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# 思林水库荧光溶解性有机质的特征、来源及其转化动力学

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**摘要:** 利用三维荧光光谱(EEM)结合平行因子分析(PARAFAC), 研究了思林水库冬季(1月)、春季(4月)、夏季(6月)和秋季(10月)上游入库水体、库区表层水(0 m)、库区深层水(20 m)、出库水体的荧光溶解性有机质(FDOM)不同组分的特征、来源及其转化动力学。结果表明, 思林水库的溶解性有机质由3种荧光组分组成, 分别是: 陆源类腐殖质(C类, C1)、浮游植物源的微生物类腐殖质(M类, C2)和浮游植物源的类蛋白或类色氨酸或类酪氨酸(C3)。其中陆源类腐殖质的荧光强度随着入库水、库区表层水、库区深层水和出库水逐渐减少, 这表明由于光化学作用、微生物作用、大坝拦截效应等环境因素的影响, 类腐殖质随着水体由入库向出库的流动而逐渐降解。相反, 微生物类腐殖质(M类)的荧光强度结果表明, 在入库-出库过程中, 微生物类腐殖质处于产生及部分或完全降解的波动中, 这表明微生物类腐殖质是浮游植物的原生产物, 并且对于光化学作用、微生物作用和大坝拦截效应有很强不稳定性。类蛋白或类色氨酸或类酪氨酸主要新产生于夏季和秋季的表层水体中, 在冬季和春季表层和深层水体中也有产生; 并在出库过程中逐渐减少。这表明类蛋白或类色氨酸或类酪氨酸是浮游植物的原生产物; 并且它们受到光化学作用、微生物作用和大坝拦截效应的共同影响, 在表层和深层水中生成和降解。因此, 这些结果意味着通过平行因子分析确定的荧光溶解性有机质组分的方法, 对于更好地理解溶解性有机质在水库水体的转化动力学机制至关重要。

**关键词:** 思林水库; 荧光溶解性有机质(FDOM); 三维荧光光谱(EEMs); 平行因子分析(PARAFAC); 荧光组分

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## Sources, Characteristics and Transformation Dynamics of Fluorescent Dissolved Organic Matter in the Silin Reservoir

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**Abstract:** The aim of this study was to examine the sources and characteristics of various fluorescent dissolved organic matter (FDOM) components as well as their transformation dynamics. FDOM was determined in the incoming, surface (0 m), deeper (20 m), and outflowing waters of the Silin Reservoir in winter (January), spring (April), summer (June), and autumn (October) using excitation-emission matrix (EEM) spectra coupled with parallel factor (PARAFAC), EEM-PARAFAC modelling. The EEM-PARAFAC modelling results demonstrated that dissolved organic matter (DOM) in the Silin Reservoir waters was composed of three fluorescent components. These included terrestrial humic-like substances (C type) of terrestrial origin (component 1), microbial humic-like substances (M type) of phytoplankton origin (component 2), and protein-like or tryptophan-like or tyrosine-like (component 3) of phytoplankton origin. In addition, the terrestrial humic-like substances (C type) was identified from two fluorescence peaks (peak C at  $E_x/E_m = 305-355/414-458$  nm and peak A at  $E_x/E_m = 245-270/414-458$  nm) while the microbial humic-like substances (M type) was identified from peaks that included peak M at  $E_x/E_m = 280-305/380-398$  nm and peak A 230-235/380-417 nm. Similarly, protein-like or tryptophan-like or tyrosine-like components were also detected from two fluorescence peaks, including peak T 270-285/316-354 nm and peak  $T_{uv}$  225-230/316-354 nm. The fluorescence intensity of terrestrial humic-like substances gradually decreased in incoming waters to surface (0 m), deeper (20 m), and subsequently, in outflowing waters. This indicates the gradual degradation of the humic-like substances and their recalcitrant nature during water transport during the incoming-surface-deeper-outflowing water cycle in both summer and winter seasons by numerous environmental factors. These included photochemical, microbial, and dam barrier-affected physical processes. Conversely, from the fluorescence intensity results of microbial humic-like substances (M type), production or partial (in some cases complete) degradation in surface-deeper-outflowing waters, fluctuated. This suggests that microbial humic-like substances are autochthonously produced from phytoplankton, but are highly labile in response to photochemical, microbial, and dam barrier-affected physical processes. From the fluorescence intensity results of protein-like or tryptophan-like or tyrosine-like substances, it demonstrated that they were newly produced in surface (0 m) waters in the summer season, but in the winter season they were significantly produced in both surface and deeper waters of the reservoir, and

