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河北洨河溶解性有机物光谱学特性

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摘要:基于荧光光谱、紫外吸收光谱与水质基本化学指标,联合主成分分析与相关性分析,对典型城市纳污河流——河北洨河的溶解性有机物(DOM)进行光谱学特性研究.结果表明,河流水体中DOM主要有类蛋白和类腐殖质两类,其中含氮化合物及DOM与水体COD之间相关性较高,尤其以氨氮对类腐殖质贡献较大.因此降低洨河水体中COD可通过减少氨氮与DOM来实现,同时此两类指标也应作为日后水体监控指标.干流水体样品中DOM下游相对上游类蛋白逐渐减少,而类腐殖质则呈现增加的趋势,并以类胡敏酸为主要存在形式.代表支流4种样品中,S1、S2水体DOM主要以类胡敏酸为重要成分,其组成有机物多为大分子量、芳香性高的有机物质,而S3、S6水体中主要为相对易降解的类蛋白,其相对分子质量相对较小、芳香性程度较低.针对代表支流的4个污水处理单位出水水体中的DOM特征,建议S1与S2应添加或改进对大分子物质有较好去除效果的膜处理设备,以加强对水体中相对难降解类腐殖质物质的去除;S3与S6应优化相关厌氧与好氧生物处理工艺,从而提高易降解的类蛋白物质的去除能力.

关键词: 洨河; 可溶性有机物; 三维荧光光谱; 同步荧光光谱; 紫外光谱

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Spectral Characteristic of Dissolved Organic Matter in Xiaohe River, Hebei

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Abstract: The spectral characteristic of dissolved organic matter (DOM) in Xiaohe River, Hebei, was investigated by fluorescence spectroscopy, ultraviolet-visible absorption spectroscopy, and basic chemical water quality indicators. The data was then statistical analyzed using principal component analysis and correlation analysis method. The result based on 3D excitation-emission matrix fluorescence spectroscopy showed that DOM in Xiaohe River contained both protein-like and humus-like components. DOM and N-containing compounds were obviously correlated with COD, especially between NH₄⁺-N and humic-like component, indicating that COD of water in Xiaohe River can be reduced by removing NH₄⁺-N and DOM, which could be good indicators for monitoring water quality in the future. The relative content of protein-like component reduces gradually along the downstream, while that of humic-like component showed an increasing trend. DOM in samples S1 and S2 was mainly consisted of humic-like components with larger molecular weight and higher aromaticity, while that in samples S3 and S6 was mainly consisted of protein-like components with smaller molecular weight, lower aromaticity, which are easier to be degraded. Therefore, in order to enhance the remove of refractory humic-like substances, sewage treatment plants of S1 and S2 or improved membrane treatment equipment with better removal effect of macromolecules should be provide. On the other hand, the anaerobic and aerobic biological treatment processes should be optimized in S3 and S6, so as to better remove these degradable protein-like substances.

Key words: Xiaohe River; dissolved organic matter; three-dimensional fluorescence spectroscopy; synchronous fluorescence spectroscopy; ultraviolet-visible spectra

城市污染河流水体中溶解性有机物 (dissolved organic matter, DOM) 占总有机物含量的 30% ~ 40%,影响水质中多种有机物指标,同时也是污水处理的主要对象 [1]. 水体中 DOM 指可以通过 0.45 μm 滤膜的有机混合体,组分主要是腐殖酸、亲水性有机酸、氨基酸、碳水化合物及脂类等 [2],其在污染河流中主要来源为人类生产活动污水、工业废水及死生物的自然消解或被细菌分解后产物 [3]. 水体

中 DOM 的组分类别、质量分布、腐殖质化程度以及分子结构特征对水体水生态变化及重金属的迁移转化有重要影响^[4].因此,DOM 研究对于城市纳污

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河流保护及其生物地球化学研究等有重要意义.

