Excitation-Emission Fluorescence Measurements of Dissolved Organic Matter in Pasig River, Metro Manila, Philippines

Jumar G. Cadondon[1,2,*], Maria Cecilia D. Galvez [1], Edgar A. Vallar[1], Lawrence P. Belo[3], and Aileen H. Orbecido [3]

[1] *Environment And RemoTe sensing researcH (EARTH) laboratory, Physics Department, College of Science, De La Salle University, 2401 Taft Avenue, Manila, Philippines 1004*

[2] *Division of Physical Sciences and Mathematics, College of Arts and Sciences, University of the Philippines Visayas, Miagao, Iloilo, Philippines 5023*

[3] *Chemical Engineering Department, De La Salle University, 2401 Taft Avenue, Manila, Philippines 1004*

**Corresponding Author: jumar_cadondon@dlsu.edu.ph*

Abstract: Pasig river is an important river in Metro Manila, Philippines, since it provides livelihood and transports to its residents, and connects Laguna bay and Manila bay. Using excitation-emission fluorescence spectroscopy, the optical characteristics of dissolved organic matter (DOM) in Pasig River were assessed. There are seven sampling sites based on the Pasig River Ferry system, water quality and fluorescence indices were measured. Fluorescence index of mean 1.23 showed that all river water samples are terrestrial in origins. EEM using Surfer v16 was utilized in the assessment of protein-like and humic-like fluorescence peaks. Peak T fluorescence measurements showed good estimation of the BOD concentrations with correlation coefficient of 0.8929. Other water quality parameters were also measured.

Key Words: Fluorescence Spectroscopy; Excitation-Emission matrix; Dissolved Organic Matter; Pasig River

1. INTRODUCTION

According to World Health Organization, domestic liquid waste contributes 45% of the pollution load, another 45% accounts for industrial pollution, and the remaining 10% accounts for solid waste of the total pollution in Pasig river. The Pasig River is the main river that flows through the center of Metro Manila and is one of the largest bodies of water in Luzon connecting two major bodies of water namely, Laguna de Bay, a freshwater ecosystem, and Manila Bay, a saltwater marine ecosystem. Since Manila is located in the subtropical monsoon zone, rainy season and the dry season are clearly divided. December until the following May is considered the local dry season. Generally, the river flow rate is relatively low and water quality becomes worse during these months accordingly (Belo, 2008). With the ongoing river rehabilitation, studies have been conducted on water quality and physico-chemical measurements (Belo, 2008; Gorme et al., 2010; Galvez, et al., 2015) and water purification processes (Okamoto et al., 2019). In rivers, lakes and man-made reservoirs, dissolved organic matter (DOM) are commonly found. It consists of complex mixtures of organic molecules such as carbohydrates, proteins, lignins, organic acids, and various humic substances (Guo et al., 2012). These components are derived from different sources such as agriculture or sewage or pollutants discharged from petroleum products and industrial effluents (Wilson & Xenopoulos, 2009; Zhao et al., 2018). Several fluorescence spectroscopy studies have been carried out in river waters with excitation-emission matrices (EEM) (Coble et al., 1998; Cory & Mcknight, 2005; Fellman et al., 2011) and traditional methods (Reyes & Crisoto, 2016). The measurement of river water fluorescence is a promising measuring tool in determining DOM composition. Hence, this study was conducted to measure excitation-emission fluorescence spectra of DOM found along seven sampling sites in the Pasig River Water System.

2. METHODOLOGY

Seven (7) sampling sites were selected, as shown in Fig. 1. It is based on the Pasig River Ferry System, namely: (St 1) Lawton Station, (St 2) P.U.P. Station, (St 3) Lambingan Station, (St 4) Valenzuela Station, (St 5) Hulo Station, (St 6) Guadalupe Station, and (St 7) San Joaquin Station.

