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Original Article

Tracking seasonal changes of natural organic matter in a water treatment plant in Bangkok using EEM-PARAFAC approach

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Abstract

This study aims to evaluate spatial and seasonal changes in natural organic matter (NOM) in Bangkhen Water Treatment Plant, Thailand. Water samples were analyzed for UV absorbance at 254 nm (UV_{254}), dissolved organic carbon (DOC), and fluorescence excitation−emission matrix (EEM) with parallel factor analysis (PARAFAC). DOC concentrations of the raw water in wet and dry seasons were in the range of 4.01-5.75 and 2.34-4.97 mg-C/L, respectively. Fluorescence character of the water samples could be represented by five PARAFAC components, including terrestrial humic-like (C1 and C2), microbial humic-like (C3), microbial protein-like (C4), and fulvic-like (C5) components. Component C2 significantly correlated to DOC and UV_{254} (R^2=0.73-0.88, $p<0.01$). Coagulation had preferential removal for humic-like materials (C1 and C2). Overall, the results demonstrate that tracking NOM using EEM was more sensitive than UV_{254} or DOC, which benefits WTP in term of adjusting their processes for better water supply quality.

Keywords: natural organic matter, fluorescence, Excitation–Emission Matrix, EEM, PARAFAC

1. Introduction

Fluorescence Excitation−emission matrix (EEM) spectroscopy, which is a series of fluorescent emission scans from a range of excitation wavelength, has been successfully used for natural organic matter (NOM) characterization (Coble, 1996). The advantages of EEM measurement includes rapid analysis, minimal sample preparation and small sample size requirement. According to Stedmon, Markager, and Bro (2003), EEMs analysis provides information regarding types, structures, and abundance of functional groups of NOM.

Traditionally, EEM can be used to characterize NOM based on location of the maximum fluorescence intensity as appeared on the EEM contour plot. Previously determined maximum excitation/emission EEM peaks included: humic-like, fulvic-like , and protein-like peaks (Coble, 1996). Parallel factor analysis (PARAFAC) was developed as a mathematical tool to decompose EEMs into individual fluorescent components (Stedmon *et al*., 2003). The PARAFAC analysis relies on statistical factors through the separation of individual components and also tracing their behaviors in various environments (Ishii & Boyer, 2012). Previously, EEM-PARAFAC was successfully used to track changes of NOM in marine environment (Cawley, Ding, Fourqurean, & Jaff́, 2012), evaluate the removal of NOM fractions of interest in drinking water treatment plants (Baghoth *et al*., 2011) and wastewater recycling plants (Murphy *et al*., 2011). Correlations between disinfection-by-products (DBPs) and specific NOM fractions extracted from PARAFAC were also established (Jutaporn, Armstrong, & Coronell, 2020; Lyon, Cory, & Weinberg, 2014). There is no evidence in a peer-reviewed literature of PARAFAC analysis of EEM data has been conducted in Thailand.

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This aim of this study is to evaluate spatial and seasonal changes in NOM to through unit processes of Bangkhen Water Treatment Plant (WTP) and its pipelines. Bangkhen WTP is the largest water supply facility in Bangkok, Thailand, and produces about 3 million m^3/day. We investigated NOM variations in the WTP using dissolved organic carbon (DOC), UV Absorbance at 254 nm (UV_{254}), specific UV absorbance (SUVA), and EEM spectroscopy for data analysis. PARAFAC modeling was applied to optimize the findings as follows: (1) maxima wavelength locations in EEM, (2) types of NOM components, and (3) changes in NOM composition during water treatment. This approach would be the first PARAFAC model ever conducted in Thailand, which is well suited to track composition of NOM. The results obtained from EEM-PARAFAC approach can be applied for raw water quality monitoring and NOM removal efficacy of variable treatment processes, in which the disinfection process can be modify to reduce the risk of DBPs. Moreover, monitoring quality of raw water can also benefit the WTP as an early warning for an aeration system in the raw water canal to increase dissolve oxygen (DO) in case of high NOM concentration in the raw water.