三维荧光光谱(excitation-emission matrix, EEM)是一种能得到图像直观、信息丰富谱图的光谱分析技术,对 DOM 分子内与分子间的动力学特性、含有苯环或共轭双键的有机物组成特征均能准确地反映,是灵敏区别和表征水体中不同 DOM 特征的最佳光谱分析技术之一^[5]. 紫外-可见吸收光谱(ultraviolet-visible, UV-Vis)因具有仪器普及、操作简单、所需样品量少等优点,是研究 DOM 的来源及样品结构特征差异时快捷便利的方法. 近年来该类光谱技术已被广泛应用于湖泊、河口及海湾等水环境 DOM 研究^[6],但大多研究者采用寻找特定峰值法解析荧光信息,因此未能充分解读荧光指纹携带的所有信息. 而荧光区域积分是一种识别和表征多组分体系中荧光光谱的重叠对象的解析方法,能一定程度克服以上不足.

河北洨河为典型北方城市纳污河流,其以接纳城市污水处理出水及农村生活污水为主要补给水,因而各支流对其干流水质情况有重要影响.本研究联合紫外吸收光谱、三维荧光区域积分法、同步荧光及统计分析方法对洨河水体中 DOM 的组成特征、分子结构特征及芳香性等进行表征,揭示各支流补给水源水体中 DOM 特征及支流汇入后干流水体中 DOM 的变化特征,以期为洨河治理和生态修复提供理论依据.

1 材料与方法

1.1 研究区概况及样品采集

河北洨河是石家庄市南部一条重要的行洪、排污河流,目前无天然水源补给,以市区及周边污水处理厂出水为主要水源,是子牙河南支滏阳河主要污染支流之一,为典型接纳生活污水、制药和食品加工行业排放废水而严重污染的城市纳污河流. 桥东污水处理厂尾水、桥西污水处理厂尾水及窦妪经简单处理后生活污水为洨河源头主要补给水源,窦妪出水口下游为洨河湿地,沿途还接纳赵县污水处理厂出水,其余支流已处于干涸.

为研究洨河此 4 种主要水源补给点水体 DOM 特征及干流水体中 DOM 变化特点,因此将该 4 处所采集水样定义为洨河支流样品,均采集于污水出口;尾水补给点上游因水量较少基本处于干涸,河流水源主要由上游 3 座污水处理厂提供,因此将洨河湿地下游所采集水样作为干流第一个样品.按上游至下游原则依次编号,其中支流对应编号为 S1、S2、

S3、S6; 干流 4 个采样点 S4、S5、S7、S8, 具体采样 点位置见图 1.

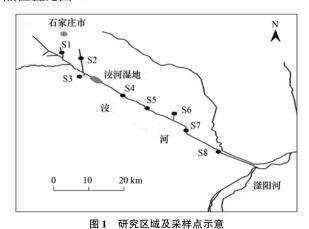


Fig. 1 Location of the study area and sampling sites

1.2 样品采集与前处理

于 2014 年 6 月对洨河支流及干流共布设 8 个点位,每个点位随机采集 4 次水样,每次采集 500 mL,将其混合成 2 L混合样品,使用棕色瓶室温保存. 采集样品同时测定 pH、溶解氧 (表 1). 样品采集后立即用孔径 0.45 μm 的 Millipore 聚碳酸酯滤膜过滤,滤液中的有机物即为 DOM,避光冷藏保存. 测试荧光之前对浓度较高样品进行一定的稀释,降低 DOC 浓度,同时使 pH 值控制在 6~7 之间.

过滤后水样带回实验室后进行水质基本指标测试,其中 DOC 采用总有机碳分析仪器(multi N/C-2100 TOC, Analytik Jena, GER),氨氮采用纳氏试剂法,总氮采用碱性过硫酸钾消解紫外分光光度法,COD 采用重铬酸钾滴定,TP 采用钼酸铵分光光度法.

1.3 样品光谱学分析

1.3.1 荧光光谱测定及分析

荧光光谱采用日立公司生产的 Hitachi F-7000 型荧光光度计进行测定. 激发光源为 150 W 氙弧灯,光电倍增管电压为 700 V,信噪比 > 110,扫描速度为12 000 nm·min⁻¹,激发和发射单色仪的狭缝宽度均为 10 nm,响应时间为自动. 荧光同步扫描光谱激发光谱波长 E_x = 300 ~ 600 nm, $\Delta \lambda = \lambda_{E_m} - \lambda_{E_x} = 18$ nm. 激发波长(E_x)范围为 200 ~ 450 nm,增量 5 nm;发射波长(E_m)范围为 280 ~ 550 nm,增量 5 nm,分算当激发波长 E_x = 370 nm、发射波长 E_m = 450 nm、500 nm 两处荧光强度比值记为 $f_{450/500}$ [7];当 E_x = 254 nm 时, $\int (E_m = 435 ~ 480 \text{ nm}) / [\int (E_m = 300 ~ 345 \text{ nm}) + \int (E_m = 435 ~ 480 \text{ nm})]$ 记为 $HIX^{[8]}$.

