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白洋淀夏季汛期入淀河流水体溶解性有机物的光谱特 征及来源

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摘要:溶解性有机物(DOM)是全球最大的有机碳储存库,在天然水体的生物地球化学循环中起着至关重要的作用.河流是连接源头与受纳水体的过渡区,是进行DOM交换的关键环节.因此,运用紫外-可见光谱技术(UV-vis)和三维荧光光谱技术(EEMs)结合平行因子分析法(PARAFAC),分析了夏季汛期白洋淀流域府河、小白河、白沟引河和瀑河水体中溶解性有机物的光谱特征及其来源.结果表明,府河和小白河水体的 a₂₄₅和 a₃₅₅显著高于白沟引河和瀑河;E₂/E₃显示入淀河流水体 DOM 相对分子质量大小为:瀑河>白沟引河>府河>小白河.三维荧光通过 PARAFAC 共解析出 3种组分,分别为类酪氨酸(C1)、陆源类腐殖质(C2)和类色氨酸(C3);各荧光组分间不存在差异(P>0.05),C2和C3组分在不同入淀河流间存在差异(P<0.05);易降解类蛋白质组分(C1+C3)占比高于类腐殖质组分 C2.各入淀河流自生源指数 BIX都大于1,腐殖化指数 HIX 都小于4,表明入淀河流水体自生源特征明显,腐殖化程度较弱;府河水体具有最高的FI指数(1.96±0.25)和最低的 HIX 指数(0.46±0.08), 且沿入淀河流方向自生源特征逐渐加强,表明府河水体呈现更高的内源特征.经入淀河流水体 DOM 的荧光组分与特征参数相关性分析得出,府河水体与小白河水体相关性呈现相似关系,白沟引河水体与瀑河水体呈现相似关系;各入淀河流水体 DOM 的荧光组分与水质参数的相关性呈现明显差异,并且与水体氮、磷关联较强;堡多元线性回归分析,各入淀河流在C1组分之间不存在显著差异,在C2组分和C3组分之间存在显著差异.综上所述,通过对夏季汛期入淀河流水体的 DOM 光谱特征及来源的研究,进一步认识了白洋淀入淀河流的碳循环过程.

关键词:白洋淀;入淀河流;溶解性有机物(DOM);紫外-可见光谱(UV-vis);三维荧光光谱(EEMs) 中图分类号:X522 文献标识码:A 文章编号:0250-3301(2024)05-2640-11 DOI:10.13227/j.hjkx.202304118

Spectral Characteristics and Sources of Dissolved Organic Matter in Inflow Rivers of Baiyangdian Lake Water in Summer Flood Season

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Abstract: DOM is the largest reservoir of organic carbon in the world, and it plays a crucial role in the biogeochemical cycles of natural water bodies. A river is a transition area connecting source water and receiving water that controls the DOM exchange between them. Therefore, in this study, ultraviolet visible spectroscopy (UV-vis) and three-dimensional fluorescence spectroscopy (EEMs) combined with parallel factor analysis (PARAFAC) were used to analyze the spectral characteristics and sources of dissolved organic matter in the Fuhe River, Xiaobai River, Baigouyin River, and Puhe River of Baiyangdian. The results showed that a₂₄₅ and a₃₅₅ in the Fuhe River and Xiaobai River were significantly higher than those in the Baigouyin River and Puhe River. E,/E, showed that the DOM relative molecular mass of the inflow river water body was Puhe River > Baigouyin River > Fuhe River > Xiaobai River. Three components, tyrosine-like (C1), terrigenous humus (C2), and tryptophan-like (C3), were determined using three-dimensional fluorescence through PARAFAC. There was no difference among the fluorescence components (P>0.05), but there were differences among the C2 and C3 components (P<0.05). The proportion of easily degradable protein-like components (C1+C3) was higher than that of humus-like components (C2). The autogeny index BIX was greater than 1, and the humification index HIX was less than 4, indicating that the autogeny characteristics of the river bodies were obvious, and the humification degree was weak. The FI index was the highest (1.96±0.25), and the HIX index was the lowest (0.46±0.08), and the self-generated source characteristics gradually strengthened along the direction of the river entering the lake, indicating that the water body of the Fuhe River showed higher endogenous and autogenic characteristics. Based on the correlation analysis of fluorescence components and characteristic parameters of DOM, the correlations between the Fuhe River and Xiaobaihe River and between the Baigouyin River and Puhe River bodies were similar. The correlation between fluorescence components of DOM and water quality parameters of each lake was significantly different, and it was strongly correlated with nitrogen and phosphorus in water. According to multiple linear regression analysis, there was no significant difference among C1 components, but there was a significant difference between C2 and C3 components. In summary, the carbon cycle process of Baiyangdian Lake was further understood through the study on the DOM spectral characteristics and sources of the inflow river waters in the summer flood season. Key words: Baiyangdian Lake; inflow rivers; dissolved organic matter(DOM); ultraviolet-visible spectroscopy(UV-vis); three-dimensional fluorescence spectroscopy(EEMs)