2. Materials and Methods

2.1 Sampling plan

The water samples were collected from different points along the process trains (Figure 1) of Bangkhen Water Treatment Plant (WTP), Bangkok, Thailand. Sampling points included raw water canal from Chaopraya river to WTP (A1-A23), raw water storage tanks (RW1 and RW2), clarified water (CW1 and CW2), tap water after sand filtration and chlorination with chlorine gas (TW1-TW3), and distribution systems 29-48 km from the WTP (DS1-DS3). Grab sampling was performed once a month during September 2015 to February 2016, resulting in 282 samples. Samples were transferred to a laboratory and then filtered through 0.2 µm cellulose nitrate membrane filter (ACN, Whatman) and analyzed within 48 hours.

2.2 Characterization of natural organic matter (NOM)

NOM character of the samples was measured by UV_{254}, DOC, SUVA, and fluorescent EEM. DOC concentration (mgC/L) in water was determined by a TOC-L CPH organic carbon analyzer (Shimadzu, USA). UV_{254} data was obtained using an Evolution 60S UV-Visible spectrophotometer (Thermo Scientific). SUVA was calculated as the sample's UV_{254} (m^{-1}) divided by the DOC concentration. EEM spectra were measured using Jasco FP-8200 Spectrofluorometer at excitation wavelengths from 220 to 600 nm at 5 nm intervals and emission wavelengths from 230 to 650 nm at 0.5 nm intervals. 282 EEMs have been spectrally corrected for instrument biases, corrected for inner filter effects and Raman calibrated. Blank EEMs using spectra of milliQ water were obtained daily. Sample EEMs were blank subtracted and then normalized to the area under the water Raman peak of blank (ex = 350 nm, em = 368–450 nm) to account for the variation of the lamp intensity over time and to produce data in Raman Units (Stedmon & Bro, 2008).

2.3 PARAFAC Modeling

PARAFAC analysis was applied to decompose 282 obtained EEMs using Matlab and DOMFluor Toolbox following a tutorial by Stedmon and Bro (2008). The data set included 161 samples from water canal, 14 samples from raw water storage tanks, 14 samples from clarified water, 21 samples from tap water, and 72 samples from distribution systems. Samples were categorized into two groups according to season in Thailand, which are the wet season (Sep-Nov 2015) and the dry season (Dec 2015- Feb 2016). During an initial exploratory analysis, six samples were determined as outliers due to instrumental measurement error and removed from the data set. For model validation, split-half analysis (Stedmon *et al*., 2003) was performed to determine the proper number of components. Residual EEMs (residual = data - model) and sum-of-squared error (SSE) of the models were visually inspected. Five-component model was selected according to its randomness of residuals, smaller SSE value, and similarity of components profiles compared to OpenFluor database (Murphy, Stedmon, Wenig, & Bro, 2014). The similarities of component profiles were confirmed by Tucker congruence coefficient exceeding 0.95 on the excitation and emission spectra simultaneously ($\theta = \theta_{ex} \times \theta_{em} \geq 0.95$). The 5-component model could explain more than 99.7% of the variation of this EEM dataset. The intensities and the relative distributions of PARAFAC components are representative the composition of fluorescent DOM.

3. Results and Discussion

3.1 NOM character of the water source

Table 1 shows pH, conductivity, UV_{254}, DOC, and SUVA of water samples starting from Chaopraya River (A1) to raw water (RW) storage tank of Bangkhen WTP, clarified water (CW), finished tap water (TP), and its distribution system (DS). pH and conductivity of all samples during 6 months of the study varied slightly within the range of typical surface water. A1 inlet had average UV_{254} of 0.119 $cm^{-1}$and DOC of 4.30 mg/L. DOC at A1 and RW agree well with a previous study using the same water source having a DOC of 4.8 mg/L (Panyapinyopol, Marhaba, Kanokkantapong, & Pavasant, 2005) and 4.2 mg/L (Tongchang *et al*., 2018). CW had lower DOC concentration, suggesting that adding coagulant was able to remove some of DOC as well as turbidity. There was no significance change of DOC between CW and TW, indicating that sand filtration and chlorine disinfection did not remove DOC, as stated by Gray (2014) that the main objective of chlorination is pathogen inactivation, not NOM removal. SUVA was used as an indicator of NOM hydrophobicity (Archer & Singer, 2006). Average SUVA values of RW was 2.57 L $mg^{-1}m^{-1}$, which considered moderate SUVA compare to the range of 1.7 – 3.1 L $mg^{-1}m^{-1}$ for SUVA in natural water sources of Thailand (Kueseng, Suksaroj, Musikavong, & Suksaroj, 2011).

