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Variation in Optical Properties of Chromophoric Dissolved Organic Matter in A Shallow Lake During Rainy Season

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Variation in optical properties of chromophoric dissolved organic matter (CDOM) in a shallow lake during rainy season was investigated by UV/VIS absorption and fluorescence spectroscopy. Two humic-like components mainly from terrestrial origin (C1 and C2) and one protein-like component derived from autochthonous production (C3) were identified by applying fluorescence excitation-emission matrix combined with PARAFAC modeling. The mean values of autochthonous production and chlorophyll concentration increased from 0.28 to 0.30 µg/L and 165 to 197 µg/L, respectively. Their correlation was different in temporal pattern, demonstrating that the dominant source of autochthonous chromophoric dissolved organic matter was altered from phytoplankton to other sources such as release from sediment and runoff during the rainy season. Mean values of C1 and C2 increased significantly from 0.36 and 0.35 to 0.42 and 0.37 respectively, coupled with a (355) increasing from 2.86 m^{-1} to 3.86 m^{-1} suggesting that precipitation process may increase terrestrial chromophoric dissolved organic matter in the lake. The low values of humification index (HIX) ranging from 3.52 to 4.62 were caused by the dominant origin of autochthonous chromophoric dissolved organic matter, although input of terrestrially-derived chromophoric dissolved organic matter could make mean value of humification index increase from 3.82 to 4.35.

Key Words: Chromophoric dissolved organic matter, Precipitation, Parallel factor analysis, Humification index.

INTRODUCTION

The optically active fraction of dissolved organic matter (DOM) and chromophoric dissolved organic matter (CDOM) is known to play an important role in aquatic ecosystem, influencing the biogeochemical and ecological processes in many environmental compartments[1,2]. Due to its strong absorption of ultraviolet radiation, CDOM can restrict the attenuation of light to protect the living organisms[3]. However, absorption of CDOM at visible wavelength regime overlaps that of phytoplankton, affecting primary productivity and remote sensing of surface water[4-6]. Photochemical reactions of CDOM absorbing UV-B radiation can produce many inorganic carbon and nitrogen compounds, which is the fueling of microbial respiration[7]. Furthermore, variations in optical properties of chromophoric dissolved organic matter can give information about organic pollution degree in aquatic environment[8] and identification of organic pollution sources[9]. Therefore, the behaviour of chromophoric dissolved organic matter has profound impact on biogeochemical cycles, nutrient bioavailability, biological productivity and microbial food web processes in aquatic ecosystem.

Chromophoric dissolved organic matter in aquatic ecosystem consists of a complex mixture of organic compounds including polysaccharides, amino acids, fatty acids and humic substances, which are released by the degradation of terrestrial plants, aquatic macrophytes and phytoplankton[10]. In general, CDOM in natural water originates from two types of sources: allochthonous and autochthonous[11]. The main source for allochthonous CDOM is terrestrial humic substances in runoff, while the autochthonous CDOM production is assigned to microbial and phytoplankton activity[12,13].

As an important natural phenomenon, precipitation can influence the solution chemistry of water bodies depending on catchment's types and land uses, thus change the characteristics of CDOM significantly by rainwater input, runoff scour and other paths[14,15]. Accordingly, studying on source and sink of CDOM during precipitation combined with surrounding environment is helpful to understand the behaviour and effect of CDOM in natural water. Chongming island in the estuary of Yangtze river was exposed to extreme levels of precipitation in rainy season between June and July. Rainy season of the island in 2009 lasted from June 16 to July 10. In this period, the high precipitation with 264.8 mm recorded for this region arose mainly from intense distinct rain events. Qianwei Lake is a shallow lake in the central area of island with water surface area of 50000 m^2 and mean depth of 1.5 m. Due to existence of bank revetment around, Qianwei Lake is regarded to be an enclosed ecosystem, which is sensitive to the influence of terrestrial environment in lake islands. The source of water in Qianwei Lake is only provided by rainwater. So it may be the ideal experimental system to study the dynamic on variation of CDOM characterization during rainy season.

Present study focused on the CDOM composition and identification of its major sources in Qianwei Lake during rainy season in 2009 with the major purpose to provide a better understanding of the variation on optical properties of CDOM during precipitation in natural aquatic environment using the spectral technology. For this purpose, variations of CDOM fluorescence, absorption coefficients and chlorophyll concentration were investigated.

