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不同水文情景下高邮湖、南四湖和东平湖有色可溶性有机物的生物可利用性特征

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摘要: 有色可溶性有机物(CDOM)的生物可利用性直接反映其生物可降解潜力, 影响水体中污染物质的迁移转化和水质优劣状况。本研究运用三维荧光光谱-平行因子分析法(EEMs-PARAFAC)结合室内微生物培养实验, 分析了高邮湖、南四湖和东平湖CDOM光谱组成和荧光组分的生物可利用性特征, 并进一步阐述其对丰水和枯水两种水文情景的响应。结果表明: ①运用EEMs-PARAFAC方法解析出4种荧光组分, 微生物作用类腐殖酸C1和陆源类腐殖酸C4, 类色氨酸C2和类酪氨酸C3。②3个湖泊丰水期吸收系数差值 $\Delta a(254)$ (培养前-培养后)均为正值, 而枯水期 $\Delta a(254)$ 部分为负值, 这意味着CDOM生物可利用性对季节的响应存在较大差异。③不同水文情境下, 南四湖和东平湖类腐殖酸组分%ΔC1、%ΔC4均为负值, 南四湖丰、枯水期和东平湖丰水期类蛋白组分ΔC2~ΔC3为正值(t -test, $P < 0.001$, $P = 0.005$)。而丰水期高邮湖类蛋白组分ΔC2~ΔC3也为正值(t -test, $P = 0.008$, $P = 0.005$), 这意味着不稳定类蛋白组分更容易被微生物矿化, 可能生成更稳定的类腐殖酸。3个湖泊腐殖化指数HIX、荧光峰积分比值 $I_c : I_T$ 均大于培养前, 同时斜率 $S_{275-295}$ 均减小进一步证实该结论。④丰、枯水期3个湖泊的类蛋白组分C2~C3的生物可利用性在入湖区域较高, 同时该类湖泊入湖口区域类腐殖酸累积也较高, 因而需要进一步加强入湖河流水质管理, 减少外源CDOM输入以确保上述3个湖泊供水安全。

关键词: 高邮湖; 南四湖; 东平湖; 有色可溶性有机物(CDOM); 生物可利用性; 平行因子分析(PARAFAC)

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Bioavailability Characteristics of Chromophoric Dissolved Organic Matter in Lake Gaoyou, Lake Nansi, and Lake Dongping Under Different Hydrological Scenarios

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Abstract: The bio-lability of chromophoric dissolved organic matter (CDOM) directly reflects its biodegradability potential, and also affects the migration and conversion of pollutants and impacts water quality. This study combines excitation-emission matrices and parallel factor analysis (EEMs-PARAFAC) with laboratory 28 days of bio-incubation experiments, and analyzed the bioavailability characteristics of CDOM samples collected from Lake Gaoyou, Lake Nansi and Lake Dongping in flood season and dry season. Our results showed that: ① four fluorescent components were obtained using EEMs-PARAFAC, including a microbial humic-like C1, a terrestrial humic-like C4, a tryptophan-like C2, and a tyrosine-like C3. ② The differences of CDOM absorption pre-and post-incubation, i.e. $\Delta a(254)$ of the three lakes were positive in the three lakes in the flood season, while partially negative in the dry season, indicating a quite different response of CDOM bioavailability to hydrological seasons. ③ Under different hydrological scenarios, the two humic-like components C1 and C4 increased post-bio-incubation compared with that pre-incubation for the samples collected from Lake Nansi and Lake Dongping, and the two protein-like components in Lake Nansi in both the flood and dry seasons and in Lake Dongping in the flood season (t -test, $P < 0.001$, $P = 0.005$) were lower in the post-than those pre-incubation. In Lake Gaoyou, C1-C3 post-incubation were significantly lower than pre-incubation (t -test, $P = 0.008$, $P = 0.005$). In the dry season, in comparison, C1-C4 except for C2 increased post-incubation than pre-incubation for Lake Gaoyou. This indicated that the protein-like components are unstable and more easily uptaken by microorganisms and may be potentially converted into more stable humic-like components. HIX and $I_c : I_T$ of the three lakes increased post-incubation while the spectral slope $S_{275-295}$ decreased, which further confirmed the aforementioned conclusion. ④ During both the flood and dry seasons, the bioavailability of the protein-like components C2-C3 and the fluorescence intensity of C1 and C4 in the inflowing river mouths of the three lakes were higher than in the remaining lake regions. It is

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therefore necessary to strengthen the water quality management in the inflowing river mouths of the three lakes to maintain the water quality of the lakes.

Key words: Lake Gaoyou; Lake Nansi; Lake Dongping; chromophoric dissolved organic matter (CDOM); bioavailability; parallel factor analysis (PARAFAC)

有色可溶性有机物质(chromophoric dissolved organic matter, CDOM)广泛存在于天然水体中,是可溶性有机物(dissolved organic matter, DOM)中能强烈吸收紫外和可见光的部分。湖泊中CDOM主要来源于地表径流、降雨淋溶和人类活动等^[1,2],其在生物地球化学循环过程中起到核心作用,同时也是水生生物生命活动能量的直接来源^[3,4]。CDOM的生物可利用性还会直接影响以CDOM为络合剂或吸附剂的重金属及有机污染物的生理毒性和环境行为,同时对饮用水处理工艺与流程起决定性作用。另外CDOM的生物可利用性高低直接影响水生态系统中C和N等生源物质的循环与再生速率,作用于水体富营养化过程,并且对揭示CDOM的迁移转化过程、潜在温室气体效应以及对水质的影响均起到不可忽视的作用^[5],因此对CDOM的生物可利用性研究具有重要价值,国内外有部分学者开始关注天然环境中CDOM的生物可利用性特征^[6]。钱伟等^[7]的研究表明可见-紫外光谱和荧光光谱能很好地分析研究内河水体DOM的分解和转化过程。Wu等^[8]的研究发现得克萨斯州南部沿海水域河流DOM生物有效性受季节和人为影响较明显。三维荧光结合平行因子分析法(EEMs-PARAFAC)被广泛用于分析河流、湖泊和海洋中CDOM的光学指标特征,能快速、准确地鉴定出CDOM的荧光组分以及分析光谱特征^[6,9]。

