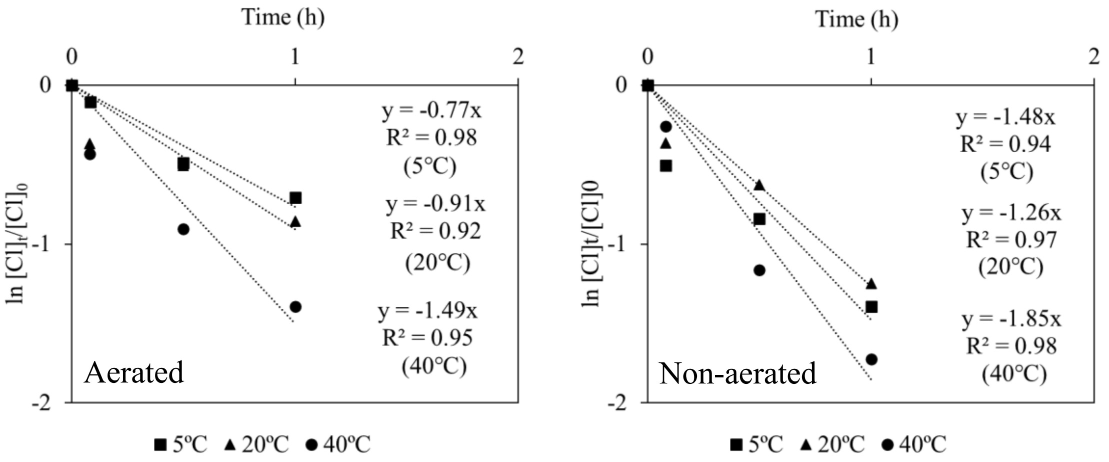

Fig. 5.3. Estimation of the first-order rate constant (*k*) of the reaction of chlorine with the water from stored DWTS by the model fitting of observed data for the initial 1 hour. The initial DOC concentration was 2 mg/L, and the temperature was 25°C for the chlorine consumption experiment.

5.3.2. Reactivity evaluation based on chlorine consumption

The relationships between DOM parameters and chlorine consumption are shown in Tables 5.1–5.6. Since UV$_{260}$ reveals the composition of aromatic compounds in the water (Imai *et al*., 2002), the result showed that UV$_{260}$ is associated with chlorine consumption, and this good correlation is obvious. The result suggests that samples with high aromatic organics will consume more chlorine during chlorination; in this study, high UV$_{260}$ was found in water from non-aerated DWTS and was thought to have more aromatic organics compared to aerated DWTS. The aromatic compositions of DOM in water from DWTS are responsible for most of UV$_{260}$. However, not all aromatics can primarily react with chlorine, resulting in a poor correlation between chlorine consumption and UV$_{260}$ in water from aerated DWTS. The poor correlation is probably because only certain sites of the molecule (functional groups) are involved in a chemical reaction with chlorine and not the whole molecule (Luilo *et al*., 2012).

Peak 2 and Peak 5 have a good relationship with chlorine consumption in the water from non-aerated DWTS. The possible reason is that those two types of DOM composition can react with chlorine through the hydrolysis and/or electrophilic aromatic substitution reactions (Wang *et al*., 2020). This is thought that more reactive DOM was presented as Peak 2 and Peak 5, even the intensity of Peak 1 and Peak 3 was observed with high intensity in water from both aerated and non-aerated DWTS, the residual intensity of those substances still presented after 48 h chlorination (Table 3.7). As reported in the literature, the reactivity of chlorine with organic compounds and different functional groups from high to low is sulfur moieties > primary and secondary amines > phenol, tertiary amines > double bonds, other aromatics, carbonyls, and amides (Deborde and von Gunten, 2008). The compositions of DOM in water from non-aerated DWTS can preferentially react with chlorine, resulting in a good correlation between Peak 5 and chlorine consumption. The findings hypothesize that Peak 5 may contain hydroxyl phenolic groups and be ready for oxidization during chemical oxidation processes through electrophilic aromatic substitution and addition, resulting in cleavage of the aromatic ring and formation of low UV absorbance oxidation products (Wenk *et al*., 2013). This study also showed that the high molecular DOM released from non-aerated DWTS stored at 40°C could strongly influence their reactivity during chlorination. The good correlation between the chlorine consumption, Peak 2 and Peak 5 in water from non-aerated DWTS suggested that those two DOM compositions can be used as a parameter to rapidly predict the consumption of oxidant during chlorination.

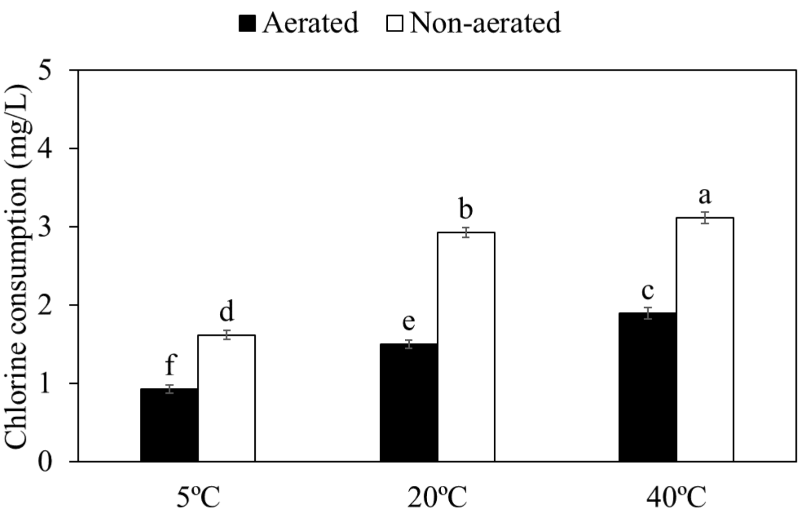

Fig. 5.4. Comparison of chlorine consumption in water after storage of DWTS under different conditions (n = 3). The initial DOC concentration was 2 mg/L, and the temperature was 25°C for the chlorine consumption experiment. The different letters (a–f) indicate that the observed differences are statistically significant at $p < 0.05$.

