Organic Fluorescent Characteristics of Five Tributaries in Gaoping River Basin in Dry Season

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Abstract. In this research, fluorescence excitation emission spectrometry (Excitation emission fluorescent matrix, EEFM) and total organic carbon Analyzer were main instruments applied into evaluating the property and amount of natural organic matter in dry season for Gaoping River basin located in Southern Taiwan. Dissolved non-volatile organic carbon in water (non-purgeable dissolved organic carbon, NPDOC) was measured and SUVA, (UV254/NPDOC), BIX (Biological index, BIX) were compared in whole samples belonging to five segments. Results showed that NPDOC values of whole samplings in Gaoping River basin were less than the criteria of Source Water Standard of Drinking Water except for Jiouru bridges. SUVA values and BIX for whole samplings were less than 1, indicating that the source pollution in the Gaoping River Basin was mainly attributed to the human activity and microbial organic matter produced in the River. The variance of peak fluorescence locations and intensity, and the difference of fluorescence intensity among five fluorescent organic groups revealed that the significant divergences existed in the five segments in Gaoping River Basin. Peak fluorescent intensity belonging to humic-like substance, those values in Qishan River, Laonong River and Ailiao River were less than 100. Peak fluorescent intensity belonging to fulvic-like substance, only Laonong River was below 100. The average fluorescence intensity in Gaoping River mainstream was the highest value followed by Mino River; however, the lowest existed in Ailiao River.

Keywords: excitation emission fluorescent matrix (EEFM), non-purgeable dissolved organic carbon (NPDOC), SUVA, (UV254/NPDOC), Biological index (BIX), Fulvic-like substance, humic-like substance

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 [1]. 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 [2]-[3]. 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.

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. EEFM (Excitation emission fluorescent matrix) applied on the dissolved organic matter have several advantages including keeping the integrity of water sample, a little volume analysed, less labour and less time consumed [4]. Fluorescence spectroscopy has been increasingly used for on-line monitoring of DOM [5].

In this research, fluorescence spectrometry as well as total organic carbon analyser was applied to evaluate the property and amount of natural organic matter in dry season for Gaoping River basin located in Southern Taiwan. Dissolved non-volatile organic carbon in water (non-purgeable dissolved organic carbon, NPDOC) was measured and SUVA (UV254/NPDOC), BIX (Biological index, BIX) were compared in whole samples belonging to five segments.

2. Material and Methods

2.1. Sampling Locations

In this study, respective samples from Gaoping River on Dec.2016 were selected to compare to distinguish the organic property owing to dry season. 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 171 km.

Fig. 1: Locations for whole samples relative to Gaoping River

2.2. Analytical Parameters

2.2.1. EEFM (Excitation Emission Fluorescent Matrix).

Regarding to the organic characteristic of water samples, fluorescent spectrometry (F-4500, Hitachi, Japan) was applied in this research. Whole samples must be filtered by 0.45 µm membrane filter (Mixed cellulose ester, Advantec MFS Inc., USA) before fluorescent measurement. EEFMs of whole samples were obtained by deducting from the background signal of pure water.

2.2.2. UV-VIS.
Ultra-violet and visible measurements were carried out with 1 cm quartz UV-visible cells at room temperature (22–24 °C) by UV-visible double beam spectrophotometer (U-2900, Hitachi, Japan). UV-vis absorption spectrum of water samples was obtained at wavelength 200 to 600 nm. Before analyzed, all samples were filtered by 0.45 µm membrane filters and filtrate were put into one cm path of the cell to measure.

2.2.3. NPDOC (Non-purgeable dissolved organic matter).

All water samples for DOC measurement were prefiltered through a 0.45 µm membrane sand filter to decrease the interference from microorganisms. The filtered water sample was acidified to pH of 2 by adding an appropriate volume of 85% phosphoric acid. Inorganic carbon was then degassed with highly pure nitrogen. The DOC of water sample was finally quantified by a total organic carbon analyser (Lotix, TELEDYNE TEKMAR, USA.) equipped with high-temperature (680 °C) combustion and a non-dispersive infrared absorption detector. The value of DOC measured was called NPDOC. Additionally, calibration curves were prepared by using a series of standard solutions consisting of anhydrous potassium biphthalate (C₈H₅KO₄).

3. Results and Discussion

3.1. NPDOC and SUVA

Figure 2 shows the variations of NPDOC and SUVA of whole samplings in Gaoping River basin. Observed from this figure, maximal NPDOC values of 5.27 mg-C/L occurred in Jiouru bridges located in main Gaoping River (Figure 2 A). High organic content exceeding the standard of source water as drinking water, may be attributed to the pollutant drainage of livestock industry. NPDOC values of samplings respectively belonging to five side-rivers basin looked so different, revealing that the difference pollutants existing in point or non-point source steadily flew into rivers in dry season.