高邮湖、南四湖和东平湖是南水北调东线工程重要枢纽湖泊,其水质优劣对东线调水工程的顺利开展起到了关键性作用,同时是受水区人们生产生活和城市经济发展的重要命脉^[10]。但随着城市的快

速发展,工业、农业和生活等污染源产生的污染物直接或间接地排放到湖泊、河流等,导致其水环境质量受到较大影响,污染物来源和种类越来越复杂^[11]。目前国内外对湖泊CDOM生物可利用特征的研究较少,且鲜见报道运用EEMs-PARAFAC揭示上述3个湖泊CDOM的生物降解特征。鉴于此,本研究在丰、枯季节开展对高邮湖、南四湖和东平湖样品采集,开展室内CDOM的生物降解特征分析,并进一步探讨3个湖泊CDOM生物可利用性如何响应于不同水文情景及其潜在影响机制,通过丰富3个湖泊CDOM及其生物可利用性特征的研究资料,以期为东线调水工程水质管理提供科学依据。

1 材料与方法

1.1 样品采集与处理

在高邮湖、南四湖和东平湖分别布设7个、13个和6个采样点(见表1、图1),于2018年4月和7月采集水样。样品采集完毕当日运回实验室后立即使用0.22 μm Millipore滤膜过滤水样200 mL以去除水样中微生物,其中100 mL立即用于测定生物培养前CDOM紫外-可见吸收光谱和三维荧光光谱,另外100 mL滤液装入经酸洗和高温灭菌的棕色玻璃瓶,加入2 mL菌种(菌种为对应样点原水),为避免生物培养实验过程中可能存在的营养盐限制,添加2 mL营养液将样品的营养盐水平提升至80 μmol·L⁻¹ NH₄⁺-N及10 μmol·L⁻¹ PO₄³⁻-P^[12,13]。样品置于室温[(20±2)℃]和避光好氧条件下(每日轻晃数次)培养28 d后再次测定CDOM紫外-可见吸收光谱和三维荧光光谱。

表1 高邮湖、南四湖和东平湖采样点经纬度

Table 1 Latitude and longitude of sampling points in Gaoyou Lake, Nansi Lake, and Dongping Lake

高邮湖		南四湖		东平湖	
经度	纬度	经度	纬度	经度	纬度
119.409 44°	32.799 44°	117.314 17°	34.607 22°	116.199 44°	36.054 44°
119.386 67°	32.827 22°	117.228 06°	34.558 61°	116.221 94°	35.996 67°
119.331 11°	32.841 11°	117.150 56°	34.680 00°	116.234 72°	35.940 56°
119.301 11°	32.876 94°	117.116 11°	34.729 17°	116.178 89°	35.953 06°
119.272 50°	32.802 50°	117.003 61°	34.840 56°	116.189 44°	35.987 22°
119.218 89°	32.795 83°	116.980 56°	34.893 06°	116.187 78°	36.021 39°
119.284 72°	32.753 61°	116.906 94°	34.948 33°	—	—
—	—	116.801 39°	35.039 17°	—	—
—	—	116.787 50°	35.060 56°	—	—
—	—	116.696 11°	35.083 06°	—	—
—	—	116.668 89°	35.151 11°	—	—
—	—	116.652 78°	35.217 22°	—	—
—	—	116.608 61°	35.257 22°	—	—

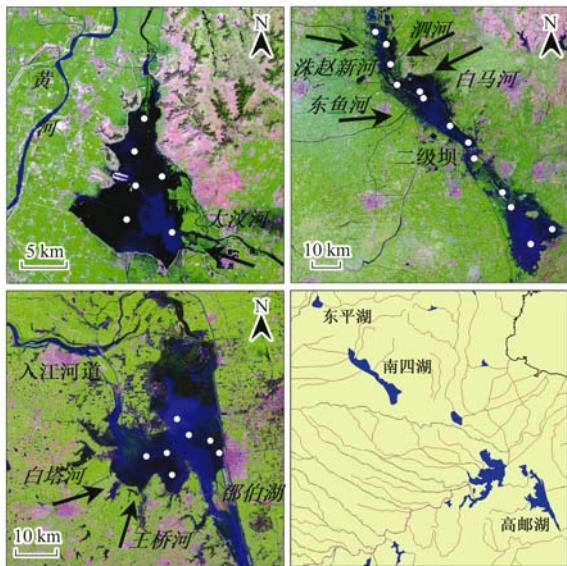


图1 高邮湖、南四湖和东平湖采样点布设示意

Fig. 1 Location of sampling sites in Lake Gaoyou, Lake Nansi, and Lake Dongping

1.2 水文数据

本研究所用淮河流域降雨量水文数据采集自淮河水利委员会(<http://www.hrc.gov.cn/>)。

1.3 紫外-可见吸收光谱参数和水质参数

主要水质参数 TN、TP 和 Chla 根据 Zhu 等^[14]的方法测定。采用 Shimadzu UV-2550 分光光度计及与之匹配的 5 cm 石英比色皿测定 CDOM 吸光度, 以 Milli-Q 水为空白对照, 在 200 ~ 800 nm 范围内每间隔 1 nm 测量 CDOM 的吸光度。扣除 700 nm 处吸光度以消除潜在颗粒物带来的散射效应, 根据公式(1)计算对应波长的吸收系数^[15]:

$$a(\lambda) = 2.303 \times D(\lambda)/r \quad (1)$$

式中, $a(\lambda)$ 表示 CDOM 在波长 λ 处对应的吸收系数 (m^{-1}), $D(\lambda)$ 表示扣除 700 nm 处吸光度后在波长 λ 处的吸光度, r 表示光程路径 (m)。