EXPERIMENTAL

Collection of samples: Surface water samples were collected from Qianwei Lake on June 16 and July 10, 2009. Additionally, rainwater, lake water, runoff and pore water at the certain sampling site (QW-3) during continuous precipitation event were collected on July 6, 2009. All water samples in acid-washed sampling bottles were transported to the laboratory as soon as possible and filtered through pre-combusted 0.7 µm Whatman GF/F filters to remove large particles and phytoplankton cells. The accurate positions of all the sampling sites were shown in Fig. 1.

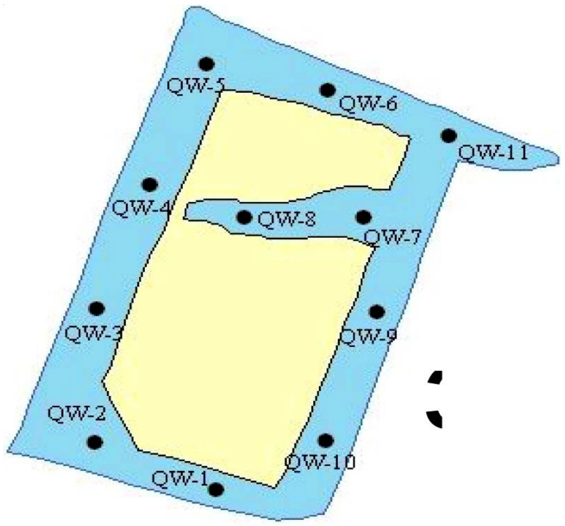

Fig. 1. Map of the study area and sampling stations (QW-1~QW-11) in Qianwei Lake

Measurement of chlorophyll concentration: Chlorophyll concentrations were measured by Phytoplankton Analyzer (Phyto-PAM, Walz, Germany).

Absorption spectroscopy: Chromophoric dissolved organic matter absorption spectra were determined between 200 and 700 nm at 1 nm interval using UV-VIS spectrophotometer (Shimadzu UV-2450) equipped with 1 cm quartz cells. Deionized water was used in the reference cell. All samples were analyzed at least at 20 °C. The absorption coefficients were obtained by:

$$a(\lambda) = 2.303 \cdot A(\lambda)/l$$

where a(λ) was uncorrected CDOM absorption coefficient at a wavelength λ, A(λ) was the absorbance at wavelength λ and l was the cell path length in meters.

Absorption coefficients were corrected for backscattering of small particles and colloids which pass through filters using equation:

$$a(\lambda') = a(\lambda) - a(700) \cdot \lambda/700$$

where a(λ') was absorption coefficient corrected for scattering[16].

Fluorescence spectroscopy: Excitation-emission matrix (EEM) fluorescence spectra were created by measuring fluorescence intensity using fluorescence spectrophotometer (Hitachi F-4500) across excitation wavelengths ranging from 220-400 nm in 3 nm intervals and emission wavelengths ranging from 250-500 nm in 2 nm intervals. Deionized water blank correction was applied to eliminate water-Raman peaks. Excitation-emission matrix were corrected for instrument bias and Raman normalized using the area under the water Raman peak at excitation wavelength 350 nm. The value of humification index was calculated as: Humification index (HIX) = $(\Sigma F_{435/480})/(\Sigma F_{300/345})$, where F was the fluorescence emission intensity for an excitation at 254 nm.

PARAFAC modeling: The PARAFAC analysis was performed in MATLAB6.5 (Mathworks), using the "N-way toolbox for MATLAB version 2.0", with default numerical settings[9]. Introduction and realization of the PARAFAC model refer to previous study[17]. This study gave a data array of size 22 samples × 61 excitations × 125 emissions. Results of the PARFAC model were highly sensitive to the number of components. In this study, several methods were used to select appropriate number of components including jack-knife technical, split-half analysis and examination of residual error plots. Finally, three components was a proper component number for the PARAFAC model.