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then decreased in the outflowing waters. This suggests that protein-like or tryptophan-like or tyrosine-like substances are autochthonously produced by phytoplankton that simultaneously reproduced and then were degraded in surface and deeper waters by photochemical, microbial, and dam barrier-affected physical processes. These results therefore imply that the FDOM components identified by EEM-PARAFAC modelling are crucial to better understand the source characteristics of bulk DOM, its transformation mechanisms, and its the dynamics in a reservoir water system.

**Key words:** Silin Reservoir; fluorescent dissolved organic matter (FDOM); excitation-emission matrix spectra (EEMs); parallel factor analysis (PARAFAC); fluorescence component

荧光溶解性有机质 (fluorescent dissolved organic matter, FDOM) 是溶解有机质 (dissolved organic matter, DOM) 的重要组成部分, 它可以吸收太阳能并发射荧光. 地表水中关键的荧光溶解有机质主要由外源腐殖质 (胡敏酸和富里酸)、各种微生物类腐殖质、类蛋白质、芳香类氨基酸 (色氨酸、酪氨酸和苯丙氨酸) 及它们的降解产物组成<sup>[1-3]</sup>. 类腐殖质物质 (主要是陆源富里酸类物质) 的荧光被认为主要发现于河流、湖泊和沿海地区<sup>[4-8]</sup>. 在湖泊或水库水体中通常会观察到微生物类腐殖质和类蛋白质或类色氨酸物质, 它们主要来自浮游植物或藻类物质<sup>[4,9,10]</sup>.

FDOM 组分通常由各种官能团组成, 例如含苯环的羧基 ( $-\text{COOH}$ )、甲氧基 ( $-\text{OCH}_3$ ) 及酚羟基 ( $-\text{OH}$ )、 $-\text{NH}_2$ 、 $-\text{NH}-$ 、 $-\text{CH}=\text{CH}-\text{COOH}$ 、 $-\text{OCH}_3$ 、 $-\text{CH}_2-(\text{NH}_2)\text{CH}-\text{COOH}$  和含 S、O 或 N 的芳族化合物<sup>[1,11-14]</sup>. FDOM 中的这些官能团可以影响水体酸碱特性、营养物质的有效性以及污染物的环境行为, 例如毒性、迁移和转化特性以及水环境中污染物的生物降解性<sup>[15,16]</sup>. 有研究表明, FDOM 组分在自然光照下 (地表水或实验条件下) 可发生光化学分解<sup>[17-20]</sup>. FDOM 的降解过程, 无论是自然光下的光化学降解还是深层水中的微生物降解, 都可以诱导各种光化学和微生物产物的释放, 如低分子量的 DOM、 $\text{CO}_2$ 、溶解性无机碳 (DIC, 通常定义为溶解的  $\text{CO}_2$ 、 $\text{H}_2\text{CO}_3$ 、 $\text{HCO}_3^-$  和  $\text{CO}_3^{2-}$ )、 $\text{PO}_4^{3-}$ 、 $\text{NH}_4^+$ 、 $\text{H}_2\text{O}_2$  和有机过氧化物等<sup>[17,19-21]</sup>. FDOM 的产物及其在光化学过程、微生物降解过程或物理过程等条件下的转化, 与地表水 (特别是在湖泊或水库) 环境中的微生物食物链及碳氮循环直接相关, 并在其中起到重要作用<sup>[21-26]</sup>. 因此, 这些 FDOM 成分在水生态系统的关键生物地球化学过程中发挥着重要作用<sup>[1]</sup>.

三维荧光 (激发-发射矩阵, EEM) 光谱结合平行因子分析 (EEM-PARAFAC), 被广泛用于精确和简便地识别水、雪、沉积物和土壤中的 FDOM 组分<sup>[1,3,5-8]</sup>. EEM-PARAFAC 目前用于表征 FDOM 组分的来源及其在淡水和海水中的季节-时空-垂直-日变化、光化学和微生物变化、金属-DOM 络合、细胞

外聚合物物质及其与类腐殖质分子水平的连接、沉积物孔隙水的史前变化、海底热液系统、以及牛粪中酪氨酸的检测<sup>[1-3,5-8,27-29]</sup>.

