

方知库
Eco-Environmental
Knowledge Web

环境科学

ENVIRONMENTAL SCIENCE

ISSN 0250-3301 CODEN HCKHDV

HUANJING KEXUE

■ 主办 中国科学院生态环境研究中心

■ 出版 科学出版社



2019

Vol.40 No.6

第40卷 第6期

目 次

北京城区大气金属元素干湿沉降特征	张国忠, 潘月鹏, 田世丽, 王永宏, 熊秋林, 李广, 顾梦娜, 吕雪梅, 倪雪, 何月欣, 黄威, 刘博文, 王跃思 (2493)
北京城郊 PM _{2.5} 中金属元素的污染特征及潜在生态风险评价	徐静, 李杏茹, 张兰, 陈曦, 杨阳, 刘永桥, 赵清 (2501)
上海城区二次气溶胶的形成: 光化学氧化与液相反应对二次气溶胶形成的影响	高杰, 乔利平, 楼晟荣, 严茹莎, 周敏, 刘瑜存, 冯加良, 黄丹丹 (2510)
天津市 2017 年重污染过程二次无机化学污染特征分析	徐虹, 肖致美, 陈魁, 李立伟, 杨宁, 高璟赞, 李源, 孔君, 毕温凯, 邓小文 (2519)
典型非金属矿物制造工艺过程源成分谱特征	赵雪艳, 于高峰, 王信梧, 张向炎, 殷宝辉, 刘盈盈, 王歆华, 杨文, 赵若杰 (2526)
垃圾焚烧厂排放颗粒物组分粒径分布特征	余卓君, 吴建会, 张裕芬, 张进生, 冯银厂, 李蒲 (2533)
天津市春季样方法道路扬尘碳组分特征及来源分析	马妍, 姬亚芹, 国纪良, 赵静琦, 李越洋, 王士宝, 张蕾 (2540)
霾天气下城市气溶胶吸湿性的观测	杨素英, 田芷洁, 张铁凝, 于兴娜, 李艳伟, 安俊琳, 赵秀勇, 李岩, 王梓航, 吴尚 (2546)
宁东能源化工基地大气 PM _{2.5} 中硝基多环芳烃污染特征及呼吸暴露风险	刘攀亮, 剧媛丽, 毛潇萱, 黄韬, 高宏, 马建民 (2556)
2014 ~ 2016 年间郑州市控制 PM ₁₀ 和 PM _{2.5} 污染的健康效益评估	韩士杰, 王佳, 燕启社, 杨留明, 赵庆炎, 王申博, 李晨, 张轶舜, 张瑞芹 (2565)
1990 ~ 2017 年中国地区气溶胶光学厚度的时空分布及其主要影响类型	刘莹, 林爱文, 覃文敏, 何利杰, 李霄 (2572)
北京春季一次霾-沙天气污染特性与成因分析	王耀庭, 李青春, 郑祚芳, 窦有俊 (2582)
江苏省内河船舶大气污染物排放清单及特征	徐文文, 殷承启, 许雪记, 张玮 (2595)
亚热带稻区大气 NO ₂ 、HNO ₃ 及硝态氮污染特征及干湿沉降	欧阳秀琴, 王波, 沈健林, 朱潇, 王杰飞, 李勇, 吴金水 (2607)
长江源区降水氢氧稳定同位素特征及水汽来源	汪少勇, 王巧丽, 吴锦奎, 何晓波, 丁永建, 王利辉, 胡召富 (2615)
基于高山湖泊沉积记录的贵州北部大气重金属污染历史重建	梁梦瑶, 刘恩峰, 张恩楼, 纪明, 李小林 (2624)
青岛 4 个海水浴场微塑料的分布特征	罗雅丹, 林千惠, 贾芳丽, 徐功娣, 李锋民 (2631)
鄱阳湖湿地候鸟栖息地微塑料污染特征	刘淑丽, 简敏菲, 周隆胤, 李文华, 吴希恩, 饶丹 (2639)
三峡库区消落带土壤溶解性有机质溯源: 基于氮/碳比值的线性双端元源负荷分析	江韬, Joeri Kaal, 梁俭, 刘江, 张耀玲, 王定勇, 魏世强, 赵铮 (2647)
水生生物光合作用对雪玉洞岩溶水体中 CDOM 的影响	范佳鑫, 蒋勇军, 贺秋芳, 王家楠, 何瑞亮, 张彩云, 马丽娜, 汪啟容 (2657)
水化学和环境同位素对济南东源饮用水源地地下水演化过程的指示	张雅, 苏春利, 马燕华, 刘伟江 (2667)
崇左响水地区地下水水质分析及健康风险评价	周巾枚, 蒋忠诚, 徐光黎, 覃小群, 黄奇波, 张连凯 (2675)
云南荞麦地流域地下水水化学特征及物质来源分析	张勇, 郭纯青, 朱彦光, 于爽 (2686)
鄱阳湖流域多尺度 C、N 输送通量及其水质参数变化特征	陆瑶, 高扬, 贾璐杰, 宋贤威, 陈世博, 马明真, 郝卓 (2696)
合流制面源污染传输过程与污染源解析	房金秀, 谢文霞, 朱玉玺, 沈雷, 马玉坤, 李佳, 姜智绘, 李叙勇, 赵洪涛 (2705)