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溶解性有机物是一种复杂的有机化合物,主要由类蛋白物质(类色氨酸、类酪氨酸等)和类腐殖质(类富里酸等)组成^[1,2],具有影响水环境中的营养物质转化与碳循环的作用^[3,4].天然水体 DOM 主要来自于土壤中类腐殖质、动植物死亡降解等的陆源输入以及浮游植物释放、浮游生物残体降解等的内源贡献^[5].河流^[6]是连接陆地与江、海、湖泊之间^[7]的过渡区,在碳传递过程中发挥着重要作用.河流 DOM 的变化与流域周边土壤类型、人类活动以及城市污水排放有关^[8].此外,水体中微生物的降解也会使河流的 DOM 发生变化^[9].

白洋淀是我国华北地区最大的湿地系统,素 有"华北之肾"的美誉[10],具有一定自我调节能 力,且受入淀河流影响较大,其特殊性直接影响 雄安新区水环境安全及生态文明建设[11]. 经相关资 料显示,为维持白洋淀的生态功能,将黄河水、 南水北调水、水库水以及再生水汇入不同入淀河 流对白洋淀淀区水体进行补给^[11],造成不同来源 的入淀河流水质情况错综复杂.例如,宁成武等[12] 在研究夏季巢湖溶解性有机质中发现南淝河作为 合肥市纳污河流,受城市污水排放的影响,其腐 殖化程度和内源特征明显不同于其他入湖河流; 张紫薇等^[13]研究的岗南水库沉积物 DOM 发现其具 有低腐殖化、强自生源的特征,而张柳青等^{14]}在 南水北调湖泊中发现其水体可溶性有机物来源主 要为陆源类腐殖质.由此可得,河流来源不同致使 水体中 DOM 的性质和特征也会有所差异,造成不 同河流水体 DOM 与水质参数关联性呈现出不同特 征,进而对研究受纳水体DOM的演变和环境效应 带来挑战.因此,研究不同来源入淀河流 DOM 特 征非常有必要.

与此同时,DOM的组成与结构也影响水系统中 有机污染物的吸收和降解^[15],并且受人为活动影响 较为强烈.DOM作为水环境中最大的溶解性有机碳 储存库^[16],在生物地球化学循环中起着重要作用. 众所周知,夏季高温加快微生物活动,从而影响河 流水体的DOM降解;同时由于汛期到来,大量降水 会使陆地DOM随着水流流入江河湖泊中,使水体的 DOM发生变化.然而,关于白洋淀入淀河流DOM的 研究却鲜见报道,尤其是对夏季汛期入淀河流DOM 特征的研究更少.因此,本研究通过对夏季汛期白 洋淀不同来源的入淀河流DOM的组成以及特征进行 解析,并对各来源河流水体DOM的环境关联特性进 行分析,以期为深入探究白洋淀入淀河流DOM转化 机制提供支持.

1 材料与方法

1.1 研究区概况及样品采集与测定

白洋淀位于河北省保定市,是河北地区最大的 内陆湖泊^[17],具有一定的自我调节能力,但受入 淀河流影响较大.历史上白洋淀共接收了由北、 西、南而来的白沟引河、萍河、瀑河、府河和小白 河等八大入淀河流.府河作为保定市的纳污河道, 水体主要来源于再生水,贯穿整个市区;小白河承 接黄河水,为白洋淀淀区输送了大量水源;白沟引 河是人工开挖的河流,水体主要来源于南水北调工 程,主要流经农业地区;瀑河是河北省滦河的主要 支流之一,现在作为承接水库水的河道.基于对白 洋淀入淀河流来源进行分析,确定府河、小白河、 白沟引河和瀑河这4条来源不同的入淀河流为研究 对象.

目前,本研究根据文献[11]以及实地调查,选 取府河、小白河、白沟引河以及瀑河这4条入淀河 流共20个具有代表性的采样点(图1),于夏季7、8 和9月对入淀河流水体进行采样,并分析该采样点 水体DOM光谱特征.采集的水样在现场测定pH、水 体温度(T)和溶解氧浓度(DO),24h内完成水样氨 氮、硝氮、亚硝氮、总氮、总磷、溶解性总氮、溶 解性总磷和高锰酸盐指数的测定,同时完成BOD。的 测定,水样经0.45μm 微孔纤维滤膜过滤得到溶解 性有机物水体样品并放入4℃的冰箱中进行保存.



Fig. 1 Schematic diagram of sampling sites in inflow rivers of Baiyangdian Lake

1.2 紫外-可见吸收光谱测定

利用紫外-可见分光光度计(DR6000,美国 HACH公司)测定吸光度.测定波长范围为200~700 nm,间隔1nm,仪器扫描速度为600 nm·min⁻¹,以 Mill-Q超纯水调节空白,用1 cm 石英比色皿测得吸 光度.紫外-可见吸收光谱参数计算如表1所示.吸收 系数公式为[18]:

$$\alpha'(\lambda) = 2.303 \times D(\lambda) \div \gamma \tag{1}$$

$$\alpha(\lambda) = \alpha'(\lambda) - \alpha'(700) \times \lambda \div 700$$
(2)

式中, λ 为实际扫描波长,nm; γ 为光程路径,m; $\alpha'(\lambda)$ 为未经散射矫正时在 λ 处的吸收系数,m⁻¹; $\alpha(\lambda)$ 为经散射矫正后在 λ 处的吸光度系数,m⁻¹; $D(\lambda)$ 为吸光度.