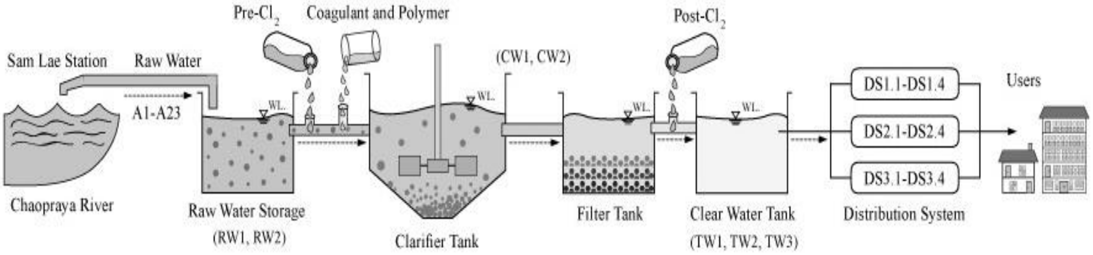

Figure 1. Water sampling location at Bangkhen water treatment plant (WTP)

Table 1. Variation of water quality parameters through Bangkhen WTP during September 2015 to February 2016

Sample points	pH -	Conductivity (μs/cm)	UV$_{254}$ (cm^{-1})	DOC (mgC/L)	SUVA (L-m^{-1}mg^{-1})
Chaopraya river (A1)	7.51 ± 0.22	375 ± 56	0.119 ± 0.03	4.30 ± 0.77	2.73 ± 0.42
Raw water (RW)	7.54 ± 0.18	373 ± 37	0.101 ± 0.03	3.89 ± 0.97	2.57 ± 0.33
Clarified water (CW)	7.16 ± 0.11	385 ± 40	0.077 ± 0.03	3.45 ± 0.78	2.15 ± 0.56
Finished tap water (TW)	7.12 ± 0.23	389 ± 34	0.075 ± 0.02	3.43 ± 0.37	2.17 ± 0.50
Distribution system (DS)	7.50 ± 0.17	321 ± 28	0.060 ± 0.02	3.25 ± 0.46	1.84 ± 0.39

Variation of DOC concentration of the water source along the raw water canal is illustrated in Figure 2. For seasonal analysis, two timeframes including wet season (Sept to Nov 2015) and dry season (Dec 2015 to Feb 2016) were divided. The DOC concentrations in wet and dry seasons were in the range of 4.01-5.75 and 2.34-4.97 mg-C/L, respectively. Thus, DOC concentration of Chaopraya river was higher in the wet season, consistent with a previous study (Tungsudjawong, Leungprasert, & Peansawang, 2018), which was explained by rainfalls causing surface runoff into the river. Among dry months, Jan had the highest DOC concentration due to out of season rainfalls in Jan 2016 (National Hydro informatics and Climate Data Center, 2016). Despite a large seasonal variation (more than two folds), spatial variation of DOC concentration along the canal in each month was smaller. Spatial variations ranged between 15-28% in wet season and 27-35% in dry season.

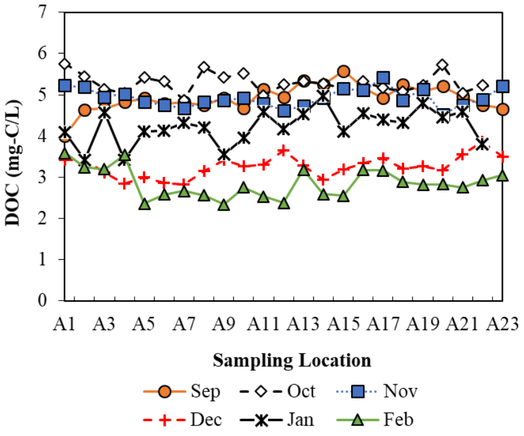

Figure 2. Seasonal change in DOC concentration in the 18-km raw water canal

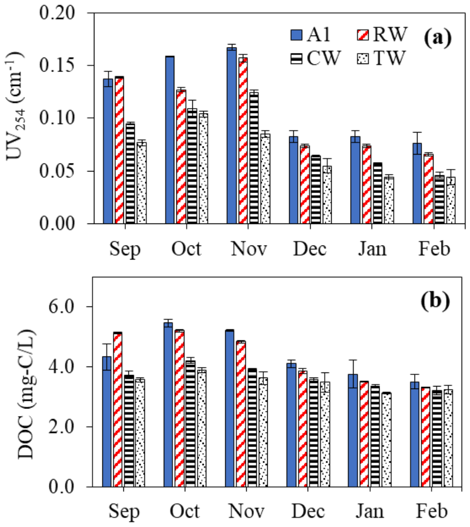

Figure 3. (a) UV$_{254}$ and (b) DOC concentration at Chaopraya river (A1), Raw water (RW), Clarified water (CW), and Finished tap water (TW) of Bangkhen WTP