强化浅基质层干植草沟对道路径流的脱氮效果	段进凯, 李田, 张佳炜 (2715)
水源水库暴雨径流过程水体锰的迁移及其影响	邓立凡, 黄廷林, 李楠, 李凯, 吕晓龙, 毛雪静 (2722)
巢湖十五里河沉积物磷吸收潜力及对外源碳的响应	李如忠, 鲍琴, 张瑞钢, 陈慧 (2730)
金盆水库沉积物磷的来源及分布特征	毛雪静, 黄廷林, 李楠, 徐金兰, 苏露, 吕晓龙, 邓立凡 (2738)
水库水体热分层的水质及细菌群落分布特征	王禹冰, 王晓燕, 庞树江, 杨晓明, 刘洋 (2745)
不同水温分层水库沉积物间隙水营养盐垂向分布与细菌群落结构的关系	王慎, 张思思, 许尤, 官卓宇, 杨正健, 刘德富, 马骏 (2753)
表面流人工湿地长期运行后的底泥营养盐累积特征与释放规律	朱伊梦, 姜翠玲, 朱立琴, 杜观超, 高旭, 陈红卫, 李峰东, 张海阔, 张雪, 秦文凯, 李一平 (2764)
针铁矿改性生物炭对砷吸附性能	朱司航, 赵晶晶, 尹英杰, 商建英, 陈冲, 瞿婷 (2773)
改性稻壳生物炭对水溶液中甲基橙的吸附效果与机制	史月月, 单锐, 袁浩然 (2783)
厌氧膜生物反应器处理含盐废水运行效能及膜污染特性	闫欢沙, 许振钰, 金春姬, 邵梦雨, 郭亮, 赵阳国 (2793)
污水处理厂出水有机磷污染特征及强化去除	王小东, 王子文, 陈明飞, 王燕, 王硕, 李激 (2800)
碱度对沸石序批式反应器亚硝化的影响	王瑞鑫, 陈婧, 汪晓军, 胡浩林, Karasuta Chayangkun (2807)
活性污泥物理结构对呼吸过程的影响	郭耀, 李志华, 杨成建, 王慧娟, 李亚明, 姜阳 (2813)
好氧颗粒污泥处理畜禽养殖沼液污染物的特性	廖杰, 叶嘉琦, 曾志超, 刘琳, 徐开钦, 刘超翔 (2821)
快速城市化区河流温室内空气排放的时空特征及驱动因素	刘婷婷, 王晓峰, 袁兴中, 龚小杰, 侯春丽 (2827)
生物炭对潜流人工湿地污染物去除及 NO ₃ -N 排放影响	邓朝仁, 梁银坤, 黄磊, 方丹丹, 陈玉成, 杜刚 (2840)
曾用抗生素磺胺二甲嘧啶对稻田 N ₂ O 排放的影响及其微生物机制	吴杰, 李志琳, 徐佳迎, 王珏, 蒋静艳 (2847)
不同施氮水平对紫花苜蓿草地土壤呼吸和土壤生化性质的影响	胡伟, 张亚红, 李鹏, 张鹏, 李满友, 尤璟涛, 田水泉 (2858)
典型城市化区域土壤重金属污染的空间特征与风险评价	何博, 赵慧, 王铁宇, 孟晶, 肖荣波, 刘胜然, 周云桥, 史斌 (2869)
西南高锡地质背景区农田土壤与农作物的重金属富集特征	刘意章, 肖唐付, 熊燕, 宁增平, 双燕, 李航, 马良, 陈海燕 (2877)
基于 GIS 和受体模型的枸杞地土壤重金属空间分布特征及来源解析	白一茹, 张兴, 赵云鹏, 王幼奇, 钟艳霞 (2885)
喀斯特地区小尺度农业土壤砷的空间分布及污染评价	汪花, 刘秀明, 刘方, 唐启琳, 王世杰 (2895)
黄土高原不同植被带人工刺槐林土壤团聚体稳定性及其化学计量特征	瞿晴, 徐红伟, 吴旋, 孟敏, 王国梁, 薛蓑 (2904)
秸秆还田配施氮肥对喀斯特农田微生物群落及有机碳矿化的影响	徐学池, 苏以荣, 王桂红, 刘坤平, 胡亚军, 陈香碧, 郑小东, 何寻阳 (2912)
生物炭施用及老化对紫色土中抗生素吸附特征的影响	阴文敏, 关卓, 刘琛, 何杨, 杨飞, 唐翔宇 (2920)
稳定性同位素 DNA-SIP 示踪中性紫色土的氨氧化过程	刘天琳, 王智慧, 闫小娟, 赵永鹏, 贾仲君, 蒋先军 (2930)
纳米银和银离子对土壤中硝化微生物及其氨氧化速率的影响	伍玲丽, 张旭, 舒慧慧, 张丽, 司友斌 (2939)
农田沟道土壤中锰氨氧化 (Mn-ANAMMOX) 过程的探究	陈湜, 李正魁, 覃云斌, 丁帮环, 陈志浩 (2948)
污泥四要素含量对蚯蚓堆肥中氨氧化菌群的影响	吴颖, 黄魁, 夏慧, 陈景阳 (2954)
《环境科学》征订启事 (2929) 《环境科学》征稿简则 (2947) 信息 (2646, 2656, 2857)	