1.3 三维荧光光谱测定

利用F-7000荧光分光光度计进行三维荧光光谱

的测定.具体设置如下:发射波长(*E*_m)为250~600 nm,间隔为1nm;激发波长(*E*_x)为200~450 nm, 间隔为5nm;扫描速度为1000 nm·min⁻¹.用 Mill-Q 超纯水去除散射的影响,用 Delaunnay 三角形内插值 法消除瑞利散射和拉曼峰散射影响^[19].利用核一致 性分析确定荧光组分数,用折半分法分析数据结 果,以R.U.为单位对数据进行标准化处理^[20],并计 算出入淀河流组分的荧光强度.三维荧光光谱参数 计算如表1所示.

	Table 1 Description of parameters related to UV-Vis and three	e-dimensional fluorescence
光谱参数	参数定义	环境意义及特征描述
E ₂ /E ₃	A_{250}/A_{365}	表示 DOM 相对分子质量大小 ^[21]
E_3/E_4	A_{300}/A_{400}	表示水体 DOM 腐殖化程度 ^[22]
E_4/E_6	A_{465}/A_{665}	表示 DOM 腐殖化程度和芳香性 ^[23]
S_{R}	$S_{275\sim 295}/S_{350\sim 400}$	表示 DOM 来源和相对分子质量信息 ^[23]
FI	$F(E_{\rm m} = 450 \text{ nm}) / F(E_{\rm m} = 500 \text{ nm}), E_{\rm x} = 370 \text{ nm}$	表示 DOM 来源 ^[24]
BIX	$F(E_{\rm m} = 380 \text{ nm}) / F(E_{\rm m} = 430 \text{ nm}), E_{\rm x} = 310 \text{ nm}$	表示 DOM 自生来源的相对贡献 ^[25]
HIX	$AREA(E_m = 435 \sim 480 \text{ nm}) / ARFA(E_m = 300 \sim 345 \text{ nm}), E_x = 370 \text{ nm}$	表示 DOM 的腐殖化程度 ^[26]
β / α	$F(E_{\rm m} = 380 \text{ nm}) / F_{\rm max}(E_{\rm m} = 420 \text{~~} 435 \text{ nm}), E_{\rm x} = 310 \text{ nm}$	反映新生 DOM 所占比例 ^[27]
Fn_{280}	$F_{\rm max}(340\sim360 \text{ nm}), E_x = 280 \text{ nm}$	反映类蛋白相对丰度[28]
Fn ₃₅₅	$F_{\rm max}(440 \sim 470 \text{ nm}), E_{\rm x} = 355 \text{ nm}$	反映类腐殖质相对丰度[28]

表1 紫外-可见光谱和三维荧光光谱相关参数描述

1.4 数据分析

在 Matlab R2014a 软件中使用 N-way 和 DOMFluor 工具箱对三维荧光光谱进行平行因子分析;应用 SPSS(24.0)软件对夏季汛期入淀河流水体 DOM 中紫 外-可见吸收光谱参数、荧光组分以及三维荧光特征 指数进行相关性分析,并用单因素方差分析法分析 水体样品中各参数的差异性;利用多元线性回归分 析对荧光组分和光谱参数及水质参数进行解析;利 用 OpenFluor数据库对三维荧光光谱组分进行筛分对 比;利用 Origin(2021)绘制箱型图等有关图形;应 用 R软件进行主成分分析和相关性分析.

2 结果与讨论

2.1 紫外-可见吸收光谱特征参数分析

本研究用 a₂₅₄和 a₃₅₅表示白洋淀不同入淀河流 DOM 相对浓度的变化情况,水体 DOM 的相对浓度 呈现显著差异(图 2).由图 2可知,小白河和府河水 体 DOM 的 a₂₅₄和 a₃₅₅较高,白沟引河的 DOM 相对浓 度次之,瀑河水体的 a₂₅₄和 a₃₅₅最低,分别为(30.04 ± 3.37)m⁻¹和(7.89±1.29)m⁻¹.其中,府河流经区域主 要以城市为主,并且作为城市的纳污河道一直受生 活污水污染,瀑河流经区域主要以农村为主,沿途 多为森林和农田.因此,水体 DOM 的 a₂₅₄与 a₃₅₅差异 变化可以一定程度上反映入淀河流水体 DOM 的来 源.同时府河和小白河分别与白沟引河和瀑河呈现 显著差异(P < 0.05); 白沟引河各个采样点的 a₃₅₅分 布较分散,差异性较大.其中,4条入淀河流 a₃₅₅的 值要高于白洋淀冬季冰封期淀区^[20](a₃₅₅为 2.57 ~ 6.77 m⁻¹).

