

# Environmental characteristics and changes of sediment pore water dissolved organic matter in four Chinese lakes

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**Abstract** Sediment pore waters were examined in four Chinese lakes (Bosten, Qinghai, Chenghai and Dianchi) to characterise the sources of dissolved organic matter (DOM) and their microbial changes in the sediment depth profiles. Parallel factor (PARAFAC) modelling on the sample fluorescence spectra confirmed that the pore water DOM was mostly composed of two components with a mixture of both allochthonous and autochthonous fulvic acid-like substances in three lakes, except Lake Dianchi, and protein-like components in Lake Bosten. However, DOM in Lake Dianchi was composed of three components, including a fulvic acid-like, and two unidentified components, which could originate from mixed sources of either sewerage-impacted allochthonous or autochthonous organic matter (OM). Dissolved organic carbon (DOC) concentrations were typically high (583–7410  $\mu\text{M}$  C) and fluctuated and increased vertically in the depth profile. The fluorescence intensity of the fulvic acid-like substance and absorbance at 254 nm increased vertically in the sediment pore waters of three lakes. A significant relationship between DOC and the fluorescence intensity of the fulvic acid-like component in the sediment pore waters of three lakes, except

Lake Dianchi, suggested that the fulvic acid-like component could significantly contribute to total DOM and could originate via complex microbial processes in early diagenesis on OM (*ca.* phytoplankton, terrestrial plant material) in these lakes. Pore water DOM components could therefore be a useful indicator to assess the DOM sources of the lake sediment during sedimentation over the past several decades, which have been heavily affected by ambient terrestrial vegetation and human activities.

**Keywords** Sediment pore waters · Dissolved organic matter · Fluorescent dissolved organic matter · PARAFAC modelling · UV absorbance · Fulvic acid-like component

## Introduction

The organic matter (OM) in dissolved and particulate forms of lake sediments originates from two major pathways. First, phytoplankton produced in lake epilimnion water could deposit as sediments on the lake floor (Bernasconi et al. 1997). Sediment-trap studies demonstrated that approximately 1 to 35% of the organic carbon synthesised in the photic zone reached the sediment surface in marine and lacustrine waters (Bernasconi et al. 1997; Hernes et al. 2001; Lehmann et al. 2002). Note that photosynthesis mostly depends on several important factors such as contents of dissolved organic matter (DOM), nutrients, water temperature, residence time, depth of the lake water, global warming, river runoff and water pollution (Mostofa et al. 2013). Second, the terrestrial runoff via rivers may bring the terrestrial organic material and organic pollutants resulting from anthropogenic (human) activities at and around the watershed areas to deposit them in the lake sediment layer (Thomsen et al. 2004). This process mostly depends on land management and natural effects

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(precipitation, flood and drought), and types and nature of terrestrial plant material in soil in the lake watershed (Mostofa et al. 2013). OM in sediments is of great importance because of its release of several classes of organic substances, nutrients and other chemical components under microbial or other oxidation processes either in surface waters or sediment depths (Fu et al. 2006; Thomsen et al. 2004; Aoki et al. 2008). It has been demonstrated that OM, such as plant material, algae (e.g., phytoplankton) and bacterial polymers, are decomposed extensively at different rates at different sediment depths (Thomsen et al. 2004; Harvey et al. 1995). Degradation rates of plant material generally depend on type, ages, densities and structural compositions of terrestrial plants (Harvey et al. 1995; Kristensen et al. 1995). Studies demonstrate that autochthonous and allochthonous organic matter sources are generally regarded as fast and slowly decomposing organic carbon, respectively, in lake sediment profile (Gudasz et al. 2015). Therefore, the sources of organic substances produced from sediments might be greatly varied, and thus, identification of organic components could be a useful indicator to understand the environmental conditions in and around the water ecosystem. It is evidenced that the compositions of sediments generally reflect the environmental conditions in and around a water body during deposition (Routh et al. 2004). The key importance of lake sediment pore waters is the redistribution of its bottom sediment-origin DOM and chemical compositions with entire lake waters during the winter convective mixing (Kim et al. 2006; Li et al. 2008; Mostofa et al. 2005; Weiss et al. 1991). This, subsequently, may influence all lake water properties that affect the photosynthesis and water quality in the lake ecosystem.

Currently, DOM compositions in natural waters are optically characterised by fluorescence (excitation-emission matrix, EEM) spectroscopy along with the parallel factor (PARAFAC) analysis on the sample fluorescence spectra (Cory and McKnight 2005; Borisover et al. 2009; Kowalczuk et al. 2009; Mostofa et al. 2010; Stedmon et al. 2003; Yamashita and Jaffe 2008). Currently, the PARAFAC model has been applied to identify and separate various DOM components and to understand the biogeochemical changes of those components in natural waters (Cory and McKnight 2005; Borisover et al. 2009; Kowalczuk et al. 2009; Stedmon et al. 2003), including interactions between trace elements and DOM (Yamashita and Jaffe 2008), sources along with seasonal variation of DOM and extracellular polymeric substances (EPS) (Stedmon et al. 2007a; Mostofa et al. 2010; Shammi et al. 2017a), degradation effects on DOM and EPS (Stedmon and Markager 2005; Mostofa et al. 2010; Shammi et al. 2017b) and formation mechanism of transparent exopolymer particles/floc from EPS under the irradiation processes (Shammi et al. 2017b). The combination of fluorescence and PARAFAC was, therefore, applied to distinguish the DOM components in lake pore water sediments in this

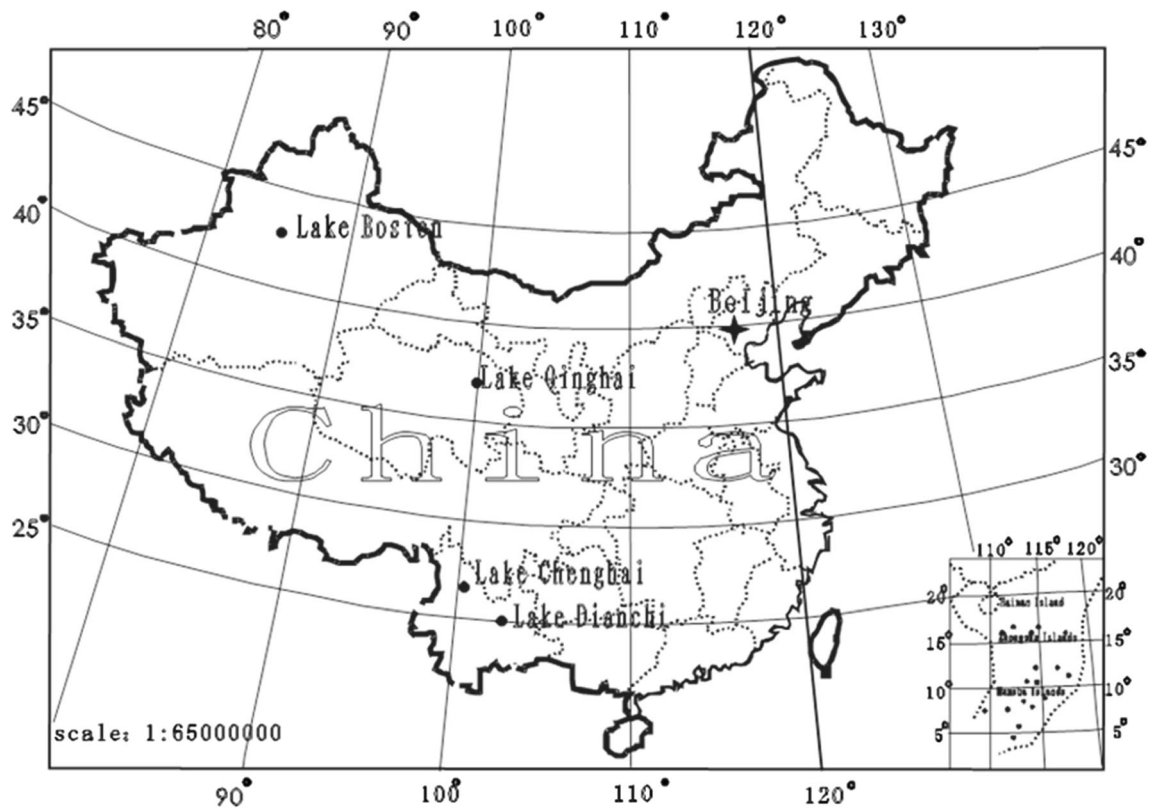
study. On the other hand, the UV absorbance at 254 nm ( $UVA_{254}$ ) represented the total contents of DOM because of their significant correlation between dissolved organic carbon (DOC) concentrations and  $a_{254}$  (Edzwald et al. 1985; Fu et al. 2006). In addition, the specific ultraviolet absorbance at 254 nm ( $SUVA_{254}$ ) normalised to DOC concentration was correlated with aromatic the contents of DOM, whereas low  $SUVA_{254}$  values typically reflected the autochthonous production or in situ transformations of DOM in the aquatic environments (Traina et al. 1990; Weishaar et al. 2003). Few studies have been conducted to investigate the composition and contents of low molecular weight organic acids in the sediment pore waters of these Chinese lakes or to determine the climate history, environment changes, and the trophic states of these lakes using sediment isotopic methods (Xiao et al. 2009; Zhang et al. 2002). The characterisation of DOM components and their sources in lake sediment pore waters is vital to better understand the sediment sources, the dynamics of pore water DOM and long-term changes in the biogeochemical processes of the lake watershed environments.

This study choose four Chinese lakes in different locations to compare and to distinguish the autochthonous and human-induced allochthonous DOM for better understanding of in and around past environmental history of the lake ecosystem. The aim of this study is to examine the DOM sources in sediment pore waters in four Chinese lakes (Bosten, Qinghai, Chenghai and Dianchi) using fluorescence and PARAFAC modelling. Determination of the fluorescence properties and  $UVA_{254}$  or  $SUVA_{254}$  in vertical sediment depths will provide the differences and changes in the fluorescent components, and aromaticity of pore water DOM over the last several decades. Finally, this study also distinguishes the allochthonous and autochthonous fulvic acid-like components of different origins in the sediment pore waters of different depth profiles.

## Materials and methods

### Site description

The samples of the sediment pore waters were collected from four lakes (Bosten, Qinghai, Chenghai and Dianchi) located from north to south of China (Fig. 1). The geographical locations and the hydrologic parameters of these lakes are presented in Table 1. Lake Bosten is the largest inland freshwater lake in China and the lake watershed areas typically belong to a strong inland desert climate with low temperatures, low rainfall and one of the four main reed regions in China (Zhong and Shu 2001). The hydraulic retention time of this lake was 4.7 years. It was reported that the chlorophyll *a* concentration was  $184 \mu\text{g L}^{-1}$  in 2006 in Lake Bosten (<http://www.stats.gov.cn/tjsj/qtsj/hjtjzl>). Lake Qinghai is the largest inland saline



**Fig. 1** Four Chinese lakes and sampling sites from which sediment pore water samples were collected in 2006

lake in China, located at the northeast of the Tibet Plateau. The climate along the lake location is generally semi-arid with a long cold season. The mean water level from the ice, cloud and land elevation satellite (ICESat) rose 0.67 m from 2003 to 2009 with an increase rate of 0.11 m/year (Zhang et al. 2011). It is reported that the chlorophyll *a* concentration is 0.5–1.2  $\mu\text{g L}^{-1}$  (Zhu et al. 2005). Lake Chenghai is a tectonic fault lake formed in the Early Pleistocene and a closed inland plateau deep-water lake. The average water temperature of this lake is 15.9 °C and the average annual rainfall is 738.6 mm. The lake usually shows a long hydraulic retention time (Wan et al. 2005). It is reported that the chlorophyll *a* concentration is 0.7  $\mu\text{g L}^{-1}$  (Zhang et al. 2009a, b). Lake Dianchi is located on the western side of the Kunming Basin in the Central Yunnan Plateau. The inflowing rivers run through farmlands, cities and phosphorite areas before reaching the lake. The lake

is severely polluted and has become eutrophic because of the input of domestic sewerage and industrial effluents from Kunming City (Zhu 2004). It was also reported that the chlorophyll *a* concentration was 3–475  $\mu\text{g L}^{-1}$  and the hydraulic retention time was 2.7 years (Li et al. 2009). The evaporation rates in the regions of Lakes Bosten and Qinghai in Northwest China is 3.8 times greater than the rainfall, and the salinity increased accordingly (Jin et al. 1990).

