

# UV-Vis Absorbance and Fluorescence Characterization of Pasig River Surface Water Samples Towards the Development of an LED Fluorescence Lidar System

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**Abstract**—The status of water quality in Pasig River was studied using UV-Vis absorbance, 3D excitation-emission matrices (EEMs), fluorescence measurements of dissolved organic matter (DOM), and physicochemical parameters measurements. The study was conducted at seven selected sampling stations in Pasig river from April 2019 to June 2019. It has been years since the government has conducted rehabilitation on the Pasig river and we want to determine its current water quality status with the additional information provided by the UV-Vis absorbance and fluorescence spectroscopy. Several surface water samples were collected using the Pasig River ferry system at (St 1) Lawton Station, (St 4) Valenzuela Station, and (St 7) San Joaquin Station. After computing for the absorbance values at 280-nm, 250-nm/365-nm, 253-nm/203-nm, and 226-400, we have used this method to determine the presence of organic carbon and its aromatic substituents. The results showed low humification degree and aromatic structure and vary from April to June 2019. (St 3) shows higher stability organic molecules containing benzene ring structures. A seasonal variability has been observed from the water quality parameters, which is also present from the fluorescence measurements. DOM sources were measured using fluorescence index (FI), the results showed that all surface water samples were terrestrially derived DOM concentrations. The variance can be attributed to the effluents from the land use types near the sampling stations such as industrial and residential waste. Based on the water quality, absorbance and fluorescence results, the impact of marine waters greatly affects the characterization and production of organic materials.

**Keywords**— Pasig river; water quality; absorbance; excitation-emission matrix; fluorescence spectroscopy.

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## I. INTRODUCTION

Climate change and human activities have increased the intensity of pollutants and blooms in lakes, reservoirs, and coastal areas. 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 [1]. It has been considered as one of the biologically dead rivers in the Philippines. It connects two

major water bodies, namely, Laguna de Bay, a freshwater system, and Manila Bay, a marine water system. Metro Manila is in the subtropical monsoon area, where dry and wet season are distinct. During the dry season which starts end of November and ends in May, the river flow rate is relatively low and water quality becomes worse during these months accordingly [2]. In January 1999, Pasig river rehabilitation commission (PRRC) was created to ensure that the Pasig river is rehabilitated to its historical condition conducive for the propagation of fishes and other aquatic resources as well as

for transport, recreation, and tourism [3], [4]. There had been programs and projects on housing and resettlement of informal settlers, riverbank development and flood control, environmental management, advocacy, and tourism, and other PRRC projects [5], [6]. Water quality monitoring stations and data analysis are conducted through Pasig river monitoring systems (PRUMS) project with the initiative of Department of Environment and Natural Resources-Environment Management Bureau (DENR-EMB)-National Capital Region and Central Office, Laguna Lake Development Authority (LLDA), and PRRC which provides coherent water quality report. According to PRRC's quarterly report, some of the sampling stations failed the minimum water quality standards based on the water quality guidelines and general effluent standards of DENR [3]. Tissue analysis on sample fishes caught in the different ferry stations has exceeded the fecal form's permissible limit for good fish [7]. Also, the presence of heavy metals was observed in the suspended sediments [8], fishes [7], and water lilies [9]. With the ongoing river rehabilitation, studies have been conducted on water quality and Physico-chemical measurements [2], [9], [10], and water purification processes [11].

The water quality of inland lakes, reservoirs, and estuaries in Pasig river measured by such factors as biochemical oxygen demand has not improved in a decade. Numerous water quality issues had been connected to dissolved organic matter (DOM). These dissolved organics are commonly found in rivers, lakes, and man-made reservoirs. It consists of complex mixtures of organic molecules such as carbohydrates, proteins, lignin, organic acids, and various humic substances [12]. These components are derived from different sources such as agriculture or sewage or pollutants discharged from petroleum products and industrial effluents [13]. High levels of DOM correspond to poor water quality. Therefore, composition of DOM is important in characterizing water quality and its potential risk to human health and the ecosystem.

Standard methods such as physico-chemical, biological, and bacteriological analyses have high acceptability when water quality is evaluated. However, these analyses require longer time before it can provide an accurate result. This study suggests the use of spectroscopy techniques such as absorbance and excitation-emission fluorescence along with the physico-chemical analyses to evaluate water quality in river systems. With the direct correlation of UV absorption of organic solutes to the content of aromatic compounds using UV-Vis spectra, we can estimate the amount of organic carbon in DOM. Also, the degree of humification and its aromatic constituents can be estimated with the UV-Vis absorbance values [14], [16]. Several fluorescence studies have been carried out in river waters with excitation-emission matrices (EEM) [12], [13], [17], [21] and traditional methods [22]. The ability to measure a wide range of excitation and

emission wavelengths to graph fluorescence excitation-emission matrix has impacted the characterization of DOM. The 3D fluorescence EEMs show significant differences as a function of water samples types and its origins. For the recent years, it is used to characterize and differentiate water masses and provides information on the mixture of coastal and estuarine environments [17], [23], [24]. In this study, UV-Vis absorbance, 3D EEM fluorescence measurements of dissolved organic matter and physico-chemical parameters were conducted on surface water samples collected from Pasig river, specifically at seven ferry stations along the Pasig river ferry system for three months. Several peaks from EEM fluorescence and absorbance values can be used to design a mobile LED-based lidar system for water quality monitoring. This study reiterates the possible use of these methods in measuring DOM's optical properties and to characterize water quality in river systems, which leads to the development of a mobile LED-based lidar system. The water quality monitoring using physico-chemical characteristics with the aid of absorbance and fluorescence spectroscopy measurements delivers information on the current status of Pasig river. This research can improve the status of Pasig river and its tributaries; hence, in-situ water quality monitoring is important.

## II. MATERIALS AND METHODS

### A. Site Description and Surface Water Collection

1) *Sampling site description:* Pasig river is about 27 kilometers comprising five cities and municipalities such as Manila, Mandaluyong, Pateros, Makati, Taguig, and Rizal. It has an average depth of 4-5 meters, with water volume of 6.458 million cubic meters, and a current flow of approximately 2.75 kph [2,26]. There are seven sampling stations based on Pasig River Ferry System (Fig. 1). These stations provide information on the surface water quality monitored from April to June 2019. St (1) Lawton Station, St (4) Valenzuela Station, and St (7) are labelled in yellow pins.

The water quality data in this study were obtained from the sampling stations provided in Table 1. It also shows land use data which offers information on the current inhabitants along the riverbanks of Pasig river. The Metro Manila land use 2003 where Pasig river is located provides sixteen variations from very low residential density (VL-1 to VL-3), low residential density (L-1 to L-3), medium residential density (M-1 to M-3), high residential density (H-1 to H-3), very high residential density (V-1 to V-3), informal settlers (S), commercial & business, industrial, government & Quasi-public, education & cultural, health & welfare, park & recreational, religious & cemetery, transport & service facility, military, agricultural land, grassland, forestland, water-related and open spaces.