为进一步了解白洋淀夏季汛期入淀河流水体 DOM 的特性,本研究就紫外-可见光谱中相关参数 E_2/E_3 、 E_3/E_4 、 E_4/E_6 以及 S_R (图2)进行分析,以此 来判断水体DOM相对分子质量大小、腐殖化程度以 及来源等信息.结果表明,小白河各采样点E₂/E₃值 为4.06±0.49, 府河、白沟引河次之, 值分别为 4.06±0.49和3.74±0.29, 瀑河的E₂/E₃值最小为3.56 ±0.23, 由于 E₂/E₃的值与 DOM 相对分子质量大小呈 反比,即瀑河 DOM 相对分子质量最大,并与府河、 小白河和白沟引河呈显著差异(P<0.001); 岳龙飞 等^[29]在研究白洋淀入淀河流溶解性有机物时, 府河 的 E₂/E₃值低于白沟引河,与本研究结论相反,表明 府河与白沟引河采样点 E₂/E₃沿程具有明显变化;府 河、小白河、白沟引河和瀑河水体 DOM 的 E₃/E₄值 在2.17~3.68之间,各入淀河流间变化不明显,府 河和小白河水体分别与白沟引河和瀑河水体DOM的 E_3/E_4 值呈现显著差异(P < 0.05); E_4/E_6 值与水体 DOM 腐殖化程度呈反比,小白河各采样点的 E4/E6值 最高为1.47±0.05, 白沟引河和瀑河水体的E₄/E₆值 较小,分别为1.39±0.08和1.42±0.05,与E₃/E₄值得 出结论相同,表明白沟引河和瀑河水体腐殖化程度

较高,小白河水体腐殖化程度最弱,并且小白河水体的 E_4/E_6 与白沟引河和瀑河呈显著差异(P < 0.05); 本研究中入淀河流所有采样点 S_R 值均小于 1,府河、 小白河、白沟引河和瀑河水体 DOM 的 S_R 值分别为 0.79 ± 0.07 、 0.78 ± 0.05 、 0.78 ± 0.05 和 0.75 ± 0.04 .瀑 河水体 DOM 的 S_R 值明显低于其他入淀河流(P < 0.001),且 S_R 值与DOM相对分子质量大小呈现负相 关关系,表明瀑河水体DOM相对分子质量高于其他 入淀河流,与 E_2/E_3 结论相同.此外,入淀河流水体 DOM的 S_R 值(0.70~0.92)与鄱阳湖蝶形湖区(0.83 ± 0.24)和通江水域(0.75 ± 0.15)沉积物中DOM的研究 结果相似^[30].



图 2 白洋淀入淀河流水体 DOM 的 a_{254} 、 a_{355} 、 E_2/E_3 、 E_3/E_4 、 E_4/E_6 和 S_R Fig. 2 The a_{254} , a_{355} , E_2/E_3 , E_3/E_4 , E_4/E_6 , and S_R of the DOM in inflow rivers of Baiyangdian Lake

2.2 汛期水体 DOM 荧光组分特征分析

2.2.1 DOM的荧光组分解析

通过平行因子分析对夏季汛期白洋淀4条入淀 河流水体进行三维荧光解析,分析DOM组分构成. 汛期入淀河流水体样品共解析到3种组分.其中,组 分1有2个激发峰为240 nm和295 nm;组分2有2个 激发峰为245 nm和310 nm;组分3有2个激发峰为 200 nm和275 nm(表2),综合分析得到:C1为类酪 氨酸,C2为陆源类腐殖质,C3为类色氨酸.

表 2 白洋淀入淀河流水体样品 DOM 的荧光组分特征

 Table 2
 Characteristics of components of DOM in water samples

	in infle	ow rivers of Baiyang	gdian Lake
组分	$E_x/E_m/nm$	物质	文献中波长/nm
C1	295(240)/340	类酪氨酸	275/340,220/325 ^[11]
C2	245(310)/426	陆源类腐殖质	260/425,315/415 ^[31,32]
С3	200(275)/338	类色氨酸	200~250/330~380 ^[33]