More chlorine is consumed by DOM in water from non-aerated conditions compared to those other conditions (Fig. 5.4). There is an obvious influence of temperature on chorine consumption; chlorine consumption increased with the increase in temperature. The difference between aerated and non-aerated conditions is quite significant. The lack of oxygen under non-aerated conditions could probably limit the degradation of DOM, resulting in more DOM accumulated and remaining in the water after storage.

Table 5.1. Pearson correlation matrix for water from DWTS after storage for 3 days under the aerated condition at 5°C.

Variables	pH	EC	DO	DOC	UV_{260}	NO_3^--N	NH_4^+-N	TN	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	CC
pH	1													
EC (mS/m)	0.478	1												
DO (mg/L)	0.396	0.053	1											
DOC (mg/L)	0.182	0.410	0.599	1										
UV_{260} (m^{-1})	-0.194	0.434	0.495	0.820	1									
NO_3^--N (mg/L)	-0.432	-0.060	-0.998	-0.554	-0.453	1								
NH_4^+-N (mg/L)	-0.360	-0.855	0.149	0.080	-0.138	-0.116	1							
TN (mg/L)	-0.451	-0.130	0.185	-0.282	0.257	-0.200	-0.209	1						
Peak 1 (QSU)	0.142	0.558	0.456	0.975	0.856	-0.410	-0.088	-0.268	1					
Peak 2 (QSU)	0.043	0.477	0.434	0.974	0.870	-0.383	-0.002	-0.251	0.994	1				
Peak 3 (QSU)	-0.683	0.164	0.069	0.387	0.815	-0.027	-0.097	0.555	0.471	0.522	1			
Peak 4 (QSU)	-0.065	0.528	0.375	0.923	0.933	-0.325	-0.110	-0.098	0.972	0.980	0.662	1		
Peak 5 (QSU)	-0.892	-0.388	0.036	0.070	0.496	0.000	0.321	0.670	0.070	0.158	0.839	0.272	1	
CC (mg/L)	0.024	-0.126	0.015	0.246	0.448	0.064	0.025	-0.075	0.410	0.551	0.625	0.413	0.656	1

CC: chlorine consumption; Peak 1: tyrosine-like; Peak 2 and 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM.

Table 5.2. Pearson correlation matrix for water from DWTS after storage for 3 days under the aerated condition at 20°C.

Variables	pH	EC	DO	DOC	UV_{260}	NO_3^--N	NH_4^+-N	TN	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	CC
pH	1													
EC (mS/m)	0.011	1												
DO (mg/L)	0.785	-0.005	1											
DOC (mg/L)	-0.833	0.260	-0.956	1										
UV_{260} (m^{-1})	-0.835	0.217	-0.964	0.991	1									
NO_3^--N (mg/L)	-0.297	-0.359	-0.661	0.468	0.562	1								
NH_4^+-N (mg/L)	-0.663	0.622	-0.594	0.787	0.712	-0.168	1							
TN (mg/L)	-0.314	0.678	-0.494	0.650	0.556	-0.175	0.888	1						
Peak 1 (QSU)	-0.824	0.180	-0.954	0.982	0.954	0.407	0.798	0.689	1					
Peak 2 (QSU)	-0.581	0.461	-0.565	0.714	0.614	-0.230	0.949	0.912	0.783	1				
Peak 3 (QSU)	-0.860	0.189	-0.959	0.993	0.976	0.437	0.789	0.644	0.995	0.745	1			
Peak 4 (QSU)	-0.818	0.268	-0.957	0.997	0.997	0.518	0.753	0.617	0.965	0.662	0.982	1		
Peak 5 (QSU)	-0.705	0.423	-0.684	0.820	0.737	-0.090	0.966	0.876	0.871	0.984	0.846	0.775	1	
CC (mg/L)	0.125	0.014	-0.126	0.325	0.400	0.035	-0.145	-0.246	0.326	0.513	0.702	0.403	0.712	1

CC: chlorine consumption; Peak 1: tyrosine-like; Peak 2 and 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM.

Table 5.3. Pearson correlation matrix for water from DWTS after storage for 3 days under the aerated condition at 40°C.