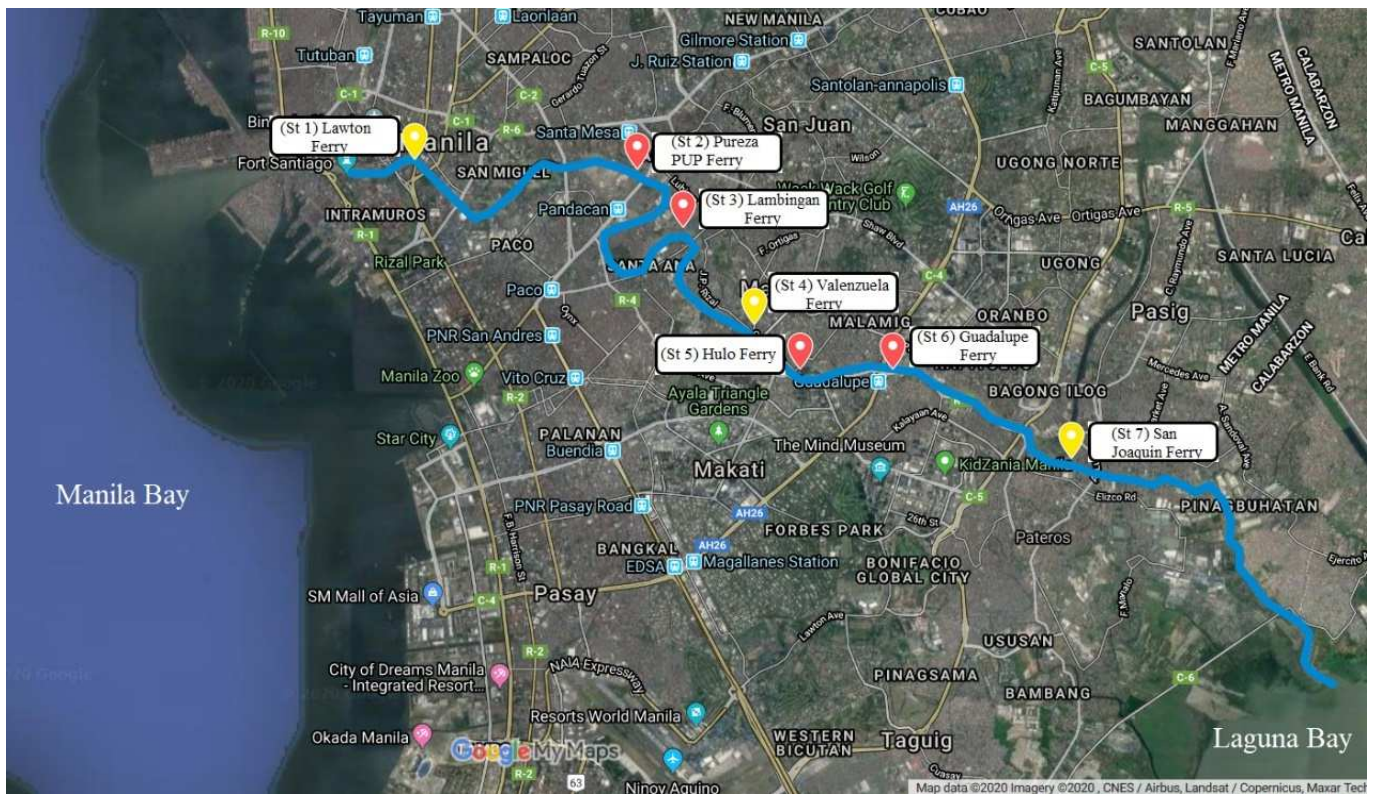


Fig. 1 Pasig River System and the sampling sites [27]

Pasig riverbanks are known for informal settlers and mainly affected by different activities such as industrial, commercial, and predominantly of domestic origin (Table I). According to Pasig River Rehabilitation Commission, there are approximately 800 industries and 250 establishments along the river [28].

TABLE I  
SUMMARY OF THE GIS AND LAND USE OF PASIG RIVER SAMPLING STIES  
[3][27]

Station	Coordinates		Land Use
	Latitude	Longitude	
St (1) Lawton	14° 35' 45.078"	120° 58' 53.0508"	Industrial, Commercial and Business, Park and Recreational, Residential Educational and Cultural,
St (2) Pureza PUP	14° 35' 45.024"	121° 0' 40.536"	Government and Quasi-public, Industrial
St (3) Lambingan	14° 35' 16.332"	121° 1' 4.008"	Highly Industrial, Highly residential
St (4) Valenzuela	14° 34' 26.263"	121° 1' 33.045"	Highly Industrial, Residential
St (5) Hulo	14° 34' 6.348"	121° 2' 3.336"	Very Highly Residential
St (6) Guadalupe	14° 34' 6.348"	121° 2' 50.316"	Very Highly Residential, Industrial
St (7) San Joaquin	14° 33' 17.0316"	121° 4' 26.202"	Highly Residential, Industrial, Agricultural Land

2) *Surface Water Collection and Flow rate Measurements*: The Pasig River Ferry was used as a mode of transportation starting at the St (1) Lawton Station until St (7) San Joaquin Station. Surface water samples were collected every Friday of the month from April to June 2019 starting from 9:00 AM to 10:30 AM. The whole area is highly residential and large built-up of land-use types are present with the on-going rehabilitation; hence, it is a good sampling collection to investigate the water quality and DOM characteristics in a river system with domestic effluents.

In measuring the river's flow rate, an Arduino-based flow rate sensor with an output pulse of 4.5 for every liter of water passing through it per minute were used. Following the standards on water sampling, the water samples were collected and separated into three containers based on the following tests: (i) the 5-day Biochemical Oxygen Demand (BOD<sub>5</sub>) test, (ii) other physico-chemical parameters, and (iii) absorbance and fluorescence measurements. Only three out of seven sampling stations were monitored for physico-chemical characteristics on surface river water samples collected along Pasig river. The three sampling stations were chosen based on their land use land cover representation and characterized by specific DOM. The sampling stations are as follows:

- St (1) Lawton Station: It represents the confluence of Manila Bay and Pasig River
- St (4) Valenzuela Station: It represents the mid-flow of Pasig River
- St (7) San Joaquin Station: It represents the confluence of Pasig River and Laguna Lake.

### B. Physico-chemical Parameters and Analysis

DENR has classified Pasig River as Class C water. This classification is intended for fisheries, agriculture, irrigation, livestock watering, and for recreational activities such as boating, fishing, or any similar activities, i.e., according to the DENR Administrative Order No. 08, Series of 2016 (DAO 2016-08) also known as the “water quality guidelines and general effluent standards of 2016”. As shown in Table II, the primary parameters are the required minimum water quality parameters for the said classification.