$S_{275-295}$ 是由 275 ~ 295 nm 波长范围内的吸收系数经指数函数拟合得到的光谱斜率, CDOM 在紫外及蓝光波段吸收光谱随波长增加呈指数函数递减。 $S_{275-295}$ 随 CDOM 腐殖化程度增大而减小, 根据公式(2)计算^[16]:

$$a(\lambda) = a(\lambda_0) \times \exp[S(\lambda_0 - \lambda)] \quad (2)$$

式中, $a(\lambda)$ 和 $a(\lambda_0)$ 分别指在波长 λ 和参考波长 $\lambda_0 = 440$ nm 下 CDOM 的吸收系数。

本研究使用生物培养前与培养后的 CDOM 相关指标差值, 即 $\Delta a(254)$ 和 $\Delta S_{275-295}$ 来表征生物培养后 CDOM 相对浓度和结构变化特征。

1.4 三维荧光光谱测定及平行因子分析

使用 F-7000 型荧光光度计(Hitachi 公司)测定样品 CDOM 荧光激发-发射光谱矩阵 (excitation-

emission matrices, EEMs), 设置激发光谱在 200 ~ 450 nm 范围, 间隔 5 nm; 发射光谱范围 250 ~ 600 nm, 间隔 1 nm。测得的三维荧光光谱先扣除超纯水 EEMs 以进行水拉曼散射校正, 同时用当日测得超纯水 EEMs 中 350 nm 激发条件下的荧光强度将所有 EEMs 定标为拉曼单位 (Raman unit, R. U.)^[17]。再采用 MATLAB 软件中的 drEEM 工具包通过切除及插值的办法进行瑞利散射校正, 同时使用每个样品 EEMs 激发发射波长相对应的吸光度进行内滤波效应校正^[18]。本研究使用荧光峰 C 峰与 T 峰积分比值 $I_C : I_T$ 来表征 CDOM 陆源类腐殖酸输入信号及 CDOM 光谱组成的变化, 该比值越大, CDOM 腐殖化程度越强^[19]。腐殖化指数 (humification index, HIX) 是 254 nm 激发条件下(本研究中由于激发波长间隔为 5 nm, 因而该处为 255 nm), 发射波长 435 ~ 480 nm 与 300 ~ 345 nm 的荧光强度积分的比值, 该指数越大, CDOM 腐殖化程度越高, 用于判定 CDOM 来源^[20,21]。

平行因子分析 (PARAFAC) 采用 MATLAB R2015b 的 drEEM 工具箱(ver. 0.2.0)完成, 共选取 104 个 [培养前后高邮湖共 7 个采样点 × 2 次采样 × 2(培养前后), 南四湖 13 个采样点 × 2 次采样 × 2(培养前后), 以及东平湖 6 个采样点 × 2 次采样 × 2(培养前后)] EEMs 矩阵进行运算, 每个矩阵对应 251 个发射波长、45 个激发波长。数据被剖分成 6 个随机子集, 取 3 个子集用于建模, 另外 3 个用于模型验证, 每个 EEMs 子集均逐步从 3 个组分模型逐步到 6 个组分检验。最终确定 4 个组分模型能很好地通过对半检验 (split-half analysis)、随机初始化分析 (random initialization analysis) 及残差分析 (residual analysis)。本研究采用每个荧光组分的最大荧光强度 (F_{\max}) 作为各类荧光物质浓度和荧光组分强度的表征^[22]。同时以生物培养前与培养后各组分 F_{\max} 的差值, 及差值占培养前组分 F_{\max} 的百分比值, 即 $\Delta C1 \sim \Delta C4$ 以及 $\% \Delta C1 \sim \% \Delta C4$ 来表征各个荧光组分的生物可利用性特征。

1.5 数据处理

采用 SPSS23.0 软件进行独立样本 t -test 和 Pearson 相关分析, 使用 ArcGIS10.2 绘制插值图, Origin 9.5 绘制图表, MATLAB R2015b 软件的 drEEM 工具箱进行平行因子分析建模。

2 结果与分析

2.1 水文特征及主要水质参数

高邮湖、南四湖均属于淮河流域, 东平湖分为老湖区和新湖区, 主要由老湖区蓄水且属于黄河流域,

而新湖区属于淮河流域，3个湖泊均地处季风影响显著的黄淮海平原区。由图2可知，淮河流域5~8月的月降水量为89.4~196.9 mm，1~4月和9~12月降水量在5.4~58.2 mm范围内。根据降水情况，本研究将2018年4月划为枯水期，2018年7月划为丰水期。3个湖泊主要水质参数见表2。