3.2 NOM removal by WTP

Figure 3 shows in UV$_{254}$ and DOC concentration at different sampling points of Bangkhen WTP. Both UV$_{254}$ and DOC concentration were higher in wet season compared to dry season. From A1 to RW, changes in UV$_{254}$ and DOC were marginal. The water treatment process, including coagulation, sand filtration, and chlorination resulted in decrease of UV$_{254}$ and DOC concentration of TW. Bangkhen WTP used either alum or polyaluminium chloride (PACl) as coagulant to remove turbidity as well as NOM. With a raw water with low turbidity (14-19 NTU) in dry season, the plant used mainly 10-50 mg/L alum as their coagulant. In wet season, the turbidity increased to 17-51 NTU, thus the plant switched to 10-30 mg/L of PACl as coagulant. 0.03 mg/L Polyacrylamide ($(C_3H_5NO)_n$) was used as polymer to aid coagulation process. pH adjustment was not conducted as the pH of the raw water was near neutral all year round.

UV$_{254}$ and DOC removals by coagulation were 22% and 16% in wet season and 22% and 4% in dry season. This result suggests using PACl in wet season achieved greater

DOC removal than using alum in dry season. The advantages of using PACl over alum are that PACl works effectively in a wider range of pH between 6-9, while an optimum pH of alum is in the range of 6.5-7.6 (Kumar & Balasundaram, 2017). However, the higher cost of PACl limits its usage only when the turbidity of raw water is greater than 20 NTU. Noted that DOC removal at the WTP was relatively lower than a previous study using the same water source reported that an optimum PACl dose was 80 mg/L (at pH 7), which 43% of DOC reduction could achieved (Tongchang *et al*.,2018). We suspected that this low DOC removal was due to the lower coagulant dose applied and lack of pH control due to limited cost of operation at the WTP.

Comparing TW to RW, all processes in the WTP removed DOC by 21% and 7.8% in wet and dry season, respectively. The lower removal of DOC can be explained by the lower SUVA of 2.41 L/mg-m in dry season compared to 2.94 L/mg-m in wet season, as coagulation was more effective in water sources with high SUVA (Archer & Singer, 2006). Water with SUVA values between 2 and 4 L mg^{-1} m^{-1} comprised of a mixture of non-aromatic functional groups in the NOM pool (Musikavong, Inthanuchit, Srimuang, Suksaroj, & Suksaroj, 2013). In wet season, sand filtration and chlorination combined achieved 19% and 6.4% removals of UV_{254} and DOC, respectively. These removals were decreased to 13% and 4% in dry season. Despite some degree of NOM removal by could be achieved by chlorination, reaction between NOM and chlorine-based disinfectants leads to formation of DBPs. The affinity of WTP processes to remove UV_{254} absorbing materials over other fractions of NOM resulted in a tap water with lower SUVA values.

3.3 Fluorescent EEMs and PARAFAC analysis

Five-component PARAFAC model was validated from 276 EEM spectra of water sample collected during Sep 2015 to Feb 2016. Table 2 shows the excitation and emission wavelength pairs of the five components, their description, as well as a comparison to similar components identified in previous studies. Spectrum of the five components with emission and excitation loadings obtained from one of the four split-half data sets are illustrated in Figure 4. Data from each subset has high degree of overlapping, indicating that the same spectral loadings were obtained from different set of samples. Two of the components (C1 and C2) have previously been attributed to humic-like fluorophores which may have a terrestrial origin. C3 was previously identified as microbial humic-like NOM. C4 has been associated with protein-like fluorophores, while C5 was determined as terrestrial derived fulvic acid-like NOM (Cawley *et al*., 2012; Coble, 1996; Lyon *et al*., 2014; Murphy *et al*., 2011; Stedmon *et al*., 2003).