表1 水样基本性质

Table 1 Basic parameters of water samples

		DO	NH ₄ ⁺ -N	TN	DOC	TP	COD
样品	pН	/mg·L -1	/mg·L ⁻¹	/mg·L ⁻¹	/mg·L ⁻¹	/mg·L ⁻¹	/mg·L ⁻¹
S1	5. 4	5. 20	1. 33	52. 7	35. 80	0. 87	120. 3
S2	5. 6	6. 34	0.69	17. 2	25. 20	1.88	61. 4
S3	5.8	4. 20	14. 01	17. 7	51. 20	1.06	232. 3
S4	5. 43	7. 33	0.90	19. 3	15. 09	0.68	104
S5	4. 85	7. 28	0.75	22. 6	16. 94	0.44	152
S6	5. 0	2. 70	82. 88	94. 0	68. 10	0.46	179. 3
S7	5.38	6. 33	6. 28	29. 5	17. 81	0.83	133
S8	5. 19	5. 82	4. 39	27. 9	16. 46	0. 37	83

通过 Origin 软件采用荧光区域积分法对荧光谱峰进行识别,将 3D-EEM 区域分成 5 个部分,分别在对应波长范围内计算荧光区域的积分体积 Φ_i ;全光谱总荧光强度(TOT)积分;各荧光团(峰)占总荧光强度比例 P_i . 具体方法参见文献[9,10]. 采用多元统计软件 SPSS 对水样同步荧光进行主成分分析(PCA)及水质参数间相关度水平检测.

1.3.2 紫外光谱分析

紫外光谱分析采用日本岛津公司生产的 UV1700 紫外-可见分光光度计,扫描波长范围为 200~400 nm,扫描间距为 1 nm. 此外,分别测定 254、250、365 nm 处的吸光度 (cm⁻¹),以 UV₂₅₄、 E_2 、 E_3 表示. E_2 与 E_3 比值为 E_2/E_3 [11], UV_{254} 乘上 100 与 DOC 浓度之比记为 SUVA₂₅₄ [L·(m·mg) $^{-1}$] [12].

2 结果与讨论

2.1 水体 DOM 荧光光谱特征

图 2 所示 S1、S2、S3 和 S6 分别为洨河 4 条支流样品稀释后的三维荧光光谱图,S3、S6 为稀释 25 倍后呈现的光谱图,其余均为稀释 5 倍后图谱.图 2显示荧光主要分布在 5 个区域,荧光中心 I 区: $E_x/E_m = 245/330$ 附近、II 区: $E_x/E_m = 225/340$ 附近、III 区: $E_x/E_m = 240/435$ 附近、IV区: $E_x/E_m = 280/340$ 附近、V 区: $E_x/E_m = 330/430$ 附近、根据荧光中心位置及相关研究报道可知^[13,14],I 区、II 区和IV区所呈现的荧光物质与类蛋白有关;III区和V区荧光物质与类腐殖质相关.对比各区荧光峰强度可发现 S3、S6 水体 DOM 组成主要为类蛋白;而 S1、S2 水体中 DOM 组成除含有类蛋白外,还存在大量类腐殖质.支流样品均采自各污水处理单位出水,居民生活产生的食物残渣、人畜粪便及各种生活洗涤用品等类蛋白大量汇入城市污水系统,因此在 4