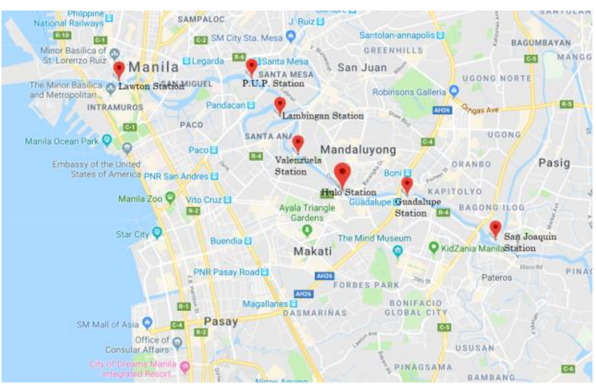

Fig. 1. Map of Pasig River Water Sampling Stations

In-situ measurements of pH, electrical conductivity (EC), temperature, and dissolved oxygen (DO) were carried out using Hach HQd/intelliCAL Rugged Field kit. Measurements were conducted during Low tide to control the inflow of water from Laguna bay going to Manila bay as well as to represent water quality values during lower flow. Following standard methods for transport and handling of water/wastewater samples, river water samples were collected at surface water level and transported in the laboratory for excitation-emission fluorescence measurements and third party laboratory for the following water parameter analyses: Color, Biological Oxygen Demand (BOD), Total Dissolved Oxygen (TDS), Total Suspended Solids (TSS), and Total Organic Carbon (TOC).

Table 1 shows the following optical measurements used in analyzing the fluorescence DOM.

Table 1. Summary of fluorescence indices and commonly observed natural fluorescence peaks of aquatic DOM.

Index/ Component	Parameters	Peak Name	Probable sources*	Description
Fluorescence Index (FI)[4]	Calculated as the ratio of emission (em) 470 nm and em at 520 nm at excitation (ex) 370 nm.			This index differentiates water samples as microbial (approximately 1.8) or terrestrial (approximately 1.2) origins.
Biological Index (BIX)[12]	Intensity at em 380 nm divided by max intensity between em 420 nm and 435 nm a t ex 310 nm.			Indicates proportion of newly produced DOM.
Tryptophan like	Ex 270 – 275 nm and em 304 312 nm	T	T,A,M	Amino acids, fre or bound in proteins, fluorescence resembles free tyrosine, may indicate more degraded peptide material
Ultraviolet A (UV A) humic like	Ex 290 325 nm and em 370 430 nm	M	T,A,M	Low molecular weight, common in marine environments associated with biological activity but can be found in wastewater, wetland, and agricultural environments
UVC humic like	Ex 320 360 nm and em 420 460 nm	C	T	

* T – Terrestrial plant or soil organic matter; A – autochthonous production; M – microbial processing

Initial measurements of the fluorescence index were done to determine the peak components to be measured. In fluorescence measurements, the samples were immediately prepared in a 10-mm UV-Vis cuvette and measured with the spectroscopy set-up. A Xenon lamp source (180- 2000 nm) was controlled using scanning monochromator (MonoScan

2000) before it hits the sample. The output source of the MonoScan 2000 were connected to an optical fiber splitter, one cable goes to Ocean optics USB 4000, and the other cable is connected to the cuvette holder. Ocean optics 2000+ XR1-ES measured the emission peaks of the sample using Ocean View application. The excitation wavelength ranges from 250-450 nm and the emission wavelength ranges from 300- 600 nm. Fluorescence emission spectrum was obtained in every 5 nm-interval of the excitation wavelength. After measuring FI, EEM were graphed using Surfer v16 and Matlab application with Parallel Factor Analysis.

3. RESULTS AND DISCUSSION

The water samples were collected on April 5, 2019, Friday starting at 8:30 am. The researchers used the Pasig river ferry as mode of transportation, in-situ collection of water samples along with water quality measurements were done at the designated sampling stations. Inflow of saline water coming from Manila Bay and goes through the Pasig river were observed. Table 2 shows the water quality and fluorescence indices parameters at seven sampling stations. The pH values are near neutral (mean: 6.957). There are changes in the EC values due to the continuous discharge of ionic matter during the flow of river water and its temperature dependence. High EC values were found in (St1) Lawton Station and (St2) P.U.P. Station.

Also, Dissolved Oxygen (DO) values located at (St 1) Lawton, (St 2) P U P, (St 3) Lambingan, (St 4) Hulo and (St 5) Valenzuela Stations are hypoxic since these concentrations are below 2 mg/L (Bodamer & Bridgeman, 2014). This may prevent organisms from growing, and lead to unhealthy and less biologically diverse communities. On the other hand, (St 7) San Joaquin Station had 1. 84 mg/L of DO concentration. TSS concentrations of 90 mg/L and above were found at (St 5) Valenzuela Station, (St 6) Guadalupe Station and (St 7) San Joaquin Station. This is high compared to the minimum standard provided by the Department of Environment and Natural Resources Administrative Order No. 2016-08 on water quality guidelines and general effluent standards for conventional and other pollutants contributing to the aesthetics and oxygen demand for fresh, brackish and marine waters. Also, the required minimum BOD concentration is 7 mg/L.