For a quantitative study, fluorescent intensities of the five components were reported as the sample-specific maximum fluorescence (F_{max}), which represents a relative concentration of the component in Raman units (RU) (Stedmon *et al*., 2003). Figure 5 shows seasonal and spatial variation of F_{max} along the raw water canal from Chaopraya river (A1) to Bangkhen WTP (A23). The raw water was enriched in terrestrial humic-like materials as C1 and C2 presented at the highest florescent intensities, follow by C3 (microbial humic-like) and C4 (protein-like). C5 (fulvic-like) presented at the lowest intensity. The greater F_{max} of terrestrial humic-like materials over other components were previously reported in surface water (Jutaporn *et al*., 2020; Stedmon *et al*., 2003).

Compared to DOC measurement, EEM-PARAFAC allows tracking changes in NOM composition between seasons. The F_{max} values of components C1-C4 were higher in wet season compared to dry season, which agreed well with higher DOC concentration in wet season (Figure 2). There was no significant pattern observed in the difference of C5 (fulvic-like) between seasons, which suggests that fulvic-like DOM presented at relatively lower concentration and its abundance did not markedly varied between seasons. The differences between seasons were greater in the case of terrestrial humic-like C1 and C2 than those of microbial-derived C3 and C4, which suggests that season change and rainfalls had greater effect on concentration of humic-like NOM. High fluctuation in the F_{max} of C1-C4 was observed after A13 sampling points in Nov, which can be explained by rainfalls that typically occurs during this month. Thus, NOM monitoring with EEM, which is a sensitive and quick measurement, could provide an early warning to WTP in term of adjusting their processes to handle higher amount of NOM in wet season.

Figure 6 shows average F_{max} of the five PARAFAC components across treatment train of the WTP in wet season and dry season. There was no significant difference observed between fluorescent profile of NOM at Chaopraya river (A1) and raw water (RW). NOM at these two sampling points showed greater abundance of terrestrial humic-like NOM (C1 and C2) over other components.

Table 2. Primary (and secondary) fluorescence excitation/emission (Ex/Em) maxima and description of five components (C1-C5) identified from PARAFAC model and a comparison to similar components identified in previous studies.

Component	Ex/Em (nm/nm)	Description and probable source	Previously identified components
C1	325/403	Humic-like; terrestrial derived	Peak A, 260/ 380–460[a] C1, <240/ 436[b] C3, <290/ 340-500[c]
C2	270(370)/453	Ubiquitous humic-like; terrestrial derived	Peak C, 350/ 420–480[a] C1, <290(330-400)/ 400-500[c] C2, <250(360)/434[e]
C3	275(420)/499	Marine and terrestrial humic materials, microbial humic-like; possible microbial reprocessing	Peak M, 312/ 380–420[a] C4, 250(325)/ 416[b] C2<260(280-340)/ 340-460[c] C1, <250(320)/ 414[e]
C4	285/353	Protein-like; Tryptophan-like; microbial derived, amino acids	Peak T, 275/340[a] C5, < 240(280)/ 368[b] C4, <250(280)/ 357[e] C4, 240 (280)/ 350[d]
C5	240/429	Fulvic acid-like; terrestrial derived, autochthonous,	C1, <290(330-400)/ 400-500[c] C2, 250 (400)/ 512[d] C1, 390/ 472[f]

[a](Coble, 1996), [b](Stedmon *et al*., 2003), [c](Shutova *et al*.,2014), [d](Cawley *et al*., 2012), [e](Lyon *et al*.,2014), [f](Murphy *et al*., 2011)