种水样中均检测出大量类蛋白. 城市污水大多由管道输送,污水中类腐殖质来自土壤腐殖质含量较小[15]. 因此,在 S1、S2 中出现大量高强度类腐殖质荧光峰,主要为经过污水处理简单物质大量去除所剩的难降解物质[16]. 图 2 中 S4、S5、S7、S8 为干流样品三维荧光光谱图,样品呈现荧光中心分布,支流类似,均由类蛋白与类腐殖质组成. 对比干流 S7、S8 与 S4、S5 荧光谱图可发现,在 S6 汇入干流后其下游 S7 相对上游 S5 荧光强度增大,同时 S7 相对 S8 比较可看出类蛋白区荧光逐渐减弱,类腐殖质荧光强度呈增强趋势,表明在洨河干流水体中 DOM 含量受支流影响较大,也验证了水体 DOM 中类蛋白组分在自然条件下相对类腐殖质更易发生降解.

三维荧光光谱总荧光强度(TOT)和各荧光团分区强度进行区域积分的方法是对三维荧光光谱定量分析的一种有效手段,能更具体解释 DOM 物质组成和荧光团的变化 $^{[17]}$. 本研究 8 种水体样品中DOM 的三维荧光光谱均可划分为 5 个区,样品所得区域积分均按稀释倍数恢复其对应原始浓度的荧光强度值. 根据 Chen 等 $^{[13]}$ 的研究报道,激发波长/发射波长范围分别为 200 ~ 250/280 ~ 325 nm,200 ~ 250/325 ~ 375 nm 的 \mathbb{I} 区、 \mathbb{I} 区与类蛋白物质(类色氨酸,类酪氨酸)有关, \mathbb{I} 区在 E_x/E_m > 250/280 ~ 375 与可溶性微生物降解产物等类蛋白物质有关, \mathbb{I} 区与 \mathbb{V} 区分布在 \mathbb{E}_x/E_m : 200 ~ 250/375 ~ 550 nm, > 250/375 ~ 250 nm, > 250/375 ~ 2

表 2 各支流 TOT 值比较可发现,在洨河 4 条主要支流补给水源中 S3 与 S6 中 DOM 含量高于上游 S1、S2,其中 S6 水体 DOM 含量最高,干流下游 S7、S8 中 TOT 值升高与其有重要关系. S4 为洨河湿地下游第一个干流采样点位,较其它干流点比较 TOT 值最低,推测与洨河湿地微生物降解及湿地植物和湿地填料对 DOM 的吸附吸收有关. 对比干流 S4 与

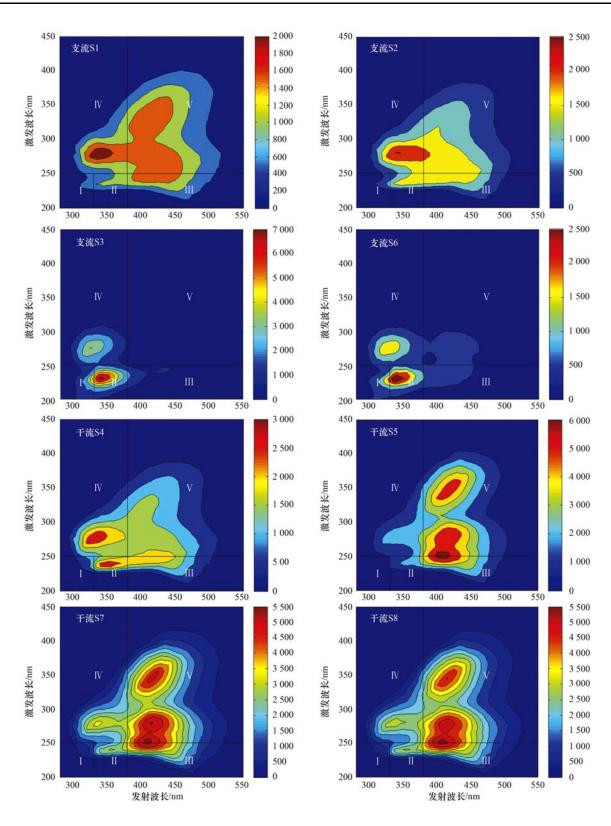


图 2 水体三维荧光光谱

Fig. 2 EEM spectra of water samples

S5、S7 与 S8 中各荧光团(峰) P_i 值可发现,除代表 胡敏酸的 V 区从下游相对上游呈增大趋势外,其余 各荧光团(峰)均呈减小趋势. 一方面可能为湿地植