Variables	pH	EC	DO	DOC	UV_{260}	NO_3^--N	NH_4^+-N	TN	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	CC
pH	1													
EC (mS/m)	-0.291	1												
DO (mg/L)	0.158	0.482	1											
DOC (mg/L)	-0.256	0.349	-0.440	1										
UV_{260} (m^{-1})	-0.263	-0.041	0.057	0.475	1									
NO_3^--N (mg/L)	-0.450	-0.183	0.032	0.254	0.935	1								
NH_4^+-N (mg/L)	-0.188	0.754	0.322	0.707	0.558	0.317	1							
TN (mg/L)	0.799	-0.032	-0.182	0.348	-0.132	-0.438	0.181	1						
Peak 1 (QSU)	-0.265	0.298	-0.659	0.891	0.059	-0.108	0.418	0.357	1					
Peak 2 (QSU)	0.045	0.240	-0.636	0.711	-0.256	-0.454	0.233	0.585	0.923	1				
Peak 3 (QSU)	-0.217	0.715	-0.209	0.827	0.012	-0.217	0.703	0.359	0.869	0.815	1			
Peak 4 (QSU)	-0.173	0.380	-0.387	0.995	0.457	0.209	0.739	0.423	0.875	0.720	0.844	1		
Peak 5 (QSU)	-0.074	-0.092	0.722	-0.577	0.389	0.537	-0.025	-0.551	-0.860	-0.978	-0.691	-0.579	1	
CC (mg/L)	0.021	0.004	-0.068	0.523	0.813	0.003	0.300	0.453	0.500	0.753	0.726	0.687	0.824	1

CC: chlorine consumption; Peak 1: tyrosine-like; Peak 2 and 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM

Table 5.4. Pearson correlation matrix for water from DWTS after storage for 3 days under the non-aerated condition at 5°C.

Variables	pH	EC	DO	DOC	UV_{260}	NO_3^--N	NH_4^+-N	TN	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	CC
pH	1													
EC (mS/m)	-0.892	1												
DO (mg/L)	0.321	-0.572	1											
DOC (mg/L)	-0.780	0.947	-0.654	1										
UV_{260} (m^{-1})	-0.503	0.505	-0.815	0.593	1									
NO_3^--N (mg/L)	0.355	-0.629	0.175	-0.713	0.087	1								
NH_4^+-N (mg/L)	-0.579	0.244	0.056	0.272	0.509	0.154	1							
TN (mg/L)	-0.829	0.659	0.097	0.631	0.208	-0.487	0.719	1						
Peak 1 (QSU)	0.203	0.192	-0.808	0.385	0.451	-0.290	-0.432	-0.426	1					
Peak 2 (QSU)	-0.792	0.943	-0.499	0.980	0.436	-0.805	0.262	0.718	0.261	1				
Peak 3 (QSU)	-0.429	0.720	-0.938	0.728	0.636	-0.354	-0.213	-0.023	0.727	0.616	1			
Peak 4 (QSU)	-0.727	0.635	0.016	0.359	-0.060	-0.214	0.068	0.486	-0.437	0.427	0.260	1		
Peak 5 (QSU)	-0.059	0.307	-0.618	0.177	0.188	0.016	-0.619	-0.469	0.499	0.087	0.759	0.365	1	
CC (mg/L)	-0.235	0.046	0.015	0.503	0.663	0.036	0.258	0.413	0.626	0.712	0.712	0.633	0.645	1

CC: chlorine consumption; Peak 1: tyrosine-like; Peak 2 and 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM.

Table 5.5. Pearson correlation matrix for water from DWTS after storage for 3 days under the non-aerated condition at 20°C.

Variables	pH	EC	DO	DOC	UV_{260}	NO_3^--N	NH_4^+-N	TN	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	CC
pH	1													
EC (mS/m)	-0.800	1												
DO (mg/L)	0.747	-0.899	1											
DOC (mg/L)	-0.823	0.963	-0.828	1										
UV_{260} (m^{-1})	-0.470	0.318	-0.617	0.150	1									
NO_3^--N (mg/L)	0.067	-0.318	0.060	-0.146	-0.016	1								
NH_4^+-N (mg/L)	-0.392	0.009	0.057	0.260	-0.292	0.644	1							
TN (mg/L)	-0.629	0.943	-0.893	0.931	0.202	-0.132	0.014	1						
Peak 1 (QSU)	-0.363	0.593	-0.216	0.702	-0.557	-0.336	0.289	0.586	1					
Peak 2 (QSU)	-0.751	0.450	-0.258	0.638	-0.144	0.205	0.846	0.341	0.587	1				
Peak 3 (QSU)	-0.949	0.576	-0.529	0.642	0.410	0.069	0.570	0.374	0.248	0.833	1			
Peak 4 (QSU)	-0.846	0.660	-0.444	0.804	-0.064	0.024	0.691	0.541	0.695	0.965	0.851	1		
Peak 5 (QSU)	-0.843	0.479	-0.296	0.608	0.057	0.028	0.710	0.282	0.478	0.954	0.931	0.941	1	
CC (mg/L)	-0.026	0.075	-0.069	0.358	0.648	0.156	0.092	-0.125	0.538	0.841	0.713	0.801	0.769	1

CC: chlorine consumption; Peak 1: tyrosine-like; Peak 2 and 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM.

Table 5.6. Pearson correlation matrix for water from DWTS after storage for 3 days under the non-aerated condition at 40°C.

Variables	pH	EC	DO	DOC	UV$_{260}$	NO$_3^-$-N	NH$_4^+$-N	TN	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	CC
pH	1													
EC (mS/m)	-0.722	1												
DO (mg/L)	0.835	-0.550	1											
DOC (mg/L)	-0.598	0.126	-0.845	1										
UV$_{260}$ (m^{-1})	0.163	-0.172	0.426	-0.090	1									
NO$_3^-$-N (mg/L)	0.111	-0.478	0.230	0.252	0.850	1								
NH$_4^+$-N (mg/L)	0.690	-0.230	0.309	-0.178	0.012	-0.128	1							
TN (mg/L)	-0.244	0.086	-0.360	0.676	0.582	0.639	0.180	1						
Peak 1 (QSU)	-0.699	0.350	-0.501	0.638	0.539	0.595	-0.491	0.754	1					
Peak 2 (QSU)	-0.045	-0.079	0.163	0.187	0.960	0.886	-0.060	0.761	0.731	1				
Peak 3 (QSU)	-0.044	-0.194	0.280	0.055	0.938	0.914	-0.306	0.536	0.680	0.939	1			
Peak 4 (QSU)	0.309	-0.262	0.547	-0.198	0.988	0.823	0.113	0.509	0.406	0.913	0.894	1		
Peak 5 (QSU)	0.818	-0.552	0.938	-0.660	0.657	0.462	0.429	-0.018	-0.279	0.441	0.474	0.763	1	
CC (mg/L)	0.015	-0.199	-0.427	0.633	0.715	0.064	0.255	0.503	0.602	0.903	0.626	0.702	0.851	1