RESULTS AND DISCUSSION

PARAFAC model results: The PARAFAC model validated three independent components in this study, which should be viewed as the dominant fluorescence groups identified by PARAFAC (Fig. 2). These components had two excitation spectral peaks and single emission peak. C1, C2 and C3 present fluorescence centers at Ex/Em wavelength pairs of 232(310)/412 nm, 262(352)/472 nm and 238(280)/340 nm, respectively. Table-1 listed excitation/emission characteristics of both the components and corresponding components in other researches. Chromophoric dissolved organic matter derived from different aquatic environment in previous studies had similar fluorescence components focused on humic-like and protein-like substance. In the present study, C1 has been identified as representing marine original humic-like substance and present also as potential terrestrial humic-like substance related to microbial reprocessing[17]. C2 was humic-like substance mainly from terrestrial source which is common in river, marine and lake environments. Its excitation/emission characteristic was associated with terrestrial organic matter that is composed of high molecular weight and aromatic organic compounds[18,19]. C3 presented a similar fluorescence peak close to autochthonous protein-like compound derived from biological production and activity of microorganisms[19].

TABLE-1
SPECTRAL CHARACTERISTICS OF THE FLUORESCENT COMPONENTS IDENTIFIED BY PARAFAC MODELING COMPARED WITH PREVIOUSLY IDENTIFIED COMPONENTS

Component	Excitation (nm)	Emission (nm)	Previously identified components				Description
			Lapierre *et al.*[1]	Murphy *et al.*[17]	Kowalczuk *et al.*[15]	Wang *et al.*[9]	
C1	232 (310)	412	C7	C2	C3	C1	Humic-like substance
C2	262 (352)	472	C2	C3	C4	C2	Humic-like substance
C3	238 (280)	340	C8	C7	C6	C3	Protein-like substance