三峡库区消落带土壤溶解性有机质溯源：基于氮/碳比值的线性双端元源负荷分析

江韬^{1,2}, Joeri Kaal^{3,4}, 梁俭^{1,5}, 刘江¹, 张耀玲⁶, 王定勇¹, 魏世强¹, 赵铮^{1,7}

(1. 西南大学资源环境学院环境科学与工程系, 重庆 400716; 2. Department of Forest Ecology and Management, Swedish University of Agricultural Sciences, Umeå SE-90183, Sweden; 3. Ciencia do Sistema Terra, Departamento de Edafología e Química Agrícola, Universidade de Santiago de Compostela, Campus Sur s/n, Santiago de Compostela 15782, Spain; 4. Pyrolyscience, 15706 Santiago de Compostela, Spain; 5. 百色学院化学与环境工程学院, 广西 533000; 6. 中国科学院青海盐湖研究所, 西宁 810008; 7. 贵州省环境监测中心站, 贵阳 550081)

摘要: 土壤溶解性有机质 (soil DOM) 作为陆地系统天然有机质的重要组成部分, 以其活跃的生物地球化学性质, 在污染物的环境行为中扮演着极其重要的作用. 而了解其来源和结构组成是进一步明确其“结构-反应活性”的关键和前提. 本文以三峡库区消落带土壤 DOM 为研究对象, 基于传统氮/碳比值 (N/C) 及衍生的双端元源负荷模型, 讨论该溯源方法在分子水平上的合理性; 同时采用光漂白试验, 进一步讨论各样本反应活性与其源负荷的相关性. 结果表明, N/C 值和双端元线性混合模型值均表明土壤 DOM 具有“陆源”和“内源”的双重特性——这与其他高级分析技术溯源结果基本一致. 这种传统溯源分析结果在分子水平上具有合理性, 但仅仅反映 DOM 结构和来源在特定面相上的信息, 只能证明库区土壤 DOM 属于“混合型来源”, 却无法提供分辨率更高的特定组分来源信息. 另外, N/C 元素比值及源负荷分别和光漂白动力学过程极显著相关, 因此可作为较方便的指标, 快速简单判断 DOM 的光化学反应活性. 但在关注 DOM 本身生物地球化学的研究工作中, 仍建议使用多重方法的比较分析, 以便于提高单一解析方法的分辨率.

关键词: 三峡库区; 消落带; 溶解性有机质 (DOM); 土壤; 天然有机质; 元素组成; 源负荷模型; 结构-反应活性

中图分类号: X142 **文献标识码:** A **文章编号:** 0250-3301(2019)06-2647-10 **DOI:** 10.13227/j.hjxx.201810128

Use of the Nitrogen/Carbon Ratio (N/C) and Two End-Member Sources Mixing Model to Identify the Origins of Dissolved Organic Matter from Soils in the Water-Level Fluctuation Zones of the Three Gorges Reservoir

JIANG Tao^{1,2}, Joeri Kaal^{3,4}, LIANG Jian^{1,5}, LIU Jiang¹, ZHANG Yao-ling⁶, WANG Ding-yong¹, WEI Shi-qiang¹, ZHAO Zheng^{1,7}