**Sampling**

Approximately 50–80-cm-long sediment cores were obtained in these four lakes using a portable gravity corer (with a tube of 10 cm in diameter and 100 cm in length). The sediment cores were collected from the deepest water area of these four lakes in early summer or autumn, 2006. Sediment/water

**Table 1** The hydrological characteristic parameters in four Chinese lakes

Sampling date	Lakes	Reservoir capacity ( $\times 10^8 \text{ m}^3$ )	Trophic level	Maximum depth (m)	Catchment area ( $\text{km}^2$ )	Lake water area ( $\text{km}^2$ )	Elevation (m)	Latitude (N)	Longitude (E)
September 2006	Bosten	88	Mesotrophic	16	55,597	1067	1045	41°47'–43°21'	82°58'–86°55'
August 2006	Qinghai	7380	Oligotrophic	27	29,660	4400	3193	36°15'–38°20'	97°50'–101°20'
May 2006	Chenghai	20	M-Eutrophic	35	229	79	1503	26°27'–26°38'	100°38'–100°41'
May 2006	Dianchi	16	Eutrophic	8	2920	311	1889	24°40'–25°02'	102°36'–102°47'

interface was markedly separated, whereas the cores were undisturbed during the sampling processes. The drill core was sliced into 1-cm sections in the field at 1-cm intervals. Hand gloves were used to prevent any contamination while slicing the cores from the gravity corer. All samples were added to 50-ml centrifuge tubes, and the tubes were all sealed and kept frozen. All samples were transported to the laboratory and pore waters were extracted from the sediments using centrifugation (3500 rpm for 20 min) at 4 °C kept under dark conditions to refrain from any light-induced effects on pore water DOM. The samples were then stored in a freezer (−20 °C) and analysed within 1 week. The pore water samples were filtered through 0.45-µm cellulose acetate membranes and kept in well-sealed 15-ml centrifuge tubes at 4 °C under dark conditions before analyses.

### Analytical methods

DOC was measured by high-temperature catalytic oxidation, with a High TOC/TN Analyser (Model: High TOC II, Elementar, Germany). Potassium hydrogen phthalate was used as a standard. The relative standard deviation (RSD) of the replicate measurements ( $n = 5$ ) of DOC was less than 2%, and the detection limit was 16 µM. UV absorbance measurements were carried out on a Shimadzu UV-3000 double-beam spectrophotometer at room temperature with 1 cm quartz cells. Milli-Q water was used as the reference. The measured absorbance at wavelength  $\lambda$  ( $A_\lambda$ ) was converted to an absorption coefficient ( $a_\lambda$ ) with the equation  $a_\lambda = 2.303A_\lambda/l$ , where  $l$  is the cell path length, and specific UV absorption  $SUVA_{254} = a_\lambda/DOC$ . The fluorescence properties were measured using a fluorescence spectrophotometer (Hitachi, Model F-4500) with a 150-W ozone-free xenon arc lamp and a 1-cm quartz cell. The fluorescence spectra were collected at an excitation wavelength ranging from 200 to 400 at 5-nm increments and at an emission wavelength ranging from 250 to 550 at 2-nm increments using a scanning speed of 1200 nm min<sup>−1</sup>. The fluorescence measurements were operated under the conditions of 5 nm slit width for excitation and 10 nm slit width for emission at room temperature and photomultiplier voltage of 700 V. Milli-Q water was measured as a blank. The sensitivity and instrumental response for corrected spectra was performed as according to the company's guidelines and to Coble et al. (1993). For normalisation of fluorescence, we used a quinine sulphate (QS) solution of 4 µg L<sup>−1</sup> in 0.01 N H<sub>2</sub>SO<sub>4</sub>. The fluorescence intensities of all samples were calibrated using intensity (1 µg L<sup>−1</sup> = 1 QS unit, QSU) at the peak (Ex/Em = 350/450 nm) for QS standard. The fluorescence index ( $F_{index}$ ) determined in an earlier study (Mostofa et al. 2013) is the ratio of the fluorescence intensity at peak A-region (Ex/Em = 250/440–450 nm) divided by the fluorescence intensity at peak C-region (Ex/Em = 330/440–450 nm); whereas, the average

fluorescence intensity of emission wavelengths (440–450 nm) were used. Note that differences in the  $F_{index}$  values in the earlier study (McKnight et al. 2001) were due to its application in the original fluorescence spectra, which are the compact of all fluorescent components studied in samples. Currently, fluorescent components are identified from fluorescence spectra using PARAFAC modelling in all reported studies and it is, therefore, important to characterise the allochthonous and autochthonous fluorescent components to apply the new  $F_{index}$  values.

### PARAFAC modelling

Parallel factor (PARAFAC) modelling is a three-way multivariate statistical analysis which is extensively used on EEM spectra to isolate and quantify the individual fluorescence component in terms of fluorescence intensity by decomposing the fluorescence matrices (Stedmon et al. 2003; Mostofa et al. 2010). The PARAFAC analysis was performed in MATLAB using the N-way Toolbox for MATLAB version 3.1 with methods described elsewhere (Stedmon et al. 2003). The data fluorescence spectra of the samples were modelled with an excitation wavelength ranging from 200 to 400 nm every 5 nm and emission wavelength from 280 to 550 nm every 2 nm. To avoid the mix up of components with a variety of lake samples, the PARAFAC model was used on each lake pore water sample's fluorescence spectra separately. The detailed procedures for PARAFAC modelling were reported elsewhere (Mostofa et al. 2010).

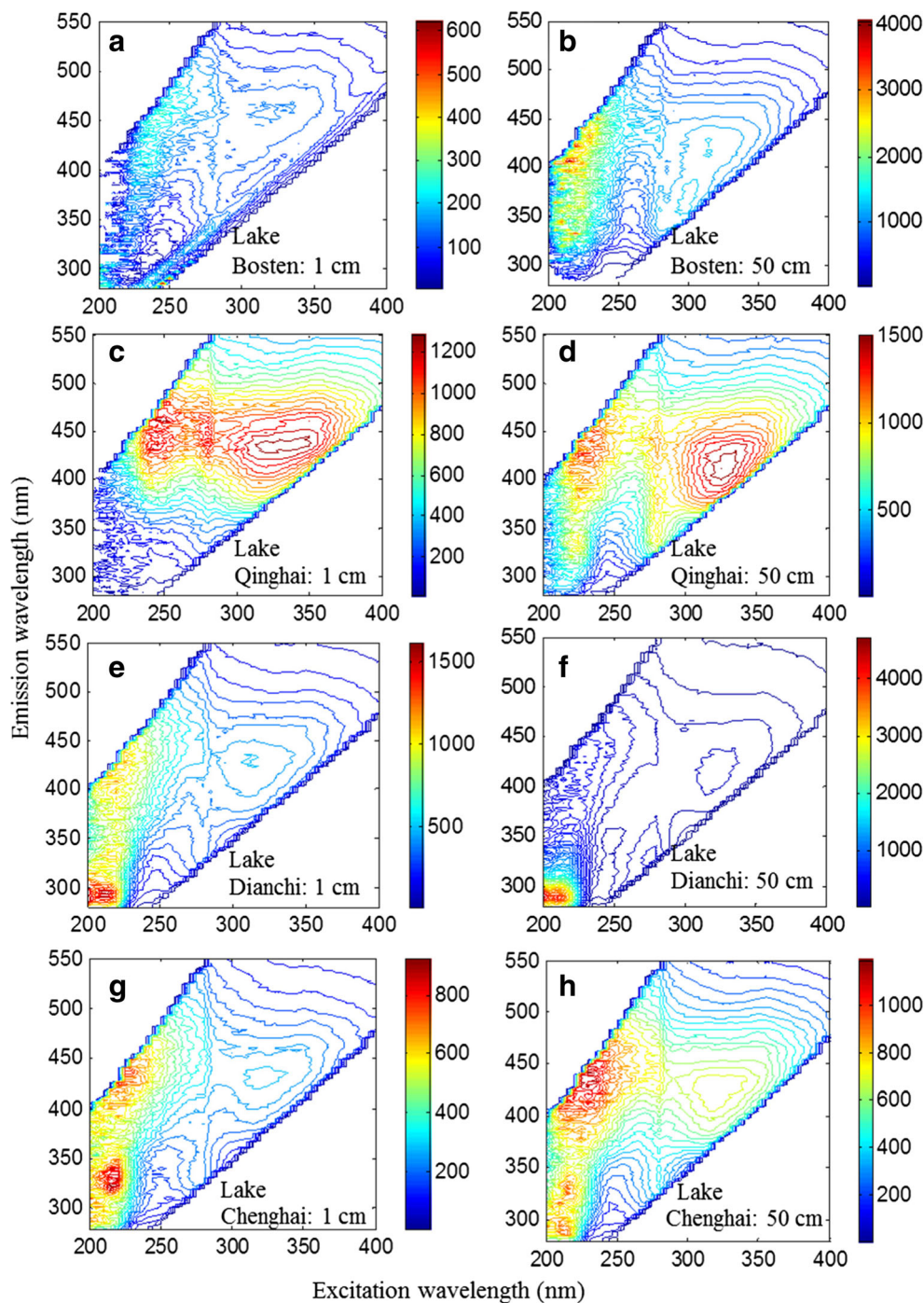
## Results and discussion

### Characterisation of FDOM components and their sources in sediment depth profiles

#### Lake Bosten

The fluorescence images of the sediment pore waters at 1 and 50 cm depths in four lakes are presented in Fig. 2. The fluorescent components of Lake Bosten pore waters identified using PARAFAC modelling on sample fluorescence spectra are depicted in Fig. 3. Two components were detected in each upper (1–20 cm), middle (21–40 cm) and deeper layers (41–50 cm) of sediment pore waters in Lake Bosten. Component 1 (Fig. 3a–e) showed two fluorescence peaks (peak C at 315/436 nm and peak A at 260/436 nm in 1–20 cm; peak C at 330/460 nm and peak A at 270/460 nm in 21–40 cm; peak C at 315/436 nm and peak A at 250/436 nm in 41–50 cm, respectively, Table 2). Component 1 in upper pore waters thus corresponded to an allochthonous fulvic acid-like component by comparison with fluorescence images and peak position of the standard Suwannee River Fulvic Acid (SRFA): peak C at