2.2.2 DOM的荧光组分强度及分布特征

图3展示的是夏季汛期白洋淀4条入淀河流采

样点,府河、小白河、白沟引河和瀑河的三维荧光 组分荧光强度情况.结果表明,入淀河流组分间不 存在差异(P>0.05), C2和C3组分在各入淀河流间 存在显著差异(P<0.05); C1组分为类酪氨酸,府 河水体 C1 组分含量最高,为(0.37±0.37) R.U.,瀑 河、小白河次之, 白沟引河水体含量最低, 为(0.19 ±0.12)R.U.. 束乐乐等^[34]在研究长江口门附近水体的 溶解性有机质时发现,夏季温度升高致使水体微生 物生长繁殖速度加快,类酪氨酸与微生物活动密切 相关, 证实府河水体微生物含量较高[图3(a)]. C2 组分作为陆源类腐殖质,大多来源于陆源输入以及 动植物降解,府河和小白河的C2组分含量远高于白 沟引河与瀑河, 依次为(0.26±0.05)、(0.26±0.03)、 (0.19±0.04)和(0.18±0.06)R.U. [图 3(b)]. C3 组分 为类色氨酸,与水中浮游植物降解和微生物代谢过 程相关,小白河水体C3组分含量最高,为(0.27± 0.12)R.U., 小白河承接于黄河水, 在研究黄河水清 水河流域中发现其类色氨酸组分占比最高[35] [图3 (c)]. 总荧光强度在不同入淀河流之间存在差异, 府 河水体的总荧光强度值最大,达到(0.83±0.40)R. U., 府河水体汇集了人们生活用水及城市面源污染 水体,严重影响水体水质情况,与滇河流域入湖河 流中污染最严重河流的总荧光强度的结论一致[36]. 而经农业流域的白沟引河水体总荧光强度最小,达 到(0.56±0.15)R.U., 充分说明了人类活动会严重导 致水体中 DOM 含量的增加.并且府河与白沟引河水 体的总荧光强度间存在显著差异(P < 0.05).

图 3(d)~3(f)为各入淀河流水体三维荧光组分 相对丰度变化情况,以分析水体DOM的结构组成情 况. 入淀河流水体中各组分占比情况如下: C1组分 在府河水体中占比最高,达到(40.40±11.97)%,在 白沟引河水体中占比最低,为(31.41±18.53)%,并 且白沟引河与瀑河水体在C1组分丰度上呈现显著差 异(P<0.05); C2组分在白沟引河水体中占比最高, 达到(37.25±17.94)%,并与瀑河水体呈现显著差异 (P < 0.05); C3 组分中小白河水体占比最高,为 (32.87 ± 9.37)%; 府河水体占比最低, 为(24.46 ± 5.56)%,并与小白河、白沟引河和瀑河水体之间呈 现显著差异(P<0.05).从整体来看,白洋淀4条入 淀河流水体各采样点的类蛋白质组分(C1+C3)占比 基本都大于陆源类腐殖质C2(除白沟引河7月采样 点外),并且各入淀河流水体7月类蛋白物质含量明 显低于8月和9月,因为7月雨量最多,污染物质会 随着雨水进入入淀河流中,致使水体陆源类腐殖质 物质增多.从整体来看,瀑河水体类蛋白质组分 (C1+C3)组分占比最高,为(70.33±11.38)%; 白沟

引河水体 C2 组分占比最高为(37.25 ± 17.94)%,其 原因可能是白沟引河流经流域多以农田、森林为 主,陆源输入相对明显.

2.3 DOM的荧光特征参数分析

为了进一步分析夏季汛期白洋淀各入淀河流水体 DOM 的光谱特征,本研究对 DOM 的荧光特征参数进行分析,分析结果如图4所示.

荧光指数 FI 代表入淀河流水体 DOM 来源情况^[37].当 FI > 1.9 时,水体中 DOM 主要以微生物内源 产生为主,当 FI < 1.4 时,水体中 DOM 主要以陆源 输入为主.如图 4(a),小白河和瀑河水体的 FI 值分 别为 1.90 ± 0.20 和 1.91 ± 0.30,表示水体 DOM 主要 以微生物内源产生为主.白沟引河水体 FI 值最小为 1.73 ± 0.23, FI 值在 1.4 ~ 1.9之间,说明水体 DOM 同时受内源和外源的双重影响,符合白沟引河水体 三维荧光组分丰度的变化情况.府河除 P4采样点(FI 为 1.66 ~ 1.77)外,其他点位 FI 值均大于 1.9,且 FI 值为 1.96 ± 0.25,显著高于其他入淀河流,与小流 域庐江水体研究结果相似^[38],表明城市纳污河流水 体 DOM 的自生源特征要比受农田、森林或其他径流 影响的河流更强.

自生源指标 BIX 代表入淀河流水体内源物质对 DOM 的相对贡献程度^[39].如图 4(b),府河水体的 BIX 为1.95±0.90,小白河水体的 BIX 为1.69±0.38, 白沟引河水体的 BIX 为2.02±0.83,瀑河水体的 BIX 为2.42±0.97.4条入淀河流的 BIX 值大于1,微生物 活动明显,水体 DOM 主要以自生源特征为主.其中, 府河从上游到下游采样点 BIX 值明显升高,指示水 体自生源特征沿入淀方向愈发明显.此外,瀑河与 小白河、白沟引河呈现显著差异(P<0.05).本研究 与宁成武等^[12]研究夏季巢湖入湖河流南淝河中溶解 性有机物的 BIX 结果一致,且南淝河也作为城市的 纳污河流,BIX 值均大于1.00,与府河情况相同.