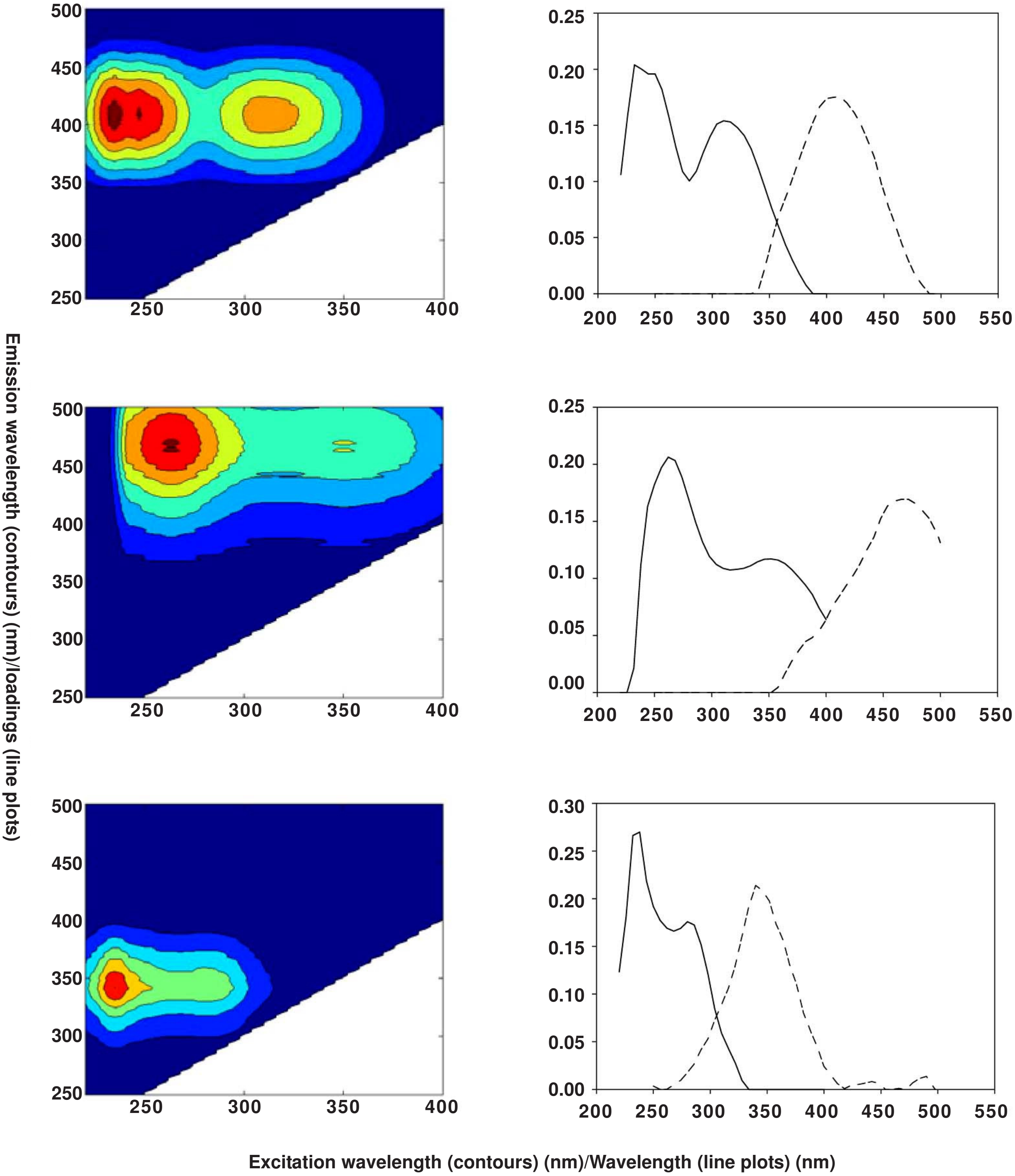

Fig. 2. Excitation (solid lines), emission (dotted lines) loadings and contour plots of fluorescent components

TABLE-2
CHLOROPHYLL CONCENTRATION AND OPTICAL PROPERTIES OF CDOM IN QIANWEI LAKE DURING THE RAINY SEASON

	Chl-a (µg/L)		a355 (nm^{-1})		C1 (R.U.)		C2 (R.U.)		C3 (R.U.)		HIX	
	6-16	7-10	6-16	7-10	6-16	7-10	6-16	7-10	6-16	7-10	6-16	7-10
QW-1	179.93	186.51	2.99	3.45	0.39	0.43	0.36	0.37	0.30	0.31	3.82	4.13
QW-2	140.47	200.80	2.88	3.80	0.36	0.42	0.36	0.37	0.26	0.30	4.01	4.13
QW-3	135.76	155.89	2.72	3.68	0.35	0.42	0.36	0.37	0.22	0.31	4.24	4.25
QW-4	138.22	156.07	2.97	3.80	0.36	0.42	0.36	0.37	0.24	0.30	4.29	4.59
QW-5	146.09	178.29	2.68	3.68	0.36	0.42	0.35	0.37	0.24	0.29	4.33	4.60
QW-6	186.17	178.91	3.11	3.45	0.36	0.41	0.36	0.38	0.31	0.33	3.52	4.03
QW-7	160.13	221.64	2.70	4.15	0.38	0.43	0.36	0.39	0.30	0.32	3.65	4.34
QW-8	158.95	189.53	2.84	4.15	0.37	0.43	0.35	0.39	0.26	0.30	3.81	4.57
QW-9	165.29	220.96	2.55	4.03	0.34	0.41	0.35	0.38	0.33	0.28	3.55	4.37
QW-10	177.99	215.91	2.63	3.92	0.34	0.42	0.33	0.38	0.26	0.27	3.57	4.62
QW-11	231.57	263.72	3.34	4.38	0.35	0.42	0.35	0.38	0.35	0.33	3.24	4.17