**Fig. 2** a–h Typical examples of the fluorescence spectra of sediment pore waters collected from four Chinese lakes

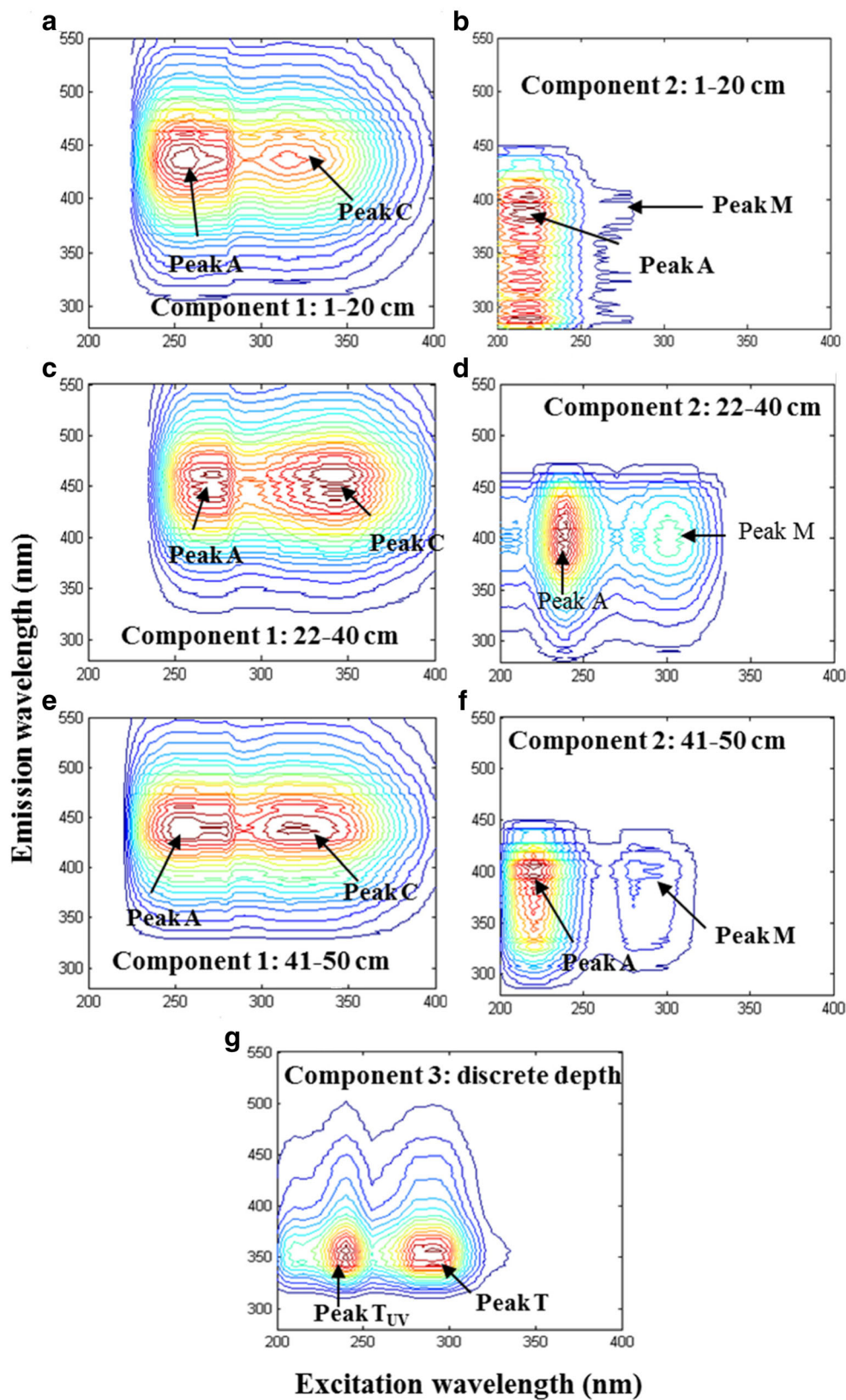


325–330/442–462 nm and peak A at 230–255/441–462 nm and standard Suwanee River Humic Acid (SRHA): peak C at 320–350/461–498 nm or 300–320/440–461 nm and peak A at 255–280/430–461 nm or 230/436 nm when they were dissolved in Milli-Q waters (Table 2; Mostofa et al. 2013). The fluorescence images of component 1 showed relatively low fluorescence intensity of peak C compared to peak A showing higher  $F_{index}$  values than one ( $F_{index} = 1.29$  for standard SRFA and  $F_{index} = 1.25$  in 1–20 cm depth and vice versa for phytoplankton showing lower  $F_{index}$  values than one,  $F_{index} = 0.96$

for lake phytoplankton, Table 2). The  $F_{index}$  values estimated using McKnight et al. (2001) cannot distinguish component 1, and because they used the original fluorescence spectra that overlap many peaks together and the new  $F_{index}$  values (peak C  $F_{index} < 1.00$  is for algal/phytoplankton origin and for SRFA = 1.40 and for SRHA = 1.28) are, thus, used in the present study on component 1, which is identified using PARAFAC modelling on the fluorescence spectra.

The upper and deeper layer pore waters showed a shorter Ex/Em wavelength of fluorescence peak C (Ex/Em = 315/

**Fig. 3** a–g Various fluorescent components identified with the PARAFAC model on the fluorescence spectra of pore waters extracted from various vertical sediment depths in Lake Bosten. Protein-like component identified in some discrete sediment depths (6, 11, 14–15, 22, 24, 34, 47 and 49 cm) in Lake Bosten. The excitation-emission (Ex/Em) maxima of these peaks are mentioned in Table 1



436 nm) than in the middle sediment pore waters (Ex/Em = 330/460 nm). But, fluorescence images (e.g.,

fluorescence intensity of peak C is generally higher or equivalent to peak A) and the  $F_{index}$  ( $F_{index} = 0.76$  in 22–40 cm or

**Table 2** The excitation-emission maxima of various fluorescent components identified using the PARAFAC modelling on the fluorescence spectra and the fluorescence index ( $F_{index}$ ) values estimated for the component 1 in the sediment pore waters of four Chinese lakes

Pore waters, river and lake water samples	Depth (cm)	Fluorescence peak (Ex/Em)				Component 3				Component 4				References		
		Component 1		Component 2		Component 3		Component 4		Component 3		Component 4				
		Peak C (nm)	Peak A	Peak M	Peak A	Peak M	Peak A	Peak A	Peak M	Peak A	Peak M	Peak A	Peak A			
Lake Bosten	1–20	315/436	260/436	280/386	220/386	–	–	–	–	–	–	–	1.25	2.13	This study	
	22–40	330/460	270/460	300/396	240/396	–	–	–	–	–	–	–	0.76	1.62	This study	
	41–50	315/436	250/436	280/406	220/406	–	–	–	–	–	–	–	1.05	2.11	This study	
Lake Qinghai	Discrete depths	–	–	–	–	290/356	240/356	–	–	–	–	–	–	–	–	This study
	1–20	340/460	280/460	305/402	225/402	–	–	–	–	–	–	–	0.80	1.67	This study	
	22–40	315/436	280/436	–	–	–	–	–	–	–	–	–	0.83	2.05	This study	
Lake Chenghai	41–50	315/436	280/436	–	–	–	–	–	–	–	–	–	0.77	2.00	This study	
	1–20	315/436	250/436	–	–	270/322	215/322	–	–	–	–	–	1.32	2.13	This study	
	22–40	355/460	275/460	310/416	240/416	–	–	–	–	–	–	–	0.66	1.53	This study	
Lake Dianchi	42–60	315/436	260/436	280/388	215/388	–	–	–	–	–	–	–	1.04	1.97	This study	
	62–74	315/436	280/436	280/388	220/388	–	–	–	–	–	–	–	0.86	1.76	This study	
	75–87	315/436	270/436	280/406	220/406	–	–	–	–	–	–	–	1.12	2.12	This study	
Lake Chenghai	1–20	310/426	225/426	–	–	–	–	–	–	–	–	–	1.93	2.73	This study	
	22–40	310/426	225/426	–	–	–	–	–	–	–	–	–	1.52	2.73	This study	
	42–55	320/442	250/442	–	–	270/298	220/298	–	–	–	–	–	1.25	2.05	This study	
Lake Dianchi	Surface waters	310/438	270/438	–	–	290/346	240/346	–	–	–	–	–	1.33	2.58	This study	
	Surface waters	310/438	270/438	–	–	290/346	240/346	–	–	–	–	–	1.33	2.28	This study	
	River waters	310/428	255/428	–	–	–	–	–	–	–	–	–	2.14	2.24	This study	
Rivers connected with Lake Bosten	Downstream waters	300–310/428–447	235–255/425–447	–	–	–	–	–	–	–	–	–	3.38	2.06	This study & Mostofa et al.	
	Freshwater	310–340/442–464	260/456–464	–	–	–	–	–	–	–	–	–	0.97–1.50	1.53–2.25	This study & Mostofa et al.	
	Freshwater	310–350/442–456	255–265/442–456	–	–	–	–	–	–	–	–	–	0.91–1.57	1.68–2.23	This study & Mostofa et al.	
Lake Baihua (0–20 m)	Standard SRFA	330/462	250/462	–	–	–	–	–	–	–	–	–	1.45–2.14	1.68–2.02	This study & Mostofa et al.	
	Standard SRFA	330/462	250/462	–	–	–	–	–	–	–	–	–	1.29	1.40	This study & Mostofa et al.	
	Standard SRFA	330/462	250/462	–	–	–	–	–	–	–	–	–	1.29	1.40	This study & Mostofa et al.	

**Table 2** (continued)

Pore waters, river and lake water samples	Depth (cm)	Fluorescence peak (Ex/Em)				F index (component 1)		References		
		Component 1		Component 2		Component 3	Component 4			
		Peak C (nm)	Peak A	Peak M	Peak A					
Standard SRHA	Standard	300/350/461	255/461	–	–	–	–	2.08	1.28	et al. 2013 This study & Mostofa et al. 2013 Mostofa et al. 2013
<i>o</i> -Cresol (dissolved in Milli-Q water)	Standard	–	–	–	–	275/303	215/304	–	–	Mostofa et al. 2013
Allochthonous fulvic acid (M-like)	River waters	285–310/387–429	230–260/387–429	–	–	–	–	–	–	Mostofa et al. 2013
Allochthonous fulvic acid (M-like)		305/412	< 250/412	–	–	–	–	–	–	Stedmon and Markager 2005
Autochthonous fulvic acid (C-like)	Lake phyto-plankton	365/453	270/453	–	–	–	–	–	–	Zhang et al. (2009a, b); Mostofa et al. 2013
Autochthonous fulvic acid (C-like)	Lake phyto-plankton	340/442, 448	260/442, 448	–	–	–	–	0.96	2.55	Mostofa et al. 2013
Autochthonous fulvic acid (M-like)	Lake phyto-plankton	–	–	300/405	240/405	–	–	–	–	Mostofa et al. 2013
Autochthonous fulvic acid (M-like)	Lake phyto-plankton	–	–	330/412	255/412	–	–	–	–	Zhang et al. (2009a, b); Mostofa et al. 2013
Humic-like (peak M)	Marine sediment	–	–	302–357	410–436	–	–	–	–	Mostofa et al. 2013 Burdige et al. 2004
Autochthonous fulvic acid (M-like)	Lake Hongfeng	–	–	295–300/396–422	235–240/296–422	–	–	–	–	Mostofa et al. 2013; Fu