腐殖化指数 HIX 表示入淀河流水体 DOM 的腐殖 化情况^[40].当 HIX > 3 时,水体腐殖化程度强,当 HIX 为 1.5~3 时,水体腐殖化程度较弱,当 HIX < 1.5 时,水体 DOM 主要来源于微生物.本研究中4条 入淀河流水体各采样点的 HIX 指数在 0.22~0.75 之 间,数值远小于1.5,表明4条入淀河流水体 DOM 腐 殖化程度较弱.其中,府河水体 DOM 的 HIX 值在4 条入淀河流中最小(0.46±0.08),从上游到下游,整 体上 HIX 值逐渐降低,腐殖化程度逐渐减弱,水体 自生源特征不断增强,充分说明府河水体 DOM 内源 特征明显,并且与 BIX 结果一致.此外,瀑河与白沟 引河呈现显著差异(*P*<0.01).

新鲜度指数(β/α)反映新生DOM所占的比例同

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Fig. 3 Fluorescence intensity and percentages of components of DOM in water samples in inflow rivers of Baiyangdian Lake

时也是评估水体生物活性的重要依据.本研究中瀑 河水体的 β/α 值最高,为1.94±0.81,小白河水体 的 β/α 值最低,为1.48±0.29,表明瀑河水体新生 DOM 所占比例较高.其中,瀑河与小白河呈现显著 差异(P < 0.05).本研究与何杰^[41]等采用光谱特征法 研究不同污染景观水体河道中溶解性有机物 HIX (HIX < 3)与 β/α (景观水体 $\beta/\alpha > 0.8$)结果相一致.

Fn₂₈₀和 Fn₃₅₅分别代表类蛋白物质和类腐殖质物 质的相对浓度水平^[42], Fn₂₈₀用来表征自生源对水体 DOM组分的贡献, Fn₃₅₅表征陆源对水体 DOM组分的 贡献.从分析结果来看,该时期 Fn₂₈₀明显高于 Fn₃₅₅, 进一步验证了夏季汛期各入淀河流水体自生源特征 明显,类蛋白物质含量占比远高于类腐殖质物质占 比的情况.小白河与白沟引河水体的 Fn₂₈₀呈现显著 差异(*P* < 0.05),府河和小白河与白沟引河和瀑河水 体的 Fn₃₅₅呈现显著差异(*P* < 0.001). **2.4** DOM的荧光组分与特征参数及水质参数相关 性分析

2.4.1 DOM的荧光组分与特征参数相关性分析

为了解夏季汛期白洋淀4条入淀河流 DOM 特 征,本研究对入淀河流水体 DOM 的荧光组分与特征 参数进行分析.图5分别代表府河、小白河、白沟引 河和瀑河水体 DOM 组分与特征参数的相关性分析 结果.从中得知,府河和小白河水体荧光组分与特 征参数相关性呈现相似关系,白沟引河和瀑河水体 荧光组分与特征参数之间呈现相似关系.C1组分与 入淀河流水体的 HIX 呈显著负相关关系(*P* < 0.001), 与白沟引河和瀑河水体的相关程度明显高于府河和 小白河水体,相关系数分别为0.953、0.891、0.804 和0.827,此外,C1组分还与4条入淀河流水体的 BIX、β/α和 Fn₂₈₀呈显著正相关关系(*P* < 0.001).C2 组分与白沟引河和瀑河水体的 HIX 呈现显著正相关

b



Fig. 4 FI, BIX, HIX, β/α , Fn₂₈₀, and Fn₃₅₅ distributions of DOM in water samples in inflow rivers of Baiyangdian Lake

关系(P<0.01),与府河和小白河水体相关性不显 著,说明白沟引河和瀑河水体腐殖化程度相对高于 府河和小白河水体.C2组分与白沟引河和瀑河水体 的Fn355相关性程度明显高于府河和小白河水体(P< 0.001),表示C2组分对白沟引河和瀑河水体陆源类 腐殖质浓度影响水平更高.C3组分与C1组分同属类 蛋白组分,相关性类似,C3组分与白沟引河和瀑河 水体的E3/E4和E4/E6呈显著相关关系(P<0.05),与 府河和小白河水体无明显相关关系.

综上所述,不同入淀河流组分间不具有相关 性,说明组分C1、C2和C3之间不存在相似的来源. 值得注意的是BIX、β/α、Fn₂₈₀和HIX在C1组分和C2 组分呈现完全相反的相关性关系.说明类酪氨酸C1 主要来源于入淀河流水体中浮游植物的降解,受陆 源输入影响较小;类腐殖质物质C2主要来源于外源 输入,受水体微生物活动影响较小.这与林子深 等^[43]研究李家河水库上游水体溶解性有机物的类酪 氨酸组分与类腐殖质组分的来源情况相似.府河水 体受城市污水排放影响,小白河水体受黄河流域沿 程外来污染物影响,白沟引河和瀑河水体流经水 库,受外源污染影响较小,因此府河水体和小白河 水体荧光组分与特征参数相关性相似,白沟引河水 体和瀑河水体相关性相似.

