Global Journal of Engineering Science and Research Management

FLUORESCENCE ANALYSIS FOR A RIVER WATER POLLUTION AND WATER TREATMENT PROCESS SELECTION

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Keywords: 3D-excitation emission matrix (3D-EEM), fluorescence, protein-like, humic-like, water treatment process.

Abstract
Using a 3D-EEM, a river water and treated water samples from four cities were detected and analyzed. Fluorescence peaks appeared at excitation wavelength/emission wavelength = 290/320nm and excitation wavelength/emission wavelength = 340/425 nm, which reflects the existence of protein-like and humic-like matters, respectively. The quality of water from river was extremely influenced by human activity. Pollution of downstream was more serious than upstream. Fluorescent organic matters can be hardly removed by the traditional water treatment processes (coagulation, sedimentation and filtration). The advanced treatment technologies (ozonation and biological activated carbon filtration) are more effective. The results indicate that it is feasible to detect water quality rapidly and select water process by fluorescence technology.

Introduction
Fluorescence analysis provides a fast and sensitive method to characterize organic matter in the aquatic environment. 3D-excitation emission matrix has two significant advantages over chromatographic methods: it is fast since it does not need any sample pretreatment and it only requires very small volumes of water sample (<5 mL). More attention to it, which shows the location in optical space of fluorescence centers, is typically observed in river and waste water (Baker et al., 2003; Baker, 2001; Coble et al., 1996). The present research on the fluorescence characteristics of dissolved organic matter (DOM) has become a hot topic for water quality characterization. Fluorescent DOM in the surface water of the estuary were analyzed and the humic-like DOM mainly originated from a terrestrial source was found (Sun, 2014; Wang et al, 2014). The big dams have an environmental impact on fluorescent dissolved organic matter in large rivers that have long hydraulic retention time (Chen et al, 2013). The flow rate has great effect on river water quality by detection of the three-dimensional fluorescence (Xie et al, 2014). Carstea suggested that fluorescence spectra helped to have verified the specific nature of DOM from canal water by fluorescence spectroscopy (Carstea et al, 2014). McEnroe indicated that monitoring organic matter fluorescence properties was sensitive and specific enough for contamination of groundwater (McEnroe et al, 2013). Hambly indicated that increased fluorescence sensitivity could be obtained by online detection system (Hambly et al, 2010). Butturini determined the potential for using fluorescence spectroscopy as a monitoring tool in water treatment plant and distribution systems (Butturini et al, 2013). More studies indicated that fluorescence technique could demonstrate rapidly the organic pollution in the water bodies and replace conventional parameters (Mendoza et al, 2014; Downing et al, 2012).

A river and four cities were selected in this research work. These cities are located along the river. The drinking water is taken from the river and treated by water treatment plant in each city. With the development of the cities, more and more pollutants are discharged into this river. This work is to analyze the river water and treated water to evaluate the water pollution and select water treatment process by 3D-EEM.

Materials and methods
Scope of the research
The four cities are respectively city A, city B, city C and city D from upstream to downstream. A lake with capacity of 17 billion cubic meters is located in upstream. The river annual average flow is 44 billion cubic meters. City A: population of 72200 and fine chemical, food industry. City B: population of 110000 and knitwear and leather industry. City C: population of 120000 and chemical and paper industry. City D: population of 3560000 and comprehensive industry (Figure 1 shows the location of the cities and the river).

Sample collection and pretreatment
The river water samples were taken from the water source zones at different cities. The sampling points of river water R1, R2, R3, and R4 were respectively to be located at city A, city B, city C and city D. The treated water samples were collected from water supply pipes near water treatment plant. The sampling points of treated water T1, T2, T3 and T4 were respectively located at city A, city B, city C and city D.

Global Journal of Engineering Science and Research Management

The water samples were filtered through 0.45 μm membrane filter before the analysis.

Methods for measurements and analysis
Fluorescence 3D-EEM measurements were conducted by using a F97 luminescence spectrophotometer (Shanghai Lengguang Technology Co Ltd). PTM voltage was 500 V, the excitation interval was 10 nm and the emission interval was 1 nm. Both of the excitation and emission wavelengths were varied between 200 and 600 nm and the scan speed was set at 6000 nm/min. Analysis of 3D-EEM data was achieved by origin8.5.

Results and discussion

The 3D-EEM fluorescence spectral characteristics of the river water and treated water
The 3D-EEM fluorescence spectra of the river water and treated water from four cities were shown in Figure 1 and Figure 2. The protein-like and humic-like matters fluorescence contours were plotted. It shows the humic-like fluorescence peaks are located in excitation wavelength/emission wavelength = 320-360/410-430nm and the protein-like fluorescence peaks are located in excitation wavelength/emission wavelength = 270-290/320-350nm (Battin, 1998; McKnight et al, 2001; Baker et al, 2004). The protein-like and humic-like fluorescence peak intensities are shown in Figure 3a, b (the excitation wavelength/emission wavelength of protein-like and humic-like are at 290/320nm and 340/ 425nm, respectively).

