Water Quality and Fluorescence Measurements of Dissolved Organic Matter in Pasig River, Metro Manila, Philippines by Excitation-Emission Spectroscopy

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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. With the on-going rehabilitation, water quality and fluorescence indices were measured on the seven sampling stations based on the Pasig River Ferry system. Using excitation-emission fluorescence spectroscopy, the optical characteristics of dissolved organic matter (DOM) in Pasig River were assessed. 3D Excitation Emission Matrix (EEM) using Surfer v16 was utilized in the assessment of protein-like and humic-like fluorescence peaks. Fluorescence index (FI) of mean 1.23 showed that all river water samples are terrestrial in origins. Peak T fluorescence measurements showed good estimation of the BOD concentrations with correlation coefficient of 0.8929. FI results were correlated with the effluents discharged from the different land-use type near the sampling stations. As a result, fluorescence measurements can be a good indicator of organic matter source and water quality in natural waters. Other water quality parameters were also measured.

Keywords: Excitation-Emission Matrix, Fluorescence Spectroscopy, 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 characterization of fluorescence using instruments for the measurement of excitation and emission spectra has been recently observed (Jin, et al., 2006). Fluorescence spectroscopy has been widely used in detecting organic matters, algae and other substances. 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 (Zhao et al., 2018).

With the on-going rehabilitation program, this study was conducted to measure excitation-emission fluorescence spectra of DOM found along seven sampling sites in the Pasig River Water System. The data from this study can be used for optical design of fluorescence LIDAR system using pulsed LED light module.

2. METHODOLOGY

Seven (7) sampling sites were selected 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. 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).

For the fluorescence detection, dissolved organic matter (DOM) from Pasig river water were investigated. When ultraviolet and blue excitation light strikes the 10mm cuvette holder, DOM fluoresces. 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. OBSERVATIONS AND CONCLUSION

Pasig River water samples were collected on May 24, 2019, Friday at 9:00 in the morning. Following the standard handling and collection of river water/ wastewater samples, river water samples were collected at surface water level and prepared for fluorescence spectroscopy measurements.

EEM of the fluorescence DOM at (St1) Lawton Station is shown in Fig. 1. The color scheme provides the relative fluorescence intensity (arbitrary units) of the fluorescence DOM. 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.

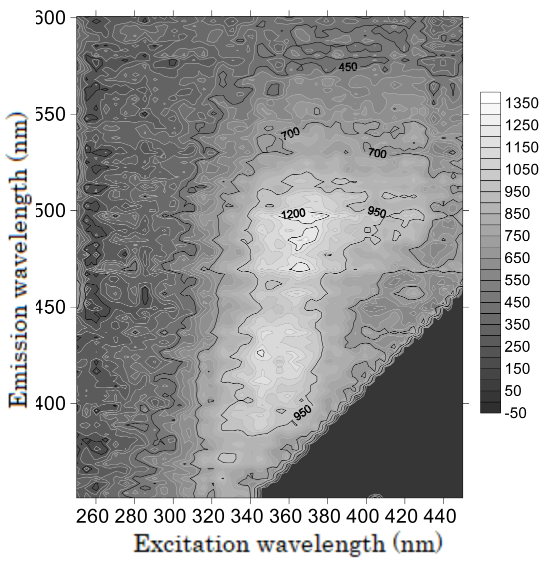

Fig. 1. EEM of fluorescence DOM at Lawton Station

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. 1 showed fluorescence peaks at ex/em, 320 nm /410 nm and 390 nm/500 nm. In Fig.2., 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).

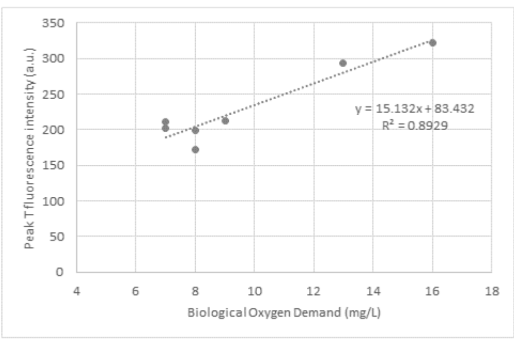

Fig. 2. Correlation of Peak T relative fluorescence intensity and BOD at the seven sampling sites.

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 (Shiina, 2019). These data can be used to develop a LIDAR monitoring system for DOM concentration and algal organic matter detection.

4. ACKNOWLEDGEMENT

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