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目 次

近 20 年来中国典型区域 PM_2 ,时空演变过程
河北香河亚微米气溶胶组分特性、来源及其演变规律分析
一股字頁禾雲和建法王信 DM 化类组式快热 LL 淡牡牡 动松黄 化姜梅 刘姬 公婉然 化组 刘旭英 几千田(2042)
温锦市秋冬季节 PM25 中碳组分特征及来源解析
················· 京盛翰,土红丽,木海林,彻独,尸浜,夏阳,宋传起,陶士康,学利,俊成宋,真成,唐伟,升玉利 (3090)
地级市域工业 VOCs 排放源产排特性及其控制技术应用现状: 以秦皇岛市为例 ····································
地级市域工业 VOCs 排放源产排特性及其控制技术应用现状: 以秦皇岛市为例 胡旭睿,虎啸宇,王灿 (3096) 青霉素发酵尾气 VOCs 污染特征及健康风险评价 郭斌,么瑞静,张硕,马磊,康汇,王姗姗 (3102) 轻型汽油车尾气 OC 和 EC 排放因子实测研究 黄成,胡馨遥,鲁君 (3110) 南京市大气降尘重金属污染水平及风险评价 田春晖,杨若杼,古丽扎尔·依力哈木,钱新,王金花,李慧明 (3118) 西安城区路面细颗粒灰尘重金属污染水平及来源分析 石栋奇,卢新卫 (3126) 三峡库区主要河流秋季 pCO。及其影响因素 罗佳宸,毛瑢,李思悦 (3134) 泾河支流地表水地下水的水化学特征及其控制因素 罗佳宸,毛瑢,李思悦 (3134) 经物滞留对城市地表径流磷的去除途径 李立青,刘雨情,杨佳敏,王娟 (3150) 淀山湖浮游植物功能群演替特征及其与环境因子的关系 杨丽,张玮,尚光霞,张军毅,王丽卿,魏华 (3158) 抚仙湖硅藻群落的时空变化特征及其与水环境的关系 杨丽,张玮,尚光霞,张军毅,王丽卿,魏华 (3158) 蓝藻水华及其降解对沉积物-水微界面的影响 年永平,谢瑞,晁建颖,姬昌辉,于剑 (3179) 生物炭对人工湿地植物根系形态特征及净化能力的影响 徐德福,潘潜澄,李映雪,陈晓艺,王佳俊,周磊 (3187)
泾河支流地表水地下水的水化学特征及其控制因素
抚仙湖硅藻群落的时空变化特征及其与水环境的关系
生物炭对人工湿地植物根系形态特征及净化能力的影响··········徐德福,潘潜澄,李映雪,陈晓艺,王佳俊,周磊(3187) Mn-Co/蜂窝陶瓷催化剂制备及催化臭氧化对苯二酚效能····································
Mn-Co/蜂窝陶瓷催化剂制备及催化臭氧化对苯二酚效能
电导率对伏氧产酸、止渗透与微生物燃料电池耦合上之运行性能的影响 ··· 陆宇孝, 对金梦, 土新华, 李秀分, 李晔(3240) 不同磷浓度下生物除磷颗粒系统的 COD 需求 ················· 李冬, 曹美忠, 郭跃洲, 梅宁, 李帅, 张杰(3247) 基质浓度对 ARR 反应器 SAD 协同脱氧除碳效能影响 ····································
采用含硫铁化学污泥作为反硝化电子供体进行焦化废水中总氮深度去除
采用含硫铁化学污泥作为反硝化电子供体进行焦化废水中总氮深度去除 (村炳炳、潘建新, 马景德, 王丰, 吴海珍, 韦朝海(3262) (古歌曜气下短程硝化耦合污泥微膨胀稳定性
气水比对后置固相反硝化滤池工艺脱氮及微生物群落影响 ····································
PFOS 前体物质(PreFOSs)降解菌的分离鉴定及其降解特性 赵淑艳,周涛,王博慧,梁田坤,柳丽芬(3321) 采油井场土壤微生物群落结构分布
广西某赤泥堆场周边土壤重金属污染风险 郭颖,李玉冰,薛生国,廖嘉欣,王琼丽,吴川(3349)邻苯二甲酸酯在重庆市城市土壤中的污染分布特征及来源分析 杨志豪,何明靖,杨婷,卢俊峰,魏世强(3358)
塔里木盆地北缘绿洲不同连作年限棉田土壤有机碳、无机碳含量与环境因子的相关性 ····································
塔里木盆地北缘绿洲 4 种土地利用方式土壤有机碳组分分布特征及具与土壤环境因子的关系 ····································
施硼对水稻幼苗吸收和分泌砷的影响 朱毅,孙国新,陈正,胡莹,郑瑞伦(3400) 不同改良剂对铅镉污染农田水稻重金属积累和产量影响的比较分析 胡雪芳 田志清 梁亭 陈俊德 张志民 朱祥民 王士奎(3409)
南京大气臭氧浓度的季节变化及其对主要作物影响的评估 赵辉,郑有飞,魏莉,关清 (3418) 三峡库区涪陵和忠县两地居民发汞含量水平及影响因素分析 程楠,谢青,樊宇飞,王永敏,张成,王庆勇 (3426)
不同改良剂对铅镉污染农田水稻里金属积累和产量影响的比较分析 胡雪芳,田志清,梁亮,陈俊德,张志民,朱祥民,王士奎(3409)南京大气臭氧浓度的季节变化及其对主要作物影响的评估 赵辉,郑有飞,魏莉,关清(3418)三峡库区涪陵和忠县两地居民发汞含量水平及影响因素分析 程楠,谢青,樊宇飞,王永敏,张成,王定勇(3426)人粪便好氧堆肥过程中典型抗生素的消减特性 时红蕾,王晓昌,李倩(3434)COD/SO4-对青霉素菌渣厌氧消化影响 强虹,李玉友,裴梦富(3443)果蔬类垃圾主发酵堆肥产物储放和利用的恶臭释放特征 何品晶,蒋宁羚,徐贤,韦顺艳,邵立明,吕凡(3452)兽用抗生素磺胺二甲嘧啶对稻田 NH,挥发的影响 庞炳坤,张敬沙,吴杰,李志琳,蒋静艳(3460)《环境科学》征订启事(3141) 《环境科学》征稿简则(3202) 信息(3229, 3433, 3451)
告用玩生系頓胺—中嘧啶对稻田 NH ₃ 挥发的影响 ·················