(1. Department of Environmental Science and Engineering, College of Resources and Environment, Southwest University, Chongqing 400716, China; 2. Department of Forest Ecology and Management, Swedish University of Agricultural Sciences, Umeå SE-90183, Sweden; 3. Ciencia do Sistema Terra, Departamento de Edafología e Química Agrícola, Universidade de Santiago de Compostela, Campus Sur s/n, Santiago de Compostela 15782, Spain; 4. Pyrolyscience, 15706 Santiago de Compostela, Spain; 5. College of Chemistry and Environmental Engineering, Baise University, Baise 533000, China; 6. Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, Xining 810008, China; 7. Guizhou Provincial Environmental Monitoring Center, Guiyang 550081, China)

Abstract: Soil dissolved organic matter (soil DOM) plays a crucial role in the environmental fate of pollutants because of its exceptional biogeochemical reactivity. Therefore, tracing the sources and understanding the properties of DOM through chemical characterization is important for clarifying the “structure-reactivity” of DOM in the environment. In this study, traditional elementary analysis methods including nitrogen/carbon ratio (N/C) determinations and derived two end-member source-loads mixing models were applied to soil DOM extracted from the water-level fluctuation zones of the Three Gorges Reservoir (TGR) area. The results were further compared to other characterization techniques that operate on the molecular scale (e. g., FTIR and analytical pyrolysis techniques). The ultimate objective was to assess the performance of N/C ratio and two end-member modeling for identifying the DOM sources. Additionally, a photo-bleaching kinetic experiment was conducted to test the correlation between DOM reactivity and its source-loadings. Results showed, based on the N/C ratio and mixing modeling, all soil DOM samples in the TGR area share “dual-source” characteristics, namely, allochthonousness (e. g., terrestrial) and autochthonousness (e. g., internal) attributes, which is in agreement with other advanced characterization tools. The traditional method results were comprehensible in light of the data from molecular techniques, but the information revealed only reflects certain aspects of DOM compositional characteristics. It can be concluded that the N/C ratio and mixing modeling can validate general sources of soil DOM, but not information about specific

收稿日期: 2018-10-18; 修订日期: 2019-01-07

基金项目: 国家自然科学基金项目 (41403079, 41373113); 重庆市科委基础与前沿研究计划项目 (cstc2015jcyjA20021); 中央高校基本科研业务费专项基金重点项目 (XDJK2015B035); 重庆市博士后科研项目 (Xm2014023)

作者简介: 江韬 (1984 ~), 男, 博士, 副研究员, 主要研究方向为天然有机质的环境地球化学, E-mail: jiangtower666@163.com

components. Meanwhile, the significant correlation between the photo-bleaching kinetic constant and N/C and source-loadings indicated that these two parameters can be used as rapid indicators to estimate soil DOM reactivity in photochemical processes. However, it should be emphasized that it remains essential to employ multiple characterization methods to investigate the biogeochemistry of soil DOM, so as to increase the characterization resolution with regard to the heterogeneity of DOM.

Key words: Three Gorges Reservoir areas; water-level fluctuation zones; dissolved organic matter (DOM); soil; natural organic matter; elemental composition; source-loading model; structure-reactivity relationships

土壤溶解性有机质(dissolved organic matter, DOM)作为陆地系统天然有机质的重要组成部分,广泛存在于滨河带、海岸带以及消落带等水-陆毗邻环境系统中,通过地表径流、淹水释放等过程,成为水体 DOM 重要来源^[1,2]. 作为土壤有机质的一部分,土壤 DOM 以其活跃的生物地球化学性质,在环境污染物的迁移转化以及全球碳循环等过程中具有重要作用^[3~6]. 三峡库区消落带作为全球最大的水-陆交替区域之一,其环境质量和生态安全受到越来越多的关注^[7~9]. 因此,了解土壤 DOM 来源、组成及结构等信息,有助于进一步明确其在库区环境中的重要角色.

利用无机元素(例如碳、氮)组成、比值对天然有机质(NOM)进行组成和来源解析,因其分析简单快速、结果直观便于解读等优势,一直以来是传统经典方法之一^[10~13];同时,基于氮/碳比值(N/C)利用线性端元混合模型(Linear end-member mixing model)^[12,13],估算 DOM 来源中陆源和内源(或非陆源)输入贡献,进一步拓展了碳、氮元素分析应用. 虽然以光谱、质谱为代表的高分辨率技术广泛应用,学界对于 DOM 结构、组成及来源辨析越发精细^[14,15],这对传统元素分析方法提出了新的挑战. 尤其是由于样本采集、富集及制备、前处理以及基体背景干扰等因素,不同方法间结果并非完全一致^[16~18],因而多重方法的比较分析,逐渐成为目前 DOM 地化特征分析工作中重要手段之一. 过去工作中^[17,19~21],研究者利用元素分析、光谱和热解-质谱技术,重点对三峡库区土壤 DOM 结构组成信息进行了讨论,而并未对 N/C 比尤其是基于该比值的双端元溯源模型进行深入拓展^[17]. 因此,本文着眼于此,并基于如上研究背景,选取三峡库区消落带表层土壤 DOM 样本为研究对象,以国际腐殖质学会(IHSS)样本为参照,通过 $n(\text{N})/n(\text{C})$ 比值及双端元混合线性模型对样本进行溯源;通过与光谱和热解-质谱结果进行相关性比较,以讨论元素分析方法在分子水平上的合理性;同时,本文进一步讨论了各 DOM 样本反应活性及其源负荷的相关性. 本研究结果将有助于进一步完善 DOM 分析方法体系,对未来深入探究三峡库区天然有机质的环境地球化学机制提供一定的研