Spatial and temporal variability of chlorophyll concentration, fluorescence components and absorption coefficient during rainy season: Chlorophyll concentration and parameters of optical properties to quantify variability of CDOM in Qianwei Lake were given in Table-2. A wide range of variability in chlorophyll concentration was found ranging from 155.89 to 320.72 µg/L. On average, chlorophyll was at lower level on June 16, 2009 (165 µg/L) than on July 10, 2009 (197 µg/L). These results suggested high primary productivity and temporal heterogeneity in the lake. The values of components were used to quantify fluorophore's concentration in present study. The mean value of C3 was consistent with the trend observed for chlorophyll increasing from 0.28 to 0.30. The highest value of chlorophyll concentration and C3 both appeared at QW-11. According to Rochelle-Newall *et al.*[10], biological degradation of phytoplankton-derived material was associated with CDOM production. Zhang *et al.*[11] discovered that phytoplankton blooms were indeed an important source of CDOM in eutrophic lakes with high phytoplankton biomass. In accordance with these studies, we found a relationship (r^2 = 0.36, $p < 0.01$) between chlorophyll concentration and C3 (Fig. 3), indicating that their changes may be synchronous. In this study, C3 was represented by protein-like compound, which was frequently associated with autochthonous CDOM production. Hence, present result implied that phytoplankton was the important contributor and material foundation of autochthonous CDOM production in Qianwei Lake. Analyzed temporal separately, more significant correlation (r^2 = 0.66, $p < 0.01$) between chlorophyll concentration and C3 was found in June 16, 2009 while non-significant correlation was discovered at July 10, 2009 (regression not shown), suggesting that although the important contributor of protein-like matter was phytoplankton, other sources may affected C3 more than phytoplankton by the influence of precipitation. As seen from Fig. 4, compared to lake water, strong protein-like fluorophore was found in pore water and runoff from soil while no distinct protein-like fluorophore was observed in rainwater, suggesting that release from sediment and runoff generated by heavy rainfall could be the additional source of C3.

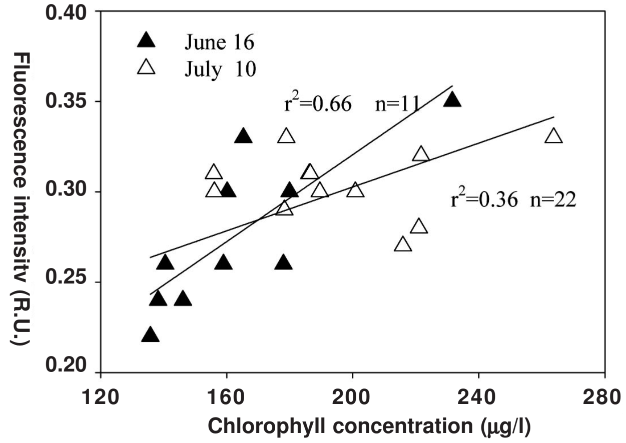

Fig. 3. Correlation between chlorophyll concentration and C3 among the 22 samples in Qianwei Lake

As seen from Table-2, there were remarked differences in temporal pattern for a(355) and terrestrially-derived components. Abundance of a(355), C1 and C2 in all samples were lower on June 16, 2009 than on July 10, 2009. Mean values of C1 and C2 increased from 0.36 to 0.42 and from 0.35 to 0.37, respectively, accompanying the increase of a355 from 2.86 to 3.86 m^{-1}. Furthermore, a(355) had significant correlations with C1 (r^2 = 0.76, $p < 0.01$) and C2 (r^2 = 0.70, $p < 0.01$) from Fig. 5, which demonstrated that a direct and stable relationship between humic-like fluorescence and a(355), thus that humic-like fluorescence was representative of CDOM absorbance in Qianwei lake in consistence with previous literature[20]. Among all the samples, QW-7 and QW-8 had highest values of C1 and C2 on July 10. This could be explained by their location features, which made QW-7 and QW-8 received more terrestrial CDOM from both islands than others. Among many literatures about the origin of CDOM, terrestrial-derived CDOM was thought to be an essential part of the CDOM pool in aquatic environments[21]. Especially during rain event, rainfall runoff can transport large quantities of CDOM leached from soils into adjacent surface waters[15]. In agreement with these studies, our study suggested that precipitation process may increase terrestrial-derived CDOM, thus change the CDOM composition in the aquatic ecosystems obviously. The average increase (extremes) of C1 during rainy season was about 17.07 % (10.26-23.53 %), which was much higher than C2 with 6.77 % (2.78-15.15 %). The result may be related to the difference about their composition and source. Although the dominant source of C1 and C2 was derived from terrestrial environment, C2 had excitation and emission maxima at longer wavelength compared to C1, which meant C2 was more complex and aromatic but less mobile component. Thus C2