蓝藻水华及其降解对沉积物-水微界面的影响

王永平1,谢瑞1,晁建颖2,姬昌辉1,于剑1

(1. 南京水利科学研究院,水文水资源与水利工程科学国家重点实验室,南京 210029; 2. 环境保护部南京环境科学研究所,南京 210042)

摘要:模拟研究了不同条件下,蓝藻水华及其降解过程对沉积物-水微界面的影响.采用丙酮法测定水体中叶绿素质量浓度,溶解氧微电极测定界面溶解氧质量浓度,毫米级分层测定沉积物中营养盐与金属元素的垂直分布.结果表明,蓝藻水华及其降解过程改变了界面附近溶解氧环境和表层约3 mm 深沉积物中营养盐与金属元素的垂直分布.扰动在蓝藻水华降解过程和C、P营养盐与 Fe、Ca、Mg、Al和 K等金属元素的早期成岩过程中起着重要作用.遮光加速了蓝藻降解,并且削弱了扰动的影响.无处理对照组沉积物表面出现了一层底栖藻,底栖藻的光合作用产生了氧气,造成表层1 mm 沉积物中大部分营养盐与金属元素质量浓度和处理组间的显著性差异.相关分析结果表明,沉积物中P的垂直分布与 Mn 显著相关,其次是C.高分辨率研究结果可见,蓝藻水华及其降解过程在毫米级厚度内即对沉积物-水界面产生了影响.

关键词:水华;降解;溶解氧;营养盐;金属元素

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Effects of Algal Blooms and Their Degradation on the Sediment-water Microinterface

WANG Yong-ping¹, XIE Rui¹, CHAO Jian-ying², JI Chang-hui¹, YU Jian¹

(1. State Key Laboratory of Hydrology-Water Resources and Hydraulic Engineering, Nanjing Hydraulic Research Institute, Nanjing 210029, China; 2. Nanjing Institute of Environmental Sciences, Ministry of Environmental Protection, Nanjing 210042, China)

Abstract: Effects of algal blooms and their degradation on the sediment-water micro-interface under conditions of disturbance and darkness were investigated. The concentration of chlorophyll a in water was determined via the acetone method, profiles of oxygen near the interface were measured using a microelectrode, and profiles of nutrients and metals in sediments were measured at the millimeter level. The results showed that algal bloom degradation at the sediment-water micro-interface decreased the concentration of oxygen and affected nutrient and metal profiles, at depths over approximately 3 mm. Disturbance played an important role in algal bloom degradation and early diagenesis processes of nutrients, such as C and P, and metals, such as Fe, Ca, Mg, Al, and K. Darkness sped up algal bloom degradation and reduced the influence of disturbance. Under control conditions of no disturbance nor algae, and supplied with enough light, a layer of benthic algae appeared at the sediment surface, whose photosynthesis produced oxygen and greatly changed the microenvironment. This brought about significant differences in the concentrations of nearly all nutrients and metals in the surficial sediment compared with those of other treatments. Correlation analyses showed that the vertical variability of sediment P concentration was most strongly related to sediment Mn, followed by sediment C. The results of this high-resolution research showed that algal bloom degradation had an effect on the sediment-water micro-interface at the millimeter level.

Key words: algal blooms; degradation; oxygen profile; sediment nutrient profiles; sediment metal profiles

湖泊富营养化引起蓝藻水华暴发已成为普遍事件. 2007 年在无锡太湖发生的影响数百万人饮用水的"水危机"事件就是由蓝藻水华在自来水厂的堆积与降解引起的^[1]. 关于蓝藻水华对水体以及沉积物影响的研究已有不少,有研究认为,蓝藻水华能显著改变水体中pH并刺激底泥中溶解性营养盐的释放^[2,3]或通过改变水体的溶解氧环境造成沉积物-水界面氮磷和 Fe、Mn、S 循环的变化^[4,5]. Boon 等^[6]认为水华能沉降在水底,并在沉积物表层发生再矿化,同时影响沉积物表层细菌活性^[7,8]. 前人对沉积物-水界面的研究大都集中在不同条件下营养盐通量^[9~11],沉积物间隙水和上覆水中营养盐和金属元

素的垂直分布[12~14]等方面.