物根系分泌物及湿地植物和沿途接纳的秸秆残体等 垃圾在下游逐渐堆积产生的腐殖降解贡献;另一方 面也说明与类蛋白和富里酸相比,类胡敏酸物质因 其具有更复杂的结构而不易在环境中被微生物降解^[18],也可能与洨河微生物群落特殊性有一定关系. 在支流样品 S3、S6 水体中类蛋白为主要荧光物质,分别占 DOM 总量的 71.3%、53.5%,而支流 S1、S2 样品中 DOM 组成 73.9% 和 67.7% 为类腐殖质,其中占大部分为 V 区所代表的类胡敏酸物质. 干流样品除 S4 以外其它点位水体样品中 DOM 组成 77%以上为类腐殖质,同时绝大部分为类胡敏酸.

基于三维荧光光谱图及区域体积积分对洨河水体 DOM 特征分析,建议代表洨河支流的 4 座污水处理单位除注重对类蛋白等易降解的物质去除,同时还应注重对类腐殖质等难降解物质的去除. S1、S2 两处在加强类腐殖质去除时更应注重类胡敏酸类物质去除,S3、S6 应改进污水处理工艺,加大削减污水中相对易处理的类蛋白物质使其达标排放.

表 2 水体 DOM 三维荧光光谱区域积分分析

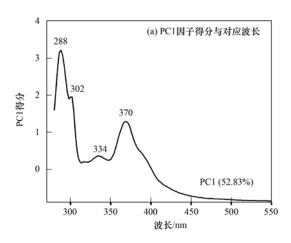
Table 2	Volume ii	ntegral of	different	area in	EEM s	spectra of	DOM

项目	区域	S1	S2	S3	S6	S4	S5	S7	S8
	I	0.04	0. 05	1. 14	1.00	0.05	0.04	0.06	0.06
	${ m I\hspace{1em}I}$	0. 12	0. 17	4. 29	5. 17	0.23	0.21	0. 26	0. 26
区域荧光体积积分值 $\Phi_i \times 10^7$ /au-	Ш	0.42	0.44	11. 12	24. 80	0.47	0.99	0. 93	0. 92
nm²-[mg·L -1 C]	${ m IV}$	0.73	0.82	20.43	27. 46	0.97	1. 10	1.30	1. 23
	V	2. 10	1.73	43. 27	124. 95	1.91	4. 99	4. 73	4. 54
	TOT	3.42	3. 21	80. 25	183. 39	3.63	7. 34	7. 27	7. 00
	I	1. 2	1.4	10. 3	7. 8	1.4	0. 5	0.8	0. 7
	${ m I\hspace{1em}I}$	3.5	5. 3	27. 1	18. 1	6.3	2.8	3.5	3.68
含量 $P_i/\%$	Ш	12.4	13.8	13.7	14. 1	13.0	13.5	12.8	13. 1
	IV	21.4	25. 4	33.9	27. 6	26.6	15.0	17. 8	17. 6
	V	61.5	53. 9	14. 9	32. 2	52.6	68. 1	65.0	64. 8

2.2 水体 DOM 组成特征

为进一步研究水体中 DOM 组成特征,通过主成分因子分析法(PCA)对同步荧光所得数据进行分析. 利用 PC 因子得分与波长作图的方法,能区别不同主成分中主要光谱波段,解释水体中 DOM 不同组分特征^[19]. 如图 3 所示,对 8 种样品所得同步荧光数据进行 PCA,可以提取 2 个主成分(PC),其方差最大旋转后特征值占总方差的 96.25%,即对此 2 个 PC(PC1 贡献总方差 52.83%、PC2 贡献总方差 43.42%)进行分析能够反映数据的绝大部分信息.

