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THE LONG -TERM VARIATION OF ORGANIC CHARACTERISTICS IN DONGGANG RIVER USING EXCITATION EMISSION FLUORESCENT MATRIX (EEFM) INTEGRATED WITH PARALLEL FACTOR ANALYSIS (PARAFAC)

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Abstract

In this study, Excitation Emission Fluorescent matrix (EEFM) integrated with Parallel factor analysis (PARAFAC) was applied to investigate the variation of organic property in Donggang River located in Southern Taiwan between Oct. 2010 and Oct. 2015. It reveals that both values of $BOD_5$and COD had a closer proximity at twice samplings; however, the four main components in both samplings showed a different location of excitation and emission wavelengths. On Oct., 2010, EX/EM (percentage of area) of four components were respectively 320/410 nm (46 %), 370/460 nm (27 %), 290/350 nm (14 %) and 280/450 nm (13 %) mainly belonging to humic-like substance. Regrading to the result on Oct, 2015, 320/420 nm (29 %), 228,278/358 nm (29 %), 240/420(29 %) nm and 228/310 nm (14 %) were found attributed in amino organic substance with low excitation wavelength. On Oct.2015, the intensities of four main components in Cinsheda Bridge higher than those in other locations may be attributed with of heavily polluted source like piggery wastewater. For the partition of N-organic and C-organic, there had a significant change on both samplings.

Keywords

Excitation Emission Fluorescent Matrix (EEFM); Parallel Factor Analysis (PARAFAC); Humic Acid-Like

1. Introduction

Dissolved organic matter (DOM), a heterogeneous mixture of organic compounds in water bodies, is composed of myriads of organic compounds which play pivotal ecological and biogeochemical roles in the environment (Wang et al., 2014; Findlay and Sinsabaugh, 2003; Hansell and Carlson, 2002). Part of DOM, named as Chromophoric DOM (CDOM) in aquatic DOM can be divided into two major classes: humic-like substances and protein-like substances (Coble, 1996; Yamashita and Tanoue, 2008). Humic-like substances with complex properties consisted of aromatic and aliphatic compounds mainly derived from the decay of organic matter; however protein-like substances are associated with high biological activities.

Currently, fluorescence excitation-emission matrix (EEFM) combined with parallel factor analysis (PARAFAC) had a widespread trend to be applied to explore the fate of DOM and understand its environmental behaviors in natural and engineering systems (Borisover et al., 2009; Ishii and Boyer, 2012; Stedmon et al., 2003; Yang et al., 2015) owing to its possibility to resolve dissimilar fluorescent components by the calculation of minimum residuals from a given EEFM dataset (Stedmon et al., 2003). For past researches, biochemical oxygen demand (BOD) and chemical oxygen demand (COD) were usually applied into the organic concentration in river; however, these parameters could not show the variation of organic characteristics. Recently, heavy piggery wastewater flew into Donggang River located in Pintung County. Naturally, the possible variation of fluorescent DOM (FDOM) in aquatic ecosystems by EEFM+PRACFAC in temporal and spatial variations attracted a glance of authors to investigate.

2. Materials and Methods

2.1 Sampling Locations

In this study, respective samples from Donggang River on Oct. 2010 and Oct.2015 were selected to compare to distinguish the organic property among water samples. The procedure and storage of water sampling were according to the regulation of Environmental Protection Administration in Taiwan. The relative locations were labelled in Fig.1. The distance of sampling location from upstream to downstream was near to 44 km. Regarding to sampling locations, related parameters of water quality including BOD, NH3-N and DO, were regularly analyzed and promulgated by EPA.