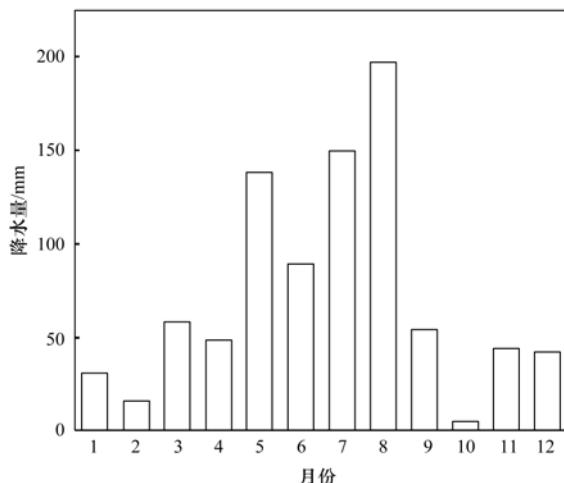


图2 2018年淮河流域月均降水量

Fig. 2 Monthly mean rainfall of Huaihe River watershed in 2018

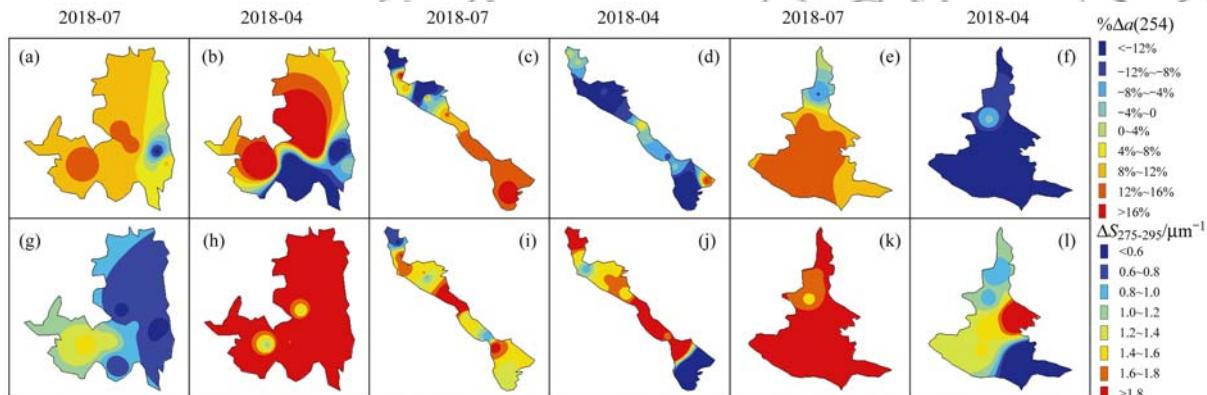


图3 不同水文情景下3个湖泊吸收系数% $\Delta a(254)$ 和 $\Delta S_{275-295}$ 空间分布

Fig. 3 Spatial distribution of % $\Delta a(254)$ and $\Delta S_{275-295}$ in Lake Gaoyou, Lake Nansi, and Lake Dongping in different hydrological scenarios

水期下游湖区% $\Delta a(254)$ 为正值，上游湖区为负值， $\Delta S_{275-295}$ 在湖区中部较高。东平湖枯水期% $\Delta a(254)$ 也为负值， $\Delta S_{275-295}$ 值在湖区中心较高，丰水期除北部出湖口外，其余湖区% $\Delta a(254)$ 为正值且 $\Delta S_{275-295}$ 值在各区域高于枯水期。

2.3 荧光组分

运用EEMs-PARAFAC对培养前后全部水样的荧光数据进行分析，鉴定出4种荧光组分（图4），两种类腐殖酸组分C1、C4和类蛋白组分C2、C3。C1激发和发射波长分别为245 nm和412 nm，组分C4分别对应两个激发和发射波长， $E_x/E_m = 265, 380/460$ nm。组分C1与微生物代谢相关，既可能是微生物矿化类蛋白，也可能来源于微生物对类腐殖酸的再处理，组分C4具有较强的陆源特征，主要来源于

表2 3个湖泊主要水质参数变化范围

Table 2 Ranges of water quality parameters of three lakes

湖泊	TP/mg·L ⁻¹	TN/mg·L ⁻¹	Chla/μg·L ⁻¹
高邮湖	0.05~0.13	1.66~2.70	20.38~78.10
南四湖	0.03~0.12	0.85~1.87	12.11~98.03
东平湖	0.03~0.12	1.04~1.58	21.62~65.67

2.2 吸收、荧光光谱参数变化特征

由表3可知，南四湖、东平湖和高邮湖吸收系数 $a(254)$ 在丰水期经生物培养28 d后，其值低于培养前，然而在枯水期略微增加。3个湖泊样品HIX值均高于培养前，且东平湖丰水期和高邮湖丰、枯水期样品显著高于培养前($P < 0.001$, $P = 0.001$, $P < 0.05$)， I_c/I_T 与HIX变化规律相似。南四湖和高邮湖丰、枯水期以及东平湖丰水期的样品 $S_{275-295}$ 值减小。图3表明，丰水期高邮湖% $\Delta a(254)$ 在西部入湖区域和湖中心均为正值且高于其他区域，其 $\Delta S_{275-295}$ 也在入湖区域较高。枯水期% $\Delta a(254)$ 在南部入湖区和北部湖区为正值且较高，湖区 $\Delta S_{275-295}$ 值大于1.8。南四湖枯水期% $\Delta a(254)$ 均为负值且空间分布较一致， $\Delta S_{275-295}$ 值在下级湖区高于上级湖区，而丰