图 3(a)为 PC1 因子得分与波长关系,在激发波长为 288 nm 及 370 nm 处出现两个主要特征峰,在 334 nm、302 nm 也分别有微小的峰.由 Chen 等[13] 和 Huir等[20]的研究可知,在 288 nm、302 nm 处分别为类酪氨酸与类色氨酸,在 334 nm、370 nm 处对应物质为类富里酸与类胡敏酸.由图 3(a)可判断 PC1 中 DOM 主要组成为类蛋白物质(类酪氨酸),并共存一定量类腐殖质.图 3(b)为 PC2 因子得分与波长关系,其中在 370 nm 处出现主要特征峰,此峰代表物质为类胡敏酸[20],说明在 PC2 中 DOM 主要由类腐殖质



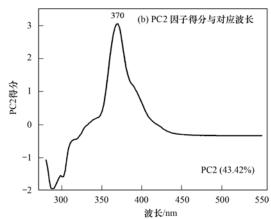


图 3 水体同步荧光主成分分析

Fig. 3 Principal component analysis of the synchronous-scan excitation spectra of the water samples

组成. 在 PC1、PC2 中出现相同的荧光波段(370 nm) 特征峰,说明此水体类腐殖质分布形态分为 2 种方式,一种通过某些载体吸附作用与类蛋白共存的方式存在;另一种为单纯赋存状态. 因此,因子 1 主要代表类蛋白物质(类酪氨酸)及其与类胡敏酸共存物质,而因子 2 主要代表类腐殖质(类胡敏酸).

图 4 为 8 种水体样品经 PCA 所得旋转空间中 成分,从样品显著正载荷分布发现,支流 S1、S2、 S3、S6 及干流 S4 以 PC1 所含物质偏多,干流 S5、 S7、S8 以 PC2 所含物质为主. 通过成分得分系数发 现,在 PC1 中 S3、S6、S4、S2、S1 得分系数分别为 0.301、0.292、0.256、0.167、0.132; 在 PC2 中其 因子得分系数大小为 S5 > S7 > S8. 由以上统计分析 结果可知,PC1 中类蛋白物质偏多主要为支流 4 种 样品及干流 S4 所贡献,PC2 中类腐殖质主要为干流 S5、S7、S8 贡献. 对 DOM 在各样品中分布,支流 S3 与 S6 中类蛋白物质含量更高,尤其以类酪氨酸为主 要组分,S1、S2 中含有大量与类蛋白共存的类腐殖 质; 在干流 S5、S7、S8 中 DOM 组成主要为类腐殖 质,以类胡敏酸为其重要有机物质. 干流 4 种样品 中类蛋白、类腐殖质组成变化可发现,干流与支流 汇合后干流水体中类蛋白和与类蛋白共存形式的腐 殖质类物质偏高,随河流而下干流水体中类蛋白物 质逐渐减少,类腐殖质逐渐增高的趋势,再次验证类 蛋白物质在水体中较类腐殖质易降解.

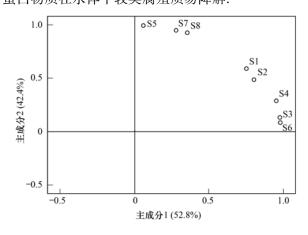


图 4 采样点旋转空间中成分

Fig. 4 Property-property plots of PCA factors of the water sample

2.3 水体 DOM 腐殖化程度及结构特征

HIX 被广泛应用于表征有机质腐殖化程度的指标. Ohno^[8]研究显示 HIX 值在 0~1 间变动,随其值的增大腐殖化程度越深,表 3显示,本研究所有样品 HIX 值均在 0.8 以下,其中 S3、S6 水体 HIX 值较其它水体 HIX 值较小. 表明水体 DOM 的腐殖化程

度较低,在环境中存在时间较短,主要来自微生物对小分子物质分解后产物及微生物自身的死亡分解;支流 S3、S6 值偏小说明其水体中易降解物质偏多. E_2/E_3 常用于湖沼学中指示有机质腐殖化程度及相对分子质量大小[21], Wang 等[22] 的研究表明,该值的大小与有机质相对分子质量呈反比关系,同时也有研究者提出 E_2/E_3 值小于 3.5 时为胡敏酸,大于 3.5 为富里酸[11]. 本次所测 8 个样品中除 S1 与 S2 外,其余 6 个样品 E_2/E_3 值基本保持在 $5 \sim 7$ 之间,表明在支流 S3、S6 及干流水体中 DOM 的分子以相对较小的富里酸为主,而相对分子质量稍大的胡敏酸含量相对较少,而 S1、S2 水体中 DOM 组成物质中相对分子质量则相对较大,表明在这两个污水处理厂中,大部分小分子有机物已经被去除,留下的都是大分子有机物.