CC: chlorine consumption; Peak 1: tyrosine-like; Peak 2 and 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM

Table 5.7. Water quality of samples from different storage conditions and after chlorination.

Samples		DOM composition/Time (h)													
		Peak 1 (QSU)		Peak 2 (QSU)		Peak 3 (QSU)		Peak 4 (QSU)		Peak 5 (QSU)		UV_{260} (m^{-1})		DOC (mg/L)	
		0	48	0	48	0	48	0	48	0	48	0	48	0	48
Aerated	5°C	0.75	0.47	0.71	0.56	0.63	0.52	0.14	0.12	0.20	0.08	1.09	0.21	2.01	0.65
	20°C	0.62	0.43	2.05	0.57	1.03	0.52	0.33	0.09	0.25	0.04	1.48	0.18	2.05	0.47
	40°C	1.06	0.43	1.43	0.68	0.84	0.70	0.41	0.15	0.24	0.11	2.26	0.23	2.10	0.40
Non-aerated	5°C	1.10	0.66	0.81	0.66	0.80	0.57	0.17	0.10	0.25	0.04	1.42	0.26	2.13	0.62
	20°C	0.75	0.64	2.09	0.85	0.87	0.79	0.47	0.28	0.15	0.15	2.69	0.30	2.03	0.42
	40°C	0.91	0.75	2.33	1.43	0.89	0.67	0.70	0.33	0.16	0.12	3.98	0.28	2.17	0.23

5.3.3. Composition changes of DOM

The composition of DOM evaluated by peak-picking fluorescence analysis shows that water from DWTS was dominated by Peak 3 and Peak 2 under aerated and non-aerated conditions, respectively. Chlorination decreased the intensity of all components (Fig. 5.5–5.6 and Table 5.7). The oxidation mechanism employs the breakdown of carbon double bonds in aromatic molecules and halogen substitution reactions which indicates the reduction in fluorescence intensity of DOM during chlorination (Korshin *et al.*, 1999). In this study, the water from non-aerated DWTS stored at 40°C had a higher reduction of DOM compared to other conditions (Fig. 5.6).

It was obvious that each sample before chlorination had different fluorescence properties, and water from aerated DWTS was dominated by humic-like fluorescence (Fig. 5.5). However, the appearance of Peak 3 was stronger than Peak 5 in water from non-aerated DWTS. In the case of water from non-aerated DWTS stored at 40°C, all the five fluorescent components were well defined in the EEM spectrum with the high fluorescence intensity for each component, suggesting the enrichment of fluorescing compounds in non-aerated DWTS stored at 40°C. The humic-like peaks in water from aerated DWTS stored at 5°C and 20°C were located at shorter excitation and emission wavelengths (blue-shifted). It is known that a blue-shift is associated with a decreasing number of highly substituted aromatic nuclei (Korshin *et al.*, 1999). Thus, aerated DWTS were mainly associated with low aromaticity and polycondensation of humic materials compared to non-aerated DWTS.

All fluorescence peaks are well-defined in water from non-aerated DWTS stored at 40°C. However, the intensity of each peak was distinct due to the release rate of DOM from DWTS during the non-aerated condition. Peak 2 and Peak 4 as the major DOM released from non-aerated DWTS stored at a high temperature were to be the most affected by chlorine. The decrease of Peak 2 and Peak 4 in the water from non-aerated DWTS at 40°C after chlorination is thought that tryptophan-like are polyphenolic that likely to have unstable structure due to dimerization/polymerization reactions against chlorine (Criquet *et al*., 2015). Meanwhile, the presence of Peak 3 with high intensity during the aerated condition of DWTS which is described as humic-like substances in this study tends to have less distinct changes in intensity even after chlorination compared to that of Peak 5. This result is hypothesized that Peak 5 was more affected by chlorine than Peak 3.