**Table 2** (continued)

Pore waters, river and lake water samples	Depth (cm)	Fluorescence peak (Ex/Em)				F <sub>1</sub> index (component 1)		References		
		Component 1		Component 2		Component 3				
		Peak C (nm)	Peak A	Peak M	Peak A	Peak A	Peak A			
Protein-like	Freshwater lake	-	-	-	-	270-290/335-375	Peak	-	-	et al. 2010 Aoki et al. 2008
Protein-like	Coastal shelf water	-	-	-	-	290/356	250/356	-	-	Kowalczyk et al. 2009
Protein-like	River	-	-	-	-	280/339-346	230/338-351	-	-	Mostofa et al. 2013
Unknown substance	Marine sediment	-	-	-	-	-	220-230/304-345	-	-	Burdige et al. 2004

Peak means that there was a peak, but not identified

\*F<sub>1 index</sub> estimated by Mostofa et al. (2013) is the ratio of fluorescence intensity (FI) at Ex/Em = 250/440-450 nm divided by the FI at Ex/Em = 330/440-450 nm

#F<sub>1 index</sub> estimated by McKnight et al. (2001) is the ratio of FI at Ex/Em = 370/450 nm divided by the FI at Ex/Em = 370/500 nm

1.05 in 41–50 cm; Table 2) and  $F_{\text{index}}$  values in the middle ( $F_{\text{index}} =$  in 21–40 cm) and deeper (41–50 cm) sediment layers are different from the upper pore waters, which is a general characteristic feature of the autochthonous fulvic acid-like component of algal or phytoplankton origin. Such phenomena can result in two possible explanations: first, component 1 may be produced from terrestrial plant material that may deposit through riverine runoff on the lake bottom. Such longer Ex/Em wavelengths of the middle sediment pore waters indicate the greater conjugations in the molecules, such as an increase in the number of aromatic rings or in certain functional groups such as carboxylic, hydroxyl or amine (Senesi 1990; Mostofa et al. 2013). It is reported that the greater conjugations in the molecule may shift to a longer Ex/Em wavelength of fluorescence (Stedmon et al. 2003). Such conjugations in the molecule may result from the long-term microbial changes in some of the functional groups, particularly the carbohydrate fraction or the aliphatic carbon bound in macromolecules (e.g., fulvic acids), which are highly susceptible to degradation in pore waters (Lehmann et al. 2002; Fu et al. 2006; Harvey et al. 1995). Such changes in the DOM might be responsible for the production of  $\text{CH}_4$  by the methanogenesis that is generally observed in sediment depths (Lovley et al. 1996). An interpolated age of OM was detected  $840 \pm 40$   $^{14}\text{C}$  year BP in 41–42 cm and  $1970 \pm 40$   $^{14}\text{C}$  year BP in 48–49 cm, respectively (Wünnemann et al. 2006), along with an interpolated age of  $102 \pm 24$   $^{14}\text{C}$  year BP in 13 cm depth (Huang et al. 2009). The input of nutrient-rich irrigation water from farmland can be caused by a strong human impact over the last 130–150 years of lake development (Wünnemann et al. 2006). It has been shown that arid plants are predominantly composed of the Lake Bosten surface sediments (Huang et al. 2009). Such impacts could affect the input of the terrestrial OM along with high precipitation in the sediments of Lake Bosten. Second, component 1 in the middle and deeper sediment layers may be produced from algal biomass or phytoplankton that deposited on the surface waters after their production during the summer stratification period through photosynthesis. The fluorescence images and the  $F_{\text{index}}$  values are the indicators of algal or phytoplankton origin. However, it is unclear whether component 1 originated from terrestrial or autochthonous OM. Future studies are warranted to resolve these issues.

Component 2 (Table 2; Fig. 3b) in the upper layer (1–20 cm) showed two fluorescence Ex/Em maxima such as peak M at Ex/Em = 280/386 nm as a minor peak with low fluorescence intensity and peak A at 220/386 nm as a strong peak with high fluorescence intensity. This corresponded to the fluorescence of an allochthonous fulvic acid-like substance that has been observed with those peaks at 285–310/414–442 nm as low fluorescence intensity and 225–250/413–448 nm as a strong fluorescence intensity, respectively, which was reviewed for freshwater and seawaters (Table 2; Mostofa

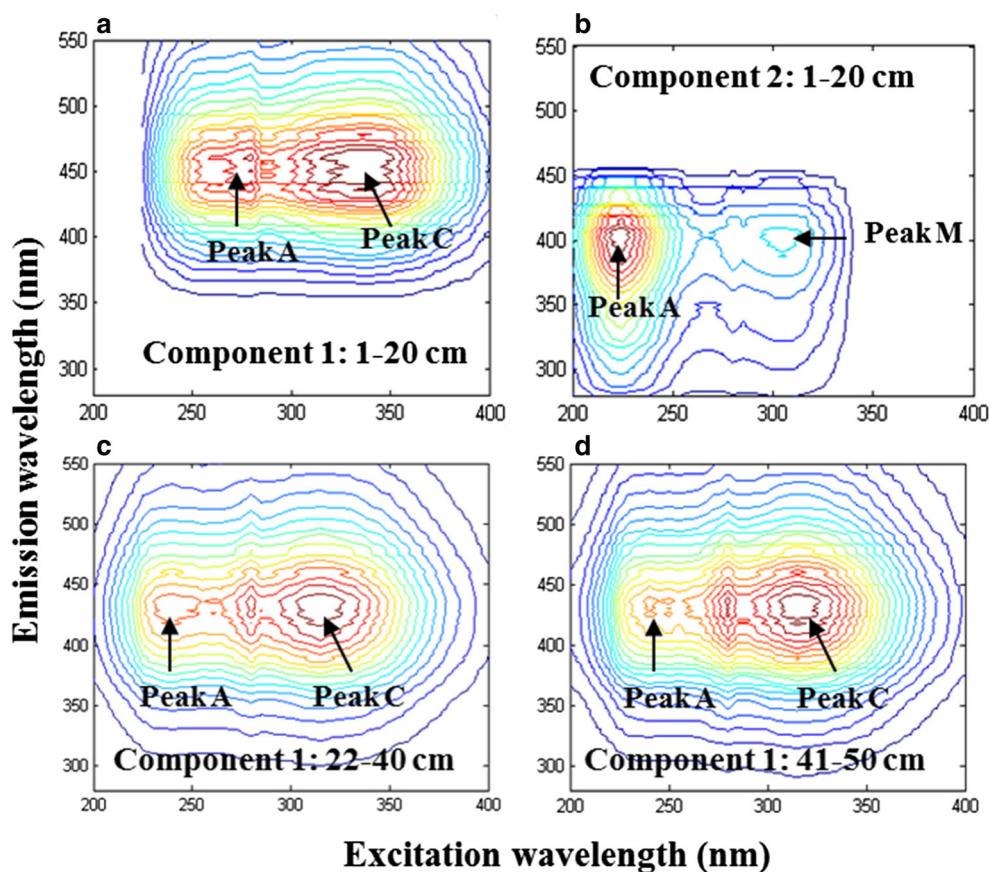
et al. 2013) or humic-like fluorophore (component 3) detected in Horsens Estuary and within its catchment, including streams, by Stedmon and Markager (2005) (Table 2). Component 2 in the middle and deeper layers showed a similar, but much longer emission wavelength (Ex/Em = 300/396 and 240/396 nm in 21–40 cm and 280/406 and 220/406 nm in 41–50 cm depth, respectively) than in the upper layer (Table 2; Fig. 3b–f). Judging from the fluorescence images of component 2 in the upper, middle and deeper sediment depths (Fig. 3b–f), it is suggested that the fulvic acid-like organic substance (or component 2) in deeper sediment pore waters might be an alternative form of that detected in the upper and middle sediment pore waters, which might take place during its long deposition period. Based on the confirmation of component 2 as an allochthonous fulvic acid-like substance, it is further considered that component 1 could also be produced from the same terrestrial plant material, claiming the first possibility, as has been discussed earlier, and that it may input through terrestrial riverine runoff in the Lake Bosten. The uppermost sediment consists of dark-grey carbonate mud (Wünnemann et al. 2006; Huang et al. 2009), which could be another indication of the origin of the terrestrial OM, as it is a typical colour of soil OM, whilst the sediments of algal origin can be a yellowish colour.

Pore waters in some discrete depths (6, 11, 14, 15, 22, 24, 34, 47 and 49 cm) of Lake Bosten were identified as mostly one component (component 3, Table 2) using PARAFAC modelling (Fig. 3g). This component corresponded to a protein-like substance with two fluorescence peaks at 290/356 and 240, 250/356 nm, as detected in earlier studies (Aoki et al. 2008; Kowalczyk et al. 2009; see also Table 2). Such fluorescent component apparently showed higher fluorescence intensity at peak T than in peak  $T_{\text{UV}}$ , an indicator of protein-like fluorescence (Mostofa et al. 2013). Component 3 likely comes from highly proteineous material (e.g., plankton and dead fish) that might be deposited from lake waters and buried at some specific sediment depths (Wu and Tanoue 2002). The contribution of a protein-like component to pore water DOM dynamics has, therefore, substantially occurred at some specific sediment depths.

#### Lake Qinghai

In Lake Qinghai, two fluorescent components were identified by PARAFAC modelling on the fluorescence spectra in the upper sediment pore water depths (1–20 cm; Fig. 4a, b), whilst only one fluorescent component was detected in the middle (22–40 cm; Fig. 4c) and deeper sediment depths (41–50 cm; Fig. 4d). Component 1 was commonly detected in the sediment pore waters with two fluorescence peaks (Table 2). The fluorescence images of component 1 showed a higher fluorescence intensity at peak C than at peak A ( $F_{\text{index}} = 0.77\text{--}0.83$ ), which is a strong indicator of the phytoplankton origin when

**Fig. 4 a–d** Various fluorescent components identified with the PARAFAC model on the fluorescence spectra of pore waters extracted from various vertical depth sediments in Lake Qinghai. The excitation-emission maxima of the peaks are mentioned in Table 1



compared with fluorescence peaks such as peak C at 340, 365/448, 453 nm and peak A at 260, 270/448, 453 nm of phytoplankton origin (Table 2; Mostofa et al. 2013; Zhang et al. 2009a, b), which corresponded to an autochthonous fulvic acid-like substance. The fluorescence peak C demonstrated a longer Ex/Em wavelength in the upper sediment pore waters than those in middle and deeper sediment pore waters, which may result from the microbial degradation of the particulate organic carbon (POC) and nitrogen (PON) bound in the organic matter during early diagenesis. This is supported by the observation of the decrease in total organic carbon (TOC) and total nitrogen (TN) with an increase in the sediment depth profiles in this lake (Xu et al. 2006). Such decrease in TOC and TN are linked with microbial degradation of POC and PON, thereby increasing the dissolved organic substances with depth. Component 2 was only detected at the 1–20 cm depth with two fluorescence peaks (Table 2) and its fluorescence image showed higher fluorescence intensity at peak A than at peak M, which is an indicator of the allochthonous origin, as discussed earlier. Therefore, it corresponded to an allochthonous fulvic acid-like substance like that in Lake Bosten (Table 2), which was discussed earlier.

The radiocarbon age determined based on the algal threads and OM showed the  $1780 \pm 23$  year BP at 47.5–49 cm depth and  $660 \pm 140$  year BP at 14–21 cm depth (Colman et al.