针对沉积物-水界面的研究存在分辨率的问题. 在微电极,薄膜扩散梯度(diffusive gradients in thin films, DGT) 和薄膜扩散平衡 (diffusive equilibrium in thin films, DET)等技术发展以前,针对沉积物-水界面开展的研究大多采用传统的方法,精度较低. 微电极等现代技术发展以后,诸如 pH、 CO_2 、 O_2 和

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作者简介: 王永平(1982~), 男, 博士, 高级工程师, 主要研究方向为水生态环境, E-mail; ypwang@ nhri. cn

H₂S 等微电极大量被应用于在湖泊和海洋沉积物水界面的实验室模拟和野外原位观测中^[15-17]. 微电极优势在于能实现较高的空间分辨率和短时间内获得大量的数据^[18]. DET 和 DGT 技术的发展使研究沉积物间隙水中金属元素的高分辨率(1 mm)的垂直分布成为可能^[19,20]. 这些技术比沉积物分层离心法,甚至是比平衡式间隙水采样技术(pore water equilibrators, Peeper)都更为先进. 但是,这些技术主要针对间隙水,目前仍然缺乏有效的技术针对沉积物自身物质的质量浓度进行高分辨率的研究,因此关于蓝藻水华对沉积物自身的高分辨率的研究结果鲜见报道.

本研究模拟了不同条件下蓝藻水华的堆积和降解过程,应用溶氧微电极测定了水体与表层沉积物中的溶解氧含量.同时对沉积物进行毫米级精确分层,分析了沉积物中多种营养盐和金属元素的垂直分布规律,目的在于从更高的精度研究不同条件下蓝藻水华及其降解对沉积物-水微界面的影响,从而提高对蓝藻水华暴发机制更精确的认识.

1 材料与方法

1.1 实验设计

本实验在中国科学院南京地理与湖泊研究所太湖站进行. 所用的沉积物,水和蓝藻均采自太湖梅梁湾. 使用彼得森抓泥器采集表层沉积物后,充分搅匀,放入18个20 L(25 cm×20 cm×40 cm)的玻璃缸中,保持泥深约20 cm. 然后在各缸中小心加入约20 cm深上覆水,静置数天后开始实验. 实验处理如表1所示,其中,"加藻(Z)"指在处理缸中加入500mL洗净的蓝藻浆,"扰动(R)"指用气泵制造扰动,"遮光(B)"指用铝箔将整个缸包裹起来,保持黑暗环境. 同时设置空白对照(CK),每种处理设置3个重复.

表 1 实验设计

Table 1	Details	of t	the	experimental	design	
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		- I	0
处理号	加藻	扰动	遮光
CK			
R		是	
Z	是		
Z + R	是	是	
Z + B	是		是
Z + R + B	是	是	是

1.2 水样采集与测定

在15 d的实验过程中,每2~3 d采集水样用于 测定叶绿素含量.叶绿素含量采用丙酮进行提取,分 光光度法测定[21].

1.3 溶解氧的测定

实验进行到第 14 d 时,用溶氧微电极(PreSens,德国)对上覆水体和沉积物中溶解氧进行测定.溶氧微电极的有效测定区小于 20 μm,涂有固态光敏荧光粉;电极反应时间小于 1 s. 在 0~100 % 空气饱和度水体中,氧气质量浓度与光强呈线性关系.每次使用前,采用饱和空气(100 % 氧气)与加入过量Na₂SO₃ 的纯净水(0 % 氧气)进行两点校准.微电极安装在精度为 0.02 mm 的操作器上.测定了界面以上 1 cm 和 1 mm 处上覆水,界面和界面以下 1 mm 沉积物中的溶解氧质量浓度.

39 卷

1.4 沉积物采样与测定

玻璃缸中的水抽干后,沉积物自然风干.将风干后的沉积物取出,避开孔洞,固定在切片机上,按1mm厚度小心切取泥样,共切10层.经玛瑙研钵研磨至过100目筛后,由元素分析仪(EA3000,意大利)测定沉积物中的C和N含量.另外按流程经王水消解后,用ICP-AES测定其中的Fe、Al、Ca、Mn、P、Mg、K和Na等金属元素含量.

1.5 统计分析

数据差异显著性分析和相关系数计算由 SPSS (16.0 版)软件进行.

2 结果与分析

2.1 水体中叶绿素质量浓度变化

实验过程的 15 d 中水体内叶绿素质量浓度变化如图 1 所示. 由于藻浆的不断降解,加藻的各处理组中叶绿素质量浓度总体呈下降趋势. 遮光使 Z+B和 Z+R+B两种处理组水体中叶绿素质量浓度下