The protein-like fluorescence peak of river water R1 from city A is not distinct. It indicates the river water in city A is in good quality. However, downstream from city A, the protein-like fluorescence of river water R2, R3 and R4 appear distinct peaks and higher intensities due to pollution from human activities. The humic-like fluorescence peak of treated water R1 from city A is distinct but low. It indicates the river water in city A contains natural humic-like matters. Downstream from city A, the humic-like fluorescence of river water R2, R3 and R4 appear more distinct peaks and higher intensities.

Comparing to river water R1, R2 and R3, the protein-like fluorescence intensity of treated water T1, T2 and T3 hardly change. However, the sample T4 from city D does not appear distinct protein-like peak. It indicates the protein-like matters were efficiently removed in city D water treatment plant. The humic-like fluorescence intensity of treated water T1, T2, T3 and T4 decreases comparing to river water in corresponding sampling sites. T1 from city A is the lowest, followed by T4, T3 and T2. It indicates the humic-like matters were removed by traditional and advanced water treatment processes, but advanced treatment process is more efficient than traditional treatment process.

Global Journal of Engineering Science and Research Management

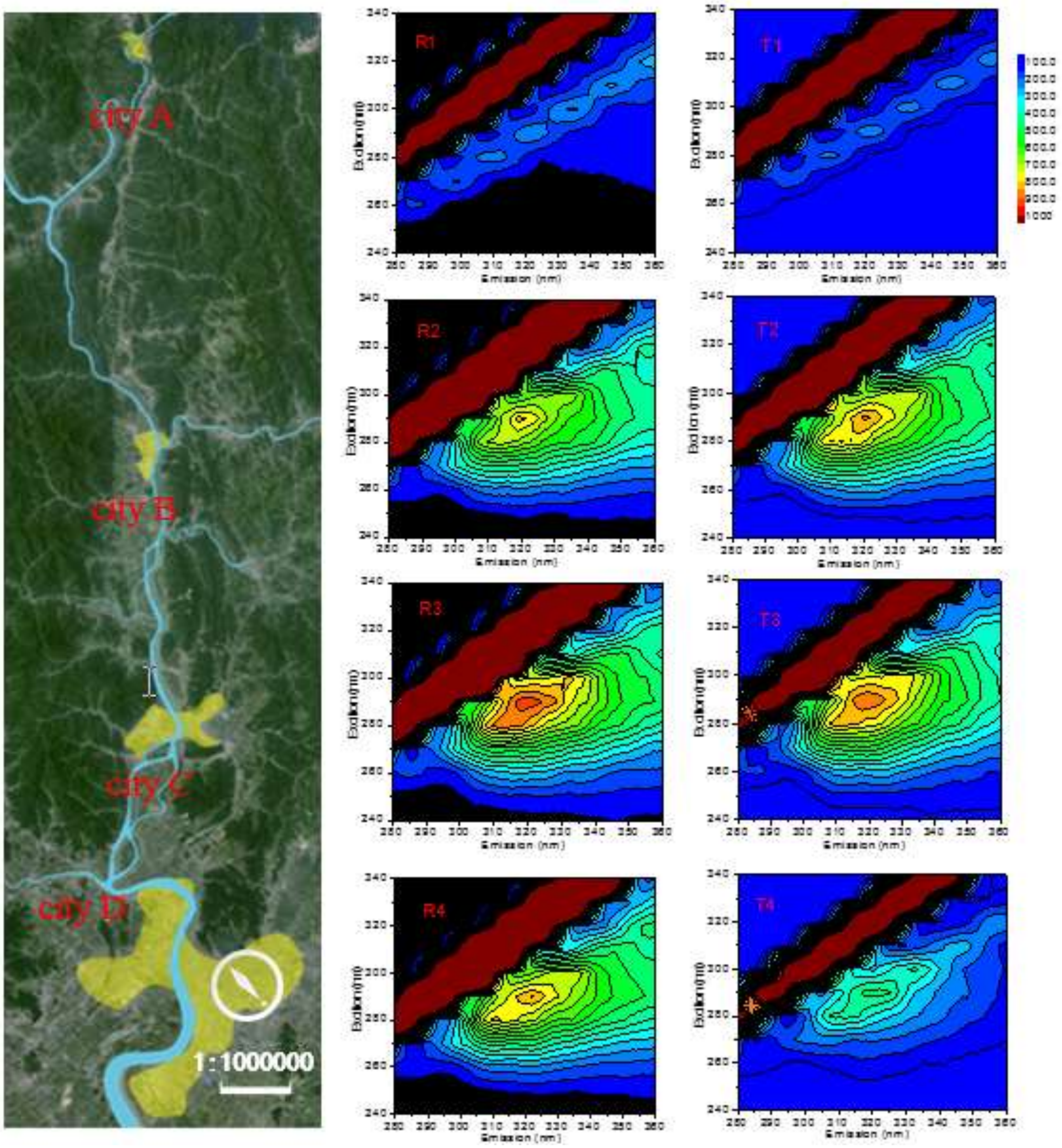

Figure 1 The Protein-Like 3D-EEM Fluorescence Spectral of River Water and Treated Water

Global Journal of Engineering Science and Research Management

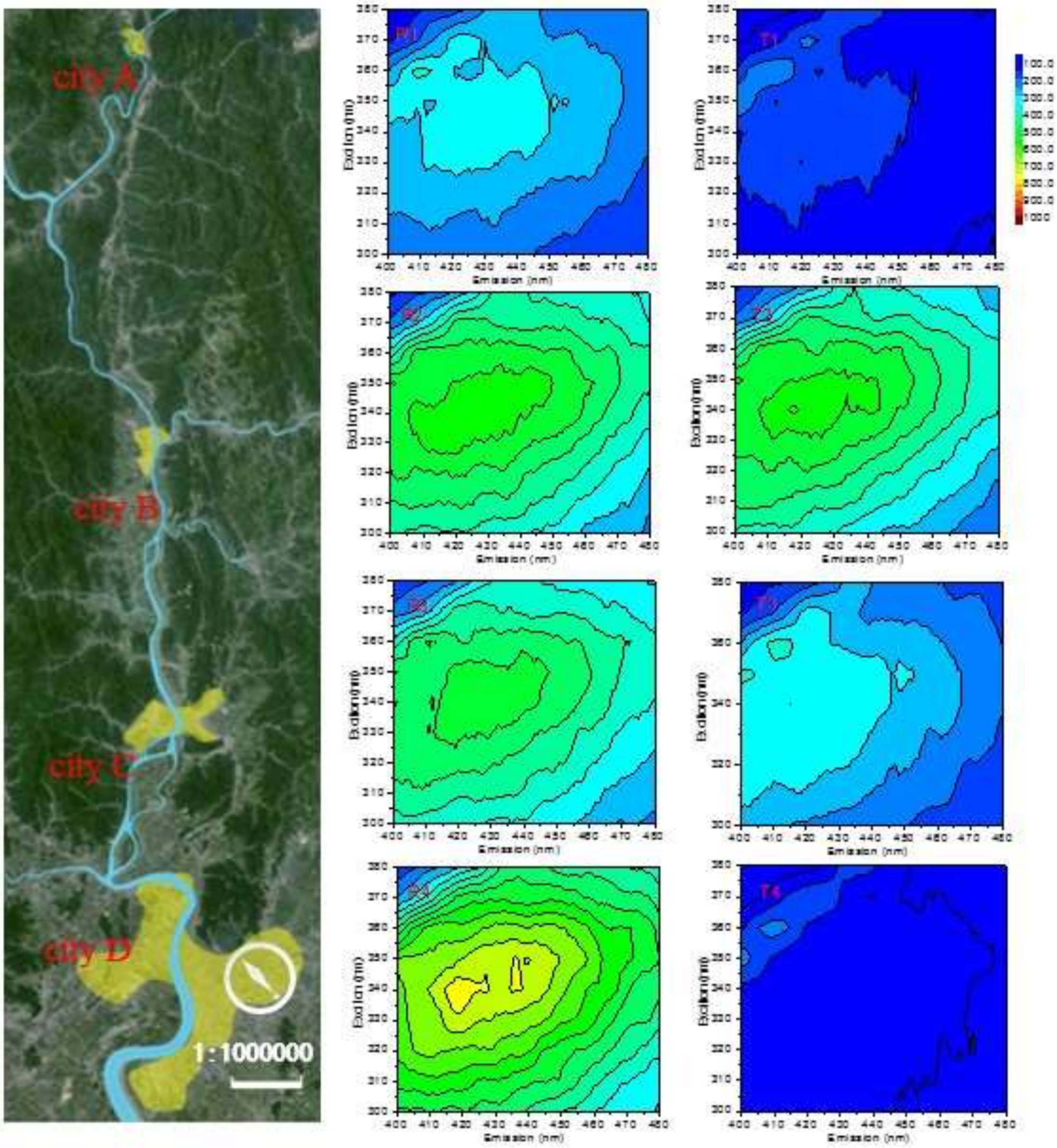

Figure 2 The Humic-Like 3D-EEM Fluorescence Spectral of River Water and Treated Water