2.4.2 DOM的荧光组分与水质参数相关性分析

为进一步了解夏季汛期白洋淀4条入淀河流 DOM 对水质的影响,本研究将基于 DOM 组分与环 境因子指标进行相关性分析,相关性分析结果如图 6所示.从中得知,在类蛋白组分(C1+C3)中,府河、 小白河和白沟引河水体的荧光组分与水质参数相关 性相似,就C1组分而言,白沟引河、府河和小白河



Fig. 5 Correlation analysis of the fluorescence components of DOM and UV-visible and three-dimensional fluorescence parameters in the water body in inflow rivers of Baiyangdian Lake

水体与NO3-N、NO2-N、TN、TDN、TP和TDP呈负 相关关系,其中,白沟引河水体与NO3--N(P < 0.001) 、 NO₂⁻-N (P < 0.05) 、 TN (P < 0.01) 和 TDN (P < 0.001)的相关性系数明显高于府河、小白河和 瀑河.在C3组分中,府河、小白河和白沟引河水体 与NO₂-N、NO₂-N、TN、TDN、TP和TDP呈负相关 关系,但瀑河水体与NO3⁻-N、NO2⁻-N、TN、TDN、 TP和TDP呈正相关关系.在C2组分中,各入淀河流 间相关性并不相似, 府河、小白河、白沟引河和瀑 河水体与NO2⁻-N、TN和TDN呈正相关关系. 瀑河、 小白河和府河水体与NH4+-N呈正相关关系,相关系 数分别为0.832、0.683和0.220、白沟引河水体与 NH_4^+ -N呈显著负相关关系(P < 0.05),相关系数为 0.536; 白沟引河、府河和小白河水体与NO₃-N呈正 相关关系,相关系数分别为0.889、0.725和0.452, 瀑河水体与 NO_3^{-} N呈显著负相关关系(P < 0.05), 相关系数为0.608.

由荧光组分与水质参数的相关性关系可知,3 种DOM组分均参与了入淀河流水体中氮、磷元素的 迁移转化.随着类酪氨酸组分C1和类色氨酸组分C3 含量的增加,水体中氮素含量降低,这是因为类蛋 白物质(C1+C3)的形成会消耗水环境中的氮素,在 赵海超等^[44]调查洱海上覆水的DOM时,其类蛋白质 组分和氮素之间的关系与白洋淀入淀河流水体的相同;由于类腐殖质组分与水体中氮、磷等营养元素均具有正相关性,表明入淀河流水体中类腐殖质与氮、磷元素联系更为密切,而类腐殖质物质大多是外源污染物输入而产生,说明入淀河流水体中氮、磷等营养元素在夏季汛期会随着降水进入入淀河流水体中.在研究芦江溶解性有机质时发现DOM会随氮、磷的外源输入进入水体^[45],表示入淀水体的DOM与氮、磷的迁移转化有关.

1

2.4.3 DOM的荧光组分与特征参数及水质参数多 元线性回归

对荧光组分与特征参数及水质参数的多元线性 回归分析.结果如表3所示,4条入淀河流DOM与特 征参数和水质参数的回归方程在C1和C2组分的相 关系数明显高于C3,并且关联的特征参数和水质参 数在C2组分、C3组分之间存在显著差异.在C1组 分中,4条入淀河流与HIX、Fn₂₈₀呈显著相关(*P* < 0.001).在C2组分中,4条入淀河流与Fn₃₅₅呈显著相 关(*P* < 0.001),此外,府河和白沟引河水体与 NO₃⁻-N呈显著相关(*P* < 0.001),小白河和瀑河水体 与NH₄⁺-N呈显著相关(*P* < 0.001).在C3组分中,府 河、小白河和瀑河水体与NO₂⁻-N呈显著相关(*P* < 0.01),白沟引河和瀑河水体与TDP呈显著相关(*P* <