近年来, 关于水库体系中 FDOM 的研究主要集中在于水库整体的来源、时空特征变化规律等<sup>[30,31]</sup>, 对于水库体系 FDOM 合成以及降解机制的研究有所欠缺. 此外, 现有研究在应用 PARAFAC 模型分析荧光组分时是将入库、库区和出库水等在内的所有样品一起分析, 从而导致对不同采样点样品中 FDOM 的真实来源尚不明晰. 本研究借助 EEM-PARAFAC 模型, 描述了乌江流域思林水库各个季节各种 FDOM 组分的来源及其动力学特征. 为了研究大坝拦截对 FDOM 动力学及其随后的生成和降解机制的影响, 本文分别分析鉴定了该水库入库水、表层水 (0 m)、深层水 (20 m) 和出库水的 FDOM 组分. 随着 PARAFAC 模型应用范围的扩大, 它可以被用来着重研究不同水文条件下河流库区陆源腐殖质和其他内源 FDOM 组分的动态变化.

## 1 材料与方法

### 1.1 研究区域

乌江是长江上游右岸最大的一级支流, 流域位于东经  $104^\circ 10' \sim 109^\circ 12'$ , 北纬  $25^\circ 56' \sim 30^\circ 22'$  之间, 南源三岔河源于贵州乌蒙山东麓的香炉山花鱼洞, 北源六冲河源于贵州省赫章县, 整个河流横穿贵州省中部, 在东北部出境入重庆市, 于涪陵汇入长江, 素有贵州人民的“母亲河”之称. 流域面积  $87\,920\text{ km}^2$ , 全长  $1\,037\text{ km}$ , 总落差  $2\,124\text{ m}$ , 多年平均流量  $1\,690\text{ m}^3 \cdot \text{s}^{-1}$ . 乌江水电开发采用 11 级方案, 坝址分别定于普定、引子渡、洪家渡、东风、索风营、乌江渡、构皮滩、思林、沙沱、彭水、大溪口.

思林水电站属于乌江流域梯级开发的第 8 级电站, 是国家实施西部大开发战略的重点工程之一, 也是贵州省“西电东送”工程的骨干工程. 电站坝址位于思南县思林乡、塘头镇、邵家桥镇交界处, 上距构皮滩电站坝址  $89\text{ km}$ , 下距思南县城  $23\text{ km}$ 、沙沱水电站  $115\text{ km}$ . 水库流域主要有两大支流: 一是左岸的六池河, 回水影响至东方红电站坝下; 二是

右岸的余庆河,回水影响至大沙坝电站坝下. 其余较小的支流还有右岸的跳墩河和左岸的辉塘河等. 水库正常蓄水位 440 m,库容 12.05 亿  $\text{m}^3$ ,淹没影响总面积 38.95  $\text{km}^2$ ,其中陆地面积 28.08  $\text{km}^2$ ,主要涉及思南、石阡、凤冈、余庆 4 县的 16 个乡镇 100 个村 297 个村民组.

## 1.2 样品的采集和处理

本研究在思林水库设置了 5 个采样点位(图

1). 入库和出库处均采集表层水(0 m),库区采集表层(0 m)和深层水(20 m). 于 2017 年的 1、4、6、10 月采集水样装于预先用超纯水清洗并烘干的聚对苯二甲酸乙二醇酯(PET)塑料瓶中,瓶子用黑色聚乙烯袋包裹,以保护水样免受太阳辐射. 水样放入保温箱中运回实验室,经 0.45  $\mu\text{m}$  玻璃纤维滤膜(GF/F, 450 $^{\circ}\text{C}$  马氟炉中灼烧 5 h 后使用)过滤后,备后续测试分析.