According to Jensen et al. (1999), BOD concentrations above 5 mg/L are doubtful water quality and higher than 10 mg/L are badly polluted water. The BOD measurements showed consistency with existing studies and monitoring on the water quality of Pasig River (Qian et al.,2000; Belo, 2008). High BOD concentrations were measured at (St2) P.U.P. and (St4) Hulo Stations which indicates low quality of water.

Table 2. Water Quality and Fluorescence indices of the seven sampling stations

Station	Water Parameters									Index	
St	Color. TCU	Temperature (oC)	pH	Conductivity (mS/cm)	Dissolved oxygen (mg/L)	BOD (mg/L)	TDS (mg/L)	TSS (mg/L)	TOC (mg/L)	Fluorescence Index	Biological Index
1	25	28.4	6.89	11.30	0.29	7	6530	28	ND*	1.38	0.99
2	25	28.0	6.92	5.48	0.23	13	3230	37	ND*	1.29	0.99
3	20	28.7	6.94	0.503	0.15	9	311	57	2.4	1.29	0.98
4	25	28.6	6.96	0.530	0.18	16	318	61	2.7	1.23	0.94
5	20	28.7	6.95	0.542	0.28	7	312	94	2.7	1.01	1.28
6	20	28.5	6.98	0.496	0.24	8	302	112	2.6	1.15	1.32
7	40	28.3	7.02	0.535	1.84	8	291	112	2.5	1.24	1.58

*ND Not detected

The differences in the measured water quality parameters can be related with the differences in human activity, effluents from different land use managements near the sampling sites. Moreover, water inflow from Laguna bay influences water quality. Also, even though Pasig River is only 27 km long, its entire stretch is a home for a variety of activities; industrial/commercial, agricultural and predominantly of domestic origin (residential purposes) with roughly 70000 informal settlers (Belo, 2008).

Table 2 also shows the fluorescence and biological indices. According to Coble et al (1998), a fluorescence index value of 1.23 indicates that the DOM found in the river water samples is terrestrial in origin. The biological index measures the freshness of the DOM produced (Fellman et al., 2010). (St 1) Lawton to (St 4) Hulo Stations showed no significant ratio of freshly produced DOM with the more decomposed DOM. On the other hand, (St 5) Valenzuela to (St 7) San Joaquin Stations indicates the contribution of recently produced DOM with more decomposed DOM. The differences in the BI shows DOM behavior in the seven sampling sites along Pasig river.

EEM of the fluorescence DOM at (St1) Lawton Station and (St 5) Hulo Station are shown in Fig. 2 (a) and Fig. 2 (b), respectively. The color scheme provides the relative fluorescence intensity (arbitrary units) of the fluorescence DOM. The EEM of the seven sampling stations provide information of the aquatic protein-like and humic-like peaks found in the river water samples. For every excitation wavelength, the average photon count in the emission region was measured. The black color at the excitation range from 340 to 450 nm and emission range from 350 to 450 nm showed the removed excitation region of the lamp source and background noise. The reduction of the excitation spectrum amplifies the fluorescence spectrum of each sample.

The study focused on the relative fluorescence measurements of the Tryptophan-like, and UV-A and UV-C humic-like optical parameters of the river water samples, which is necessary for BOD and TOC correlations. Fig. 2 (a) showed fluorescence peaks at ex/em, 320 nm /410 nm and 390 nm/500 nm. On the other hand, fluorescence peak at ex/em with ratio of 380 nm/510 nm is found at (St 5) Hulo Station. Using Parallel Factor Analysis, fluorescence optical parameters were identified. Numerical measurements of the identified fluorescence optical parameters were recorded.