水期% $\Delta a(254)$ 在各级湖区均为负值且空间分布不一致。东平湖% $\Delta a(254)$ 在丰水期和枯水期均为负值且空间分布一致， $\Delta S_{275-295}$ 值在各级湖区均为正值且空间分布不一致。高邮湖% $\Delta a(254)$ 在丰水期和枯水期均为正值且空间分布一致， $\Delta S_{275-295}$ 值在各级湖区均为负值且空间分布不一致。

2.4 荧光组分变化特征

由表4可知，不同水文情景下东平湖和南四湖的类腐殖酸C1和C4荧光强度均高于培养前，南四湖组分C2~C3和东平湖组分C2荧光强度($P < 0.001$, $P < 0.05$)低于培养前且小于30%。此外，丰水期东平湖和高邮湖(t -test, $P = 0.005$)组分C3荧光强度也低于培养前，% $\Delta C3$ 均值分别为24%和40%，高邮湖枯水期% $\Delta C1$ 、% $\Delta C3$ 和% $\Delta C4$ 为负值，3个组分累积程度较高（见图5）。

表3 不同水文情景下3个湖泊吸收系数 $a(254)$ 、 $S_{275-295}$ 、 $I_C:I_T$ 和HIX经培养28 d前后t检验Table 3 The t-test between the mean of $a(254)$, $S_{275-295}$, $I_C:I_T$ and HIX before and after 28 days

of bio-incubation of the three lakes in different hydrological scenarios

湖泊	项目	$a(254)/\text{m}^{-1}$	HIX	$S_{275-295}/\mu\text{m}^{-1}$	$I_C:I_T$
高邮湖	丰水期	0 d	22.9 ± 4.4	1.7 ± 0.4	21.5 ± 1.1
		28 d	20.7 ± 3.0	2.5 ± 0.6	20.0 ± 0.7
		P	>0.05	$=0.001$	<0.001
	枯水期	0 d	16.6 ± 1.0	1.3 ± 0.5	21.5 ± 2.1
		28 d	16.8 ± 8.6	1.7 ± 0.5	20.0 ± 1.4
		P	>0.05	<0.05	<0.05
南四湖	丰水期	0 d	24.9 ± 6.1	3.7 ± 0.4	18.1 ± 0.6
		28 d	23.4 ± 3.3	4.6 ± 2.1	17.3 ± 0.8
		P	>0.05	>0.05	<0.05
	枯水期	0 d	21.2 ± 4.6	2.2 ± 0.1	21.5 ± 0.8
		28 d	22.8 ± 2.4	2.5 ± 2.5	18.7 ± 1.5
		P	>0.05	>0.05	0.001
东平湖	丰水期	0 d	22.3 ± 2.3	2.0 ± 0.2	23.9 ± 0.7
		28 d	20.1 ± 2.2	2.7 ± 0.3	21.9 ± 0.5
		P	>0.05	<0.001	<0.001
	枯水期	0 d	23.0 ± 4.0	1.5 ± 0.2	22.2 ± 1.4
		28 d	28.8 ± 2.6	1.6 ± 0.3	21.1 ± 1.4
		P	<0.05	>0.05	>0.05

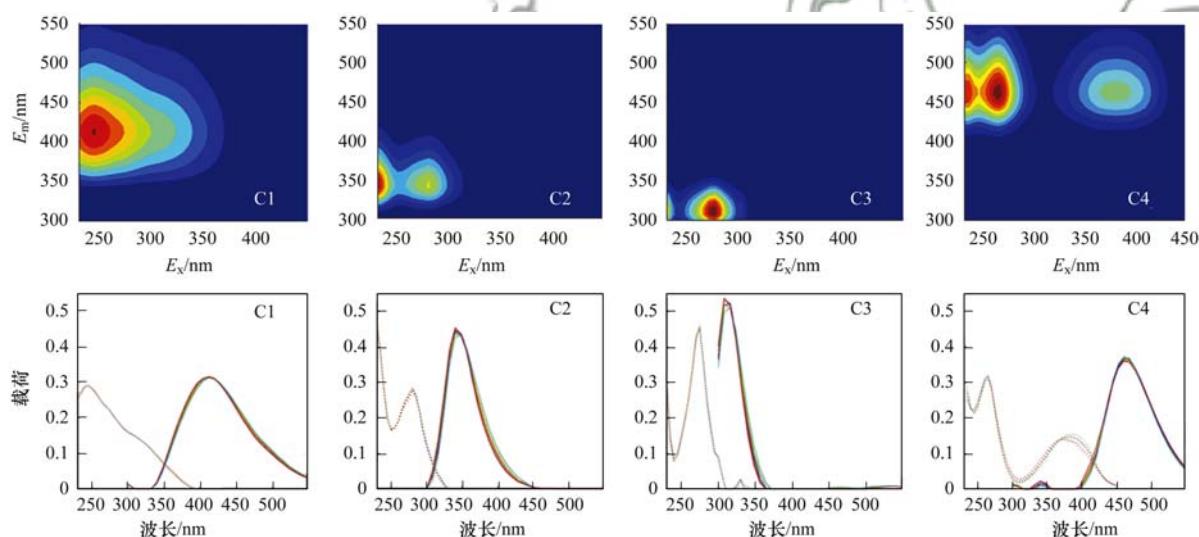


图4 对半检验和随机初始化检验PARAFAC模型得到4类荧光组分

Fig. 4 Four fluorescent components were obtained by PARAFAC modeling, and the model was validated using split-half analysis and random initialization