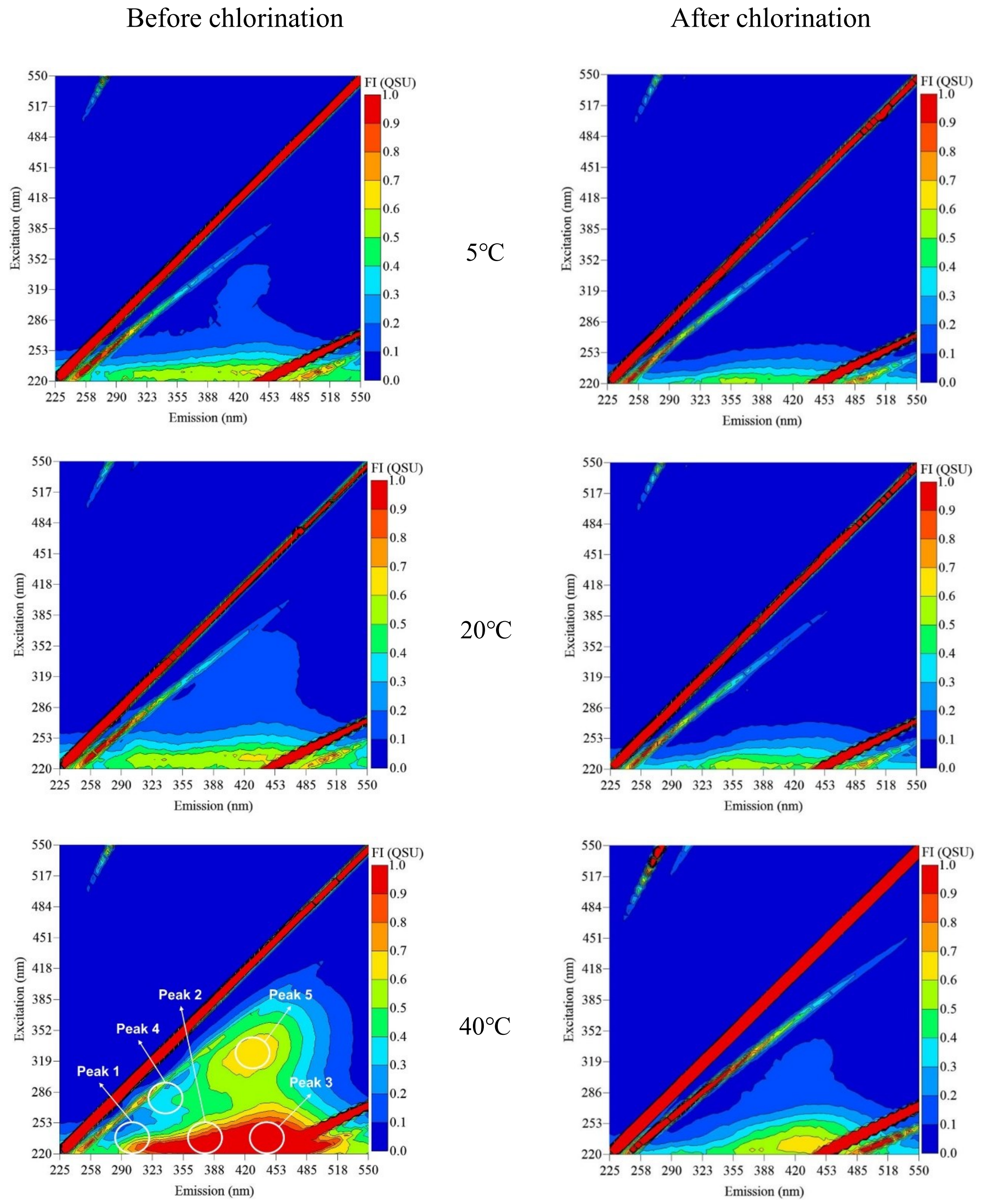

Fig. 5.5. Fluorescence spectra of water after the aerated condition of DWTS under different temperatures (5, 20, and 40℃) and their changes after chlorination. FI: fluorescence intensity; Peak 1: tyrosine-like; Peak 2 and 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM.