2007). This result suggests that OM deposits degrade for approximately 2000 years at a sediment depth at 50 cm. Studies demonstrate that the average densities of the phytoplankton and biomass are approximately 61,289–117,250 cells/L and 0.76–1.09 mg/L, respectively, during the summer period from 2006 to 2010 (Yao et al. 2011). The pore water FDOM sources in Lake Qinghai could also be understood evidently from the stable carbon isotope ( $\delta^{13}\text{C}_{\text{org}}$ ) of organic carbon, which fluctuates largely, showing the lowest level ( $-28.6\%$ ) and the highest level ( $-25.0\%$ ) at 47–48 cm (Zhang et al. 2002). Such fluctuations in  $\delta^{13}\text{C}_{\text{org}}$  signatures are linked to the occurrence of the different components such as various algae, algal tissue and their sterol-cholesterol components as  $-11.8$  to  $-27.7\%$ ; high molecular weight DOM as  $-22.0$  to  $-28.1\%$ ; nucleic acids as  $-21.2$  to  $-29.4\%$ ; phytoplankton and its end member as  $-18.0$  to  $-34.6\%$ ; macrophytes as  $-21.7$  to  $-28.9\%$ ; chloropigments as  $-20.9$  to  $-35.3\%$  (Lehmann et al. 2002; McCallister et al. 2006; Chikaraishi 2006; Ohkouchi et al. 2008). It is reported that the degradation of OM (e.g., fresh algal matter  $-24.2 \pm 0.15\%$ ) can considerably decrease the values of  $\delta^{13}\text{C}_{\text{org}}$  to  $-26.3\%$  after a 49-day incubation period; thereafter, it remains the same (Lehmann et al. 2002). Therefore, the production of FDOM components resulted from mixed sources, such as component 1 from phytoplankton or algae and component 2 from

terrestrial OM; their changes in the pore water could be an indicator of the long-term microbial degradation of DOM and OM, which generally takes place in the sediment depth profiles.

### Lake Chenghai

In Lake Chenghai, three fluorescent components were detected via PARAFAC modelling on the fluorescence spectra from the upper to the bottom sediment pore waters (Fig. 5; Table 2). Component 1 was demonstrated with two fluorescence peaks (peak C and peak A; see Table 2) in all sediment pore waters (Fig. 5a–i). The fluorescence images (Fig. 5a–i) and their  $F_{\text{index}}$  values ( $F_{\text{index}} = 1.32$  in 1–20 cm, 0.66 in 22–40 cm, 1.04 in 42–60 cm, 0.86 in 62–74 cm and 1.12 in 75–87 cm; Table 2) of component 1 corresponded to its origin from mixed sources in different pore water layers via the comparison with those of SRFA ( $F_{\text{index}} = 1.29$ ) and lake phytoplankton ( $F_{\text{index}} = 0.96$ ), as well as their respective fluorescence peaks (Table 2; Mostofa et al. 2013; Zhang et al. 2009a, b). For example, an allochthonous fulvic acid-like substance could presumably result from terrestrial plant material in 1–20, 42–60 and 75–87 cm depth, whilst an autochthonous fulvic acid-like substance could result from phytoplankton or algal biomass (Table 2; Fig. 6b; Zhang et al. 2009a, b; Mostofa et al. 2013). This can also be supported by the observation of  $\delta^{13}\text{C}_{\text{org}}$  of OM in Lake Chenghai, which fluctuates from  $\sim -27.3$  to  $< -24.0\%$  in the sediment depth profile (Wu and Wang 2003). The  $\delta^{13}\text{C}_{\text{org}}$  values could be a good signature for the occurrence of both terrestrial plant material and algal biomass or phytoplankton (Lehmann et al. 2002; McCallister et al. 2006; Chikaraishi 2006; Ohkouchi et al. 2008), which experiences a long-term microbial processes to release DOM in the sediment pore waters.

Component 2 was detected with two fluorescence peaks (a weak peak M at Ex/Em = 310/422 nm and a strong peak A at Ex/Em = 240/416 nm) at the 21–87 cm depth (Fig. 5d–j), which is similar to the allochthonous fulvic acid-like substance in Lake Bosten and Lake Qinghai (Table 2; Zhang et al. 2009a, b; Mostofa et al. 2013). However, in the successive sediment depth profile, Peak M was detected at Ex/Em = 280/388, 406 nm at 42–87 cm and became very weak with decreasing fluorescence intensity (on average, 56% at 75–87 and 21–40 m depth), whilst peak A was shifted to shorter wavelength regions and became a stronger peak with increasing fluorescence intensity (on average, 178% at 75–87 and 21–40 m depths (Fig. 5f–j)). Such changes in component 2 are presumably anticipated to be the effects of a long-term successive microbial decomposition in sediment pore waters. By comparing the fluorescence images (e.g., a higher fluorescence intensity in peak A than in peak M, also discussed in detail earlier) and their successive changes vertically in sediment depth profiles (Fig. 5d–j), it is suggested that component

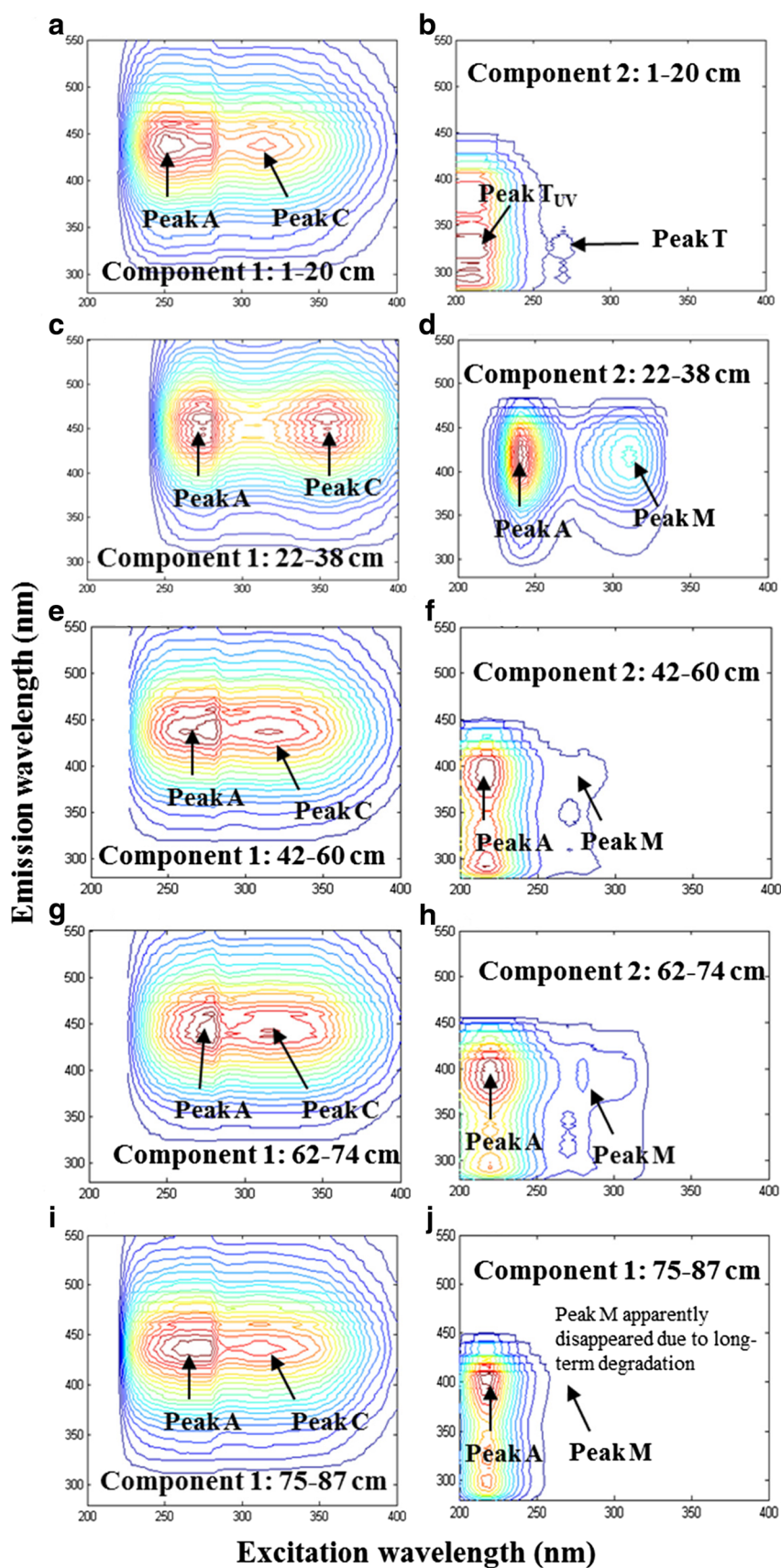
2 corresponds to an allochthonous fulvic acid-like component of terrestrial plant material origin, which might be altered by a long-term successive microbial decomposition after its origin from OM.

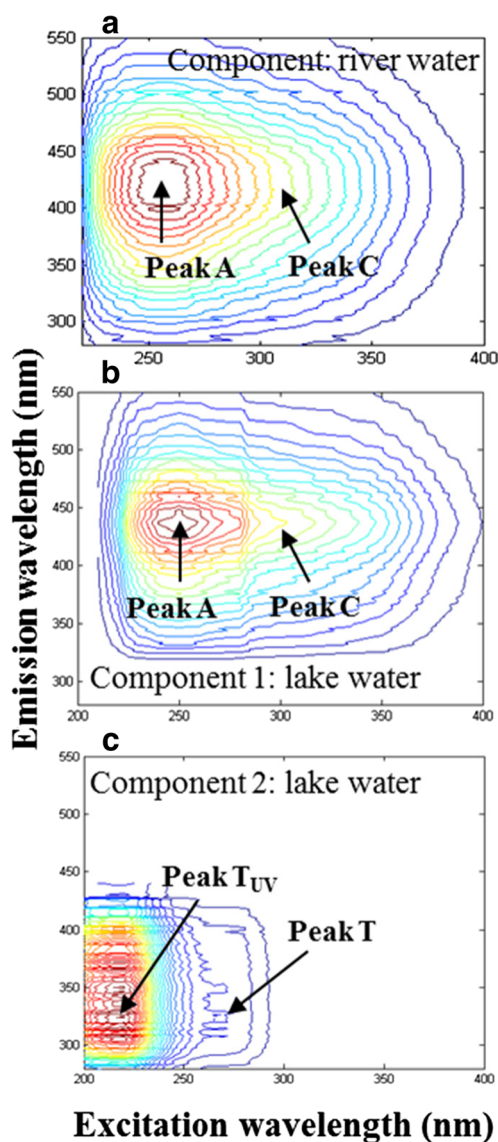
Component 2 (named component 3 in Table 2) at 1–20 cm depth showed a strong fluorescence peak  $T_{\text{UV}}$  at Ex/Em = 215/322 nm and a weak peak T at Ex/Em = 270/322 nm (Fig. 5b), representing tryptophan component identified from measurement of standard tryptophan in aqueous solution (Mostofa et al. 2013). Such a weak peak T is possibly caused by the microbial decomposition of the respective functional groups bound in the component. This component apparently corresponds to those of peak T (Aoki et al. 2008; Mostofa et al. 2013) or peak SR (220–230/304–345 nm) in marine sediments detected by Burdige et al. (2004) or peak  $T_{\text{UV}}$  (Kowalczyk et al. 2009; Mostofa et al. 2013). Because of the lack of PARAFAC modelling in the previous study (Burdige et al. 2004), they did not make any specific conclusions regarding this component. This component could, therefore, be an indication of remaining decomposed aromatic amino acids. This can be supported by the occurrence of the tryptophan-like substance (component 3, Table 2) with two fluorescence peaks (peak T at Ex/Em = 290/346 nm and peak  $T_{\text{UV}} = 240/346$  nm) in the surface water of Lake Chenghai. The source material of surface water protein-like components might be deposited and buried for long-term microbial decomposition, which could possibly produce component 3 in sediment pore waters. Detection of this component (component 3, Table 2) in both lake and marine sediments is characteristically important in the sediment pore waters and is presumably considered originate from a specific phytoplankton. This should be the focus of future studies.