TABLE II  
WATER QUALITY GUIDELINES FOR PRIMARY PARAMETERS [4]

Parameter	Unit	“Class C” Value
BOD	mg/L	7
Dissolved Oxygen (Minimum)	Oxygen <sup>(a)</sup> mg/L	5
pH (Range)		6.5-9.0
Temperature	°C	25-31
Total Suspended Solids	mg/L	80

Samples shall be taken from 9:00 AM to 4:00 PM

In-situ water quality parameters such as Temperature, pH, electrical conductivity (EC) and dissolved oxygen (DO) were measured using Hach HQd/intelliCAL Rugged Field. Other parameters, i.e., Biochemical Oxygen Demand (BOD), Total Suspended Solids (TSS), Total Organic Carbon (TOC), and Total Dissolved Solids (TDS), were monitored by grab sampling method and sent to CRL Environmental Corporation for analyses. Gravimetric method was used to measure the TSS and TDS, and Azide Modification Winkler method for BOD measurements. For optimum characterization of water quality, TOC measurements were done with three replicates. The TOC content of water is a useful indicator to determine the degree of pollution.

Field observations based on each sampling station's physical condition were also recorded during the surface water collection. The natural background temperature as determined by EMB shall prevail if the temperature is lower or higher than the water quality guidelines, provided that the maximum increase is only up to 10% and it will not cause any risk to human health and the environment.

### C. Water Quality Index

Water quality index (WQI) is a scale that quantifies the state or degree of pollution of surface water parameters collected along Pasig river to standard values. According to [33], the WQI rating reflects the composite influence of different water parameters by comparing water quality to standard set in the target usage point of view. It states that the closeness of the WQI value to the standard shows better water quality. The Weighted Arithmetic Index method using the quality rating ( $q_i$ ), and relative weight ( $w_i$ ) for each parameter was calculated using eq. (1) and eq. (2), respectively.

$$q_1 = \frac{P_1}{S_1} \times 100 \quad (1)$$

$$w_1 = \frac{1}{S_1} \quad (2)$$

where  $P_i$  is the value of the observed parameter, and  $S_i$  is the set quality. From these equations, the WQI was calculated using eq. (3),

$$WQI = \sum_1^n w_i q_i \quad (3)$$

### D. Absorption measurements

The water samples were immediately transported at the Environment And RemoTe sensing research (EARTH) laboratory for the absorbance measurements using the Ocean Optics set-up. Each sample was filtered using 0.47  $\mu\text{m}$  pore size filter and prepared in a 10-mm UV-Vis cuvette (BRAND GMBH + CO KG). The Xenon lamp (180-2000 nm) is connected using the 600- $\mu\text{m}$  fiber cable directly to the cuvette holder for the absorbance spectroscopy set-up. Another 600- $\mu\text{m}$  fiber cable is connected from the holder to the spectrometer (Ocean Optics 2000+ XR1-ES). Fig. 2 (a) shows the experimental set-up for the absorbance spectroscopy. Fifty (50) blank samples were also utilized and average to measure the power released by the light. The UV-Vis absorption spectra are obtained between 250-400 nm to measure DOM's humification degree, fulvic and humic substances.

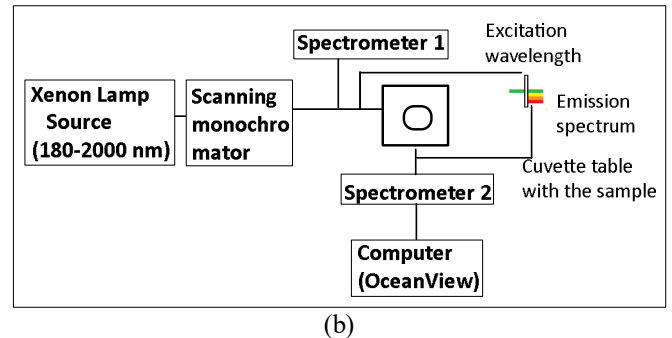
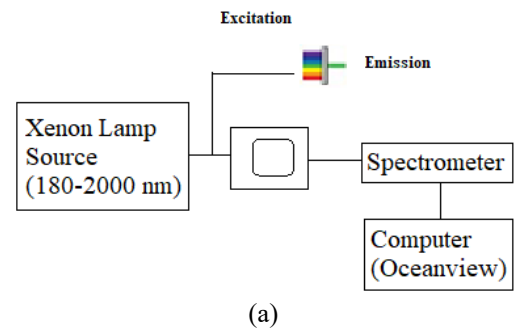


Fig. 2 The block diagram for (a) absorption spectroscopy, and (b) excitation-emission fluorescence spectroscopy

### E. Absorption Ratio

Absorption values of per unit concentration and the absorbances' ratio at specific wavelength include A280, A250/365, A254/436, A340/254 and A253/203 are calculated to determine the humification degree, aromatic structure and distribution of DOM as observed [14]. Table III shows the absorption ratios used to characterize DOM on surface water samples in the Pasig river, an estuarine environment.

TABLE III  
SUMMARY OF ABSORPTION VALUES AND RATIOS USED IN CHARACTERIZING DOM IN ESTUARINE ENVIRONMENT [15]-[19]

Absorption value/ratio	Target characteristics and relationships
A254	Organic matter characterization, DOC, and conductivity correlation
A280	Molecular size, Domestic effluent characterization, BOD and DOC correlation

A250/365	Molecular weight, negatively correlate with aromaticity and molecular weight, estuary environment
A254/436	Probable sources, estimate the relative composition of autochthonous versus terrestrial DOM, estuarine environment (seawater)
A340/254	It is used to predict DOC/TOC concentration
A253/203	Correlate positively with trihalomethane formation potential
A254	Organic matter characterization, DOC, and conductivity correlation
A280	Molecular size, Domestic effluent characterization, BOD and DOC correlation
A250/365	Molecular weight, negatively correlate with aromaticity and molecular weight, estuary environment

These absorption ratios are defined as the ratios of the absorption coefficients at two different wavelengths, which are commonly used to determine DOM sources and composition.

#### F. Fluorescence Measurements

An Ocean Optics Spectroscopy set-up was also designed for excitation-emission fluorescence measurements. A Xenon lamp source is controlled using scanning monochromator (MonoScan 2000) before it hits the sample. The output source of the MonoScan 2000 is connected to an optical fiber splitter, one cable goes to Ocean optics USB 4000 (Spectrometer 1), and the other cable is connected to the cuvette holder. Ocean optics 2000+ XR1-ES (Spectrometer 2) measured the emission peaks of the sample using Ocean View application (Figure 2 (b)). The excitation wavelength ranges from 250-450 nm and the emission wavelength ranges from 250- 600 nm. Fluorescence emission spectrum was obtained in every 5 nm-interval of the excitation wavelength.

All fluorescence measurements were conducted at room temperatures (~25°C). Fifty (50) deionized water samples were average and used as blank samples. The corrected EEM fluorescence data were analyzed. Fluorescence indices and aquatic fluorescence peaks such as Tryptophan-like (Peak T) and humic-like peaks, humic-A (peak A), and humic-C (peak C) were measured. Table IV shows the major fluorescence in aquatic samples.