表征水体中 DOM 相对分子质量与芳香性的指 标有很多,据 Nishijima 等[23]研究,有机物在 254 nm 下的紫外吸收主要是由包括芳香族化合物在内的具 有不饱和碳-碳键的化合物引起,SUVA254值与 DOM 芳香性程度呈正相关关系[12]; 荧光指数 (fluorescence index, f_{450/500}) f_{450/500} 值能灵敏地表征 DOM 芳香性,其值越低说明含有苯环结构越多,芳 香性较强,同时其还可以用于表征 DOM 来源[7]. 从 水体中 $SUVA_{254}$ 值与 $f_{450/500}$ 值可发现其干流大于支 流,河流由上游至下游 SUVA34值呈升高趋势. 以上 数据说明随水流而下水体 DOM 中芳香性组分减 少,此类芳香性组分可通过在水流过程中逐渐被底 泥及沉积物吸附、水体微生物分解及光降解等途径 减少^[24,25]. $f_{450/500}$ 值大小在2~4之间,根据 McKnight 等 $^{[26]}$ 提出 $f_{450/500}$ 值大于 1.9 时其来源主要 为生物源,而大部分河流、湖泊的f450/500 值接近 1.5^[27,28]. 说明其中 DOM 中腐殖质来源主要为生物 源,以污水处理厂尾水为水源的水体中腐殖质组成 不同于以地表水为水源的河水. 代表支流 S1、S2、 S3 和 S6 的 SUVA₅₄值大小均依次为 S6 > S3 > S1 > S2,表明 S1 与 S2 水体中 DOM 含有较多的具有不饱 和碳-碳键的芳香族化合物,芳香性较强、相对分子 质量大; 而 S3 和 S6 水体的 DOM 组成中相对分子 质量相对小、芳香性较弱. 建议在 S1、S2 处理工艺 中应添加或改进相关膜处理设备,加强大分子有机 物的去除效率;针对S3、S6 在处理过程中应注重 厌氧与好氧生物处理工艺的优化,提高对小分子的 去除能力[29].

表 3 水体 DOM 相对分子质量及芳香性特征参数

Table 3 Parameters for molecular weight and aromatic character of waters DC	Table 3	Parameters	for molecular	weight and	aromatic	character	of waters	DOI
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项目	S1	S2	S3	S4	S5	S6	S7	S8
HIX	0.711	0. 746	0. 251	0. 577	0.758	0. 358	0.703	0. 754
E_2/E_3	3. 321	2. 279	7.096	6.308	5. 303	5. 293	5. 647	5. 469
SUVA_{254}	0.076	0.035	0.082	1. 255	1. 333	0. 100	1.419	1. 453
$f_{450/500}$	2. 246	2. 148	2. 567	2. 282	3.716	2. 583	3. 829	3. 815

2.4 水体 DOM 浓度与水质化学指标关系

DOM 为水体中重要的有机物,在某种程度上其 浓度能体现水体有机物含量的大小,通过对 DOM 荧光分析能一定程度上反映水体污染状况. 通过对 样品荧光光谱区域积分体积与水体化学指标进行分 析,发现众多指标间都体现很好的相关显著性,表4 为其 Pearson 相关性分析结果. TOT 由水体中每个 荧光团所贡献,能全面反映 DOM 荧光团浓度,其与 水体 NH_4^+ -N和 COD 呈极显著相关(P < 0.01),与 TN 呈显著相关(P < 0.05),说明水体中 DOM 荧光 强度能很好反映水体状况. 从各荧光区与水质化学 指标间相关性发现,Ⅲ区、V区与水质 TN、NH₄-N 呈显著关系,尤其与 NH_{\star}^{+} -N相关显著性更强(P <0.01),而 TP 与各荧光区均无明显相关性,可推测 洨河水体 DOM 组成以氮类元素为主,而磷类元素 对其贡献相对较少. 因此,在对洨河水体有机质去 除可通过降低水体NH₄-N与 COD 实现,同时对洨河 治理应注重氮素的去除与降解.