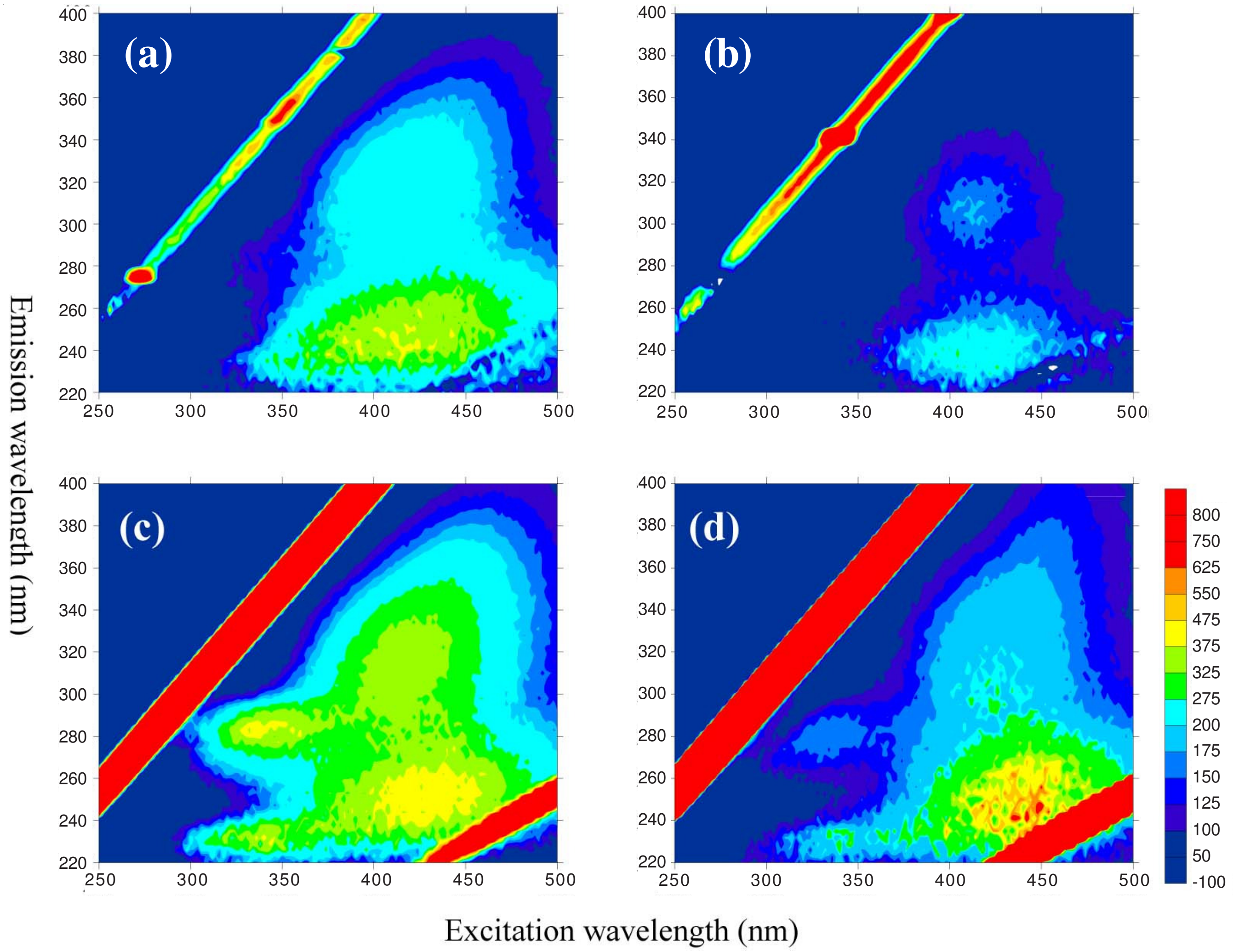

Fig. 4. Typical EEM fluorescence plot detected at sample station QW-3 (July 6) for (a) surface water; (b) rain water; (c) pore water; (d) runoff from soil