图 1 思林水库采样点位置示意

Fig. 1 Distribution of sampling sites in the Silin Reservoir

## 1.3 分析方法

在室温下,使用 700 V 电压氙灯作为激发光源,使用日立 F-7000 荧光分光光度计测定水样的三维荧光光谱. 激发波长( $E_x$ )扫描范围为 220 ~ 400 nm,发射波长( $E_m$ )扫描范围为 280 ~ 500 nm,激发波长的增量为 5 nm,发射波长的增量为 1 nm,狭缝宽度为 5 nm,扫描速度为 1 200  $\text{nm}\cdot\text{min}^{-1}$ . 分析前比色皿经 5% 硝酸溶液冲洗并超声处理. 使用硫酸奎宁溶液( $4 \mu\text{g}\cdot\text{L}^{-1}$ 溶于  $0.05 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{SO}_4$ 中)在  $E_x/E_m = 350/450 \text{ nm}$  处的荧光强度将三维荧光光谱的荧光强度(FI)校准为硫酸奎宁单位(QSU). 为了消除内滤效应,对扫描的样品进行紫外吸光度检测,确保其在波长 254 nm 处的吸光度小于 0.1<sup>[32]</sup>.

## 1.4 平行因子分析

在 MATLAB 中使用 N-way Toolbox for MATLAB version 3.1,按照先前研究中描述的方法对不同季节和采样点的 28 个样品进行平行因子分析<sup>[33]</sup>. 使用自制的 Excel 程序,从样品的三维荧光光谱中减去超纯水背景,并对荧光强度很低、含有荧光信息很少的三角区域和瑞利散射明显的区域置 0. 模型

通过对半检验法(split-half analysis),将数据库分为 2 个随机的子数据库;通过对比不同组分时模型的激发和发射光谱的误差平方和曲线来初步确定模型的组分. 若这 2 组对应的曲线越平滑,含有波峰越少,则模型的拟合效果越好. 通过对比 2 个子数据库激发和发射波长的载荷,以及模型拟合的三维荧光光谱同实测的三维荧光光谱,分析三者是否基本一致,来进一步验证模型的可靠性,并最终确定组分的个数<sup>[34]</sup>.

## 2 结果与讨论

### 2.1 入库、库区、出库水体的荧光组分特征

根据平行因子模型分析识别出的组分特征见图 2、图 3 和表 1. 总体上有以下结果:夏季和秋季思林水库的入库水体和库区深层水体含有两种荧光组分,在库区表层水中含有 3 种荧光组分,在出库水中发现了一种荧光组分(图 2 和表 1). 在冬季和春季所有的采样点均发现了 3 种荧光组分(图 3 和表 1). 以下详细阐述这 3 种荧光组分.

组分 1 被确定为具有两个荧光峰的陆源类腐殖质(夏季和秋季:峰 C 305 ~ 355/414 ~ 440 nm,峰 A

245 ~ 270/414 ~ 440 nm, 冬季和春季: 峰 C 305 ~ 335/440 ~ 458 nm, 峰 A 260 ~ 270/440 ~ 458 nm; 表 1). 夏季和秋季陆源腐殖质组分的激发/发射波长最大值发生了显著变化, 其中出库(峰 C 305/415 nm, 峰 A 245/415 nm)和入库水(峰 C 330/414 nm, 峰 A 260/414 nm)比库区表层(峰 C 355/431 nm, 峰 A 270/431 nm)和深层水(峰 C 305/440 nm, 峰 A 260/440 nm)的最大发射波长要低(称为“蓝移”)(表 1), 这可能是由于水体迁移和大坝拦截效应造成的. 在冬季和春季则没有观察到这种“蓝移”现象(表 1), 这可能是由于冬季和春季较低的气温和较低的光照强度, 使得入库、库区和出库水中 DOM 的荧光组分不能分解或转化. 这些结果表明, 陆源的类腐殖质在光化学、微生物和物理过程中(由于大坝拦截造成的水体坠落碰撞)是不易被降解的. 早期的研究也报道了陆源类腐殖质的这种稳定性<sup>[3,7,11,18,35]</sup>.

组分 2 代表了微生物类腐殖质. 在夏季和秋季, 仅在库区深层水体中检测到两个荧光峰, 但在入库和库区表层水中只有一个荧光峰(峰 A), 而在出库水中完全降解(图 2 和表 1). 而在冬季和春季, 在入库(峰 M 280/381 nm, 峰 A 235/381 nm)、库区表层(峰 M 280/380 nm, 峰 A 230/380 nm)、库区深层(峰 M 285/380 nm, 峰 A 230/380 nm)和出库水(峰 M 305/398 nm, 峰 A 235/398 nm), 中均发现了这类腐殖质(图 3 和表 1). 基于之前的研

究, 这些结果表明微生物类腐殖质可能来自浮游植物<sup>[1~3,10]</sup>. 对比分析不同季节的结果表明, 冬季和春季在入库、库区表层和深层以及出库水体中的微生物类腐殖质对光化学和大坝拦截效应物理过程不敏感, 不易发生降解作用, 这可能是由于冬季和春季较低的光照强度以及较低水温的共同作用. 据报道, 浮游植物源的 DOM 是比陆源 DOM 更有效的光化学底物<sup>[36,37]</sup>. 因此, 夏季和秋季的微生物类腐殖质在光化学作用、微生物作用和大坝拦截效应物理过程作用下是高度不稳定的.