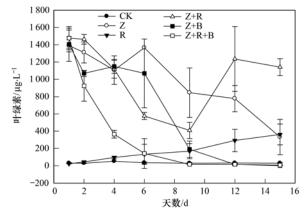


图 1 实验过程中各处理水体中叶绿素质量浓度变化

Fig. 1 Concentration of Chl-a for all treatments during the experiment

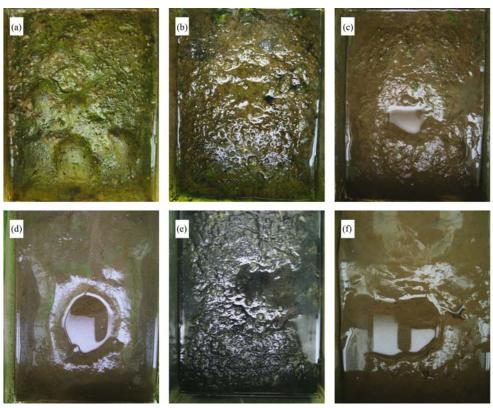
降速度更快,分别在第9和第12d降至0.Z+R处理组的叶绿素质量浓度在第9d达到低谷,随后又逐渐升高,可能是新一代蓝藻生长所致.R处理组并未加入藻浆,但在整个实验过程中的叶绿素质量浓度逐渐升高,可能是由于扰动引起底泥悬浮,同时提供了原来在沉积物中的蓝藻开始生长和繁殖的条件,对照组叶绿素质量浓度始终保持在较低水平,主要是由于在充足阳光和无扰动的条件下,沉积物表面出现一层底栖藻类,从而抑制了浮游藻类的生长,并且保持水体清澈.

2.2 沉积物性状

图 2 是实验结束后各处理组沉积物的照片. 在对照组沉积物表面可以看到明显的底栖藻层, Z 处理组表面有蓝藻和底栖藻的混合物. R、Z + R 和 Z + R + B 这 3 个处理组的沉积物由于受扰动影响而呈新鲜的黄褐色. 只有 Z + B 处理组的沉积物呈黑色,可能受缺氧条件下蓝藻降解和某些金属离子被还原所致.

2.3 溶解氧的垂直分布

各处理组水体和沉积物中溶解氧的垂直分布如



(a)~(f)分别代表对照、加藻、扰动、加藻+扰动、加藻+遮光、加藻+扰动+遮光处理 图2 沉积物性状照片

Fig. 2 Sediments statuses for all treatments

图 3 所示. 由于缺光和无扰动的条件加速了蓝藻降解, Z + B 处理组的沉积物-水界面环境完全缺氧. 而其余处理组界面以上 1 cm 上覆水中溶解氧质量浓度均为 8 mg·L⁻¹左右. Z + R + B 和 Z 处理组在界面以上 1 mm 处溶解氧质量浓度迅速降低,可能分别是由于缺光和缺乏扰动而导致氧气消耗速率增加. 但是,受底栖藻光合作用影响,对照组呈现出较高的溶解氧质量浓度,其结果与 Zhang 等^[22]观察到的一致. 各处理组界面以下 1 mm 处沉积物中溶解氧都接近 0 mg·L⁻¹. 此处沉积物表层溶解氧层的厚度小于其他研究结果,可能是由于沉积物经充分混合,与野外条件存在差异所致.

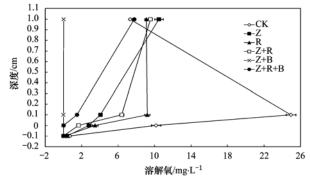


图 3 各处理组水体和沉积物中溶解氧质量浓度

Fig. 3 Vertical profiles of oxygen in the water and sediment for all treatments

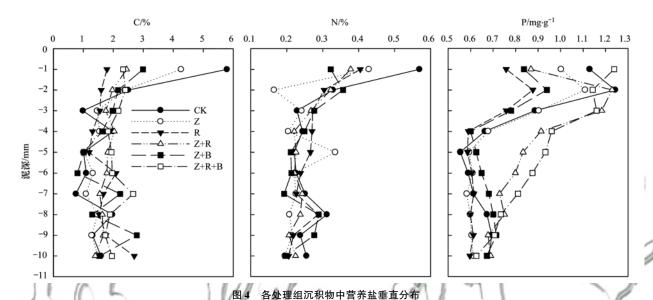
2.4 营养盐的垂直分布

各处理组沉积物中 C、N 和 P 垂直分布如图 4 所示. 由于微生物能分解有机物从而向间隙水中释放 HPO_4^{2-} 和 $NH_4^{+[23]}$,影响了沉积物中 P 和 N 的含量.

各处理组间 C 含量没有明显差异,但对照组和 Z 处理组表层 1 mm 沉积物内 C 含量(质量分数)比 其它处理组都高.各处理组的 N 含量(质量分数)垂直分布的总趋势是在界面以下 1~2 mm 处出现峰值,然后逐渐降低并保持在一个较低的水平上.这有

可能是实验过程中蓝藻降解释放出的 N 在沉积物 表层富集.

P的垂直分布趋势较为复杂. 大部分处理组的质量浓度峰值出现在界面以下 2 mm 处,然后逐渐降低至 5 mm 处. 说明虽然蓝藻降解释放出的 P 沉降到沉积物表面,但 P 的垂直分布可能主要受氧化还原边界层的影响而在边界层富集. Z + R + B 和 Z + R 处理组的沉积物 P 在界面以下 2~10 mm 段明显高于其它处理组,究其原因,可能是富集在表面的P 受扰动的影响而呈现出类似侵蚀的效果.



Vertical profiles of C, N and TP in the sediment for all treatments

表 2 是各处理组表层 1 mm 沉积物内营养盐含量的单因素方差分析结果. 受沉积物表面底栖藻的影响,对照组中 C 和 N 的含量显著高于其它处理组. Z 与 Z + R 处理组间 C 质量浓度的显著性差异和 Z + B 与 Z + R + B 处理间 P 质量浓度的显著性差异反映出扰动在其中的作用. 而遮光处理则造成了 Z 与 Z + B 处理间 P 质量浓度的显著性差异.