究基础.

1 材料与方法

1.1 土壤 DOM 样本采样及制备

本研究 DOM 样本共 12 种,其中 8 种为库区消落带土壤提取样本,4 种为标准/参照样本. 土壤样本采集自三峡库区消落带 160 ~ 170 m 高程表层土(0 ~ 15 cm),见图 1(a),包括奉节(FJ)、云阳(YY)、开县(KX)、万州(WZ)、忠县涂井(TJ)、忠县石宝寨(SB)、丰都(FD)和涪陵(FL)^[17,19,20]. 样本自然风干后碾磨过筛. 称取定量土壤,以水:土 = 10:1 加入 Milli-Q[®] 纯水,遮光 200 r·min⁻¹ 振荡 16 h 后,离心 30 min (4 000 r·min⁻¹). 离心液用 0.45 μm 醋酸纤维滤膜过滤,滤液即为土壤 DOM 稀溶液. 利用旋转蒸发仪 35 ~ 40℃ 对土壤 DOM 稀溶液浓缩直至明显出现黄褐色. 浓缩液进一步冷冻干燥成为固体,玛瑙钵碾磨成粉末状混匀,装棕色硼硅玻璃瓶保存. 另外,在国际腐殖质学会(IHSS)标准/参照样本库中,选取 4 个代表性样本作为对照,分别为:北欧典型水库 NOM(NR, 1R108N),南极 Pony 湖富里酸(PL, 1R109F),Suwannee 河水体胡敏酸(SR, 2S101H)以及 Elliott 土壤胡敏酸(ES, 1S102H),用以评估元素分析法和高级分析技术溯源结果之间的相关性. 由于缺少陆源输入, IHSS 南极样本(PL, 1R109F)目前被公认为“内源主导型”参照样本.

1.2 样本分析^[17]

本文溯源分析过程如图 1(b)所示. 样本在固体条件下,采用 Vario Microselect 元素分析仪(Elementar, 德国)进行氮和碳元素分析;红外分析在 NICOLET6700ATR-FTIR 光谱仪(Thermo, 美国)上进行,光谱扫描范围 4 000 ~ 400 cm⁻¹,分辨率 2 cm⁻¹. 紫外-可见及荧光光谱在 Horiba Aqualog 光谱仪(Horiba, 日本)完成. 另外,采用两种热解技术,包括热解-气相质谱联用(PY-GC-MS)和热助水解甲基化-气相质谱联用(THM-GC-MS)获取分子组成信息. PY-GC-MS 系统由 CDS2000 热解吸仪(CDS, 美国)、GC/MS-QP2010 气相色谱-质谱联用(Shimadzu, 日本)组成. THM-GC-MS 系统由 CDS Pyroprobe 5250 热解吸仪(CDS, 美国)、GC(6890N)-MS



图 1 三峡库区消落带土壤采样点及溯源分析流程

Fig. 1 Soil sampling sites in the water-level fluctuation zones of the Three Gorges Reservoir area and the relevant procedure for the source-identification based on the elemental ratio analysis

(5975)气相色谱-质谱联用仪(Agilent, 美国)组成. 所有热解分子结构含量均以相对峰面积表示(% TQPA). 本研究详细研究方法详见文献[17, 22, 23], 所有结构分析结果详见文献[17].