组分 3 被确定为类蛋白质或类色氨酸物质, 在夏季和秋季, 仅在库区表层水和深层水中找到具有两个荧光峰(峰 T 280/340 ~ 354 nm, 峰 T<sub>uv</sub> 230/340 ~ 354 nm)的类蛋白质或类色氨酸组分. 但在冬季和春季, 在入库、库区表层和深层水以及出库的水体中, 均发现了具有两个荧光峰的类蛋白质或类色氨酸组分(峰 T 270/316 ~ 323 nm, 峰 T<sub>uv</sub> 225/316 ~ 323 nm; 图 2、图 3 和表 1). 这些物质通常由浮游植物在光化学下产生, 或由微生物呼吸作用产生<sup>[2, 35, 38]</sup>. 通过各个季节的结果可以得出, 夏季和秋季类蛋白质或类色氨酸物质在入库、库区表层与深层以及出库水中, 均易通过微生物作用降解或大坝拦截作用物理降解. 而在冬季和春季, 类蛋白质或类色氨酸物质对光化学作用、微生物作用和大坝拦截作用均表现出稳定性.

表 1 各采样点各季节荧光组分特征及荧光强度<sup>1)</sup>

Table 1 Fluorescence characteristics and intensity in each season at each sampling site

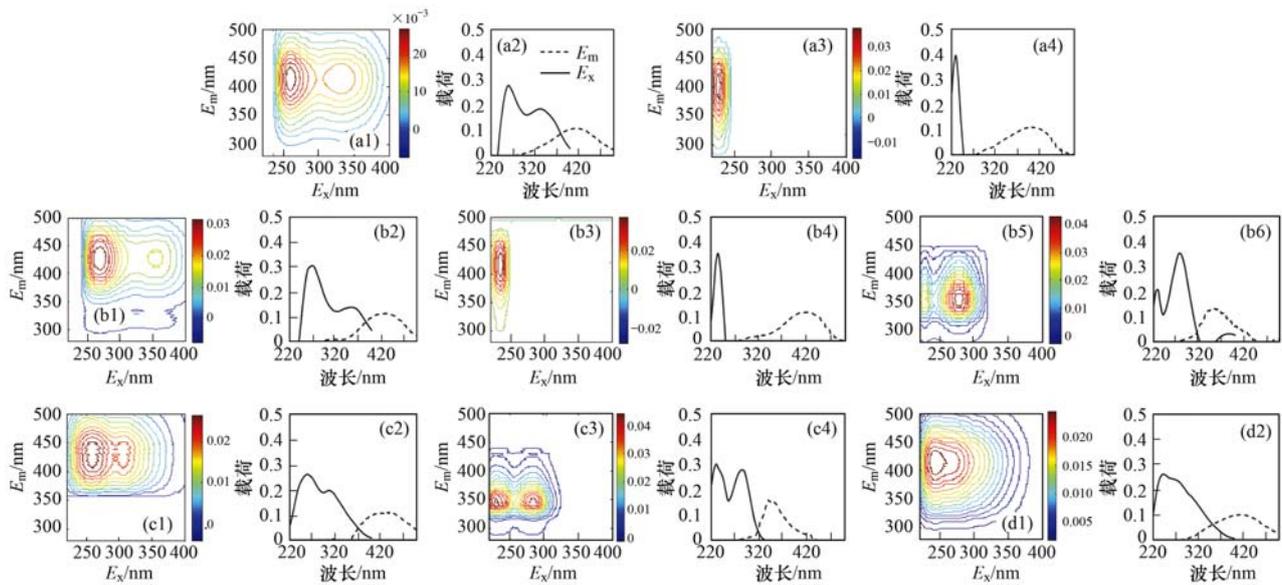
项目	组分 1		组分 2			组分 3	
	峰 A	峰 C	峰 A	峰 M	峰 T <sub>uv</sub>	峰 T	
入库水(6 月和 10 月)	260/414 (938 ~ 1080)	330/414 (622 ~ 717)	230/398 (764 ~ 1074)	—	—	—	
表层水(6 月和 10 月)	270/431 (790 ~ 1320)	355/431 (355 ~ 594)	235/417 (601 ~ 1176)	—	230/354 (228 ~ 272)	280/354 (388 ~ 463)	
深层水(6 月和 10 月)	260/440 (522 ~ 618)	305/440 (394 ~ 466)	—	—	230/340 (736 ~ 1001)	285/340 (660 ~ 948)	
出库水(6 月和 10 月)	245/415 (375 ~ 590)	305/415 (249 ~ 391)	—	—	—	—	
入库水(1 月和 4 月)	270/449 (504 ~ 647)	315/449 (271 ~ 348)	235/381 (404 ~ 507)	280/381 (300 ~ 376)	225/322 (206 ~ 560)	270/322 (363 ~ 699)	
表层水(1 月和 4 月)	270/449 (424 ~ 542)	315/449 (233 ~ 298)	230/380 (403 ~ 479)	280/380 (221 ~ 262)	225/316 (211 ~ 542)	270/316 (459 ~ 781)	
深层水(1 月和 4 月)	260/432 (446 ~ 584)	305/432 (289 ~ 379)	230/380	285/380	225/323 (540 ~ 1052)	270/323 (525 ~ 627)	
出库水(1 月和 4 月)	260/458 (283 ~ 381)	335/458 (174 ~ 235)	235/398 (473 ~ 584)	305/398 (277 ~ 342)	225/322 (147 ~ 246)	270/322 (332 ~ 557)	