表 2 各处理组表层 1 mm 沉积物中营养盐含量

Table 2	Nutrionto	in the	curficial	andimenta	for all	treatments

处理号	C/%	N/%	P/mg·kg ⁻¹
CK	6.762 ± 0.984 ^a	0.661 ±0.090 ^a	$1\ 074.47\pm 50.45^{\mathrm{bc}}$
Z	$4.190 \pm 0.208^{\rm b}$	$0.435 \pm 0.051^{\rm b}$	998.33 ± 8.14^{abc}
R	$3.043 \pm 1.194^{\rm bc}$	$0.393\pm0.051^{\rm bc}$	878.38 ± 112.11^{ab}
Z + R	$2.662 \pm 0.250^{\circ}$	$0.344\pm0.053^{\rm bc}$	798. 19 ± 110. 93 ^a
Z + B	$2.933 \pm 0.049^{\circ}$	$0.349\pm0.027^{\rm bc}$	834.09 ± 2.69^{a}
Z + R + B	2.497 ± 0.191°	$0.309 \pm 0.018^{\circ}$	1 144.31 ±81.24°

2.5 金属元素的垂直分布

各处理组沉积物中 Fe、Mn、Ca、Mg、Al、K 和

Na 等金属元素的垂直分布如图 5 所示. Fe 的峰值 与 P类似,也受氧化还原边界层影响而出现在界面 以下 2 mm 处^[24]. 而由于扰动改变了溶解氧环境, R、Z+R和Z+R+B处理中 Mn 含量也在界面以下 2 mm 氧化还原边界层处达到峰值. 在其它处理组中, Mn 在表层富集,然后逐渐降低至 4 mm 处趋于稳定.

Al、K和Na元素的趋势类似,都是在表层含量最低而后逐渐升高,说明表层沉积物中的元素在有机物降解过程中受早期成岩作用影响而逐渐溶解. Ca元素在表层富集,然后迅速降低. K元素在表层富集的垂直分布趋势和对照组与 Z处理组中 C含量垂直分布类似,而在其它处理组中随深度变化没有明显差异.

表 3 是各处理组表层 1 mm 沉积物内金属元素含量的单因素方差分析结果. 由于受沉积物表层底栖藻的影响,对照组和 Z 处理组的表层沉积物中 Fe、Ca、Mg、Al、K 和 Na 等金属元素含量与

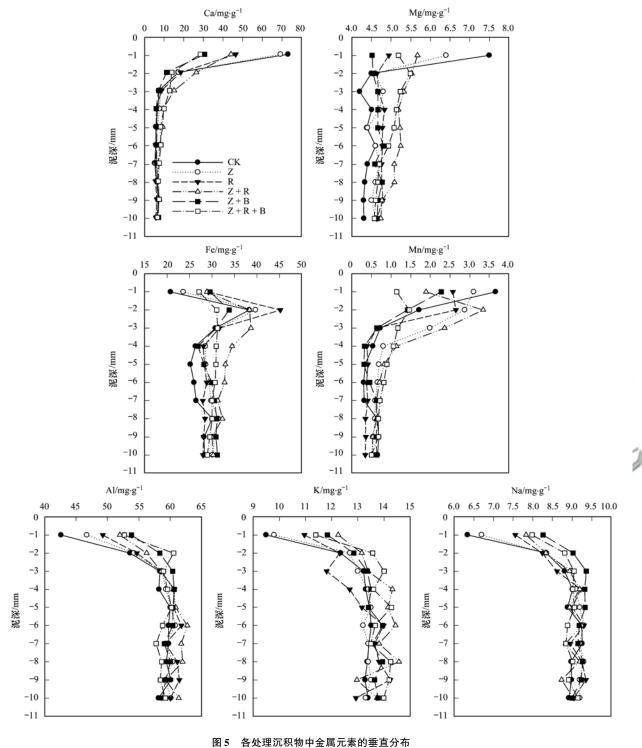


图 3 合处理机标物中显属儿系的要且万印

Fig. 5 Vertical profiles of metals in the sediments for all treatments

其它处理组都有显著差异. 底栖藻的新陈代谢产生的氧气改变了界面的微环境,同时其体内的叶绿体也利用 Ca 和 Mg 元素和营养盐含量的垂直分布结果一致, 扰动和遮光处理在金属元素的垂直分布中也具有明显的作用,如 Z 和 Z + R 处理间的 Mn、Ca、Al 和 K 元素含量的显著性差异, Z 和 Z + B 处理间的 Fe、Ca、Mg、Al 和 K 元素含量显著

性差异. 但是, 扰动的作用在遮光处理组中并不显著.

3 讨论

3.1 蓝藻水华及其降解的影响深度

很多野外和实验室研究结果指出浮游藻类能沉降在沉积物表面并发生矿化^[5-7].并且,大量有机物

质的成岩作用仅能发生在表层几毫米沉积物中^[25-26].本研究中,溶解氧的垂直分布结果显示氧气侵蚀深度仅为 1 mm 左右.而大部分沉积物中营

养盐和金属元素的垂直分布结果表明其峰值或转折 点出现在界面以下 2~3 mm 处. 这些结果说明蓝藻 水华及其降解影响深度大概在 3 mm 以内.