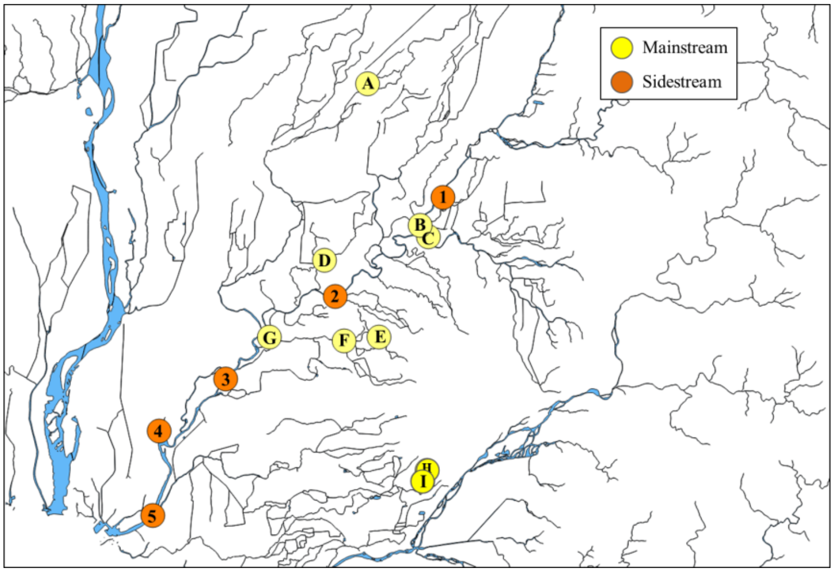

Figure 1: *Locations for whole Samples Relative to Donggang River (1: Longdon Bridge; 2: Chaojhouda Bridge; 3: Cinsheda Bridge; 4: Gangci Pomping Station；5: Donggangda Bridge*

2.2 Analytical Parameters

2.2.1 Excitation Emission Fluorescent Matrix (EEFM)

Regarding to the organic characteristic of water samples, fluorescent spectrometry (F-4500, Hitachi, Japan) was selected as a tool to measure whole samples in this research. Prior to the measurement of whole samples, 0.45 μm membrane filter (Mixed cellulose ester, Advantec MFS Inc., USA) was used as a filter. EEFMs of whole samples were obtained by deducting from the background signal of pure water.

2.2.2EEFM+PARAFAC

Regarding to the complex mixtures of DOM fluorophores in EEFM, ARAFAC is a statistical tool to availably decompose DOM into non-co-varying components. For the measurement of whole samples, the operation condition of fluorescent spectrometry was operated an excitation range of 200–450 nm (every 2 nm) and an emission range of 250–550 nm (every 3 nm). Missing values in parts of the data area replaced by zero could help PARAFAC quickly converge, resulting in solutions with physical and chemical significance. PARAFAC modeling was achieved using DOM Fluor Toolbox written by Stedmon & Bro (http://www.models.life.ku.dk/al_DOMFluor). Both programs are subroutines for the MATLAB R2010a. The three-way PARAFAC model was fitted for the entire dataset as a whole. Single value decomposition (SVD) was used as initial loadings for the original model. Of course, the correct numbers of factor could be determined by the application of PARAFAC model into analysis of whole data (Thygesen et al., 2004).

3. Results and Discussion

3.1 BOD and COD

Regarding to the difference of the amount of organic matter in Donggang River, COD and BOD_5 values at different locations at twice samplings between Dec.2010 and Dec.2015 were plotted in Fig.2. Fig.2 A reveals that COD value of No.3 was higher than that of the other locations. A similar trend of BOD_5 was also appeared on Dec., 2015, as shown in Fig.2 B; however, the highest value was happened at point 4. Owing to the difference of both methods like BOD_5 and COD, most of particulate organic matter could be measure by COD; however, dissolved organic matter with biodegradability was represented by BOD_5. Hence, the divergence of the location with highest BOD_5 or COD value could be comprehended owing to the difference of measurement. For the sample locations of point 3 and 4 in downstream looked higher values than those values of point 1 and point 2 in upstream, indicating that the pollution degree in this river showed an increasing trend from upstream to downstream owing to the agriculture activity and the influent of sewage.