### Lake Dianchi

In Lake Dianchi, the PARAFAC analysis on the fluorescence spectra identified two fluorescent components in 1–20 cm (Fig. 7a, b) and 22–40 cm (Fig. 7c, d) depths, but three fluorescent components in 42–55 cm (Fig. 7e–g). Component 1 was detected with two fluorescence peaks (peak C and peak A; see Table 2). This corresponded to a sewerage-impacted allochthonous fulvic acid-like substance in 1–55 cm depth profiles via comparison with the river waters (310/428 and 255/428 nm, respectively; Table 2), the fluorescence images (low fluorescence intensity of peak C than in peak A) and the high  $F_{\text{index}}$  values ( $F_{\text{index}} = 1.25$ – $1.93$  in 1–55 cm) with those of sewerage-impacted downstream rivers such as  $F_{\text{index}} = 2.14$  or 2.08 and three other lakes studied (Table 2; Fig. 7a–e). Component 2 (named component 3, Table 2) was merely detected in deeper sediment pore waters (42–55 cm) with two fluorescence peaks such as a weak peak T at 270/298 nm and a strong peak  $T_{\text{UV}}$  at Ex/Em = 220/298 nm (Fig. 7g; Table 2). Component 2 is presumably considered to be the decomposed

**Fig. 5** a–j Various fluorescent components identified with the PARAFAC model on the fluorescence spectra of pore waters extracted from various vertical depth sediments in Lake Chenghai. The excitation-emission maxima of the peaks are mentioned in Table 1





**Fig. 6** a–c Various fluorescent components (Comp) identified with the PARAFAC model on the fluorescence spectra of river waters and lake surface waters studied. The excitation-emission maxima of the peaks are mentioned in Table 1

forms of either unidentified components of phytoplankton origin, whereas its fluorescence image is similar to component 5 that was detected in Baltic coastal sea ice (Stedmon et al. 2007b) or an autochthonous fulvic acid-like of phytoplankton origin (see Table 2) that was deposited from surface waters and was buried for long-term microbial degradation in deeper sediment pore waters.

Component 3 (named component 4, Table 2) showed a strong fluorescence peak at Ex/Em = 210/290 nm that existed in all sediment pore waters in Lake Dianchi (Fig. 7b–f; Table 2). Component 3, identified in all sediment pore waters of Lake Dianchi, was not observed in the three other lakes or in earlier studies. Thus, these results imply that component 3 is refractory for microbial degradation and could presumably

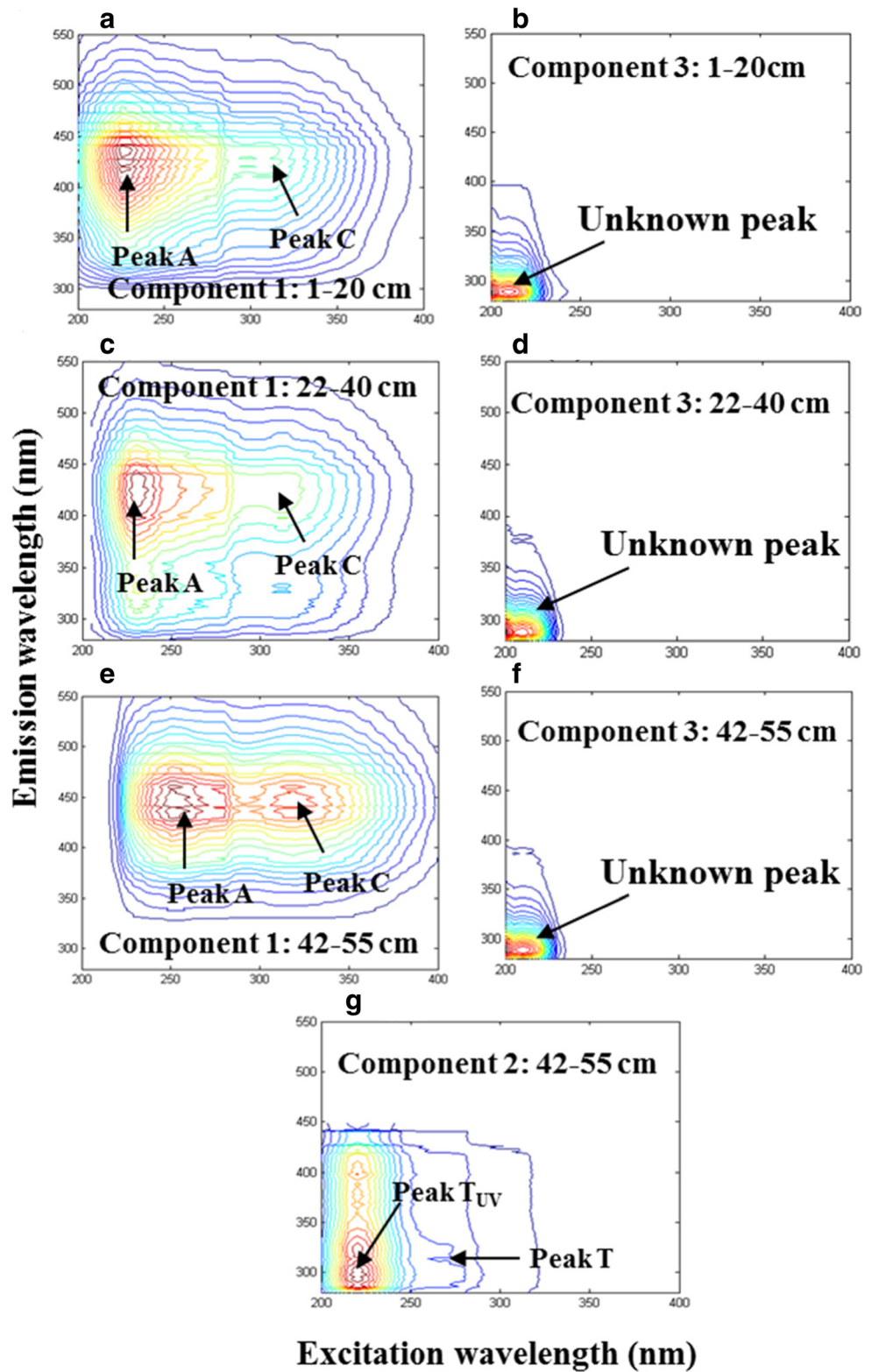
originate from polluted OM, either from sewerage or industrial waste in sediment pore waters. It has been demonstrated that Lake Dianchi is highly polluted due to the input of effluents from industrial and sewerage OM from Kunming city (Sun and Zhang 2000). Such high pollution can be justified by the observation of a high DOC concentration (862  $\mu\text{M C}$ ) in its surface waters. The results of  $\delta^{13}\text{C}_{\text{org}}$  of OM show that the  $\delta^{13}\text{C}_{\text{org}}$  value fluctuates from  $-22.2\text{‰}$  at 1 cm to  $-25.6\text{‰}$  at 63 cm in the sediments of Lake Dianchi (Wang et al. 2009). The  $\delta^{13}\text{C}_{\text{org}}$  values in Lake Dianchi in the upper sediment depth are significantly higher compared to those of the three lakes, which have already been discussed, suggesting that the OM in Lake Dianchi is substantially different from that of the three other lakes.

### Profile distributions of DOM and their dynamics in sediment pore waters

Figure 8 showed the distribution of DOC concentrations and the fluorescence intensity of peak C for both allochthonous and autochthonous fulvic acid-like substances in sediment pore water profiles of the four lakes. DOC concentrations of sediment pore waters generally increased with depth in the three lakes, except in Lake Dianchi, where DOC concentrations sharply decreased from 2861  $\mu\text{M C}$  near the water-sediment interface to 986  $\mu\text{M C}$  at 2 cm depth, and then generally increased with depth. Pore water DOC concentrations ranged from 583 to 4432  $\mu\text{M C}$  in Lake Bosten, from 1238 to 6086  $\mu\text{M C}$  in Lake Qinghai, from 654 to 3418  $\mu\text{M C}$  in Lake Chenghai, and from 803 to 7410  $\mu\text{M C}$  in Lake Dianchi. The results demonstrated that pore water DOC concentrations were relatively low in Lake Chenghai among the four lakes, possibly because of the lower rates of sediment OM mineralisation. DOC concentrations at the water-sediment interface were highest (2861  $\mu\text{M}$ ) in Lake Dianchi and lowest (713  $\mu\text{M}$ ) in Lake Chenghai among the four lakes studied. A rough estimation showed that the increase in pore water DOC concentration at deeper sediments compared to those of upper sediment (average of 1 to 10 cm) was detected at approximately 72% in Lake Bosten, 85% in Qinghai, 126% in Chenghai and 206% in Lake Dianchi. This result indicates that the lakes (Dianchi and Chenghai) in subtropical regions can produce relatively more DOC in deeper sediment pore waters compared to lakes (Bosten and Qinghai) located in temperate regions.

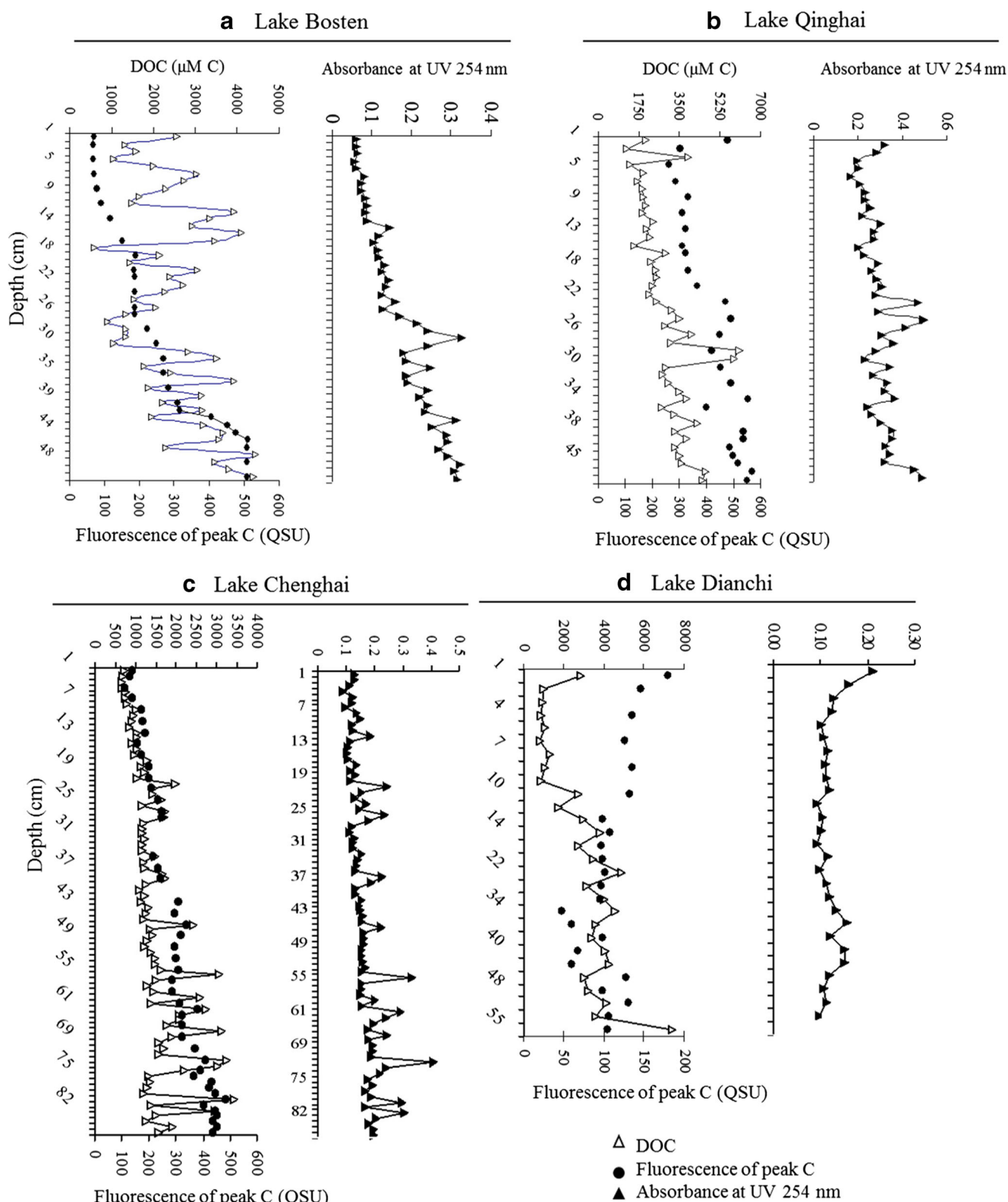
The fluorescence intensity of peak C for both autochthonous and allochthonous fulvic acid-like substances (component 1, Table 2) generally increased from the upper to deeper sediment pore waters in three lakes (Lake Bosten, Qinghai and Chenghai), except in Lake Dianchi where the fluorescence intensity fluctuated from the upper to deeper sediment pore water (Fig. 8). DOC concentrations and fluorescence intensity of peak C were positively