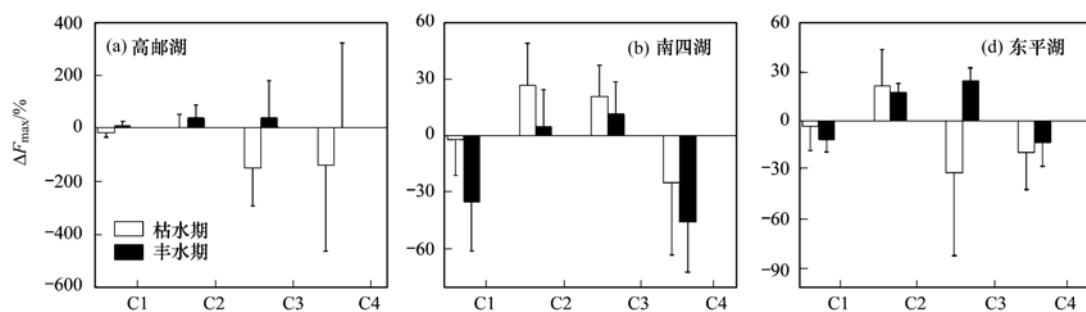


图5 不同水文情景下3个湖泊的荧光组分经生物培养28 d前后的变化

Fig. 5 Variability of the four fluorescent components of the three lakes pre-and post-28 days of bio-incubation in different hydrological scenarios

由图6(a)~6(h)可知,丰水期高邮湖% ΔC_1 和% ΔC_4 自西向东逐渐增大,东部临近运河小部分湖区正值,% ΔC_2 、% ΔC_3 在各湖区均为正值.枯水期% ΔC_1 、% ΔC_4 总体上为负值且分别在南部湖区和北

部区域最小。丰水期南四湖 $\% \Delta C1$ 和 $\% \Delta C4$ 在各湖区也为负值, $\% \Delta C2$ 同时存在正负值,无明显递变规律, $\% \Delta C3$ 在各湖区基本为正值且在入湖区域较高。枯水期 $\% \Delta C2$ 和 $\% \Delta C3$ 在各湖区为正值, $\% \Delta C1$ 在出湖口为负值且低于其他区域,湖区中部及北部区域为正值, $\% \Delta C4$ 均为负值且上级湖区较小[见图6(i)~6(x)]。

(p)].东平湖丰水期 $\% \Delta C1$ 为负值,从南到北逐渐减小,除出入湖口区域外, $\% \Delta C4$ 为负值。 $\% \Delta C2$ 和 $\% \Delta C3$ 为正值且在湖中心较大。枯水期东平湖 $\% \Delta C1$ 、 $\% \Delta C4$ 变化规律与丰水期相似,但 $\% \Delta C1$ 在中部和出湖口为正值。 $\% \Delta C2$ 在出湖口较低, $\% \Delta C3$ 仅在入湖口为正值[见图6(q)~6(x)]。

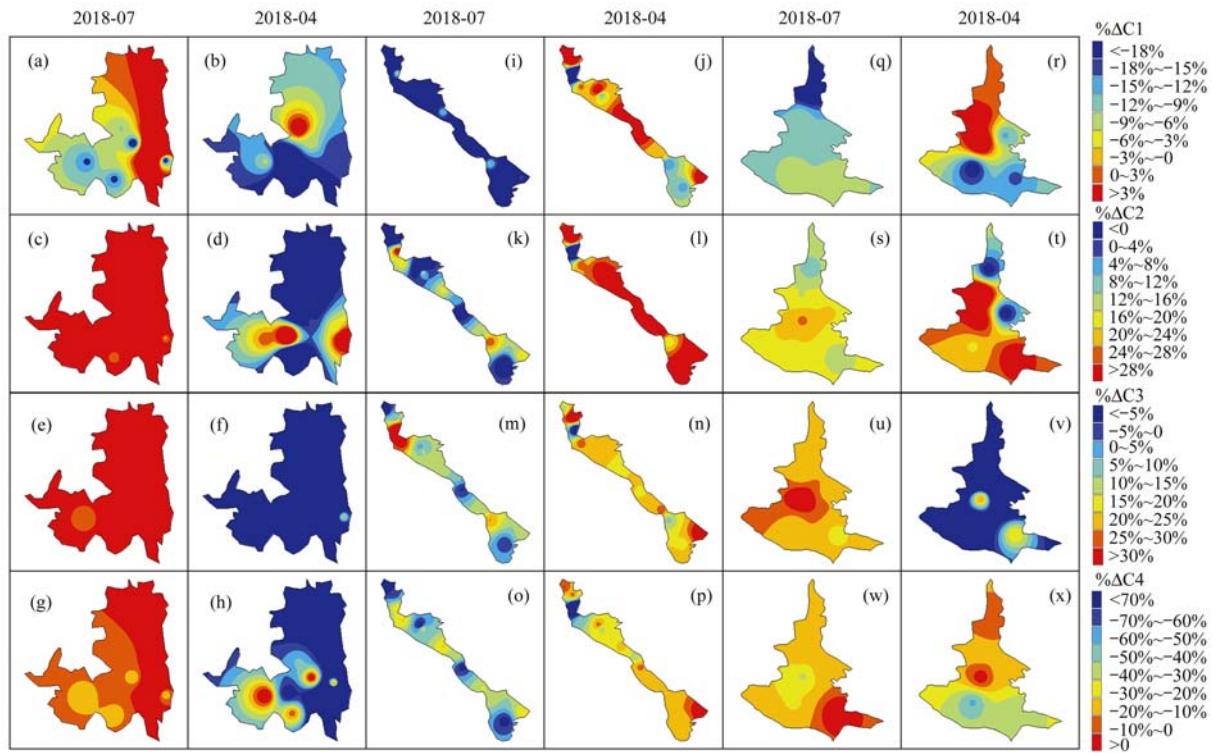


图6 同水文情景下4种荧光组分 $\% \Delta C1$ ~ $\% \Delta C4$ 的空间分布

Fig. 6 Spatial distribution of $\% \Delta C1$ - $\% \Delta C4$ in the three lakes in different hydrological scenarios