TABLE IV  
SUMMARY OF ABSORPTION VALUES AND RATIOS USED IN CHARACTERIZING DOM IN ESTUARINE ENVIRONMENT [15]-[19]

Index/Component	Parameters	Peak Name	Probable Sources*	Description
Fluorescence Index (FI)	emission (em) 470- nm/ em at 520 nm at excitation (ex) 370 nm	-	-	Differentiates water samples as microbial (~1.8) or terrestrial (~1.2) origins.
Biological Index (BIX)	em 380-nm/em 420-nm and 435-nm at ex 310-nm	-	-	Indicates proportion of newly produced DOM
Humification Index (HIX)	435-480-nm divided by area under em 300-345-nm + 435-480-nm at ex 254-nm	-	-	Indicates the presence of humic substances
Tryptophan-like	ex 270-275-nm and em 304-312-nm	T	T,A,M	Amino acids, free or bound in proteins
Ultraviolet A (UV-A) humic-like	ex 290-325-nm and em 370-430-nm	A	T,A,M	Low molecular weight, associated with biological activity, present in wastewater, wetland, and agricultural environments
Ultraviolet C (UV-C) humic-like	ex 320-360-nm and em420-460-nm	C	T	High molecular weight, highly present in wetlands, and forested environments

The fluorescence DOM components are designated based on [21] on marine and terrestrial DOM characterization using excitation-emission matrix spectroscopy. One of the basic and most widely used measurement is fluorescence index (FI), which provides information about the source of the samples or degree of degradation of DOM. Fluorescence DOM measurements are commonly calculated using 3D EEM which provides multiple spectra of increasing excitation ranges from UV to blue region.

The EEMs could provide information on the composition, origin, and processing of DOM. These indices use ratios of fluorescence intensity in different regions to provide possible sources and relative contribution of recently produced DOM. DOM characteristics are associated with the range of computed values from BIX and HIX from all sampling stations varies based on their autochthonous components and humic substances, respectively.

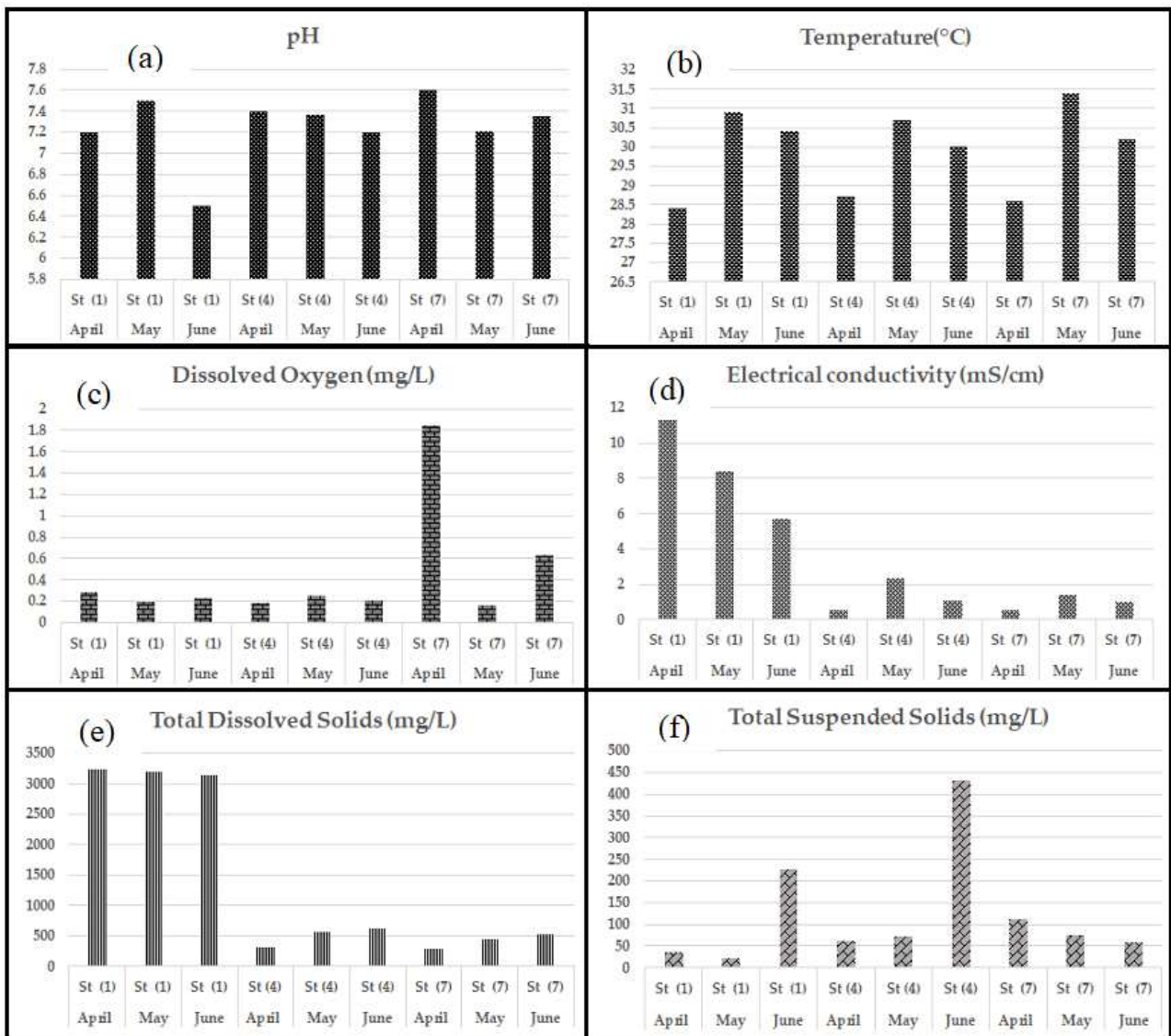


Fig. 3 Trend of physico-chemical characteristics of surface water samples such as (a) pH, (b) temperature, (c) dissolved oxygen, (d) electrical conductivity, (e) total dissolved solids, and (f) total suspended solids along Pasig river

### G. Statistical analyses

Absorbance ratios were used to correlate DOM characteristics such as molecular weight, aromaticity, TOC, and sources. Spectroscopic indices and intensity peaks were correlated to water quality parameters with all months combined. Correlations were conducted in Statistica software and GGally in R. Correlations were considered significant when the correlation coefficients were greater than 0.35 [40].

## III. RESULTS AND DISCUSSION

In April 2019, the flow rate at St (1) Lawton station is approximately 0.52 m/s and gradually decreases to 0.26 m/s at St (4) Valenzuela Station. No significant flow was observed at St (7) San Joaquin Station. However, during May 2019, the flow direction varies with upstream flow from Manila Bay to Laguna Lake and an average flow rate of 0.38 m/s. An average flow rate of 0.31 m/s were observed during June 2019 with a flow direction of downstream from Laguna Lake to Manila Bay.