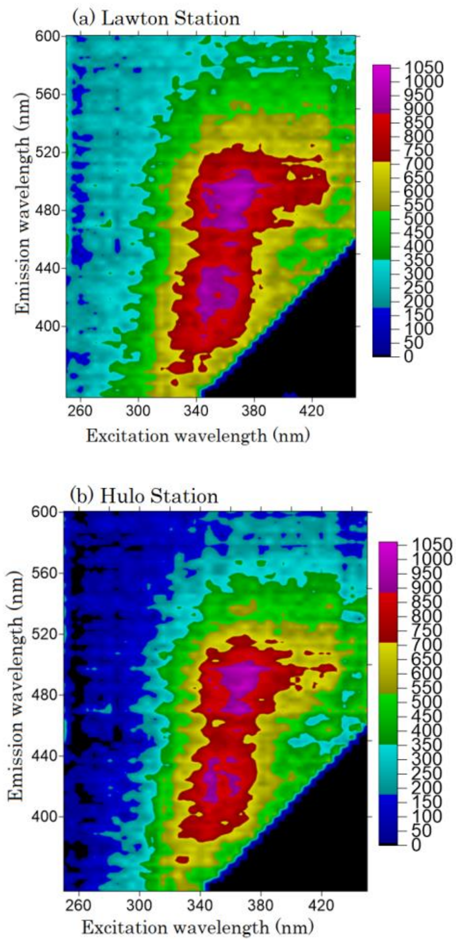

Fig. 2. EEM of fluorescence DOM at (a) Lawton Station, and (b) Hulo Station

Fig. 3 shows the different fluorescence peaks such as Tryptophan-like, UV-A humic-like and UV-C humic-like peaks. Tryptophan-like fluorescence intensities shows no significant change in all sampling stations. On the other hand, higher amount of UV-C humic-like fluorescence intensities were measured compared to UVA humic-like fluorescence intensities. This shows that high-molecular-weight humic are largely present in (St 1) Lawton Station, (St 4) Valenzuela Station, (St 5) Hulo Station, and (St 1) Guadalupe Station. The peak shifting in excitation wavelength from shorter to longer wavelengths implies an increase of molecule size and aromatic content (Yu et al. 2011).

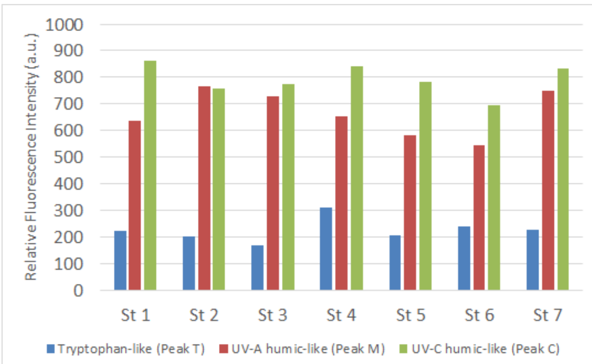

Fig. 3. Average fluorescence measurements of the seven sampling stations

Fig. 4 provides the correlation of BOD concentration and Tryptophan-like peak at the different sampling sites. The correlation coefficient of 0.8929 showed that the optical parameter, Tryptophan-like fluorescence can be used to roughly quantify BOD concentration in the surface water (Hudson et al., 2007).

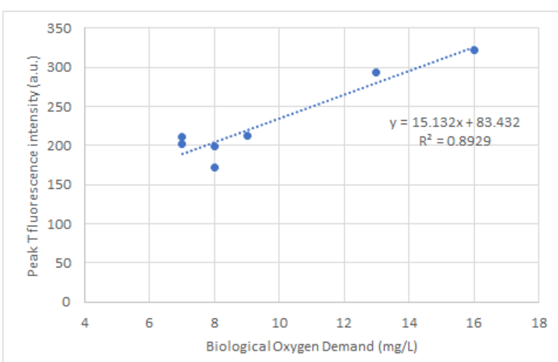

Fig. 4. Correlation of Peak T relative fluorescence intensity and BOD at the seven sampling sites.

Despite high correlation on the BOD and Peak T fluorescence, only five stations were used to estimate TOC concentration using humic-like fluorescence peaks due to no detection found in (St1) Lawton Station and (St 2) P.U.P. Station. Also, measured fluorescence is typically emitted from DOM, and large amount of BOD and TOC concentrations are extracted from suspended solids. Low correlation coefficient with value of 0.4367 were measured from TOC estimation using humic-like peaks. Although fluorescence intensities were amplified, selected fluorescence indices appear to be insufficient to represent the suspended solids contribution to BOD and TOC analysis. However, it should be noted that EEM can still be utilized for water quality monitoring in the future. Continuous water quality monitoring is necessary to identify trends which can be used to provide information in creating techniques for in-situ measurements.

4. CONCLUSIONS

Excitation-emission fluorescence spectra can provide optical DOM characteristics of the water samples along Pasig river. Based on fluorescence indices and water quality parameters, a difference from the values obtained from different sites were observed which can be attributed to be due to effluents from various sources. High correlation was calculated on the BOD and Peak T fluorescence with correlation coefficient of 0.8929. On the other hand, low correlation was found at TOC and humic-like fluorescence due to no detection of TOC at (St 1) Lawton Station and (St2) P.U.P. Station. However, it is suggested that more water sampling collection must be done from wet to dry season to compare DOM composition. Also, detailed measurements of the contents of DOM which produce fluorescence spectra must be investigated. Additional information must be gathered to correlate effluents from different land-use types and DOM compositions at different stations.