1.3 线性双端元混合模型

基于 C/N 摩尔值的线性双端元混合模型[公式(1)和(3)]^[12], 广泛应用于土壤及底泥等有机质溯源组成研究中. 虽然在利用碳、氮元素简单评估有机质组成时——不考虑端元混合模型及源负荷率, 采用 C/N 和 N/C 值本质上并无差异, 但 Perdue 等^[13]认为原混合模型^[12]过高估算了 DOM 的内源贡献, 尤其对以陆源输入比重较大(>50%)样本时, 原模型使得双端元混合边界(mixing line)出现偏差, 使得陆源输入碳的估算比例值偏低, 因此提出基于 N/C 比值(即 C/N 的倒数)对模型进行校正[公式(2)和(4)]. 现将两种计算方式列举如下^[13]:

$$\frac{C}{N} = \left(\frac{N_{\text{auto}}}{N_{\text{allo}} + N_{\text{auto}}} \right) \times \left(\frac{C}{N} \right)_{\text{auto}} + \left(\frac{N_{\text{allo}}}{N_{\text{allo}} + N_{\text{auto}}} \right) \times \left(\frac{C}{N} \right)_{\text{allo}} \quad (1)$$

$$\frac{N}{C} = \left(\frac{C_{\text{auto}}}{C_{\text{allo}} + C_{\text{auto}}} \right) \times \left(\frac{N}{C} \right)_{\text{auto}} + \left(\frac{C_{\text{allo}}}{C_{\text{allo}} + C_{\text{auto}}} \right) \times \left(\frac{N}{C} \right)_{\text{allo}} \quad (2)$$

进一步公式整理如下:

$$\frac{C}{N} = f_{\text{auto}} \times \left(\frac{C}{N} \right)_{\text{auto}} + f_{\text{allo}} \times \left(\frac{C}{N} \right)_{\text{allo}} \quad (3)$$

$$\frac{N}{C} = f_{\text{auto}} \times \left(\frac{N}{C} \right)_{\text{auto}} + f_{\text{allo}} \times \left(\frac{N}{C} \right)_{\text{allo}} \quad (4)$$

式中, 脚标 auto 和 allo 分别表示两个来源输入: 陆源(即异生源, allochthonousness)和内源(即自生源, autochthonousness); f 为各来源在土壤 DOM 组成中贡献比例, 即源负荷率(%).

基于 N/C 值的公式(4), 进一步整理可得各源贡献比例 f_{auto} 和 f_{allo} 的表达式[公式(5)和(6)]:

$$f_{\text{auto}} = \frac{\left(\frac{N}{C} \right)_{\text{allo}} - \left(\frac{N}{C} \right)}{\left(\frac{N}{C} \right)_{\text{allo}} - \left(\frac{N}{C} \right)_{\text{auto}}} \quad (5)$$

$$f_{\text{allo}} = \frac{\left(\frac{N}{C} \right) - \left(\frac{N}{C} \right)_{\text{auto}}}{\left(\frac{N}{C} \right)_{\text{allo}} - \left(\frac{N}{C} \right)_{\text{auto}}} \quad (6)$$

式中, $(N/C)_{\text{allo}}$ 和 $(N/C)_{\text{auto}}$ 分别为单一陆源或内源输入的 DOM 典型值, 一般陆生植物 N/C 值范围 0.07~0.08^[6], 发育程度较高的腐殖质在 0.01~0.06^[24]; 藻类在 0.14~0.18^[6]. 基于此, 本研究选择 $(N/C)_{\text{allo}} = 0.02$ 和 $(N/C)_{\text{auto}} = 0.1$ 作为阈值^[13], 用以计算源负荷率.

1.4 源负荷与反应活性关系

以 8 个库区土壤 DOM 样本为研究对象, 采用 DOM 光漂白动力学试验作为反应活性指标试验. 取定量样本溶于 Milli-Q® 纯水, 测定并计算有色 DOM(CDOM)含量, 以 $a(355)$ 表示^[25, 26], 即波长 355 nm 处紫外吸光系数:

$$a(355) = A(355) \times 2.303/l \quad (7)$$

式中, $A(355)$ 为 355 nm 处吸光度, l 为光程(1 cm), $a(355)$ 单位 m^{-1} .

样本浓度统一稀释到初始 $a(355) = (15 \pm$

$0.5) \text{ m}^{-1}$. 室外自然光照条件下动力学试验(5 d), 分别在第 1、3、6 和 24 h、以及第 3 d 和 5 d 取样测定 $a(355)$, 根据一级动力学方程[公式(8)], 计算反应速率 K_{bleach} :

$$a(355)_t/a(355)_0 = e^{-K_{\text{bleach}} \times t} \quad (8)$$

式中, $a(355)_t$ 和 $a(355)_0$ 分别为不同动力学时间点和初始阶段样本的 $a(355)$ 值; $[1 - a(355)_t/a(355)_0] \times 100\%$ 为样本光漂白程度(%).