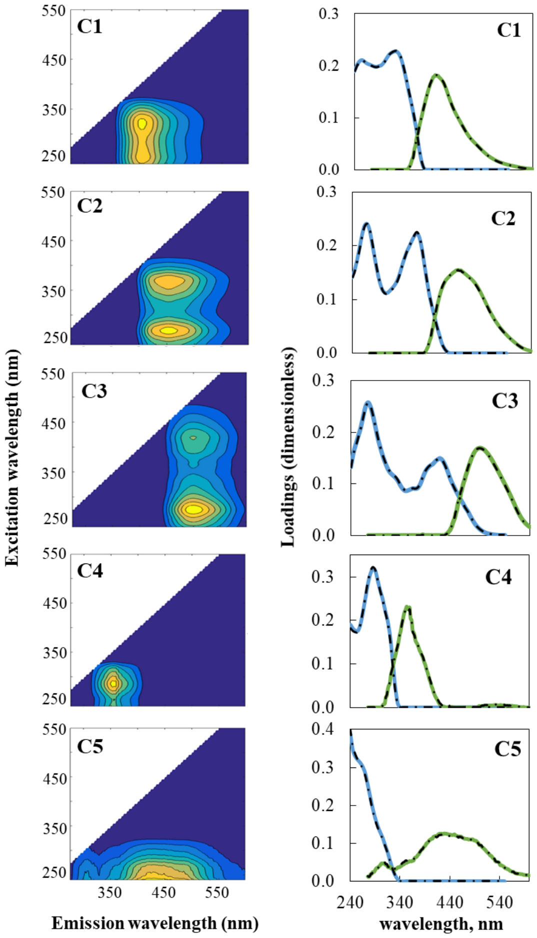

Figure 4. Fluorescence spectra of the five PARAFAC components identified from 276 EEMs of Bangken WTP during Sep 2015 - Feb 2016. The line plots on the right show split-half validations of excitation and emission loadings between the complete dataset (solid) and one of the independent halves (dotted).

Coagulation processes resulted in reduction of F_{max} at clarified water (CW) and NOM removal efficiency was greater in dry season. In wet season, reduction of F_{max} of humic-like NOM (C1-C3) by clarifier were in the range of 10-21%, while only 4% reduction of protein-like NOM (C4) was achieved. In dry season, F_{max} reduction by clarifier increased to 35-56% and 37% for humic-like and protein-like NOM, respectively. Hence, while coagulation had greater NOM removal efficiency in dry season, it has preferential removal of humic-like NOM, consistent with a previous study (Ishii & Boyer, 2012). Compared to protein-like NOM, humic-like materials were more hydrophobic and had greater charge density (Archer & Singer, 2006), thus, explained the greater removal by coagulation.

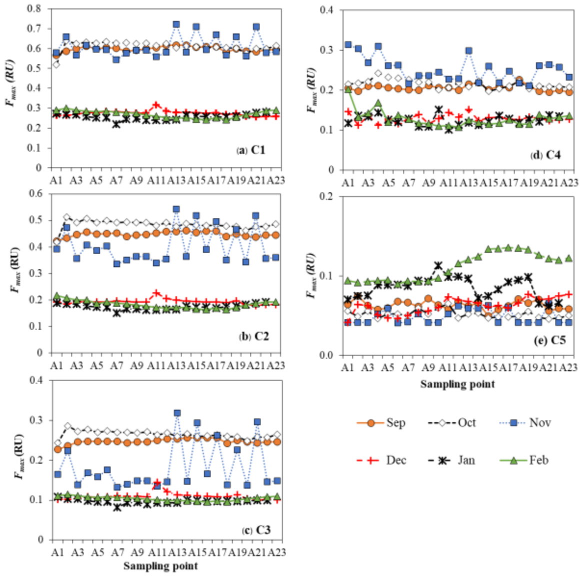

Figure 5. Fluorescence intensities (F_{max}) profile of (a) terrestrial humic-like components (C1), (b) terrestrial humic-like component (C2), (c) microbial humic-like component (C3), (d) protein-like component (C4), and (e) fulvic-like component (C5) along 23 sampling points of the raw water canal during Sep 2015 - Feb 2016

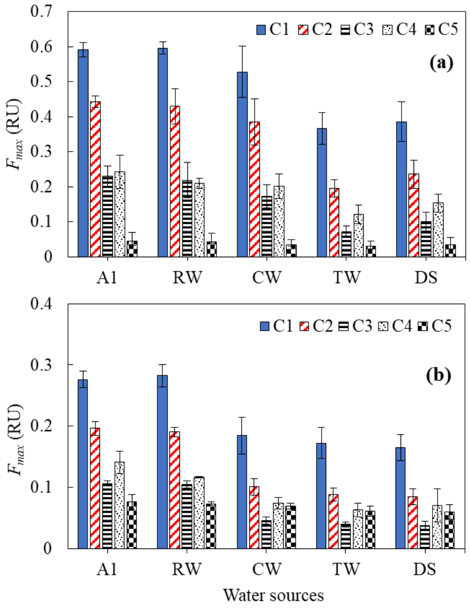

Figure 6. Average maximum fluorescence intensities (F_{max}) of five PARAFAC components at Chaopraya river (A1), raw water (RW), clarified water (CW), tap water (TW), and distribution system outlet (DS) of Bangkhen WTP in (a) wet season and (b) dry season