表 3 各处理组表层 1 mm 沉积物中金属元素含量

Table 3 Metals in the surficial sediments for all treatments

处理号	Fe/mg·g -1	Mn/mg•g ⁻¹	Ca/mg·g ⁻¹	Mg/mg·g ⁻¹	Al/mg·g ⁻¹	K/mg•g ⁻¹	Na/mg•g ⁻¹
CK	22.5 ± 1.7 a	$3550.5\pm104.4^{\mathrm{d}}$	72.7 ± 1.2°	$8.0 \pm 0.5^{\circ}$	42.5 ± 0.3 ^a	9.9 ± 0.4 ab	6.3 ± 0.1 a
Z	24.5 ± 0.9^{ab}	$3\ 034.\ 3\pm62.\ 1^{\rm cd}$	$65.4 \pm 4.6^{\circ}$	6.2 ± 0.3^{b}	45.9 ± 2.1^{ab}	9.8 ± 0.4^{a}	6.9 ± 0.6^{ab}
R	$32.3 \pm 3.4^{\circ}$	$3\ 168.\ 8\pm572.\ 1^{\rm cd}$	$46.6 \pm 8.1^{\rm b}$	5.3 ± 0.5^{ab}	$49.8 \pm 1.1^{\rm bc}$	11.4 ± 0.4 bc	$7.9 \pm 0.4^{\text{bc}}$
Z + R	29.5 ± 2.0^{bc}	1711.5 ± 537.1 ab	37.4 ± 7.1^{ab}	5.5 ± 0.2^{ab}	54.0 ± 1.9^{d}	$12.9 \pm 0.4^{\circ}$	$8.3 \pm 0.4^{\circ}$
Z + B	$30.6 \pm 1.3^{\circ}$	$2314.2\pm39.0^{\mathrm{bc}}$	31.2 ± 0.3^{a}	4.8 ± 0.3^{a}	54.1 ± 0.5^{d}	$12.6 \pm 0.4^{\circ}$	$8.3 \pm 0.0^{\circ}$
Z + R + B	$27.8 \pm 0.6^{\text{bc}}$	1 112.2 ± 80.4 a	25.2 ± 3.7^{a}	5.1 ±0.1 ^a	$53.4 \pm 1.8^{\rm cd}$	$11.9 \pm 0.4^{\circ}$	$8.5 \pm 0.5^{\circ}$

在关于早期成岩和元素的迁移过程的研究中,DGT和DET技术常用来获得高分辨率的间隙水中元素垂直分布结果,结果表明沉积物中金属元素迁移通量存在明显的梯度^[27~29].这些研究结果中的影响深度都超过了本研究.但是,以前很多针对营养盐和金属元素在沉积物中垂直分布的研究中,沉积物的分层厚度是 0.5 cm、1 cm或者更厚^[12~14].而较厚的沉积物分层很有可能错过一些更为精细的过程.同时,间隙水与沉积物性质的不同也有可能引起早期成岩作用与元素迁移过程研究结论的差异.另外,由于本研究是采集沉积物混匀静置后进行的,这可能是结果中氧气侵蚀深度较浅的原因.但是总体而言,本研究结果发现蓝藻水华及其降解对表层的初步影响深度是毫米级的.

3.2 沉积物中P垂直分布的决定因素

沉积物中 P 含量的决定因素很复杂,主要包括有机物和 Fe 等^[30]. Trolle 等^[31]在太湖的研究中也

发现沉积物中 P 和有机物显著相关. 本研究结果中 营养盐和金属元素间垂直分布的相关分析结果表 明, P和 Mn 显著相关(r=0.738), 甚至强于 P与 C (r=0.520)和 P 与 Fe(r=0.428)的相关性(表4). 反映出沉积物中 P 的早期成岩作用跟锰化合物的 关系比跟 Fe 和有机物更紧密. 历时两周的实验中, 溶解氧垂直分布结果显示氧气在沉积物中仅能侵蚀 1mm 左右. Fe 和 Mn 都是氧化还原敏感性元素,在 氧气充足的环境中形成稳定氧化物,而在缺氧条件 下能从沉积物中释放出来再在新的富氧环境中重新 沉淀. 但是, Mn 的移动性和氧化能力都强于 Fe^[32] 同时, Jensen 等[33] 对欧洲众多湖泊的调查结果表 明,沉积物的 Fe/P 控制着沉积物磷的迁移能力,比 值越高沉积物中磷的稳定性越好. 本研究结果可 知,沉积物中 Fe/P 较低,可见 Fe 对 P 的束缚较弱. 这些应该是本研究中沉积物中P垂直分布的主要 决定因素是 Mn 而非 Fe 的原因.