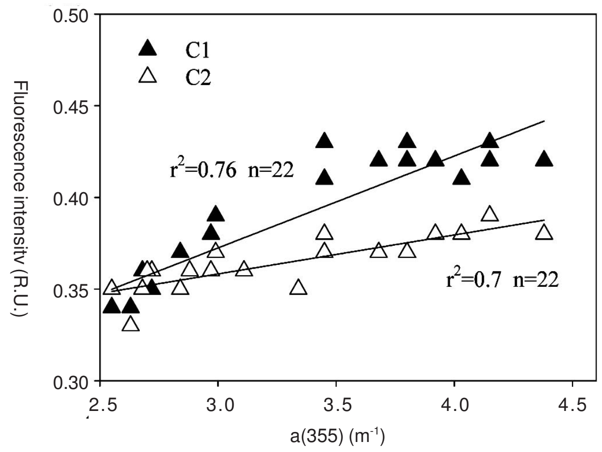

Fig. 5. Correlation between a(355) and C1,C2 among the 22 samples in Qianwei Lake

was preferentially retained in soil[22]. Besides that, it is also found that stronger fluorescence peak similar to C1 exists in rainwater and pore water (Fig. 4), indicating that appearance of other sources may be additional factor to make C1 increase higher than C2.

Variability of humification index value during rainy season: Additional parameter HIX was applied to characterize the CDOM pool. Humification index was introduced to measure the degree of humification with CDOM. High HIX value was related to high C/H ratio and presence of complex and allochthonous organic molecules, while low value is consistent with the majority of the CDOM being mainly composed of autochthonous molecules[23]. Huguet *et al.*[24] pointed that high HIX values in the range of 10 and 16 were the sign of strongly humic organic matter mainly from terrestrial origin while low values (< 4) were associated with autochthonous organic matter. In our study, the mean value of HIX increased from 3.82 to 4.35 during rainy season (Table-2), suggesting the increase of complex and allochthonous CDOM in the lake. However, all the low HIX value ranging from 3.52 to 4.62 indicated that the CDOM characteristic in the lake still corresponded well to autochthonous production despite of increase of terrestrial-derived CDOM. This was also proved by relationship between HIX and fluorescence components (Fig. 6). Non-significant relationship was found between HIX and terrestrial-derived components (C1 and C2). Autochthonous CDOM (C3) had significant correlation with HIX values if analyzed temporal separately. The relationship between HIX and C3 was weak for all samples (regression not shown), but was greatly improved when the values of C3 on June 16 (r^2 =

0.76, $p < 0.01$) and on July 10 ($r^2 = 0.48$, $p < 0.01$) were regressed separately (Fig. 5). Different correlations suggested the change in CDOM composition by the impacts of precipitation, owing to complex sources of protein-like materials and input of humic matter caused by precipitation. Our result further supported Huguet et al's theory[24], implying that as representation of autochthonous CDOM in our study, C3 can affect HIX with low value (< 4) more than other allochthonous components.

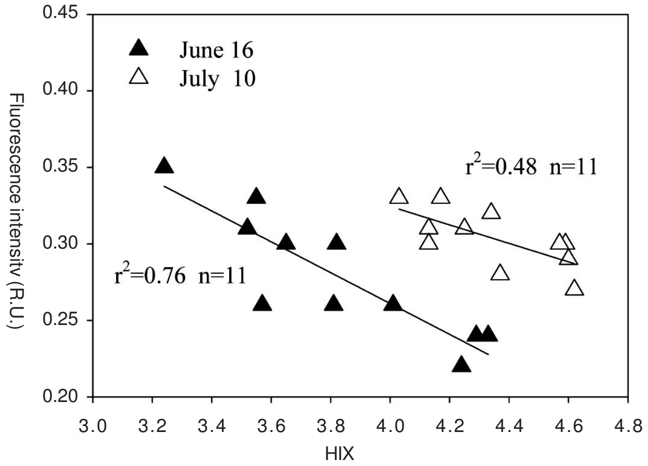

Fig. 6. Correlation between HIX and C3 among the 22 samples in Qianwei Lake

Conclusion

Variability of CDOM optical properties during rainy season in Qianwei Lake was investigated. Two humic-like components and one protein-like component were identified by PARAFAC modeling. The dominant source of protein-like component was altered from phytoplankton to other sources such as release from sediment and runoff during rainy season. Terrestrial-derived CDOM in the lake increased significantly with a(355) by the influence of precipitation. The low HIX value in the lake was caused by the dominant production of autochthonous CDOM despite of increasing input of terrestrial-derived CDOM. In general, the present study demonstrated that precipitation may change the CDOM composition in the aquatic ecosystems obviously and that fluorescence spectroscopy combined with PARAFAC modeling is a sensitive tool to characterize the variation of DOM composition.

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