On the other hand, combined sand filtration and chlorination were more effective in wet season than in dry season and no preferential removal of any component was observed. In wet season, removals of humic-like NOM (C1-C3) and protein-like NOM (C4) by sand filtration and chlorination were 30-59% and 40%, respectively, while in dry season C1-C3 removals were 6.5-15% and C4 removal was 14%. Bangkhen WTP does not have a sampling collection tap between sand filtration and chlorination, so evaluation of components removal by each unit was difficult. Typically, sand filtration had no effect on humic-like and protein-like components while chlorination had moderate reduction in fluorescence intensity of humic like component (Ishii & Boyer, 2012). Despite minor differences between UV$_{254}$ and DOC in CW and TW (Figure 3), using EEM-PARAFAC approach allowed access seasonal removal efficiencies and changes in NOM composition by sand filtration and chlorination processes.

As shown in Table 1, UV$_{254}$ and DOC concentration of water in distribution system (DS) were slightly lower than TW collected right at the WTP. However, F_{max} of the five PARAFAC components in DS were slightly higher than in TW in wet season. In the distribution pipelines 29 km from the WTP, F_{max} of C1-C5 increase in the range of 5.4-51%. The greatest increase in F_{max} values was 41% for C3, followed by 28% for C4. The increase in F_{max} values, especially for microbial derived component (C3 and C4) indicates infiltration or biogrowth in distribution pipelines (Baghoth *et al*., 2011). For dry, the largest increase was for C4 (tryptophan-like NOM) where its increased F_{max} from 0.06 RU to 0.07 RU (12% increase). Hence, microbial contamination in the pipelines also occurred in dry season, but to a smaller magnitude. Overall, the results demonstrate that fluorescence EEM was a more sensitive water quality tracer than were UV$_{254}$ and DOC. Application of PARAFAC analysis to EEM data also allowed characterization of NOM sources and properties which can be correlated to other parameters, e.g. associations between THMs formation and humic-like NOM or between biogrowth in distribution systems and protein-like NOM.

3.4 Relationship between PARAFAC components and other parameters

To investigate relationships between F_{max} and other water quality parameters, all 276 EEM samples were included in the linear regression analysis and the results are shown in a correlation matrix in Table 3. The correlation coefficient (R^2) with an asterisk (*) mark indicates a correlation that is significant at 0.01 confidence level ($p< 0.01$). There were significant correlations observed between UV$_{254}$ and DOC concentration and F_{max} of the five PARAFAC components of the water samples collected across the treatment train of the WTP. Selected regressions with the highest R^2 were illustrated in Figure 7.

Among F_{max} values of the five PARAFAC components, the strongest correlations were found between F_{max} of terrestrial humic-like component (C2) and UV$_{254}$ (R^2=0.88, p<0.01, Figure 7a) and also between F_{max} of C2 and DOC (R^2=0.88, p<0.01, Figure 7b). Our results agree well with a previous study that investigated correlations of PARAFAC components in WTPs (Baghoth *et al*., 2011). The peak location of C2 was found at Ex/Em 270(370)/453 nm/nm, this location was previously called peak C (Coble, 1996) and also highly correlated to chloroform formation potential (CHCl$_3$-FP) (Pifer & Fairey, 2012) and trihalomethane formation potential (THMFP) (Jutaporn, Laolertworakul, Armstrong, & Coronell, 2019).

We also compared our results with previous studies conducted using the same water source from Bangkhen WTP to associate our findings with water quality and DBPs formation potential (DBPFP). Panyapinyopol *et al.* (2005) reported that most of the THMFP formed in the water sample was chloroform and that CHCl$_3$-FP was generated mostly from NOM of the hydrophobic (HPO) fraction. Haloacetic acid formation potential (HAA$_5$-FP) of this HPO fraction was also higher than other NOM fractions in this source water