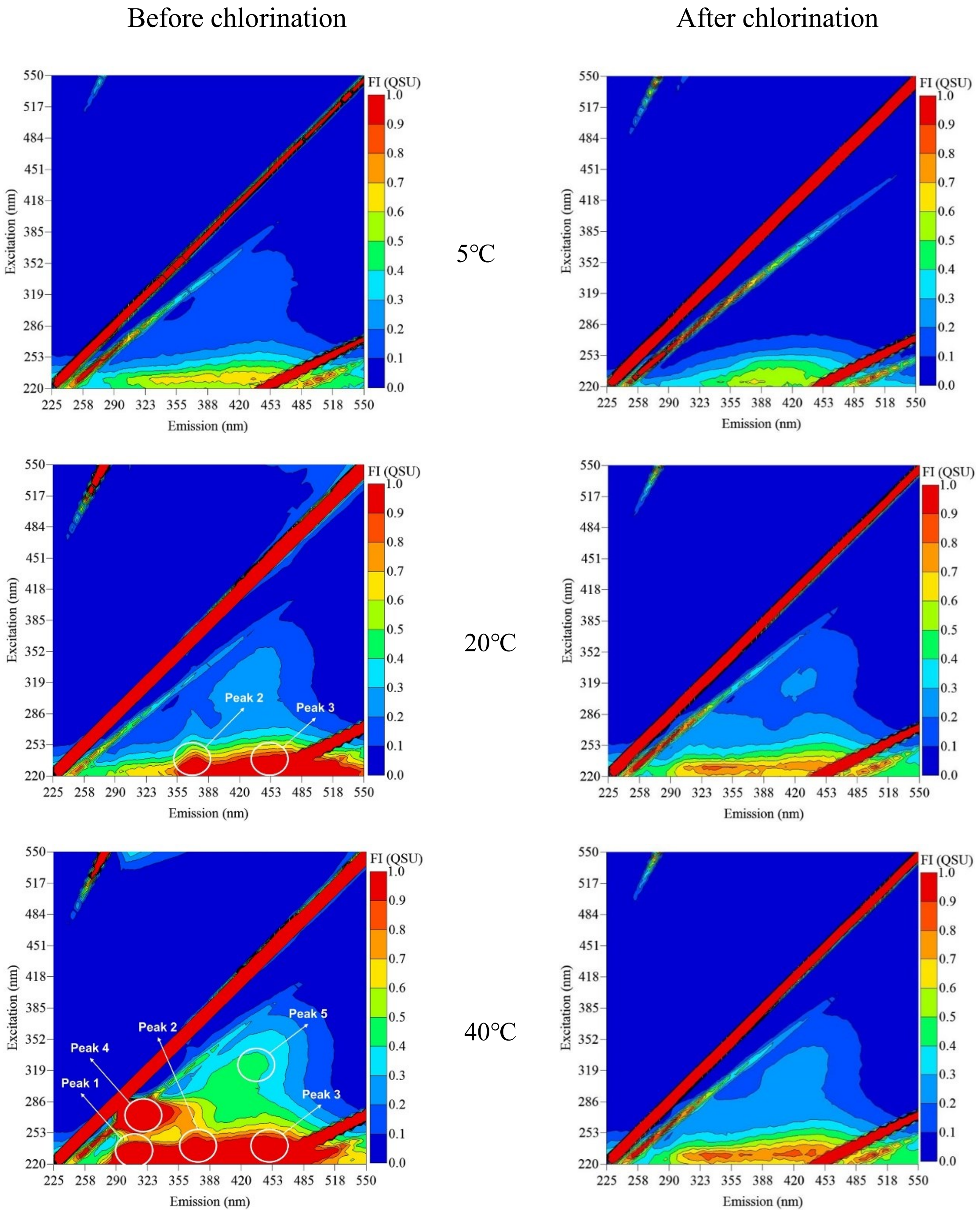

Fig. 5.6. Fluorescence spectra of water after the non-aerated condition of DWTS under different temperatures (5, 20, and 40°C) and their changes after chlorination. FI: fluorescence intensity; Peak 1: tyrosine-like; Peak 2 and 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM.

The decrease in fluorescence intensity might indicate the decomposition of fluorescing materials in the DOM structure during chlorination. Such a decrease was observed for all peaks in water from DWTS. The distinct DOM reduction during chlorination from different sample waters in this study could be explained that Peak 1 and Peak 2 had a high contribution which is accounted for 45–64% of the fluorescence compared to that of Peak 3 and Peak 5 released from non-aerated DWTS. Peak 1 and Peak 2 observed in water from non-aerated DWTS stored at 40°C completely broke down into non-fluorescent structures because of chlorination. Although Peak 3 showed a decrease in fluorescence intensity during chlorination, the changes in Peak 3 in each sample were less distinct as compared with those in the corresponding Peak 5. It was hypothesized that the humic-like Peak 5 was more susceptible to chlorine than the humic-like Peak 3.

5.3.4. Relationship between *k* and water quality indices of water from DWTS

Correlation between initial UV_{260} and *k* values for chlorinated water are presented in Fig. 5.7–5.8. Relationships between *k* and UV_{260} are obvious for the water from non-aerated DWTS and imply that the DOM structure contained carbon bonds that were reactive with chlorine. The results were suggested that some of these carbons may have contained amine or hydroxyl groups, resulting in faster reacting DOM "sites" characterized by *k* values. The weak relationships between *k* and UV_{260} for the water from aerated DWTS at a temperature of 5°C are thought that carbon bonds may have contained carboxyl groups that resulted in slowing reacting DOM "sites" as presented by those quantified by *k* values (Westerhoff *et al.*, 2004). Even though the DOC concentration was normalized to 2 mg/L for all sample waters, the non-aerated condition exhibited higher consumption rates compare to that of the aerated condition. Judging from the UV_{260}

values, the chlorination of water from different DWTS storage conditions exhibited the different DOM reductions in composition and structure as resulted in the above-mentioned.

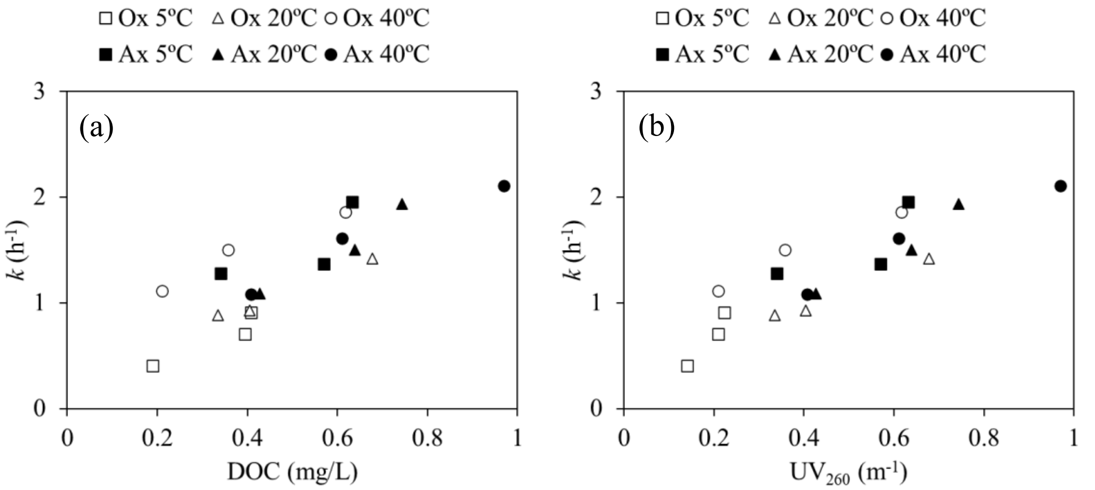

Fig. 5.7. Relationship between (a) DOC, (b) UV_{260}, and *k* of water from DWTS. Ox: aerated; Ax: non-aerated.