**Fig. 7** a–g Various fluorescent components identified with the PARAFAC model on fluorescence spectra of pore waters extracted from various vertical depth sediments in Lake Dianchi. The excitation-emission maxima of the peaks are mentioned in Table 1



correlated in Lake Bosten ( $r = 0.43, p < 0.01, n = 39$ ), Lake Qinghai ( $r = 0.48, p < 0.01, n = 43$ ) and Lake Chenghai ( $r = 0.77, p < 0.01, n = 78$ ) (Fig. 9a–c), but such a correlation was absent in Lake Dianchi (Fig. 9d).

Correspondingly, a rough estimation by comparing surface sediment (average values of 1–10 cm) and bottom sediment (average values of last 10 cm depths) demonstrated that the increase in fluorescence intensity of peak C for

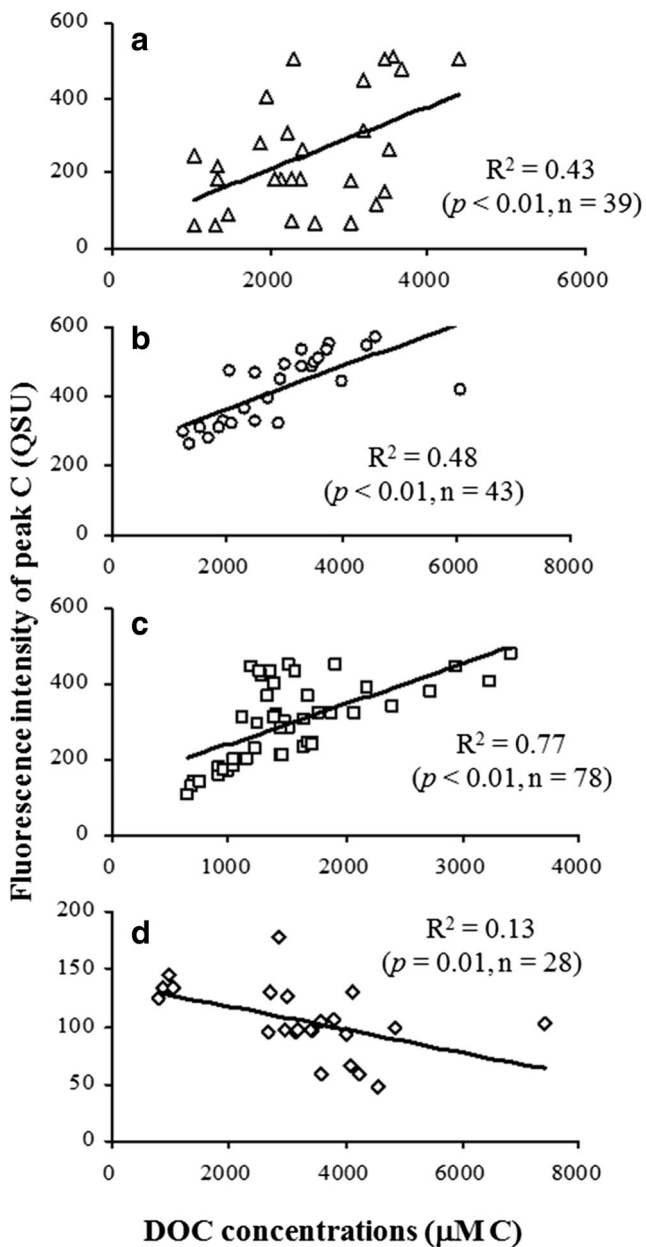


**Fig. 8** Vertical distribution of dissolved organic carbon (DOC) concentrations, the fluorescence intensity of peak C (autochthonous fulvic acid-like) and absorbance at UV-254 nm for the pore waters samples extracted from the sediments of Lakes Bosten (a), Qinghai (b), Dianchi (c) and Chenghai (d)

component 1 was 551% in Lake Bosten, 61% in Qinghai and 208% in Lake Chenghai; but fluorescence intensity

was lower (30%) in the pore waters of Lake Dianchi. These results further evidence that component 1 originated





**Fig. 9** Relationship between DOC concentrations and fluorescence intensity of peak C (fulvic acid-like component or component 1) in the sediment pore waters of Lake Bosten (a), Lake Qinghai (b), Lake Chenghai (c) and Lake Dianchi (d)

from mixed sources, such as both allochthonous (plant material) and autochthonous (algal or phytoplankton) fulvic acid-like substances, which might have contributed to the majority of total DOM in these three lakes. DOM production diagenetically originates either from plant material or phytoplankton biomass in the sediment depths via complex microbial processes in the pore waters of three lakes (Bosten, Qinghai and Chenghai). This can be supported by the atomic C/N ratios of sedimentary OM, which are used to identify the sources of OM. Note that allochthonous terrestrial OM is enriched in fibres but low in proteins

with high atomic C/N ratios (generally  $> 20$ ), while algae or phytoplankton contain more proteineous material, which has low atomic C/N ratios, generally  $< 10$  (Meyers 1997; Dean 1999). The atomic C/N ratios of OM in the surface sediments of Lake Qinghai and sediments of Lake Chenghai suggest mixed sources in these lakes (Wan et al. 2005; Xu et al. 2006). In Lake Bosten, the atomic C/N ratios of sediment OM range from 8.4 to 14.3, also suggesting a mixed source in the lake. These results, therefore, further evidence that fluorescent DOM (FDOM) is mostly originated from mixed sources such as terrestrial plant material deposited through riverine runoff or from phytoplankton deposited from surface waters after their production through photosynthesis during the summer stratification period in these three lakes (Bosten, Qinghai and Chenghai). On the other hand, the atomic C/N ratios of sediment OM in Lake Dianchi range from 9.7 to 12.6, suggesting that the sediment OM comes from mixed sources such as autochthonous (e.g., algae or phytoplankton) and terrestrial OM in the lake (Xiong et al. 2009).

On the other hand, component 1 or an allochthonous fulvic acid-like substance in Lake Dianchi may marginally contribute to its total DOM, which might be controlled by two mixed sources. First, this could be controlled by the untreated sewerage-impacted effluents, which are deposited through riverine inputs and mostly observed in earlier studies (Sun and Zhang 2000). The fluorescent component of the sewerage origin (Mostofa et al. 2010) may predominantly decompose microbially in deeper sediment layers, which could result in a decrease in fluorescence, thereby showing a negative correlation with DOM in the deeper sediments of Lake Dianchi (Fig. 9d). Observations of dissimilar fluorescent components in Lake Dianchi than in the three other lakes are also supported by the occurrence of sewerage-impacted allochthonous fulvic acid-like components along with two special fluorescent components (Fig. 7). The sources of component 4 (Table 2), commonly detected from upper to deeper sediment pore waters, and component 3 (Table 2), merely detected in deeper sediment pore waters, might have originated from polluted OM by microbial processes in the sediment pore waters of Lake Dianchi. Second, this could be controlled by the OM (*ca.* algae) that is produced autochthonously by photosynthesis in the lake surface waters, some of which is deposited on the sediment surface (Bernasconi et al. 1997; Hernes et al. 2001; Lehmann et al. 2002). There was variation in the input of these two sediment sources, presumably controlled by various factors, including precipitation, sunlight, temperature and DOC, which seemingly affected the photosynthesis inside the lake. Such differences in the lake ecosystem could, therefore, greatly influence the DOM compositions and the release of component 1 from the respective sediments in Lake Dianchi, which apparently makes it different than the other three lakes (Bosten, Qinghai and Chenghai).

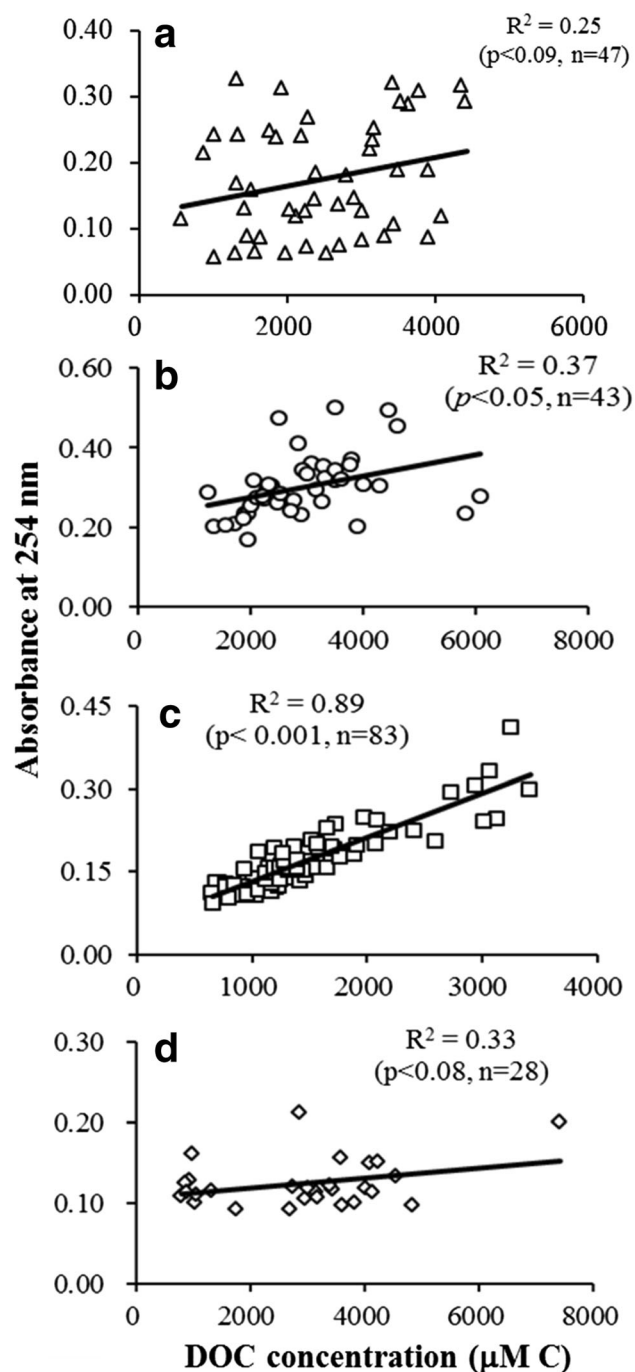
### Changes in the UV absorbance and SUVA<sub>254</sub> of DOM in the sediment depth profiles