1.5 数据分析

所有具体基础数据请参考文献[17]. 利用 Lilliefors 检验法对全部数据分组进行正态分布检验; 符合正态分布数据采用 Pearson 相关性分析(r_p); 非正态分布数据采用 Spearman 相关性检验(r_s). 所有数据统计分析由 OriginPro® 2015 完成, $P < 0.05$ 和 $P < 0.01$ 分别为“显著”和“极显著”.

2 结果与讨论

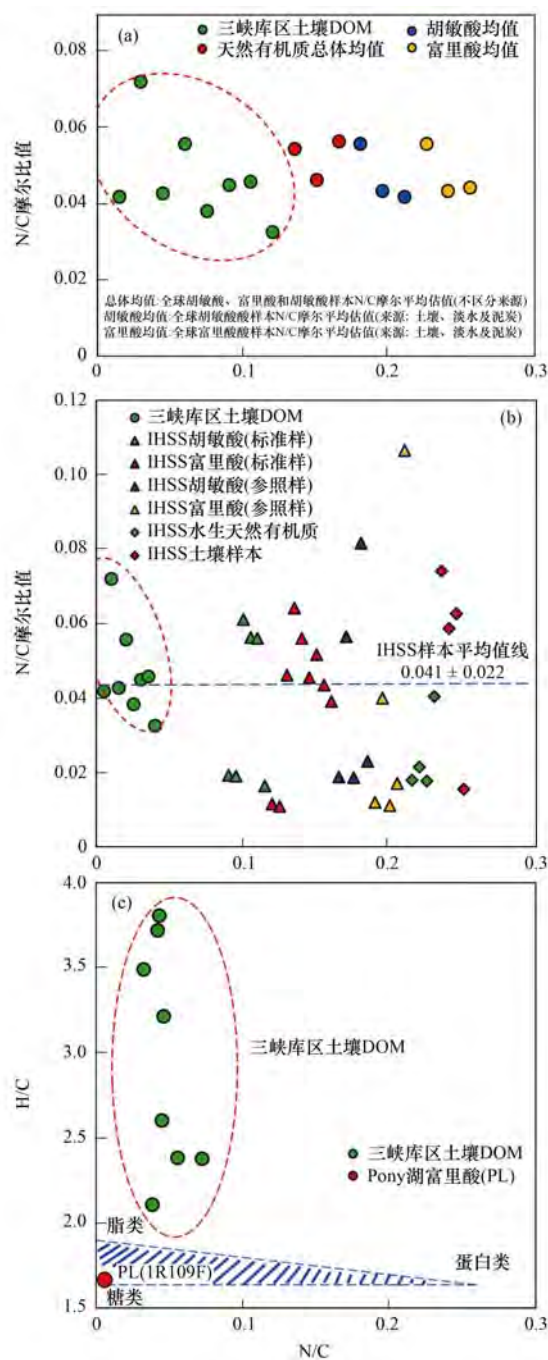
2.1 三峡库区土壤 DOM 的 N/C 摩尔比值

三峡库区消落带土壤 DOM 的 N/C 摩尔比值在 0.03 ~ 0.07 之间, 均值为 0.047 ± 0.012 , 空间分布差异性较大(变异系数达 25%)^[17]. 根据文献[24, 27]、国际腐殖质学会(IHSS)标准样及参考样本数据, 本研究将其与库区土壤 DOM 进行了比较. 除 SBZ(0.07)之外, 其余库区样本和全球天然有机质均值相比[图 2(a)], 差异不明显($P < 0.05$). 和 IHSS 的标准/参照样本库(均值 0.041 ± 0.022 , 变异系数 55%)相比, 库区样本比值范围和标准富里酸接近[图 2(b)]. 和胡敏酸不同(碱溶酸沉淀), 亲水性的富里酸在几乎整个 pH 范围内均为溶解态, 因此常规纯水或者盐溶液提取的土壤 DOM; 例如本研究以及文献[28 ~ 30], 性质和组成更接近于富里酸. 同时, 由 H/C-N/C 分布图[图 2(c)], 库区土壤 DOM 组成性质位于典型“内源区”[图 2(c)中蓝色虚线区域]^[31]之外, 而南极 Pony 湖样本则属于典型内源主导型.

因此, 通过 N/C 数值简单对比可知(图 2), 库区土壤 DOM 样本和富里酸类似, 具有一定程度内源特征, 但明显不属于“内源主导型”DOM; 后文将进一步分析这种源特征的负荷率及与分子结构上的相互关系.