1) 括号外为荧光峰的位置, 单位为 nm, 括号内为荧光强度, 单位为 QSU

## 2.2 各个季节荧光组分的转化和动力学特征

通过比较入库水、库区表层水与深层水、出库水的荧光强度, 可以得到在夏季和秋季陆源类腐殖质物质的荧光强度逐渐降低, 库区表层水和深层水与入库水相比分别下降了约 35% 和 38%. 在出库水中荧光强度降低得更显著, 与入库水、库区表层水和深层水相比分别降低了约 53%、27% 和 23% (图 4). 在冬季和春季, 库区表层水和深层水与入库水相比陆源类腐殖质的荧光强度分别降低了约

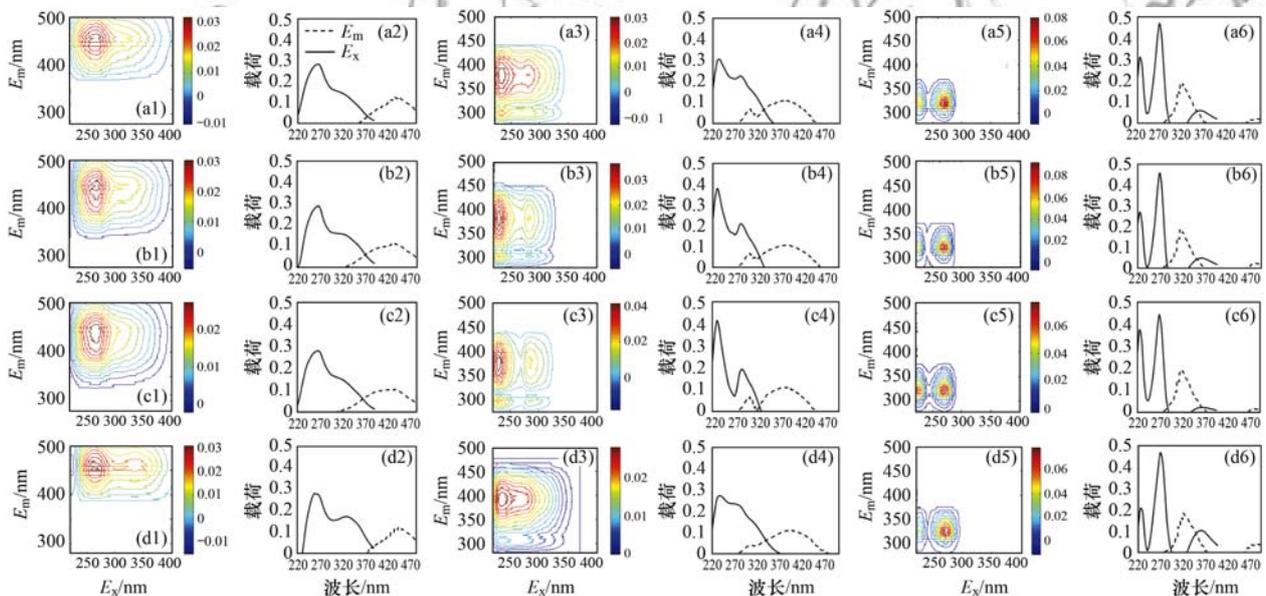
13% 和 4%, 而入库水、库区表层水和深层水与出库水相比降低了约 33%, 22% 和 30% (图 4). 夏季和秋季库区表层水体荧光强度的降低(35%)显著高于冬季和春季(13%), 这可能是由于强烈的太阳光照使得水温升高导致的夏季和秋季的光化学降解作用明显强于冬季和春季(夏季和秋季: 22.0 ~ 25.8℃, 冬季和春季: 16.2 ~ 20.1℃). 由于光照强度驱动的水温变化与光诱导产生 H<sub>2</sub>O<sub>2</sub> 直接相关, 可以推断出夏季和秋季 H<sub>2</sub>O<sub>2</sub> 产量显著增加, 冬季