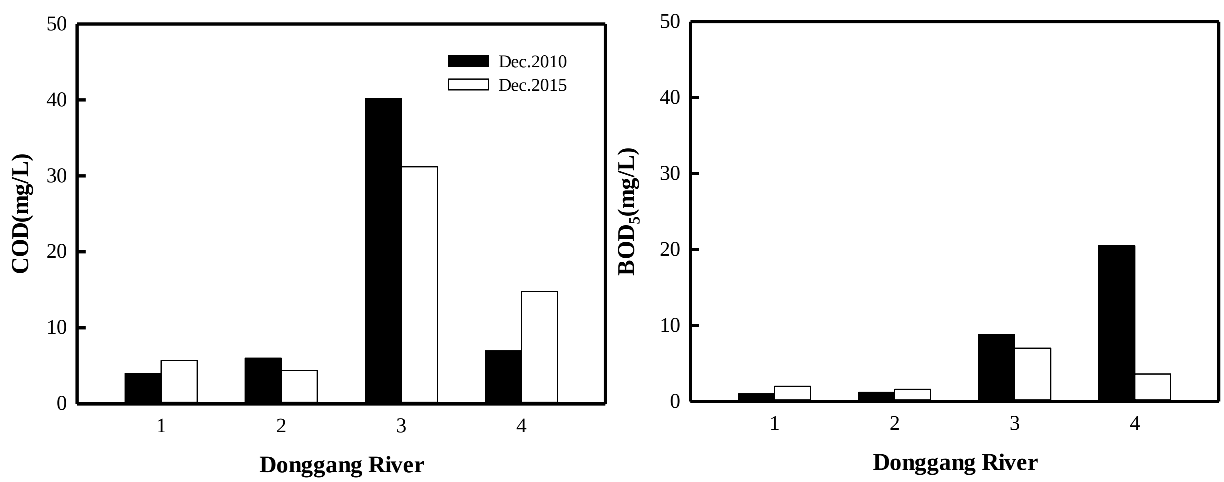

Figure 2: *The (A) COD (B) BOD_5 for Donggang River at different Sampling Locations*

3.2 Main Fluorescent Components

Owing to the absence of organic property from BOD_5 and COD value, in this study, EEFM+PARAFAC could provide more information of organic characteristic. Regarding to the decision of the factor numbers in this study, only 4 sample numbers were analyzed by the operation of PARAFAC with MATLAB. The related result was illustrated in Fig.3. Four components expressed by fluorescent intensity were decided by the following bases including the convergence criterion of 0.01, iterations of 7 and explained variation of 90%. On Oct., 2010, EX/EM (percentage of area) of four components were respectively 320/410 nm (46 %), 370/460 nm (27 %), 290/350 nm (14 %) and 280/450 nm (13 %) mainly belonging to humic-like substance. Based on the result on Oct, 2015, 320/420 nm (29 %), 228,278/358 nm (29 %), 240/420(29 %) nm and 228/310 nm (14 %) were found attributed in amino organic substance with low excitation wavelength. Apparently, the characteristic of organic matter in Donggang River wasrich in N content and less humic-substance in 2015 year than those in 2010 year, indicating that artificial activity in the offshore in this river change thoroughly the partition of organic matter while traditional organic parameters could not provide an available observation.