The ratios of UV$_{254}$ (cm$^{-1}$) to NPDOC (mg-C/L), named as SUVA, were plotted in Figure 3 B. Usually, SUVA larger than 4 represents the organic substance with hydrophobic property like humic fraction. Contrarily, SUVA less than 2 reveals organic substance with hydrophilic property like non-humic fraction [6]. Whole SUVA values in Gaoping River basin were less than 1, as shown in Fig.2 B, proving that organic matter with hydrophilic property was attributed to artificial activity, especially on the sampling locations belonging to Laonong River and Ailiao River where most of their values were declined to the 0.4.
Apparently, this area development affects the water quality, and even changes its status of utilization by water source planning.

3.2. EEFM and Characteristic Peaks

![EEFM for Gaoping River at different sampling locations](image)

**Fig. 3: EEFM for Gaoping River at different sampling locations**

Table 1 Peak locations and fluorescent intensities at different sampling locations of five tributaries located in Gaoping River Basin

<table>
<thead>
<tr>
<th>River</th>
<th>I: Excitation (nm)</th>
<th>II: Excitation (nm)</th>
<th>III: Emission (nm)</th>
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EEFM of whole samplings were shown in Figure 3. Based on the classification of related research, dominant components could be divided into five groups, group I of aromatic protein (Tyrosine): 200-250/280-330 nm, Group II of aromatic protein (BOD₅): 200-250/330-380 nm, Group III of Fulvic acid: 200-250/380-540 nm, Group IV of soluble microbial by-product-like: 250-340/280-380 and group V of humic acid-like: 250-400/380-540 nm [7]. Related peak locations and intensity were listed in Table 1.

Table 1: Peak locations and fluorescent intensities at different sampling locations of five tributaries located in Gaoping River Basin
shows minor divergences for peak locations among Qishan River, Mino River and Laonong River, Ailiao River and Main Gaoping River. Although significant fluctuation on fluorescent intensity was observed, those values in Qishan River, Laonong River and Ailiao River were lower than those in other streams. Peak fluorescent intensity belonging to humic-like substance, those values in Qishan River, Laonong River and Ailiao River were less than 100. Peak fluorescent intensity belonging to fulvic-like substance, only Laonong River was below 100. Regarding to peak fluorescent intensity of soluble microbial by-product (SMP), Laonong River and Ailiao River were close to 100. For Main Gaoping River, the variance of peak fluorescent intensity in whole organic classification became larger than other streams in this basin, especially for Group II (Aromatic protein (BOD$_3$) and SMP.

### 3.3. Fluorescent Organic Classification and Their Distribution

Figure 4 reveals total fluorescence intensity and fluorescence intensity of each kind of organic fluorescent matter in whole sampling points in the Gaoping River basin. For total fluorescence intensity, the biggest difference between sampling points in each branch is the Gaoping River mainstream, and the lowest happened in Mino River. The average fluorescence intensity in Gaoping River mainstream was the highest value followed by Mino River; however, the lowest existed in Ailiao River. Actually, the variance of fluorescent intensity and maximal fluorescent intensity for five groups of fluorescent organic matter were compared in each tributary; maximal values were found in Gaoping River mainstream, and the minimal values was appeared in Laonong River. In other words, organic pollution in Laonong River was lower than that in Gaoping River mainstream. Apparently, less development in upstream than downstream was related with current results.

![Fig. 4: EEFM for Gaoping River at different sampling locations](image)

### 3.4. Humification Index (HIX) and Biological Index (BIX)

HIX was used as the basis of organic humification. It could be calculated by total fluorescent intensity of emission wavelength of 435-480 nm divided by that of 300-345 nm at constant excitation wavelength of 254
DOM with weak humification, less than 4 of HIX, was attributed to microbial activity. DOM was mainly from terrestrial sources while HIX value ranged from 10 to 16. BIX (Biological index), calculated as fixed excitation wavelength of 310 nm, the ratio of fluorescent intensity in emission wavelength of 380 nm to that in 430 nm [9], is another judgement to explain the formation duration of organic compounds in water sample. BIX ranging from 0.6 to 0.7 represents low genetic composition (the index of Recent autochthonous contribution); 0.7 to 0.8 represents degrees in genetic composition; 0.8 to 1 represents strong native content, and BIX greater than 1 represents microbial or bacterial activity.

![HIX and BIX values at different sampling locations of five tributaries located in Gaoping River Basin](image)

Figure 5 shows the comparison between HIX and BIX in five tributaries located in Gaoping River Basin. Observed from Fig 5 A, HIX values in whole sampling points were less than 4, indicating that CDOM in Gaoping River Basin with low humification was formed from biological activities. Regarding to BIX value (Fig. 5 B), most of values ranged from 0.74 to 0.99, apparently, revealing that dissolved organic matter was freshly produced by microbial metabolism in river.

4. **Summary**

1. SUVA values and BIX for whole samplings were less than 1, indicating that the source pollution in the Gaoping River Basin was mainly attributed to the human activity and microbial organic matter produced in the River.

2. For peak fluorescent intensity belonging to humic-like substance, those values in Qishan River, Laonong River and Ailiao River were less than 100. Peak fluorescent intensity belonging to fulvic-like substance, only in Laonong River, was below 100.

3. The average fluorescence intensity in Gaoping River mainstream was the highest value followed by Mino River; however, the lowest existed in Ailiao River.

5. **Acknowledgements**

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6. **References**