水体 DOM 荧光强度与其化学指标之间的关 系,近年也有很多研究者做出相关研究,例如:Baker 等[30]对河水库水三维荧光光谱研究,发现 I 区 $[E_x/E_m(280 \text{ nm}/350 \text{ nm})]$ 与水体氮和磷浓度有很 好的相关性;施俊[31]对污水处理厂进出水三维荧 光光谱研究,发现城市污水中荧光强度与铵态氮 和总氮有很好线性关系: 王志刚等[32]研究表明腐 殖酸与 DOM 的荧光强度有很强相关性. 水体中 DOM 组成、来源和测量与水体中许多物理、化学 及生物因素有关,针对城市纳污河流还受城市污 染源结构等众多因素影响,同时水体中 DOM 的荧 光组分与非荧光组分比例不同也会影响荧光结果 与化学指标的相关性,本文主要基于荧光有机组 分对水体样品中有机质进行分析,因此针对洨河 有机质与水质化学指标之间明确的关联性还应进 一步深入研究.

表 4 水体荧光强度与水质基本指标相关性1)

Table 4 Relationship between the fluorescence intensity of water DOM and the other water quality chemical indicators

			•		1	*	
	Ⅲ区	V区	TOT	TN	TP	NH ₄ -N	COD
III 区	1.000						
$V \boxtimes$	0. 995 * *	1.000					
TOT	0. 999 * *	0. 996 * *	1.000				
TN	0. 759 *	0. 806 *	0. 765 *	1.000			
TP	-0.151	-0.181	-0.155	-0.434	1.000		
NH ₄ -N	0. 959 * *	0. 982 * *	0. 964 * *	0. 872 * *	-0. 227	1.000	
COD	0. 937 * *	0. 967 * *	0. 941 * *	0. 892 * *	-0. 257	0. 994 * *	1.000

1) * 表示在 0.05 水平(双侧)上显著相关; * * 表示在 0.01 水平(双侧)上显著相关

3 结论

(1)通过三维荧光及同步荧光光谱对洨河水体DOM分析可知,水体中DOM由类蛋白及类腐殖质物质组成,同步荧光主成分分析发现主要组成为类色氨酸、类酪氨酸、类胡敏酸和类富里酸这4种.代表支流的4种水体样品中均存在显著的类蛋白峰,S3、S6水体中类蛋白峰浓度更高;在S1、S2水体DOM主要为类腐殖质,其中类胡敏酸为其主要组分.干流水体中DOM呈现类蛋白逐渐减少,类腐

殖质出现增加趋势.

- (2)结合紫外光谱及三维荧光分析数据对水体中 DOM 相对分子质量大小及芳香性研究发现,支流 S1、S2 水体中 DOM 主要为相对分子质量相对大、芳香性强的有机物; S3、S6 水体中 DOM 组成更多为小分子量、芳香性弱的有机物,同时其腐殖化程度相对 S1、S2 较差. 干流水体中 DOM 随河流而下小分子、易降解有机质被微生物降解,最终以难降解的类胡敏酸大量存在于水体.
 - (3)针对代表洨河支流的4座向洨河排放尾水

的污水处理单位出水水质特征,建议 S1、S2 加强对水体中相对难降解的类腐殖质物质去除,可添加或改进对大分子物质有较好去除效果的膜处理设备; S3、S6 应更多优化相关厌氧与好氧生物处理工艺,增加对易降解的类蛋白物质去除效果. 在对洨河水体中有机质的去除时,可通过降低水体中NH₄-N与COD 含量实现,对水体治理应注重氮素的控制.

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《环境科学》再获"百种中国杰出学术期刊"称号

2014年9月26日,中国科技论文统计结果发布会在北京举行,会议公布了"百种中国杰出学术期刊"获奖名单.《环境科学》连续13次荣获"百种中国杰出学术期刊"称号."百种中国杰出学术期刊"是根据中国科技学术期刊综合评价指标体系进行评定.该体系利用总被引频次、影响因子、基金论文比、他引总引比等多个文献计量学指标进行统计分析,对期刊分学科进行评比,其评价结果客观公正,为我国科技界公认,并具有广泛影响.

HUANJING KEXUE

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