### A. Physico-Chemical Properties of Pasig River Water Samples

The physico-chemical parameters, such as pH, temperature, EC, DO, BOD<sub>5</sub>, TSS, TDS, and TOC are shown in Fig. 3. The pH values are nearly neutral which varies from 6.50 to 7.60 and within the range for Class C type of water. The temperature changes from April to June 2019 ranging from 28.4 °C to 30.9 °C. DO concentrations on the other hand are significantly low and considered hypoxic since all values are below 2 mg/L. It ranges from 0.16 mg/L to 1.84 mg/L. The highest DO concentration was observed only at St (7) San Joaquin station during April 2019 which is still below the minimum DO level for Class C water body. The low DO concentration indicates the presence of high concentrations of biodegradable organic matter in the water. On the other hand, EC values significantly decrease from St (1) Lawton Station to St (7) San Joaquin Station. St (1) Lawton Station has the highest EC values which is due to the confluence of Manila bay, a marine water, and Pasig river, an estuarine system. The same trend is observed in the TDS concentrations. The

observed TDS levels can be associated with the presence of dissolved salts from Manila Bay.

The TSS concentration varies on each sampling station which ranges from 22 to 432 mg/L. In April 2019, St (1) Lawton Station and St (4) Valenzuela Station are below the minimum TSS concentrations. In May 2019, only St (1) Lawton Station is below the minimum TSS concentrations. However, significant increase in TSS concentrations were observed in June 2019 for St (1) Lawton Station and St (4) Valenzuela Station.

The amount of organic matter present in river samples can be presented with the organic carbon content. Also, BOD<sub>5</sub> values quantify the strength of organic matter. Figure 4 shows the amount of organic matter using total organic carbon and biological oxygen demand from April 2019 to June 2019. No detection to low concentration below 3 mg/L were observed in three sampling stations during the month of April 2019. TOC concentration ranges from 0.11 to 0.99 mg/L in May 2019. The collected values were very low due to holding time resulting below the detection limit.

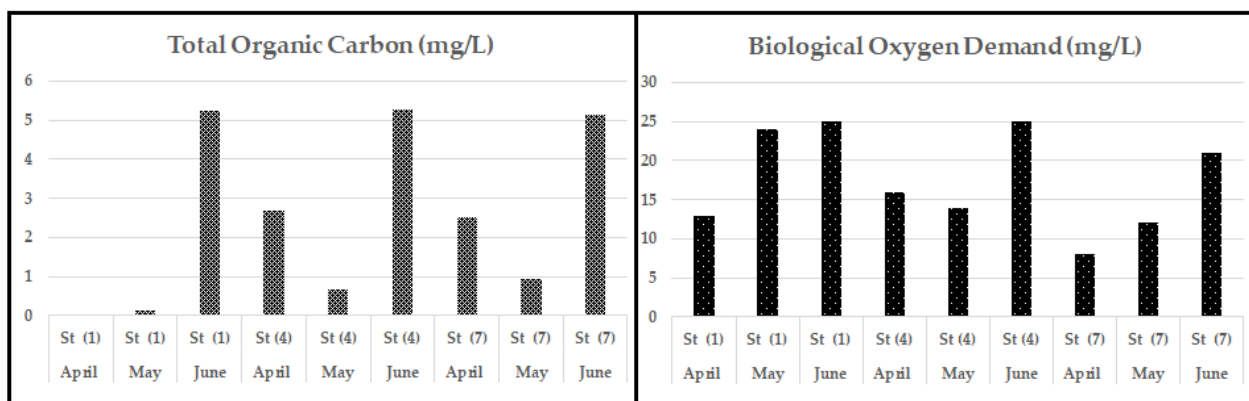


Fig. 4 Trend of organic matter characteristics of surface water samples such as total organic carbon (left) and biological oxygen demand (right) along Pasig river

High concentrations above 5 mg/L were observed during the month of June 2019. This clearly shows that high production of organic carbon associated with the presence of organic matter is observed in the month of June 2019. BOD<sub>5</sub> concentrations on all sampling stations are higher than the maximum concentration of 7 mg/L which the DENR sets for Class C water body. River water is considered clean if it has a BOD<sub>5</sub> of 2 mg/L and below. However, heavily polluted, and severely polluted rivers have BOD<sub>5</sub> concentrations of 10-20 mg/L and 20 or more mg/L, respectively [40]. This high BOD<sub>5</sub> concentration is one of the reasons for low DO concentration since biodegradation of organic matter consumes the DO in the water. The area's high organic matter is due to the untreated or partially treated sewage discharges from the neighboring cities. The water utilities responsible for treating these wastes are still currently working on increasing the coverage of sewage collection and treatment in the area. Thus, the sewage discharges are currently being mainly treated using septic tanks only.

### B. Water Quality Index

The standard values used for pH, BOD<sub>5</sub>, temperature and TSS were obtained from DAO 2016-08. Other measurements such as TOC and BOD were obtained from [2] - [3]. The standard values for the water quality index are dependent on the references used in this study. The pH standard value ranges from 6.5-9.0 and temperature ranges from 25-31. In this case, the mean value for the pH and temperature were used as standard value. Also, DO standard value is 5. For the TDS and TSS standard values are 1000, and 80, respectively. Lastly, the standard value for BOD<sub>5</sub> is 7. Not all water quality parameters were used in this study due to the standard set value's limitations.

TABLE V  
WATER QUALITY INDEX (WQI) PARAMETERS FOR THE STANDARD

Parameter	Set Value	w <sub>i</sub>	w <sub>i</sub> q <sub>i</sub>
pH	7.75 (6.5-9.0)	0.129	0.387
Temperature	28 (25-31)	0.035	0.107
DO	5	0.200	0.600
TDS	1000	0.001	0.003
TSS	80	0.013	0.038
BOD <sub>5</sub>	7	0.143	0.429
<b>WQI</b>			<b>2.313</b>

The calculated WQI for the standard is 2.313 which indicates good water quality for river waters based on the parameters used. Table VI shows the calculated WQI of the surface water samples collected along three out of seven sampling sites from April 2019 to June 2019. Each sampling station is ranked from highest to lowest for each month. The calculated WQI closest to the standard shows the best water quality condition while the farthest from the standard shows worst water quality condition.

The highest WQI is measured at St (1) Lawton Station with a value of 7.550 while the lowest WQI is St (7) San Joaquin Station with a value of 5.829 for the month of April 2019. The same rank was observed for the month of May 2019. High WQI values observed in St (1) is due to tidal effect from Manila Bay. For the month of June 2019, St (4) Valenzuela Station have the highest WQI value of 12.96, which is very close to St (1). On the other hand, St (7) has the lowest WQI on the said month. The low WQI values for St (7) can be attributed to the downstream flow from Laguna lake. All WQI values are close to each other and far from the standard value.