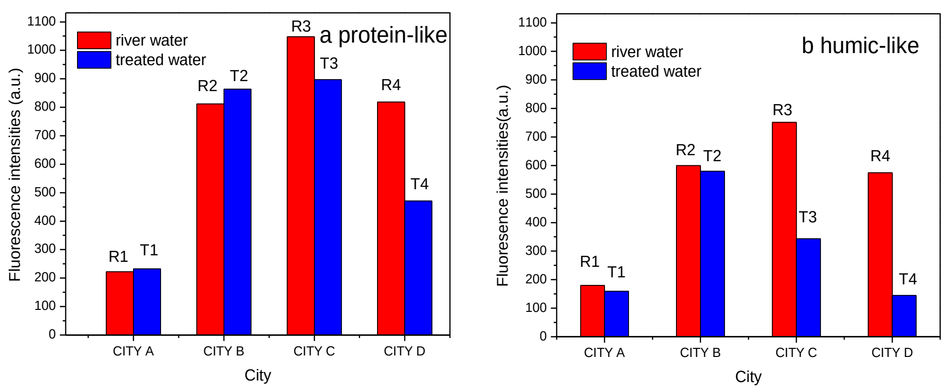

Figure 3 The Fluorescence Intensities of River Water and Treated Water

Global Journal of Engineering Science and Research Management

Characterization of river pollution and selection of water treatment process

The river water in city A is directly from a lake with much water capacity, low pollution and strong ecological self-purification ability. The water quality of river water and treated water is very good in city A though a traditional and sample water treatment process is used.

Treated wastewater from traditional wastewater treatment plant discharged into the river and non-point source pollution which is the main reasons for the increase of the protein-like matters in river water. The increase of protein-like fluorescence intensity in river water in city B is related to the pollution from the effluent from upstream municipal wastewater treatment and the fine chemical factories which is the major industry of city A. Similarly, the inefficient wastewater treatment and leakage of wastewater in city B and city C, especially a lot of paper factories in city C, play a negative effect on river water quality. The river water pollution can be indicated based on the variations of protein-like fluorescence intensities from upstream to downstream.

The humic-like fluorescence peak in river water increase from upstream to downstream, the main reasons may include: pollution of humic-like matters, inflow from farmland and forests, and the sediments release from river bottom due to wider and slower flow in downstream (Rochelle-Newall and Fisher, 2002).

The treated water quality depends on river water quality and water treatment processes. It is not efficient to remove protein-like matters by traditional water treatment processes (coagulation, sedimentation, filtration and disinfection) (Yuan et al, 2008; Han et al, 2013).

Table 1 The Protein-like and Humic-like matters Removal Rate in Different Water Treatment Process

City	Treatment process	Protein-like removal rate (%)	Humic-like removal rate (%)
City A	coagulation, sedimentation, filtration, disinfection	-4.2	+11.6
City B	coagulation, sedimentation, filtration, disinfection	-6.7	+33.3
City C	coagulation, sedimentation, filtration, disinfection	+14.4	+54.2
City D	pre-ozonation, coagulation, sedimentation, filtration, ozonation, BAC filter, disinfection	+42.5	+74.8

The water treatment process of four cities and protein-like and humic-like matters removal rates are shown in table 1, city A, city B and city C used traditional water treatment process, city D used advanced water treatment process. The protein-like matters removal is not efficient in city A, city B and city C, except for city D.

Based on comparison of fluorescence peak of treated water, the quality of treated water by advanced water treatment process (pre-ozonation, coagulation, sedimentation, filtration, ozonation, BAC filter, and disinfection) is better than traditional water treatment process. Organic compounds can be oxidized by ozone and purified by biological activated carbon (Zhang et al, 2006). Advanced water treatment process can effectively improve the water quality for city water supply (Wang et al, 2004).

For good quality raw water, it is feasible to use the traditional water treatment process like city A. It is necessary to select advanced water treatment process for polluted raw water like city B, city C and city D in river downstream. What is more important is to control pollution in river upstream.

Conclusions

The water fluorescence peaks of a river increase from upstream to downstream. It indicates that the quality of water source was polluted by the effluent from each city. The treated water quality depends on the river water and the water treatment process. River water without pollution is easier to supply good treated water. The advanced water treatment process is more efficient than the traditional water treatment processes for removing the fluorescent organic matters. It's feasible to detect the water quality rapidly and select water treatment process using 3D-EEM fluorescence technology.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51478433) and Project of Science and Technology of Zhejiang (2010R50037).

Global Journal of Engineering Science and Research Management

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