表4 不同水文情景3个湖泊生物培养28 d前后荧光组分t检验

Table 4 The *t*-test between the mean of F_{\max} of the four fluorescent components pre and post 28 days of bio-incubation of the three lakes in different hydrological scenarios

湖泊	项目	C1/R. U.	C2/R. U.	C3/R. U.	C4/R. U.
高邮湖	0 d	0.8 ± 0.2	0.4 ± 0.1	0.3 ± 0.1	0.2 ± 0.1
	28 d	0.8 ± 0.4	0.3 ± 0.1	0.2 ± 0.1	0.2 ± 0.1
	<i>P</i>	>0.05	0.008	0.005	>0.05
	0 d	0.6 ± 0.1	0.6 ± 0.1	0.3 ± 0.0	0.2 ± 0.0
	28 d	0.7 ± 0.1	0.5 ± 0.3	0.8 ± 0.5	0.4 ± 0.5
	<i>P</i>	>0.05	>0.05	<0.05	>0.05
南四湖	0 d	0.7 ± 0.1	0.8 ± 0.2	0.5 ± 0.2	0.2 ± 0.0
	28 d	0.9 ± 0.1	0.7 ± 0.1	0.4 ± 0.1	0.2 ± 0.0
	<i>P</i>	<0.001	>0.05	>0.05	<0.05
	0 d	0.7 ± 0.2	1.4 ± 0.6	0.7 ± 0.3	0.2 ± 0.1
	28 d	0.7 ± 0.1	1.0 ± 0.5	0.6 ± 0.2	0.2 ± 0.1
	<i>P</i>	>0.05	>0.05	>0.05	>0.05
东平湖	0 d	0.7 ± 0.1	0.7 ± 0.0	0.3 ± 0.1	0.1 ± 0.0
	28 d	0.8 ± 0.1	0.6 ± 0.0	0.2 ± 0.0	0.2 ± 0.0
	<i>P</i>	>0.05	<0.001	0.005	>0.05
	0 d	0.8 ± 0.1	1.2 ± 0.2	0.5 ± 0.1	0.2 ± 0.0
	28 d	0.7 ± 0.1	0.9 ± 0.2	0.7 ± 0.3	0.2 ± 0.0
	<i>P</i>	>0.05	<0.05	>0.05	>0.05

2.5 荧光组分与吸收、荧光光谱参数相关性分析

由表5可知,生物培养28 d后,高邮湖组分C1与 $a(254)$ 、HIX、 $I_c : I_T$ 显著正相关,与 $S_{275-295}$ 显著负相关,C3与 $a(254)$ 、HIX显著负相关,与 $S_{275-295}$ 显著正相关,表明组分C1、C3与CDOM丰度及结构的变化关系紧密。南四湖组分C1、C4与 $a(254)$ 显著正相关,与 $S_{275-295}$ 显著负相关,且C1与HIX和 $I_c : I_T$ 显著正相关。两种类蛋白组分与HIX、 $I_c : I_T$ 显著负

相关。表明了两种类腐殖酸累积影响CDOM结构组成特征。组分C1与C2、C3显著负相关,组分C1与C4显著正相关,说明组分C1的产生与组分C2、C3的降解有关。东平湖组分C2、C4与 $a(254)$ 显著正相关,同时C2、C3分别与HIX、 $I_c : I_T$ 显著负相关,表明组分C2和C4的生物可利用性对CDOM浓度的影响显著,类蛋白组分的降解对CDOM结构的影响也较大。

表5 生物培养后3个湖泊吸收荧光参数与4个荧光组分皮尔逊相关性分析¹⁾

Table 5 Pearson correlation analysis between absorption parameters and fluorescence

parameters of three lakes post the 28 days of bio-incubation

项目	$a(254)$	HIX	$S_{275-295}$	$I_c : I_T$	C1	C2	C3
高邮湖	C1	0.702 **	0.577 *	-0.678 *	0.741 **	—	—
	C2	0.014	-0.237	-0.009	-0.300	-0.438	—
	C3	-0.534 *	-0.558 *	0.579 *	-0.461	-0.526	0.274
	C4	0.069	0.670 **	0.096	0.440	-0.007	-0.069
南四湖	C1	0.659 **	0.758 **	-0.498 **	0.765 **	—	—
	C2	-0.114	-0.601 **	0.065	-0.710 **	-0.407 *	—
	C3	-0.247	-0.856 **	-0.269	-0.807 **	-0.457 *	0.746 **
	C4	0.567 **	0.011	-0.474 *	-0.029	0.259	0.522 *
东平湖	C1	0.549	0.014	-0.498	0.182	—	—
	C2	0.735 **	-0.790 **	-0.329	-0.809 **	0.252	—
	C3	0.554	-0.841 **	0.072	-0.778 **	0.075	0.500
	C4	0.835 **	-0.235	-0.622 *	-0.176	0.779 **	0.536