TABLE VI  
WATER QUALITY INDEX VALUES OF THE THREE SAMPLING STATIONS IN PASIG RIVER FROM APRIL 2019 TO JUNE 2019

Station	April 2019		May 2019		June 2019	
	WQI	Rank	WQI	Rank	WQI	Rank
Standard	2.313	-	2.313	-	2.313	-
St (1)	7.550	3	9.033	3	12.82	2
St (4)	6.057	2	5.712	2	12.96	3
St (7)	5.829	1	5.408	1	7.672	1

#### D. UV-Vis Absorption analysis

UV-Vis absorption is used to approximate molecular sizes, sources, and predictions of DOC from organic matter in

TABLE VII  
MEAN ABSORBANCE VALUES AT 280-NM, 253-NM/203-NM, 226-400 NM, AND 250-NM/365-NM OF THE THREE SAMPLING STATIONS FOR APRIL TO MAY 2019

St	Molecular Size A280	THMFP*	Molecular weight/Aromaticity A250/365	DOM Sources A254/A436	DOC Prediction A340/A254
APRIL 2019					
1	0.231	0.211	3.234	0.893	0.278
2	0.220	0.206	3.221	0.790	0.460
3	0.168	0.148	2.788	0.457	0.371
4	0.144	0.115	3.112	0.567	0.443
5	0.122	0.195	3.105	0.678	0.502
6	0.130	0.268	2.996	0.420	0.430
7	0.335	0.293	4.967	1.020	0.564
MAY 2019					
1	0.245	0.167	3.023	0.666	0.123
2	0.255	0.221	3.122	0.675	0.121
3	0.184	0.198	3.210	0.543	0.200
4	0.217	0.201	3.145	0.236	0.235
5	0.201	0.231	3.221	0.856	0.356
6	0.199	0.275	3.267	0.988	0.112
7	0.210	0.322	3.349	1.112	0.411
JUNE 2019					
1	0.212	0.334	3.222	0.785	1.356
2	0.197	0.354	3.108	0.877	1.400
3	0.233	0.332	3.295	0.882	1.670
4	0.275	0.337	3.645	0.679	1.256
5	0.178	0.476	3.542	0.996	1.345
6	0.201	0.589	3.206	1.221	1.550
7	0.204	0.721	3.450	1.323	1.299

\*THMFP -Trihalomethane formation potential

The absorbance at 280-nm was measured to interpret aromatic structures present in the DOM, however, this wavelength does not provide the maximum absorbance but it is normally chosen for phenolic arenes, benzoic acids, aniline derivatives, polyenes, and other aromatic hydrocarbons with two or more rings [14],[21]. It has also been used to measure the humification degree, molecular weight, and aromaticity of DOM [22]. Using the UV absorbance at 280-nm, the organic matter's molecular size is highly correlated with its absorption [14]. As seen from Table 5, the aromatic degree changes from 0.144 to 0.335. In April 2019, St (7) San Joaquin Station has higher values compared to the other sampling stations. However, during the three-month long sampling, absorbance values in June 2019 have significantly higher values compared to April and May 2019. It shows that June 2019 sampling period contain more aliphatic chains of substituents aromatic rings while April and May 2019 sampling period

may have carbonyl, carboxyl, hydroxyl, and ester substituents. In April 2019, higher absorbance values were measured from St (7) followed by St (1) and St (4), respectively. On the other hand, for May 2019, St (2) has the highest absorbance value while St (1) for the month of June 2019. The absorbance band from 226-nm to 400-nm denotes the variance of organic compounds containing benzene ring in aqueous solution [18]. This provides information on DOM's stability and degradation properties, which more likely states that more organic molecules contain benzene ring structures. St (3) shows consistent results from April to June 2019, indicating that it has higher stability than other stations. The absorbance ratio at 250-nm and 365-nm provides water carbon origin. In this study, the range varies from 3.023 to 4.967, which represents the origin of fulvic acids [38]-[39]. We can assume through these values the presence of dissolved organic carbon and the presence of fulvic acids. With the UV-



Vis absorbance values, we can approximate the presence of dissolved organic carbon and its aromatic substituents as observed on the low DO values, and the effluents from industrial, *business*, and residential near the sampling stations from April to June 2019 [43]. Poor water quality shows a

deteriorating humification degree. The poor quality of Pasig river shows the effect of effluents from the different DOM sources. On the other hand, St (3) is predominantly residential and agricultural land in the southern region where water qualities are much better.