The UV absorption coefficients at 254 nm of sediment pore waters generally increased with depth in three lakes (Bosten, Qinghai and Chenghai) (Fig. 8). However, the absorption coefficients in Lake Dianchi decreased rapidly from 0.21 near the sediment-water interface to 0.09 at the 17 cm depth, and then generally increased to 0.15 at the 42 cm depth (Fig. 8). DOC concentrations were significantly correlated with UV absorption coefficients at 254 nm in Lake Chenghai ( $r = 0.89$ ,  $p < 0.01$ ,  $n = 83$ ) and moderately in Lake Qinghai ( $r = 0.37$ ,  $p < 0.05$ ,  $n = 43$ ) (Fig. 10), but were not correlated in Lake Bosten (Fig. 10a). Because the absorption coefficients at 254 nm resulted from the aromatic structures in DOM that absorb light in this UV region (Chin et al. 1994; O'Loughlin and Chin 2004), it is, therefore, indicated that the aromatic structures of total DOM could majorly contribute to total DOM in Lake Chenghai. This is also supported by the observation of the good relationship between the fluorescence intensity of peak C for component 1 and DOC concentrations, as discussed earlier (Fig. 9). A rough estimation showed a relative increase in absorbance in deeper sediments (average values of the last 10 cm depth) than in upper sediments (average values of 1–10 cm depth) was 305% in Lake Bosten, 48% in Lake Qinghai and 73% in Lake Chenghai; in Lake Dianchi, a decrease in absorbance (2%) was detected. These results further support the increasing release of total DOM from sediments with increasing sediment depths.

SUVA<sub>254</sub> of DOM in the sediment pore waters generally decreased with depth in Lakes Qinghai, Chenghai and Dianchi; in Lake Bosten, an increasing trend with depth was observed (Fig. 11). A strong correlation of SUVA<sub>254</sub> with aromaticity for extracted DOM for a variety of waters was detected in an earlier study (Weishaar et al. 2003). The SUVA<sub>254</sub> profiles in this study, therefore, suggests that the aromaticity of DOM in sediment pore waters could decrease from the sediment surface to deeper sediments in these three lakes (not Lake Bosten). The decrease in SUVA<sub>254</sub> values with depth in these lakes might result from the FDOM components, mostly components 2 and 3, which are substantially altered vertically, together with component 1 (see Table 2). This result, therefore, suggests that microbial activities could affect substantially the aromaticity of the total DOM components in lake sediment pore waters.

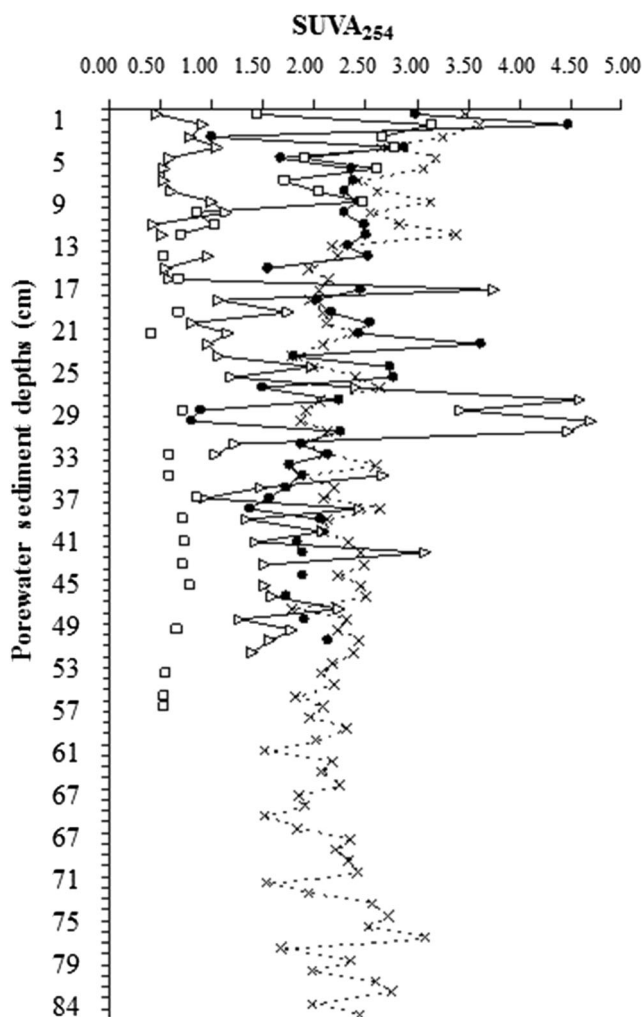
### Characteristics and importance of pore water FDOM

Several characteristic changes in the FDOM components take place in the sediment depth profiles in the four lakes studied. First, microbial degradation on both allochthonous and



**Fig. 10** Relationship between DOC concentrations and the absorbance at 254 nm in the sediment pore waters of Lake Bosten (a), Lake Qinghai (b), Lake Chenghai (c) and Lake Dianchi (d)

autochthonous fulvic acid-like components causes either a shift in the Ex/Em maxima to shorter wavelength regions, or it remains similar to those of the upper wavelength regions with increasing sediment depth in three lakes (Bosten, Qinghai and Chenghai). Such changes in the Ex/Em maxima showed opposite behaviour of the same component detected



**Fig. 11** The vertical distribution of the specific ultraviolet absorbance at 254 nm ( $SUVA_{254}$ ) values for sediment pore waters in four lakes

in the deeper waters of lakes or oceans (Coble 1996; Mostofa et al. 2005) that generally showed shifts in the Ex/Em wavelengths to longer wavelength regions in experimental observation under dark incubation (Moran et al. 2000; Mostofa et al. 2007). High and sequential degradation of functional groups bound in that component that generally produce  $CH_4$  or  $CO_2$  by biotic oxidation (Lovley et al. 1996) is presumably susceptible to such gradual changes in the pore water FDOM components. Shorter Ex/Em maxima towards sediment depth profile could be a useful indicator of the biotic oxidation of OM that is caused biologically in the sediment pore waters. Second, the microbial degradation on allochthonous fulvic acid-like components is found to decompose gradually in Lakes Bosten and Chenghai, and entirely in Lake Qinghai, after detection at the 1–20 cm depth. Third, the fluorescent components in Lake Dianchi are completely dissimilar to those of the three lakes, as opposed to the sewerage-

impacted terrestrial fulvic acid-like component identified along with two unidentified fluorescent components (Fig. 7). Fourth, protein-like components are only detected in some specific sediment pore water depths of Lake Bosten, which presumably originate from buried particulate organic matter, including phytoplankton, diatoms, other autotrophs and heterotrophs (Ríos et al. 1998; Wu and Tanoue 2002). Note that proteins are the key and ubiquitous components of living organisms and represent a significant fraction of organic matter present in marine sediments (Ríos et al. 1998; Keil et al. 2000; Chaijan et al. 2010).

Such changes in the FDOM components in the sediment pore waters are primarily caused by the geographic locations of the lakes with significant differences in the meteorological and seasonal timescale conditions, for example, Lakes Bosten [annual water temperature range (–)19.4–19.7 °C, mean – 4.6 °C and a relatively long cold season] and Qinghai [annual water temperature range (–)20–10 °C, mean = – 0.7 °C and a relatively long cold season] lie in the arid and semi-arid climate regions north of China, whilst Lakes Chenghai [annual water temperature range 2.0–31.2 °C, mean 15.9 °C and a relatively long summer season] and Dianchi [annual water temperature range 9.8–24.5 °C, mean 16.0 °C and a relatively long summer season] lie in the subtropical regions south of China (Chen et al. 2008; Zhang et al. 2009a, b; Xu et al. 2006; Zhang et al. 2014; Wan et al. 2005; Bai et al. 2012). Note that temperature is one of the fundamental controls on the degradation rate of particulate organic matter in lake and marine sediments (Gudasz et al. 2015; Malinverno and Martinez 2015). Increasing temperatures during burial could stimulate organic matter degradation in sediment depths (Malinverno and Martinez 2015). The fluorescence intensity of both allochthonous and autochthonous fulvic acid-like components and absorbance properties exhibited a similar vertically increasing trend in sediment pore waters of three lakes (Bosten, Qinghai and Chenghai). Such changes in the FDOM components are in agreement with the average DOC increase at the 40–50 cm depth (72% in Lake Bosten, 94% in Lake Qinghai, 72% in Lake Chenghai and 177% in Lake Dianchi) as opposed to the upper sediment depth layer (1–10 cm). In fact, almost similar increases in DOC in the three lakes are susceptible to be caused microbially on the OM, irrespective of the sources, due to longer residence time in deeper sediment depths, and are not affected substantially by the surrounding environmental factors. Conversely, a remarkably high increase in DOC levels in deeper sediment depths of Lake Dianchi might result from sewerage-impacted OM, which is possibly recalcitrant to microbial degradation and the increasing vertical leaching in an upward to a downward direction. Two fluorescent substances (component 3, unknown, only found in deeper sediment pore waters, and component 4, unknown, found in

all sediment pore waters, Table 2) may have originated from polluted OM in the sediment pore waters of Lake Dianchi. No clear evidence has been documented for the sources of these two components identified in the sediment pore waters of Lake Dianchi, which could be the focus of future studies. These results, therefore, indicate that sewerage-impacted OM pollution may severely influence the pore water DOM level in the lake ecosystem.

## Conclusion

The results are summarised below:

- An autochthonous fulvic acid-like component of phytoplankton origin predominantly occurred in Lake Qinghai, whilst both the allochthonous and the autochthonous fulvic acid-like components were often detected in the sediment pore waters of three lakes (Bosten, Chenghai and Dianchi), which were considered to be from mixed sources such as terrestrial plant material and autochthonously produced algae or phytoplankton. The sediment pore water FDOM components, therefore, reflected the key sources of DOM, which originated either from autochthonous OM or human-induced allochthonous OM via terrestrial runoff in and around the lake ecosystem.
- The fluorescence intensity of fluorescent component 1, both allochthonous and autochthonous fulvic acid-like substances, often increased from the water/sediment surface to the bottom sediment layers in three lakes (except Lake Dianchi), whereas the fluorescence intensity decreased from the upper to the middle and the deeper sediment pore waters.
- The absorbance properties of pore water DOM at 254 and its positive correlation with DOC (Lakes Qinghai and Chenghai) indicated that the increasing input of DOM resulted from OM microbially from the upper to deeper sediment pore waters. Conversely, decreasing SUVA<sub>254</sub> values in deeper pore waters suggests that microbial activities of total DOM components may be responsible for the changes in either the aromaticity or total functional groups bound in pore water DOM in the lakes studied.
- The identification of both allochthonous and autochthonous fulvic acid-like components (component 1 and component 2, Table 2) by PARAFAC modelling on the fluorescence spectra and their microbial changes in the Ex/Em maxima could be a useful indicator to understand the sources of sediment pore water DOM and their successive alterations in sediment depth profiles through microbial processes over the past several decades.

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