1) *表示 $P < 0.05$, **表示 $P < 0.01$

3 讨论

3.1 不同水文情景对湖泊CDOM荧光组分生物降解特征的影响

南四湖枯水期荧光组分生物可利用性高于丰水期,而其余两个湖泊与之相反,而Wu等^[8]的研究发现得克萨斯州南部的5条河流冬季DOM的生物可利用性高于夏季。这是由于是丰水期降雨水和外源输入的共同作用,引入的DOM生物活性较高,且已有研究表明雨水中DOM的生物可利用性潜力更大^[26]。丰水期3个湖泊类蛋白荧光强度均低于培养前,而类腐殖酸荧光强度有所增加,南四湖和高邮湖的类腐殖酸与HIX显著正相关进一步说明微生物作用增强了CDOM的腐殖化程度。枯水期高邮湖和东平湖类蛋白C2荧光强度降低而C3荧光强度增加,表明枯水期类蛋白组分生物活性较低,由于不同季节CDOM来源存在差异进而影响了微生物的降解能力^[27]。同时,研究发现不同季节南四湖类腐殖酸C1荧光强度与两种类蛋白荧光强度显著负相关,表明了微生物优先利用类蛋白物质与类腐殖酸C1的产生紧密相关,这与程琼等^[28]的研究结果相似,3个湖泊微生物降解作用促进了水体中类腐殖物质的转化,不稳定的CDOM组分在微生物作用下

趋向于转化为性质更稳定的物质。Dong等^[29]对黄浦江的研究也发现不稳定CDOM物质的微生物转化有助于类腐殖物质的积累,可见微生物对有机物质的分解和转化起到了不可忽视的作用。

3.2 不同水文情景对湖泊CDOM生物降解空间分布特征的影响

微生物降解能力一方面取决于CDOM自身结构特征,另一方面也受到微生物代谢强度,外源输入等因素的影响^[27]。丰水期高邮湖西部入湖口及湖中心类腐殖酸%ΔC1和%ΔC4为负值,而全湖类蛋白%ΔC2和%ΔC3高于28%,西部入湖区域受外源输入影响较大,该区域类蛋白的生物可利用性较高且伴随类腐殖酸累积,随着迁移转化过程中紫外光辐射的作用,CDOM不稳定性增强,所以东部湖区出现类腐殖酸减少的现象^[30]。类蛋白组分在丰水期显著降低可以进一步说明。枯水期高邮湖的类腐殖酸%ΔC1和%ΔC4为负值且分别在湖区南部入湖口和北部最小,而%ΔC2仅在入湖口和东南湖区为正值,表明了枯水期不同湖区各个荧光组分的活性较低。枯水期南四湖两类蛋白的生物可利用性受空间位置的影响较小,类腐殖酸主要在上级湖泊累积,上级湖泊接纳外源河流输入的影响。丰水期南四湖类腐殖酸在全湖区都有累积现象,而组分C3的生物可利用

性从北部入湖口到南部出湖口有降低的趋势,由于上级湖区主要用于蓄水,而下级湖泊保证了泄洪安全,因此上级湖泊可能截留了更多具有生物潜力的CDOM^[31]。丰水期东平湖类蛋白物质为正值且在湖中心最高,然而湖区中心和出湖口两种类腐殖酸累积也较高,意味着东平湖湖区中心类蛋白组分生物可利用性较高,这与湖泊地形位置不同有关^[32]。枯水期东平湖入湖口至出湖口方向类色氨酸的生物可利用性逐渐降低,同时两种类腐殖酸累积程度也在减少,这与迁移过程可能增加了东平湖不稳定组分的矿化程度相关^[33]。

3.3 3个湖泊 CDOM 生物可利用性特征的潜在环境指示意义

微生物作用后,高邮湖、南四湖和东平湖丰水期水样 CDOM 的吸收系数 $\Delta a(254)$ 为正值,而枯水期 $a(254)$ 值略微高于培养前,这可能是由于枯水期水样中微生物的裂解作用导致的^[34]。同时 CDOM 的类蛋白组分占比减少且微生物作用后的类腐殖酸增加,HIX 值也随之增加,意味着发生了类腐殖酸的转化,与 Shin 等^[35]的研究结果相似。一定程度上指示了微生物消耗湖泊类蛋白物质,可以减缓湖泊富营养化程度^[36]。然而,3个湖泊 $S_{275-295}$ 值在不同水文情境下也显著低于培养前, $I_C : I_T$ 均增大可以进一步印证 CDOM 腐殖化程度的增强。天然水体中类腐殖酸结构复杂,丰富的官能团对重金属离子和其他有毒污染有机物具有吸附络合作用,另一个方面说明微生物作用提高了 CDOM 的腐殖化程度可能会增加复合污染物质,降低水环境质量^[37,38]。因此,CDOM 生物可利用性特征对环境的潜在指示意义还需进一步研究。

4 结论

(1) 紫外-可见吸收光谱和荧光光谱参数能较好地表征 CDOM 生物可利用性特征。不同水文情景下,东平湖、南四湖和高邮湖 CDOM 样品均出现类蛋白物质的消耗和类腐殖酸的累积现象。微生物优先降解不稳定的类蛋白物质,并增加了 CDOM 腐殖化程度。

(2) 不同湖泊 CDOM 来源和组成存在差异,微生物降解特性不同。丰水期高邮湖和东平湖 CDOM 荧光组分生物可利用性高于枯水期,而南四湖在枯水期较高。丰水期高邮湖类蛋白组分的生物可利用性高于南四湖和东平湖,且枯水期高邮湖类腐殖酸累积程度高于其余两个湖泊。

(3) 整体上 3 个湖泊入湖河口区域类蛋白物质生物可利用性及类腐殖酸的累积高于其余湖区,因而有必要加强入湖河流周边流域人类污染物排放管

理,尤其是丰水期,以此降低因局部 CDOM 生物可利用性过高而对水质造成的潜在危害。

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