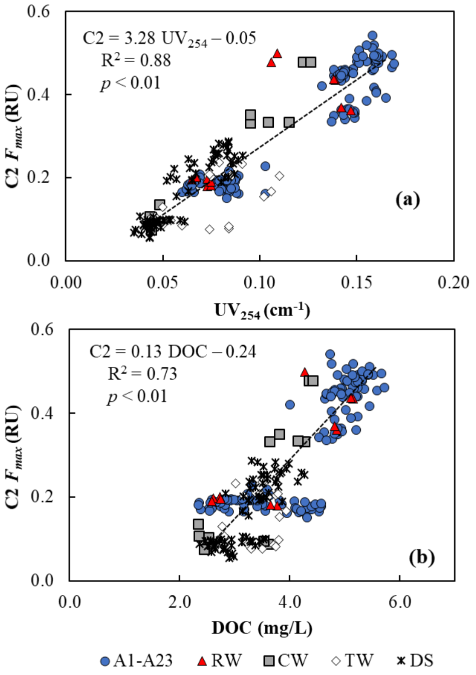

Figure 7. Regressions describing the relationships between (a) UV$_{254}$ and F_{max} of terrestrial humic-like component (C2) and (b) DOC and F_{max} of C2 (n = 250)

Table 3. Correlation matrix of UV$_{254}$, DOC, and SUVA, and F_{max} values of the five PARAFAC components of the water samples collected across the treatment train of the WTP during Sep 2015 - Feb 2016.

R^2	UV$_{254}$	DOC	SUVA	C1	C2	C3	C4	C5
UV$_{254}$	1.0	0.82*	0.76*	0.86*	0.88*	0.81*	0.84*	0.19*
DOC		1.0	0.35*	0.70*	0.73*	0.66*	0.65*	0.17*
SUVA			1.0	0.65*	0.65*	0.61*	0.69*	0.09*
C1				1.0	0.96*	0.83*	0.86*	0.17*
C2					1.0	0.94*	0.83*	0.13*
C3						1.0	0.71*	0.05*
C4							1.0	0.17*
C5								1.0

*Correlation is significant at the 0.01 level (two-tailed)

(Kanokkantapong, Marhaba, Pavasant, & Panyapinyophol, 2006). Compared to the hydrophilic fraction of NOM, the HPO fraction was often found to have higher THMFP (Singer, 1999). Humic acid or HPO fraction contributes to majority of the DOC and the strong correlations found between DOC, UV$_{254}$ and the terrestrial humic-like component C2 suggest a potential approach to monitor raw and treated water quality using fluorescent EEM. F_{max} of C2 was much higher in wet season (Figure 6), thus care must be taken in the disinfection process to reduce the risk of DBPs. Moreover, using the same water source, Tongchang *et al*. (2018) also reported a significant correlation between tryptophan-like peak and dissolved organic nitrogen (DON) which is a precursor to nitrogenous DBPs (N-DBPs). In conclusion, the ability of NOM characterization of EEM-PARAFAC provides an opportunity for its application as an alternative measurement of sub-fractions NOM that allows WTP operator to adjust their processes to respond to changes in raw water quality whenever required.

4. Conclusions

This study assessed spatial and seasonal variation of NOM properties at Bangkhen Water Treatment Plant (WTP). Our results and discussion support the following conclusions:

i. Chaopraya river water source had higher UV$_{254}$ and DOC in wet season. The clarifier unit had greater DOC removal in wet season. UV$_{254}$ and DOC values in the clarified water, tap water, and distribution networks were not significantly different.
ii. A 5-component PARAFAC model was developed, which all the components can be compared to previously determine fluorescent components in OpenFluor database.
iii. In both wet and dry seasons, raw water had the greatest F_{max} of terrestrial humic-like NOM (C1 and C2), followed by microbial humic-like and protein-like (C3 and C4), while C5 had the lowest F_{max}.
iv. Coagulation achieved greater NOM removal in dry season and it had preferential removal of humic-like NOM (C1 and C2). Sand filtration and chlorine disinfection was more effective in wet season and had no preferential removal of any PARAFAC component.
v. Humic-like component (C2) strongly correlated with UV$_{254}$ and DOC, thus monitoring fluorescent signature of the water source at this location can be used as a quick indicator for DBPs precursors, which is higher in the dry season. Also, the increase in microbial derived component (C3 and C4) indicates that biogrowth in distribution pipelines occurred more in wet season.

EEM-PARAFAC approach allowed access in seasonal changes in NOM composition and concentration, thus benefits WTP to adjust their processes to respond to changes of NOM quality and quantity in raw water whenever required. Future research is needed to access DBPs formation potential and its precursors removal by unit processes in WTP.

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