(a) 入库水(0 m, 6 月和 10 月); (b) 库区表层水(0 m, 6 月和 10 月);  
(c) 库区深层水(20 m, 6 月和 10 月); (d) 出库水(0 m, 6 月和 10 月)

图 2 平行因子分析鉴别出的夏季与秋季荧光组分及其激发发射波长载荷

Fig. 2 Fluorescence components of June and October samples identified by the PARAFAC model and their excitation and emission wavelength loading



(a) 入库水(0 m, 1 月和 4 月); (b) 库区表层水(0 m, 1 月和 4 月);  
(c) 库区深层水(20 m, 1 月和 4 月); (d) 出库水(0 m, 1 月和 4 月)

图 3 平行因子分析鉴别出的冬季与春季荧光组分及其激发发射波长载荷

Fig. 3 Fluorescence components of January and April samples identified by the PARAFAC model and their excitation and emission wavelength loading

产量则相对较低并且地表水存在强烈的昼夜变化<sup>[39~41]</sup>。同样,较低的光照强度和水温会导致 $H_2O_2$ 产量较低,可能会降低 $\cdot OH$ 的生成速率<sup>[42]</sup>;  $\cdot OH$ 是一种强氧化剂,可诱导水中 DOM 或有机污染物的光降解<sup>[43]</sup>。这种降解最终可能产生低分子量有机质和许多其他产物,包括 $CO_2$ 和 DIC<sup>[18,20,21,23,44]</sup>。因此,水中的 $CO_2$ 和 DIC 可以直接或间接释放到大气中,从而促进全球碳循环和气

候变化<sup>[45~48]</sup>,同时可以为湖泊和水库系统的初级生产力做出贡献<sup>[44,49,50]</sup>。在由大坝拦截河流所形成的水库中,水流相对缓慢,水深增加,水体滞留时间增加,有利于浮游植物生长以及光化学反应产生的 $CO_2$ 和 DIC 的吸收或释放<sup>[44,45,47,49,50]</sup>,由此光合作用逐渐成为影响水库系统有机质、养分和溶解氧循环的主要生物效应<sup>[51]</sup>。因此,浮游植物驱动的分循环是控制湖泊和水库生态系统中 C 和 N 循环

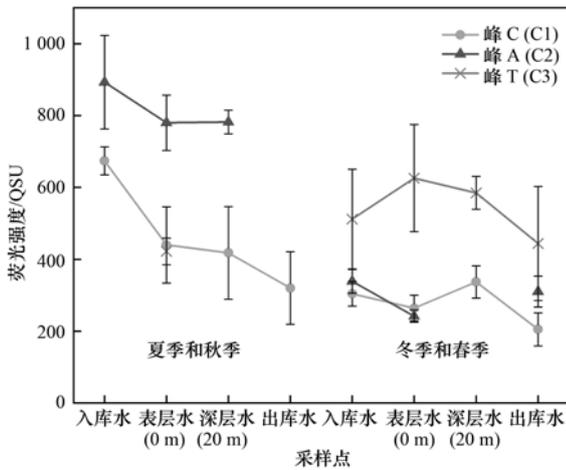


图4 各采样点各季节不同荧光峰的荧光强度变化

Fig. 4 Fluorescence intensity changes of different fluorescent peaks in each season at each sampling site