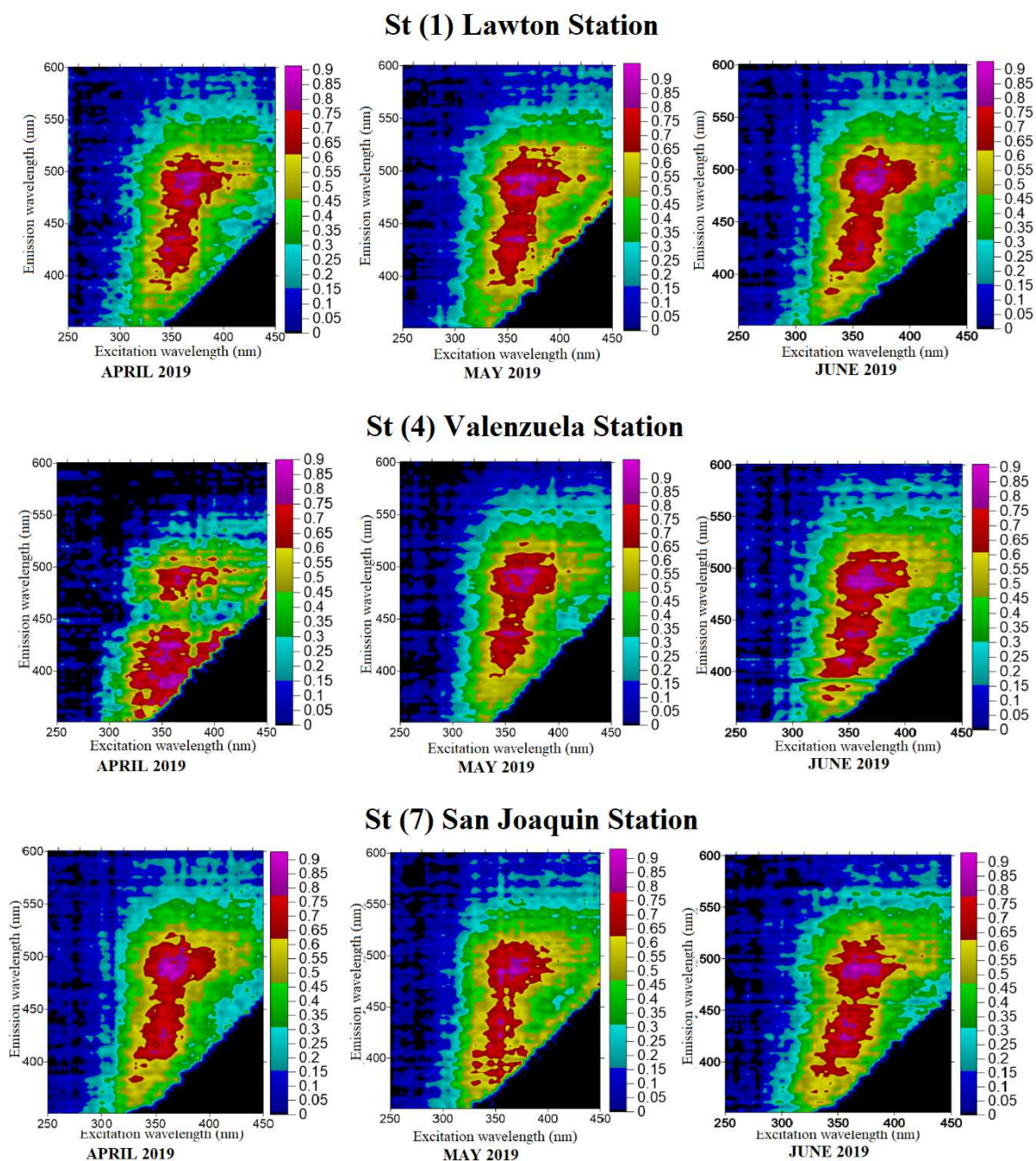


Fig. 5 3D fluorescence excitation-emission matrices of the three sampling sites from April to June 2019. Normalized fluorescence intensities are provided with arbitrary units.

Hence, it provides the highest humification degree from all the sampling stations. The absorbance ratio at wavelengths 253 nm and 203 nm were used to identify Trihalomethane formation potential. Trihalomethane formation potential is used to assess the formation of trihalomethanes in urban rivers [44]. It is shown that the trihalomethane formation increased with increasing organic matter and UV absorbance values for all water samples. This suggests that these parameters can be

used as predictors of by-products formed with chlorine in the river system [45].

#### E. Fluorescence EEM plots and analysis

There are qualitative fluorescence DOM differences observed from the EEMs of the different sampling stations from April to June 2019. Figure 5 shows the image 3D EEM maps of the different sampling stations. The EEMs for each sampling station is unique and infers that the DOM source,

composition, and its processes vary for each sampling station. The samples' fluorescence spectra were mapped on the same excitation wavelength interval of 5-nm, and emission wavelength interval of 0.5-nm. The same fluorescence intensity scale was used for all samples with arbitrary units (a.u.). The fluorescence index (FI) was used to differentiate water samples from microbial and terrestrial sources in this study. The FI values for all samples range from 0.99 to 1.34, which clearly indicates that terrestrially derived DOM compositions are present.

Peak-T (Tryptophan-like), Peak-A (terrestrial humic substances), and Peak-C (terrestrial, agriculture) were observed in all samples. Protein-like fluorescence such as tryptophan are likely derived from a mixture of dissolved amino acids and other organic materials with similar fluorescence characteristics. However, with its great potential use in ecological applications, there are still limitations on the molecular size and structure of high DOM concentrations which contributes to the detection of fluorescence protein-like signatures. Peaks -A and -C are usually associated with humic substances and vary mainly on its source and molecular size. The peak shifting in excitation wavelength from shorter to longer wavelengths implies an increase of molecule size and aromatic content [13].

The fluorescence measurements observed in all surface water samples mainly vary on the location and season. Figure 6 shows the normalized intensities of the different fluorescence peaks. It is evident that peaks -A and -C are largely present in the EEMs for each sampling station during seasonal variation. In St (1) Lawton Station, the month of May 2019 had the highest fluorescence peaks among the three-month long sampling duration.

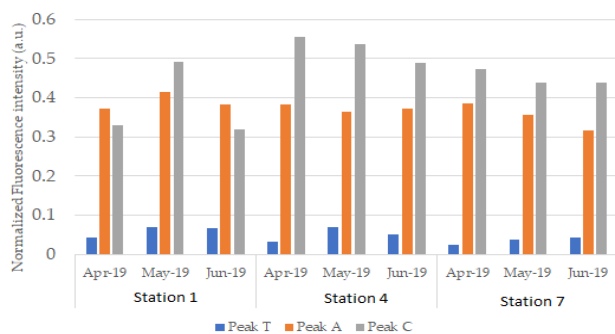


Fig. 6 Normalized fluorescence intensities (a.u.) of the different peaks at the three sampling stations from April to June 2019

Fluorescence EEMs can also be used to determine the impact of sewage effluents discharged from different land-use types near the river system [34]. The ratio of peak-T to peak-C was used to differentiate upstream and downstream water samples. According to [40], peak T fluorescence intensity is strongly correlated with biological oxygen demand in both river systems and sewage effluents. With the observation from the DOM composition's peak-C fluorescence intensity in the three sampling stations, we can correlate peak-T/peak-C ratio as the ratio of BOD<sub>5</sub>/DOC ratio terrestrial waters. Figure 7 provides the peak-T/peak-C ratio with seasonal

variance and differences in water quality. For April and May 2019, low peak-T/peak-C ratio and high peak-C emission wavelength were observed. This is due to the mixture of marine water from Manila bay as observed by the upstream flow during these months. In this case, the use of peak-T fluorescence cannot sufficiently provide pollutant interpretation due to the contributions of marine biological activity [46]. On the other hand, high peak-T/peak-C ratio but low peak-C emission wavelength was measured in the month of June 2019. As stated, downstream flow was observed this month, showing the impact of Laguna lake in the three sampling stations' water quality.

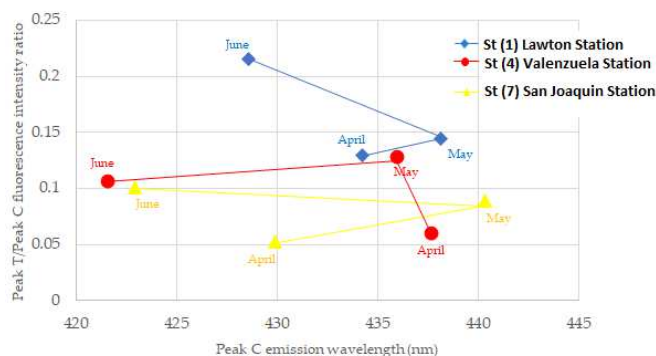


Fig. 7 Normalized fluorescence intensities (a.u.) of the different peaks at the three sampling stations from April to June 2019

The higher intensity of the fluorescence peaks indicated in Fig. 7 confirms the concentration of sewage in all sampling stations. It can be identified from the EEM analysis that the contribution of labile organic matter and presence of humic compounds varies at every station during the three-month sampling period. These combinations are commonly used to evaluate dynamic changes of organic matter in river systems. The EEM fluorescence spectra and identification of regions with higher fluorescence intensity peaks can be used to determine presence of labile organic and humic substances at certain sampling stations, i.e., St (1) Lawton Station and St (4) Valenzuela Station, having different land-use type. These results indicate the direct consequence of urban development and domestic pollution from informal settlers.