Fluorescent components reduced consistently in a function of time, where the high reduction of Peak 5 (Table 5.8) occurred under aerated conditions and exhibited a linear correlation ($r > 0.924$) (Fig. 3.8). However, the humic-like substances did not behave similarly during chlorination. Even the humic-like substances were majorly produced under aerated condition of DWTS, the high *k* (1.79 h^{-1}) between Peak 5 and chlorine was observed under the non-aerated condition at 20°C was probably due to desired species of humic-like substances reacting with chlorine which contained carbon double bonds in aromatic molecules and halogen substitution reactions (Korshin *et al.*, 1999). Meanwhile, Peak 2 exhibited a high *k* under the non-aerated condition at 40°C. A dramatic decrease of Peak 2 might be thought to be the suspectable reaction between chlorine and tryptophan-like in this study. It's noteworthy that NH_4^+-N could inhibit the decomposition of the fluorescence chemicals (Wu *et al.*, 2010). Thus, the lower reaction rate of chlorine to fluorescent components found in this study was probably due to the inhibition of NH_4^+-N.

Table 5.8. Mean reduction percentage of DOM composition and concentration.

Samples		Reduction percentage (%)						
		Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	UV_{260}	DOC
Aerated	5°C	37	21	18	18	60	81	67
	20°C	31	72	50	74	86	88	77
	40°C	59	52	17	65	56	89	81
Non-aerated	5°C	40	18	28	39	84	81	71
	20°C	15	59	9	42	29	88	79
	40°C	17	39	25	52	24	93	89

Peak 1: tyrosine-like; Peak 2: tryptophan-like; Peak 3: humic-like; Peak 4: tryptophan-like; Peak 5: humic-like substances from fluorescence EEM.

DOM in water from non-aerated DWTS has the highest *k* and the *k* became steady against Peak 2 and Peak 5 in water from non-aerated DWTS stored at 20°C. It seems that a residual chlorine level of 0.03 mg/L which is in this water is not efficient to avoid new-freshly DOM released from DWTS. Non-aerated DWTS produces the most important DOM accumulation, and this may lead to higher chlorine demand. The most significant statistical relationship was obtained between the *k* and fluorescent component of water from non-aerated DWTS. The findings showed that almost all DOM fractions had the same linear increase of *k*. *k* increased with the increase of UV_{260} in water from all storage conditions of DWTS. The temperature of storage becomes important for a short period of storage with a high DOM concentration. Even with a similar DOC concentration, *k* for the non-aerated condition is greater than the aerated one, mostly because of its high value of UV_{260}.