5. ACKNOWLEDGMENTS

Jumar Cadondon acknowledges support from DOST-SEI ASTHRDP -NSC scholarship. We also acknowledged the support from UDM CHED DARETO project entitled "Using wireless environmental monitoring sensors in assessing the impact of megacity environmental pollution and local climate on butterfly diversity in Manila, Philippines". Also, the DLSU CENSER-ARCHERS through EARTH lab for its facilities and support in finishing this project.

6. REFERENCES

Belo, L.P. (2008). Master's Thesis: Measurement of the Sediment Oxygen Demand of Different

Stations of the Pasig River Using a Bench-Scale Benthic Respirometer.

Bodamer, B.L. & Bridgeman, T. B. (2014). Experimental dead zones: two designs for creating oxygen gradients in aquatic ecological studies. Limnol. Oceanogr.: Methods. 12. 441-454.

Coble, P.G., Del Castillo, C.E., Avril, B. (1998). Distribution and optical properties of CDOM in the Arabian Sea during the 1995 Southwest Monsoon. Deep-Sea Res Part II.45(10–11):2195–2223

Cory, R.M., McKnight,D.M. (2005). Fluorescence spectroscopy reveals ubiquitous presence of oxidized and reduced quinones in dissolved organic matter. Environ Sci Technol 39(21), 8142–8149

DENR Administrative Order No. 2016-08. (2016) Retrieved from www.denr.gov.ph accessed on May 28, 2019.

Fellman, J.B., Hood, E., & Spenser, R.G.M. (2010). Fluorescence spectroscopy opens new windows into dissolved organic dynamics in freshwater ecosystems: A review. Limnol. Oceanogr. 55(6), 2452-2462.

Galvez, M. C., De Guzman, J. F., Gueco, S. D., Camelo, J., Castilla, R., and Vallar, E. (2015). SEM/EDX Analysis of the Roots of Water Hyacinths (Eichornia crassipes) Collected Along Pasig River in Manila, Philippines. ARPN Journal of Agricultural and Biological Science, 458-463.

Gorme, J.B., Manaquiz, M.C., Song,P. & Kim,L. (2010). The water quality of the Pasig river in the city of Manila, Philippines: Current status, management and Future recovery. Environ.Eng.Res. 15(3), 173-179

Guo X.J., Jiang J.Y., Xi B.D., He X.S., Zhang H., Deng Y. (2012). Study on the spectral and Cu (II) binding characteristics of DOM leached from soils and lake sediments in the Hetao region. Environ Sci Pollut R 19(6), 2079–2087

Hudson N., Baker A., and Reynolds D. (2007). Fluorescence analysis of dissolved organic matter in natural, waste and polluted waters—a review. River Res. Appl. 23, 631

Jensen, Joergen, et al.. (1999). Pasig River Monitoring and Modelling. Status Report. 1998. DENR/DANIDA.

Okamoto, K., Komoriya, T., Toyama, T., Hirano, H., Garcia, T., Baccay, M., Macasilhig, M., & Fortaleza, B. (2019). Purification Experiments on the Pasig River, Philippines Using circulation-type purification system. International Journal of GEOMATE. 16 (54), 2186-2990.

Qian, X., Capistrano, E., Lee, W. & Ishikawa, T. (2000). Flow Structure and Water Quality of Pasig River in Metro Manila. Korea Water Resources Association (KWRA), International Conference on Hydro-Science and Engineering in 2000.

Reyes, T.G. & Crisosto, J. M. (2016). Characterization of Dissolved Organic Matter in River Water by Conventional Methods and Direct Sample Analysis- Time of Flight-Mass Spectroscopy. Journal of Chemistry. Article ID 1537370.

Wilson, H.F., & Xenopoulos, M.A. (2009). Effects of agricultural land use on the composition of fluvial dissolved organic matter. Nat. Geosci. 2,37-41.

Yu, H., Xi B., Ma W., Li D., He X. (2011). Fluorescence spectroscopic properties of dissolved fulvic acids from salined flavo-aquic soils around Wuliangsuhai in Hetao Irrigation District, China. Soil SciSoc Am J 75(4), 1385–1393

Zhao, C., Gao, SJ., Zhou, L., Li, X., Chen, X., Wang, C.(2019). Dissolved organic matter in urban forestland soil and its interactions with typical heavy metals: a case of Daxing District, Beijing. Environ Sci Pollut Res 26, 2960.