的主要因素<sup>[18,52]</sup>。同时,一些研究表明,水库出库水可能是CO<sub>2</sub>排放到大气中的重要通道<sup>[47]</sup>。因此,各种FDOM组分的荧光强度是检测地表水中FDOM含量的重要指标之一,对研究水库生物地球化学循环具有重要意义。

夏季和秋季库区深层水中荧光强度的降低,可能是由于经过太阳照射后的表层水在流动过程中混入深层水中所导致的,但其荧光强度减少的关键原因尚不清楚,这将是未来研究的重点。在夏季和秋季,通常情况下在深层水中会发生荧光强度的增加或保持相对稳定的现象<sup>[35]</sup>,因此本研究中思林水库库区深层水体中荧光强度的显著降低是一种不寻常的现象。另外,冬季和春季荧光强度的略微减少(4%)可能与表面经过太阳光照射后的水混入深层水有关。库区深层水中陆源类腐殖质的荧光强度没有发生显著变化,这在自然界深层水体和黑暗条件下的对比实验中是很常见的现象<sup>[19,53]</sup>。深层水中陆源类腐殖质的荧光强度没有变化或微小变化是因为该物质的官能团受到了微生物降解的影响<sup>[17,19,39]</sup>。以上结论表明陆源类腐殖质在各种环境因素下可以逐渐分解,如光化学作用、微生物作用和大坝拦截作用。类似的现象已经在早期的研究中观察到<sup>[3,17,54]</sup>。

同时,从微生物类腐殖质的荧光强度结果可以看出:在夏季和秋季,M峰值被完全降解(图2)。并且库区表层水和深层水体微生物类腐殖质的荧光强度比入库水分别减少了约29%和51%(图4)。由此推断:微生物类腐殖质可以通过浮游植物而再次产生,并且水体生态系统中这类腐殖质在光化学作用和微生物降解作用下也是非常不稳定的。其他研究也报道了类似的现象<sup>[1-4]</sup>。

类似地,在夏季和秋季期间仅在水库的表层水中检测到类蛋白质或类色氨酸的荧光强度。但在冬季和春季,类蛋白质或类色氨酸的荧光强度在库区表层水和深层水中相对入库水有所增加,而在出库水中又逐渐减少(图4)。在此前类似的水体样品或实验样品的研究中,类蛋白质或类色氨酸或类酪氨酸物质同样有着显著的波动<sup>[19,35,38,53]</sup>。这些结果表明,本研究中水库类蛋白质或类色氨酸或类酪氨酸物质,可以从浮游植物中产生,并同时在表层和深层水体中降解,这显示了DOM在水库系统中动态的迁移转化规律。

### 3 结论

(1)陆源类腐殖质(C类)的荧光强度在库区表层和深层水体以及在出库水中逐渐减少,这表明它可能来自陆地源,并且在从入库水体、到库区表层和深层水体、最后到出库水体的运输过程中通过光化学作用、微生物作用和大坝拦截作用持续发生变化。

(2)微生物类腐殖质(M类)和类蛋白质或类色氨酸或类酪氨酸的荧光强度在水库的表层或深层水中升高,在出库水中增加或降低。这表明这些荧光组分是由浮游植物内源产生的,在表层和深层水体中同时发生这类荧光组分的再生和降解。光化学作用、微生物作用和大坝拦截作用在整体水库中DOM的转化动力学过程发挥重要作用。

(3)在冬季和春季的入库、库区表层和出库水体中检测到了三种荧光组分,而在夏季和秋季样品中则没有检测到这些组分,这表明在冬季和春季由于较低水温和较低太阳强度的影响下,这些组分的降解程度相对于夏季和秋季较低。

(4)最后,平行因子分析可以作为了解水体中溶解性荧光组分在季节-时空-垂直尺度上受控于光诱导作用、微生物作用以及大坝拦截作用而发生不同变化的有用工具。该方法对深入了解FDOM在入库水体、库区表层水、库区深层水和出库水体中的动态变化机制提供了初步的参考。

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