#### F. Correlations between physico-chemical parameters

Correlations between the absorbance values and ratios with some physico-chemical parameters were observed associated with the dissolved organic matter present in the Pasig river. Table VIII shows the correlation table of the absorbance values and ratios with physico-chemical parameters monitored using three sampling stations during the three-month sampling period. Several parameters such as dissolved oxygen, total dissolved and suspended solids, total organic carbon, and biological oxygen demand represent a different measure to organic matter and analyze water quality status in a river system. BOD<sub>5</sub> is used to evaluate biodegradable organic matter and carbohydrates. However, there are other parameters to identify different organic compounds.

TABLE VIII  
PEARSON'S R LINEAR COEFFICIENT FOR EACH REGRESSION BETWEEN PHYSICO-CHEMICAL PARAMETERS AND ABSORBANCE VALUES (P<0.0001)

		Absorbance value/ratio				
		A280 (Molecular size)	A253/203 (THMFP)	A250/365 (Molecular weight)	A254/436 (DOM sources)	A340/254 (TOC/DOC prediction)
Physico-chemical parameter	pH	0.2668	-0.1254	0.3454	0.0020	-0.5616
	Temperature (°C)	-0.1569	0.2144	-0.4139	-0.0451	0.0702
	DO	<b>0.7085</b>	0.2093	<b>0.9423</b>	0.3833	0.0448
	EC	-0.0018	-0.3192	-0.4087	-0.0928	-0.3319
	TDS	-0.0135	-0.2445	-0.4096	-0.0793	-0.1006
	TSS	0.3252	0.1291	0.1977	-0.1226	<b>0.6714</b>
	TOC	0.0071	<b>0.6196</b>	0.1993	0.2764	<b>0.9678</b>
	BOD <sub>5</sub>	-0.1900	0.2353	-0.4742	-0.1200	<b>0.5639</b>

The relationship between absorbance values and BOD<sub>5</sub> evidenced effluents' presence from organic matter in all sampling stations located in Pasig River. Highlighted values showed acceptable correlation between absorbance values and some physico-chemical parameters. The linear relationship between BOD<sub>5</sub> and A340/254 (TOC/DOC

prediction) collected from three sampling stations is  $r = 0.5639$  ( $n = 10$ ,  $p < 0.0001$ ) showed high correlation. This is highly supported with the linear relations between BOD<sub>5</sub> and TOC ( $r = 0.5383$ ,  $p < 0.0001$ ), TOC and A340/254 ( $r = 0.9678$ ,  $p < 0.0001$ ).

TABLE IX  
PEARSON'S R LINEAR COEFFICIENT FOR EACH REGRESSION BETWEEN PHYSICO-CHEMICAL PARAMETERS AND FLUORESCENCE PEAKS (P<0.0001)

		Fluorescence peak		
		Peak T (Trptophan-like)	Peak C (UV-C humic-like)	Peak A (UV-A humic-like)
Physico-chemical parameter	pH	-0.4339	<b>0.7228</b>	0.2080
	Temperature (°C)	-0.0050	-0.0050	-0.2663
	DO	-0.5828	0.0357	0.0576
	EC	0.2946	-0.5832	<b>0.4447</b>
	TDS	<b>0.4382</b>	<b>0.6601</b>	<b>0.4519</b>
	TSS	<b>0.6260</b>	0.2811	<b>0.5551</b>
	TOC	<b>0.7840</b>	0.3911	<b>0.5027</b>
	BOD <sub>5</sub>	<b>0.5781</b>	<b>0.6450</b>	<b>0.5113</b>

The presence of labile organic matter can be correlated with BOD<sub>5</sub> and fluorescence intensity peaks such as protein-like (peak T) and humic-like (peak A, peak C) substances. BOD<sub>5</sub> values were highly correlated with tryptophan-like substances (peak-T) with  $r = 0.5781$  ( $p < 0.0001$ ,  $n=9$ ) and humic-like substances such as peak C with  $r = 0.6450$  ( $p < 0.0001$ ,  $n = 10$ ), and peak A with  $r = 0.5113$  ( $p < 0.0001$ ,  $n = 10$ ). These tryptophan substances are usually associated with the presence of labile organic matter. However, not all samples may not be directly correlated with BOD<sub>5</sub> and other physico-chemical parameters.

The different sources of organic pollution in rivers such as sewage, domestic and industrial effluents, urban and agricultural run-off result in a mixture of compounds with unique absorbance and fluorescence intensities. However, effluents from polluted river samples only showed good correlation between absorbance-fluorescence and BOD<sub>5</sub> values while zero to low correlation (below

$r = 0.35$ ,  $p < 0.0001$ ) were observed for unpolluted waters. Several factors are affecting the estimated correlation between parameters such as origin and composition of organic matter, biological and physical conditions such as salinity and weather parameters.

With the strong correlations between the absorbance and fluorescence values with BOD<sub>5</sub>, we can develop a mobile LED fluorescence lidar system that can be used to characterize natural waters or effluents. *In-situ* lidar monitoring together with physico-chemical testing can provide real-time water quality status.

#### IV. CONCLUSIONS

This study provides information on the water quality status of Pasig river from seven sampling stations within the three-month sampling period. Among seven sampling stations, only three stations namely St (1) Lawton Station, St (4) Valenzuela Station, and St (7) San Joaquin Station were monitored for

physico-chemical parameters. All DO values were below 2 mg/L which are considered hypoxic and did not meet the DENR-DAO standards for “Class C” type. Physico-chemical measurements with the aid of absorbance and fluorescence spectroscopy were used to investigate organic matter contribution in the river system. Parameters such as DO, BOD, TSS, and TDS directly indicated three out of seven sampling stations were polluted and shows significant variance according to the levels of urbanization and organic pollution in Pasig river. However, TOC analyses insignificantly state variance among the stations monitored.

Absorbance and fluorescence spectroscopy set-up were assembled which measures optical properties used in investigating DOM characteristics in river systems. Absorbance values at A254/A436 showed changes in the DOM sources. Respective absorbance values indicated the presence of anthropogenic allochthonous sources such as domestic and urban effluents and humic compounds. 3D fluorescence EEMs from the fluorescence spectroscopy set-up provides detailed DOM characteristics compared to absorbance ratios. Strong correlations were observed between Peak T, A, C and BOD, which indicates labile organic matter. The results from the EEMs among the seven sampling stations were highly affected by marine waters and seasonal variance. It also showed that highly urbanized sampling stations were more affected by the presence of Tryptophan-like substances. From these values, significant peaks, and ratios from the fluorescence spectrum such as Tryptophan (Peak -T) and humic substances (Peak -A, -C) can be used to correlate with water quality parameters such as BOD<sub>5</sub> and TOC/DOC which can be used in the development of a mobile LED-lidar system.

Fluorescence peaks from 3D EEMs was proven to provide water quality data in polluted rivers. This study confirms the relationship between the spectroscopic values and water quality parameters commonly used in water quality monitoring. This could serve as a breakthrough in water quality monitoring since fluorescence remote sensing delivers spatial and real-time data. The urgency of monitoring river systems can be done rapidly with the help of mobile fluorescence lidar system, which provides quality data for water quality monitoring, and planning and management strategies by government sectors involved.

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