表 4 营养盐和金属元素间垂直分布的相关分析(n = 60)

Table 4 Correlation matrix between C, N, P, Fe, Mn, Ca, Mg, Al, K, and Na for the vertical profiles of all treatments (n = 60)

	С	N	P	Fe	Mn	Ca	Mg	Al	K	Na
С	1	0. 701 **	0. 520 **	-0.172	0. 622 **	0. 763 **	0. 729 **	- 0. 731 **	-0.619**	-0.739**
N		1	0. 463 **	-0.191	0. 665 **	0. 820 **	0. 687 **	- 0. 744 **	-0.649 **	-0.750 **
P			1	0. 428 **	0. 738 **	0. 517 **	0. 526 **	- 0. 522 **	-0.369 **	-0.548 **
Fe				1	0. 328 **	-0. 183	-0.190	0.112	0. 205	0. 103
Mn					1	0. 809 **	0. 605 **	- 0. 801 **	-0.674 **	-0.808**
Ca						1	0. 775 **	- 0. 932 **	-0. 848 **	-0.950**
Mg							1	- 0. 595 **	-0.495 **	- 0. 700 **
Al								1	0. 889 **	0. 950 **
K									1	0. 874 **
Na										1

1) **表示在 0.01 水平上显著相关

3.3 扰动处理的影响

前人研究表明扰动能引起表层沉积物的悬浮并相应地改变环境^[34,35].本研究从现象层面上看,扰

动引起了 R 处理组和 Z + R 处理组后期的蓝藻的繁殖与生长,而没有扰动引起了对照组中沉积物表面变微环境显著改变,并直接导致了底栖藻的出现.

从分析结果看,表 2 和 3 显示了扰动处理组引起了 表层沉积物中 Mn 和 P 等元素含量与其它处理组产 生显著性差异,反映出扰动影响了元素的早期成岩 过程.

统计数据表明,太湖在2001全年中有238 d 的风速超过了6.5 m·s^{-1[36]},意味着一年中有2/3 的时间存在较强的风浪扰动.从而一方面造成沉积物的悬浮,给蓝藻的繁殖和生长提供了营养,另一方面抑制了沉积物表层底栖藻的出现,这也从一定程度上解释了太湖中蓝藻水华严重的原因.

4 结论

本研究揭示了蓝藻水华及其降解对沉积物-水 微界面的影响主要体现在改变界面附近溶解氧环境和表层约3 mm 沉积物中营养盐与金属元素的垂直分布.不同处理的效应差异显著: 扰动处理在藻降解过程和 C、P、Fe、Ca、Mg、Al 与 K 等营养盐与金属元素的早期成岩过程中起重要作用. 遮光处理能加速蓝藻降解,影响多种金属元素的早期成岩过程,并削弱扰动的影响. 另外,决定沉积物 P 含量垂直分布的因素主要是 Mn,其次是 C.