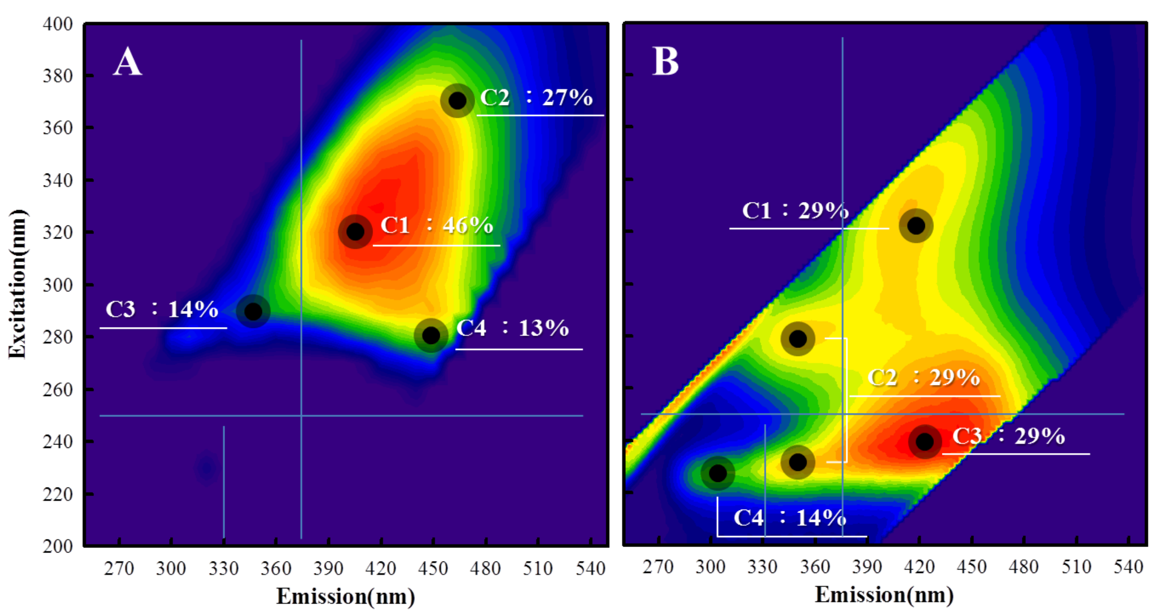

Figure 3: *The Major Fluorescent Components of Donggang River by EEFM+PARAFAC on (A) Dec, 2010 (B) Dec, 2015*

3.3 Variation of Major Fluorescent Components

The major fluorescent components varied from upstream to downstream in Donggang River were shown in Figure 4. For the fluorescent components on Dec, 2010, shown in Fig.4 A, four fluorescent components were respectively increased, especially for those at Cinsheda Bridge and Gangci Pumping Station. Similar trend was also found on Dec.2015, but the different fluorescent components and intensities were observed. On Dec., 2010 (Fig.4 A), the EX/EM change of the component from upstream to downstream, their values were in order of 320/410 nm, 370/460 nm, 290/350 nm and 280/450 nm. On Dec., 2015 (Fig.4 B), the turning point of four components was founded in point 3 of Cinsheda Bridge. The major fluorescent components were 240/420 nm and 228,278/358 nm, revealing ascending trend from upstream to downstream. Furthermore, the fluorescent intensities of water samples on Dec., 2015 were higher than those on Dec., 2015.

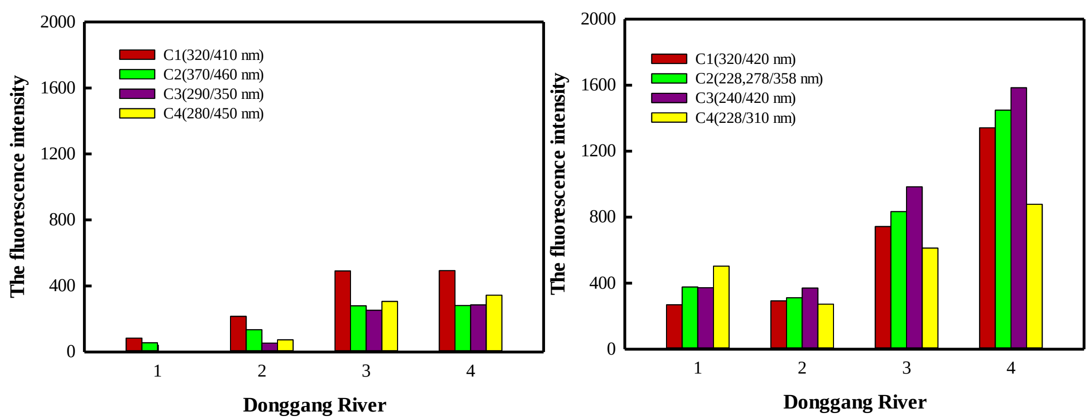

Figure 4: *The Variation of Major Fluorescent Components in Donggang River on (A) Dec, 2010 (B) Dec, 2015*

4. Conclusions

Based on the information of BOD, COD, fluorescent intensity, amount of organic pollution flew into Cinsheda Bridge. The organic pollutant in downstream was higher than that in upstream. According to major fluorescent components of both samplings, organic properties was significantly change from 320/410 nm (46 %), 370/460 nm (27 %), 290/350 nm (14 %) and 280/450 nm (13 %) on Dec.2010 to 320/420 nm (29 %), 228,278/358 nm (29 %), 240/420(29 %)

nm and 228/310 nm (14 %) on Dec. 2015. The different partitions of N-organic and C-organic may be related with the change of pollution sources.

5. Acknowledgement

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