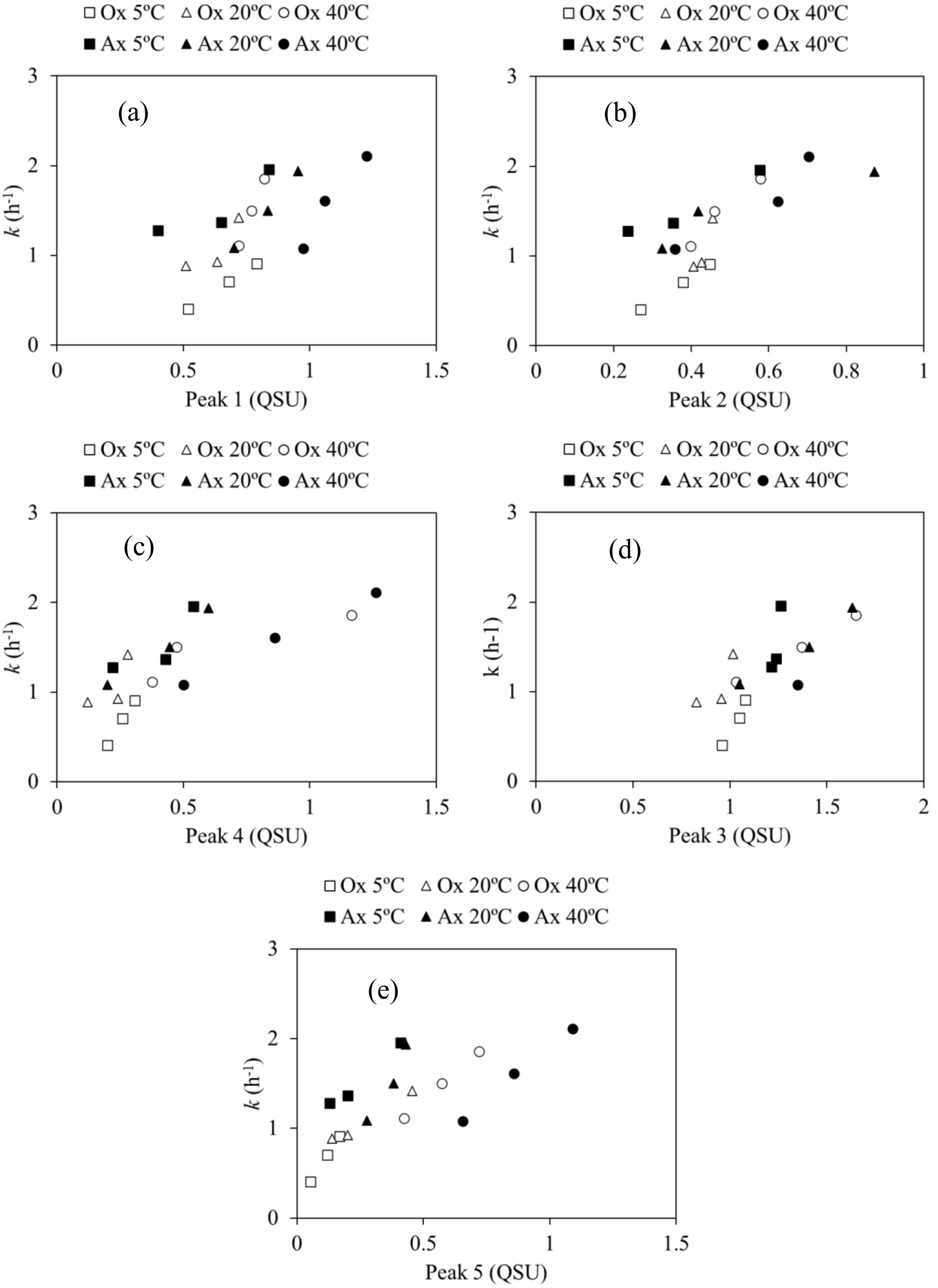

Fig. 5.8. Relationship between fluorescence EEM Peak 1, 2, 3, 4, and 5 and *k* of water from DWTS. Ox: aerated; Ax: non-aerated. Peak 1: tyrosine-like; Peak 2 and 4: tryptophan-like; Peak 3 and 5: humic-like substances from fluorescence EEM.

5.4. Summary

The study showed that the storage treatment of DWTS can change the DOM characteristics released into the water and caused rapid chlorine decay during chlorination. The composition of DOM assessed by UV_{260} value and fluorescence EEM exhibited higher in water from non-aerated DWTS than aerated one that causing the rapid decay of chlorine when DOC concentrations of samples were normalized to 2 mg/L. More consumptive DOM was presented as Peak 2 (tryptophan-like) and Peak 5 (humic-like) observed with high intensity in water from both aerated and non-aerated DWTS and were thought to have rich phenolic structures in DOM with high reactivity with chlorine. The changes in the fluorescence spectrum suggested that the fluorescent structure of DOM in water from DWTS decomposed during chlorination. The findings also showed that the first-order constant rate exhibited an obvious correlation with the UV_{260} value, where the water from non-aerated DWTS drew a higher consumption rate than the aerated one. DOM was released distinctly during aerated and non-aerated storage of DWTS, resulting in the different consumption rates of different structural DOM compositions. The results of this study show that both temperature and oxygen concentration are important factors regarding the storage of DWTS in the thickener tank of the treatment plant.

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Chapter 6 Conclusion

The study presented the DOM characteristics in source water and their changes throughout the drinking water treatment and the release of DOM from DWTS was also investigated. Based on the results obtained, the conclusions can be drawn as follow:

Chapter 3 discusses the water quality in the raw water feeding the drinking water treatment plants and the DOM changes throughout the water treatment. The result showed that the average DOM concentration was 1.84 ± 0.65 and 0.95 ± 0.19 mg/L as DOC for plants A and B, respectively. The fluorescence EEM analysis showed that plants A and B had a high proportion of humic-like substances in the raw water and showed significant differences in DOM changes during water treatment in both plants. The intensity of humic-like substances in plant B was two times higher than that in plant A. These results suggest that the significant differences in water quality in raw water feeding both plants existed. Plant A was observed with the increase of fluorescent DOM after post-chlorination, which can be explained by the degradation and transformation of DOM into humic molecules through condensation during chlorination. Fluorescence indices verified that purified water in plants A and B contained and generated new-produced organic matter during the storing. The results provide important information that can be used to optimize the water treatment process for DOM removal.

In Chapter 4, the prolonged aerated and non-aerated storage of DWTS (21 days) at different temperatures (5ºC, 20ºC, 40ºC) and DOM transformation in sludge were investigated. Non-aerated condition at high temperatures was found to promote high DOC concentrations with low SUVA values, which indicates that non-aromatic DOM formed during storage. Compositional analysis by fluorescence EEM indicated that more humic-like substances formed during aerated storage than during non-aerated storage and that more protein-like substances formed during non-aerated storage than during aerated storage. With increases in DOM, high-temperature storage was able to accelerate the humification process for aerated storage, suggesting that the bulk DOM was more humified under those conditions. Moreover, compositional analysis based on the molecular weight distribution found that the UV-absorbing DOM constituents that formed in non-aerated storage had higher molecular weights at high temperatures than the molecular weights seen with aerated storage. This result indicated that the storage treatment under an aerated condition may decrease the DOM released from DWTS.

Chapter 5 shows that the storage treatment of DWTS can change the DOM characteristics released to the water and caused rapid chlorine decay during chlorination. The composition of DOM assessed by UV_{260} value and fluorescence EEM exhibited higher in water from non-aerated DWTS than aerated one that causing the rapid decay of chlorine when DOC concentrations of samples were normalized to 2 mg/L. More consumptive DOM was presented as Peak 2 (tryptophan-like) and Peak 5 (humic-like) observed with high intensity in water from both aerated and non-aerated DWTS. The changes in the fluorescence spectrum suggested that the fluorescent structure of DOM in water from DWTS decomposed during chlorination. The findings also showed that the first-order constant rate exhibited an obvious correlation with UV_{260} value, where the water from non-aerated DWTS drew a higher consumption rate than the aerated one.

The findings of this study can provide important information to understand the changes of DOM quality from source to the treated water in drinking water treatment plant associated with the release of DOM from DWTS, and to evaluate the water treatment process in removing DOM.

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