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(a) <i>T</i>				(b) <i>T</i>				(c) T		*	***	(d) <i>T</i>		*		
					_											
DO				DO		**		DO				DO				
NH4 ⁺ -N				NH4 ⁺ -N		**		NH4 ⁺ -N		*		NH4 ⁺ -N		***		
NO ₃ ⁻ -N		**		NO ₃ ⁻ -N			*	NO ₃ ⁻ -N	***	***		NO ₃ ⁻ -N		*		
NO ₂ ⁻ -N			*	NO ₂ ⁻ -N			*	NO ₂ ⁻ -N	*		*	NO2-N		*	***	1.0
TN		**		TN		*	**	TN	**	*		TN			D	- 0.5 0
TDN		***		TDN		**	*	TDN	***	***		TDN				-0.5
TP				ТР				TP			*	TP		***		
TDP		***		TDP			*	TDP			***	TDP		***		
COD				COD				COD		**		COD		**		
BOD ₅				BOD ₅			**	BOD ₅	**	**		BOD ₅		***		
	C1	C2	C3		C1	C2	C3	1	C1	C2	C3		C1	C2	C3	
				图6 白	洋淀入	淀河流	水体D	OM的荧光	:组分与	水质参	数的相	关性分析			/ /	3)
	Fig. 6	Correl	ation an	alysis of DO	M fluor	escence	compor	ients and w	ater qua	lity para	imeters i	n inflow riv	ers of B	aiyangdi	an Lake	
		\int	1		表3 💈	炭光组 分	分与特征	E参数及水	质参数	多元线	生回归」	J p	1		Sec.	25
\cap	fable 3	Correla	tion ma	trix of DOM	indices	and thi	ee PAR	AFAC com	ponents	of water	sample	s in inflow r	ivers of	Baiyang	dian Lal	ke
61	入淀	河流			12	10	50	回归	1方程	/	. [.	1			相关	关系
11	6	11		5	C1]=0	.193×H	IX -18.2	295×Fn ₂₈₀ -	0.261	14	61	31			0.992	2****
25	府	河		[C2] = 3	1.951×I	$n_{355} - 0.$	011×(NO ₃ ⁻	-N)+0.0	16×TDN	+0.380	<tdp+0.09< td=""><td>1</td><td></td><td>0.857</td><td></td></tdp+0.09<>	1		0.857	
(all	11	C	~	(C3] = -	0.158×I	BIX+7.9	52×Fn ₂₈₀ -	0.623×(1	$NO_2^N)$	+0.343	1)		0.605	5**
191	10		r	[C1] = 0	.261×H	IX -17.1	197×Fn ₂₈₀ -	0.257						0.949	€ ^{***}
(0)	ア 小白	三河		[C2] = 4	4.209×F	$n_{355} - 0.$	04×DO -0.	0190×(I	NH4 ⁺ -N)	+0.123		0.554		0.842	2***
				[[C3] = -	$0.200 \times ($	$\frac{NO_3 - N}{11}$	+0.565×(N	$O_2 - N) - O_2 -$	-0.059×′	ΓN -0.0	$26 \times BOD_5 +$	0.576		0.614	1 4***
-	白湯	己河		l	(2) = -	U.238×1 7 466×1	11X - 14	.404×Fn ₂₈₀	-0.084	- N) ±0	005~00	D _0 222			0.9/4	+ 7***
	口仍	기내		l	(2] = 2	1.400^{\times}		TDP = 0.70	10^(INU ₃	(-10) + 0.	.003×B(, D ₅ -0.333			0.98	, 2***
				ן ר	$C_{11} = 0$	0 402×1	$\frac{2.512}{11X+15}$	254×Fn	-0.132						0.823	3***
	濕	河		ſ	(21) = 6	4.348×F	n+0 ($0.09 \times T + 0.01$	3×(NH	. ⁺ -N) –0	.218				0.949	- 3***
	140			[C3] = 1	.194×(N	0 ₂ ⁻ -N)-	1.605×TDI	P+0.137						0.794	4***

1)"[]"表示组分的浓度

0.01).

前人研究表明TDN、NO₃⁻⁻N、NH4⁺⁻N和NO₂⁻⁻N 等各种形式的氮都可能与水体中DOM结合^[46].水体 中的磷元素也与DOM的含量相关,但在生活污水含 量较多的地方,磷与DOM的相关性并不显著^[47],与 本文府河水体与磷元素之间的相关性并不显著(*P*> 0.05)相一致.程云轩等^[48]对松花江沉积物研究结果 表示,沉积物中的4个组分与TP和TN存在相关性, 而这4条入淀河流水体的C2和C3组分也与NO₃⁻⁻N、 NH4⁺-N和TDP存在一定联系.其结果与相关性分析 结果相似,展现出不同入淀河流DOM与特征参数和 水质参数关联关系的差异.综上,通过对夏季汛期 白洋淀入淀河流水体 DOM 的荧光组分与特征参数及 水质参数进行多元线性回归拟合,便于评估夏季汛 期不同类型入淀河流水体 DOM 的特征,为管理人员 治理该时期溶解性有机物提供参考.

3 结论

(1)夏季汛期白洋淀入淀河流三维荧光光谱共
 解析出了2种类蛋白物质(C1、C3)和1种类腐殖质
 (C2),荧光组分之间差异不显著;夏季汛期入淀河
 流中类蛋白物质含量(C1+C3)占比大于类腐殖质

(C2)占比情况,说明类蛋白物质为白洋淀入淀河流 DOM的主要成分.

(2)夏季汛期白洋淀入淀河流中府河和小白河的DOM相对浓度高于白沟引河和瀑河.FI指数较高, 大于或接近1.9, HIX指数均低于4,说明入淀河流 DOM主要来源于自生源且腐殖化程度较弱.

(3)府河水体和小白河水体荧光组分与特征参数相关性呈现相似关系,白沟引河水体和瀑河水体 荧光组分与特征参数之间呈现相似关系;各入淀河 流水体荧光组分与水质参数相关性呈现明显差异, 并与氮、磷的迁移转化密切相关.多元线性回归方 程可以很好地拟合水体荧光组分与特征参数及水质 参数之间的关系,有利于分析汛期入淀河流水体 DOM的特征变化.

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