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HUANJING KEXUE

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Vol. 39 No. 7 Jul. 15, 2018

CONTENTS

Spatial-Temporal Change Evolution of PM ₂₋₅ in Typical Regions of China in Recent 20 Years	LUO Yi DENG Qiong-fei YANG Kun et al. (3003)
Evaluation the Extent of Health Damage Caused by PM _{2.5} Particulate in Xi'an City	
Analysis of Chemical Composition, Source and Evolution of Submicron Particles in Xianghe, Hebei Province	IIANG Qi, WANG Fei, SUN Ye-le (3022)
Characteristics and Source Analysis of Carbonaceous Components of PM _{2,5} During Autumn in the Northern Suburb of Nanjing	XII Zu-fei CAO Fang GAO Song et al. (3033)
Comparison of Chemical Components Characteristics of PM _{2,5} Between Haze and Clean Periods During Summertime in Lin'an	
Characteristics and Sources of Carbon Components in PM _{2,5} During Autumn and Winter in Panjin City	
Aerosol Optical Properties and Light Absorption Enhancement of EC During Wintertime in Nanjing	
Concentration, Solubility, and Dry Deposition Flux of Trace Elements in Fine and Coarse Particles in Qingdao During Summer	
Characteristics and Sources of Dissolved Heavy Metals in Summer Precipitation of Taiyuan City, China	
Characteristics of and Factors Affecting Atmospheric CO ₂ Concentration in Hangzhou Characteristics of and Factors Affecting Atmospheric CO ₂ Concentration in Hangzhou	
Treatment Status and Emission Characteristics of Volatile Organic Compounds from Typical Industrial Sources	
Characteristics of Industrial VOCs Emission Sources and Control Technology Application in a Prefecture-level City Region-Based on	
Characteristics of industrial vOCs Emission Sources and Control Technology Application in a Freiecture-level City Region-based on	HII Yuzrui HII Yigozyu WANG Can (3006)
Pollution Condition and Health Risk Assessment of VOCs in Fermentation Exhaust from Penicillin Production	
Measurements of OC and EC Emission Factors for Light-duty Gasoline Vehicles	
Pollution Levels and Risk Assessment of Heavy Metals from Atmospheric Deposition in Nanjing	IAN Chun-hui VANC Ruo-zhu Culizhoer Vilibamu et el (2118)
Contamination Levels and Source Analysis of Heavy Metals in the Finer Particles of Urban Road Dust from Xi'an, China	SHI Dong-gi III Vin-wei (3126)
pCO ₂ in the Main Rivers of the Three Gorges Reservoir and Its Influencing Factors	JIIO Jia aban MAO Rong JI Si waa (2124)
Major Ionic Features and Their Possible Controls in the Surface Water and Groundwater of the Jinghe River	
Urban Runoff Phosphorus Removal Pathways in Bioretention Systems	KOU Tong-chao, KUA Kun, Li Zhou, et al. (3142)
Succession Characteristics of Phytoplankton Functional Groups and Their Relationships with Environmental Factors in Dianshan Lake	e, Shangnai
Spatio-temporal Variations of Diatom Community and Their Relationship with Water Environment in Fuxian Lake	
Effects of Algal Blooms and Their Degradation on the Sediment-water Micro-interface	
Effect of Biochar on Root Morphological Characteristics of Wetland Plants and Purification Capacity of Constructed Wetland	
Preparation of Mn-Co/Ceramic Honeycomb Catalyst and Its Performance on Catalytic Ozonation of Hydroquinone	
Degradation Mechanism of Tetracycline Using Fe/Cu Oxides as Heterogeneous Activators of Peroxymonosulfate	
Behavior and Mechanisms of Cd(II) Adsorption from Water by Niobate-Modified Titanate Nanosheets · · · · · · · · · · · · · · · · · · ·	
Trace Amounts of Phosphorus Removal Based on the in-suit Oxidation Products of Iron or Manganese in a Biofilter	
Effect of Preparation Methods on Phosphate Adsorption by Iron-Titanium Binary Oxide; Coprecipitation and Physical Mixing	
Effects of Conductivity on Performance of a Combined System of Anaerobic Acidification, Forward Osmosis, and a Microbial Fuel C	•
COD Requirement for Biological Phosphorus Removal Granule System Under Different Phosphorus Concentrations	0
Effect of Substrate Concentration on SAD Collaborative Nitrogen and Carbon Removal Efficiency in an ABR Reactor	
Evaluation of Advanced Nitrogen Removal from Coking Wastewater Using Sulfide Iron-containing Sludge as a Denitrification Electron	n Donor
2 little 23 little 23 little 24 little 25 litt	
Stability of Nitritation Combined with Limited Filamentous Bulking Under Intermittent Aeration	
Filamentous Sludge Microbial Community of a SBR Reactor Based on High-throughput Sequencing	
Impact of Nano Zero-Valent Iron (NZVI) on Methanogenic Activity, Physiological Traits, and Microbial Community Structure in August 1985.	naerobic Digestion
Effects of Gas/Water Ratio on the Characteristics of Nitrogen Removal and the Microbial Community in Post Solid-Phase Denitrifical	tion Biofilter Process
	······ ZHANG Qian, JI Fang-ying, FU Xu-fang, et al. (3297)
Comparison of Extraction Methods of Extracellular Polymeric Substances from Activated Sludge	
Identification and Characterization of a Hypothermic Alkaliphilic Aerobic Denitrifying Bacterium Pseudomonas monteilii Strain H97	
Isolation, Identification, and Biodegradation Behaviors of a Perfluorooctane Sulfonic Acid Precursor (PreFOSs) Degrading Bacterium	m from Contaminated Soil
Microbial Community Distributions in Soils of an Oil Exploitation Site	
Characteristics of Soil Physicochemical Properties and Enzyme Activities over Different Reclaimed Years in a Copper Tailings Dam	
Risk Analysis of Heavy Metal Contamination in Farmland Soil Around a Bauxite Residue Disposal Area in Guangxi	
Occurrence and Distribution of Phthalate Esters in Urban Soils of Chongqing City	
Profile Distribution of Paddy Soil Organic Carbon and Its Influencing Factors in Chengdu Plain	LI Shan, LI Qi-quan, WANG Chang-quan, et al. (3365)
Correlation Between Soil Organic and Inorganic Carbon and Environmental Factors in Cotton Fields in Different Continuous Cropping	g Years in the Oasis of the Northern Tarim Basin
	······· ZHAO Jing-jing, GONG Lu, AN Shen-qun, et al. (3373)
Soil Organic Carbon Components and Their Correlation with Soil Physicochemical Factors in Four Different Land Use Types of the N	forthern Tarim Basin
	······ AN Shen-qun, GONG Lu, LI Yang-mei, et al. (3382)
Short-term Mechanism of Warming-induced Stability for Organic Carbon in the Karst Plateau Soil	TANG Guo-yong, ZHANG Chun-hua, LIU Fang-yan, et al. (3391)
Effects of Boron Treatment on Arsenic Uptake and Efflux in Rice Seedlings	ZHU Yi, SUN Guo-xin, CHEN Zheng, et al. (3400)
Comparative Analysis of Different Soil Amendment Treatments on Rice Heavy Metal Accumulation and Yield Effect in Pb and Cd Co	ontaminated Farmland
	HU Xue-fang, TIAN Zhi-qing, LIANG liang, et al. (3409)
Seasonal Variation in Surface Ozone and Its Effect on the Winter Wheat and Rice in Nanjing, China	
Hair Mercury Concentrations in Residents of Fuling and Zhongxian in the Three Gorges Reservoir Region and Their Influence Factor	
Removal of Typical Antibiotics During Aerobic Composting of Human Feces	SHI Hong-lei, WANG Xiao-chang. LI Oian (3434)
Effect of COD/SO ₄ ² Ratio on Anaerobic Digestion of Penicillin Bacterial Residues	
Characteristics of Odor Emissions from Fresh Compost During Storage and Application	
Effects of the Veterinary Antibiotic Sulfamethazine on Ammonia Volatilization from a Paddy Field Treated with Conventional Synthet	
Luces of the Teterinary Anthonic Suntainedialate on Anthonia Tolanization from a Faculty Field Tetaled with Conventionia Synthetic	······ PANG Bing-kun, ZHANG ling-sha, WII lie et al. (3460)