2.2 线性双端元混合模型估算

根据线性双端元混合模型[公式(5)和(6)]计算源负荷. 陆源与内源负荷均对库区土壤 DOM 的组成有贡献(图 3), 其中陆源负荷率在 35% ~ 80%; 除 SB(65%)和 KX(45%)以外, 内源负荷率在 15% ~ 30% (均值 26%). 作为参照外标, PL(南



(a) 与全球均值比较(数据来源文献[24, 27]); (b) 与国际腐殖质学会标准/参照样本比较(数据来源: IHSS 官方网站 <http://humic-substances.org/elemental-compositions-and-stable-isotopic-ratios-of-ihss-samples/>); (c) H/C-N/C 分布(脂类、糖类和蛋白类分区来自文献[31], 虚线红圈内为本研究样本)

图 2 三峡库区土壤 DOM 和其他天然有机质样本 N/C 摩尔值比较

Fig. 2 Comparison of N/C molar ratio between TGR soil DOM samples and other natural organic matter samples

极样本)内源负荷率 100%, 和预期一致, 进一步支持该样本作为“单一内源输入”标准物的合理性; 而作为典型腐殖质水体(humic water), NR 和 SW 样本缺少内源输入, 其来源几乎为陆源有机质(例如腐殖质, $f_{\text{allo}} > 99\%$). 由此可见, 尽管库区土壤

DOM 作为陆地系统土壤有机质的一部分,但其内源输入对 DOM 来源组成影响仍然显著. 这与之前采用荧光光谱溯源结果类似:库区土壤 DOM 荧光指数(FI)位于两个端元阈值之间[1.4(陆源)<FI<1.9(内源)]^[17, 20, 21].

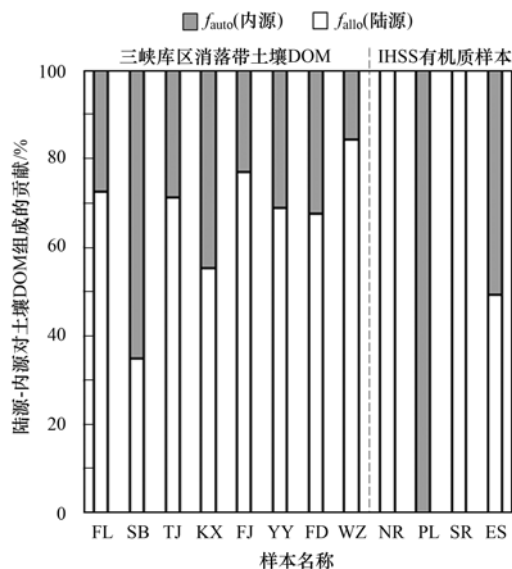


图3 线性双端元(陆源-内源)混合模型估算各来源贡献率
Fig. 3 Contributions of two end-members to the compositions of soil DOM from the TGR sites based on the linear mixing model

2.3 与光谱指标的相关性

光谱指标包括:紫外-可见光谱中的 SUVA₂₅₄、光谱斜率($S_{275-295}$)及光谱斜率比值(S_R ,即 $S_{275-295}$ 和 $S_{350-400}$ 比值)、荧光光谱中的荧光指数(FI)、内生源指数(BIX)和腐殖化指数(HIX). 光谱在水体DOM

来源传统描述中,常采用“陆源”(异生源)和“内源”(自生源)来代表两类在组成、结构上存在明显差异的来源^[13, 32, 33];前者以腐殖质、木质素等具有较强陆地发育特征的物质为主,而后者以蛋白质、多糖等和水体自身生产力或微生物代谢活动有关的物质组成^[33~35]. 类似地,土壤 DOM 来源按此划分,但和水体 DOM 区别在于:“内源”物质更多来自于微生物代谢活动,受水体初级生产力影响较小,但受人为农业活动(例如施肥)等影响较大.

虽然含碳量(C%)和光谱指标相关性显著($P<0.01$),但是 N/C 比值与主要光谱指标无显著相关^[17]. 另外,双端元源负荷率(f_{auto} 和 f_{allo})与光谱指标也无显著相关性(表1). 由于光谱分析是基于 DOM 生色团(chromophores),易受铁及无机盐离子干扰^[36, 37];而元素分析包括了生色团和非生色团在内全部组分^[17],由此造成不同方法指标间相关性缺失. Stubbins 等^[18]利用 FT-ICR-MS 高分辨率质谱分析表明,DOM 中生色团和质谱鉴别的特定分子结构组分并非完全一致. 同时,DOM 的可见-紫外吸收光谱及荧光光谱,实际提供的是更宽泛、且基于环境系统条件(例如 pH、离子强度、无机干扰离子等)和有机生色团相互作用后的“净”效应. 虽然光谱和元素分析均证实库区样本的双重来源,但基于单一方法的样本间比较仍存在较大差异;因此,溯源分析中,光谱和元素的对比分析更适合应用于大样本量的时空差异比较.

表1 端元贡献与光谱指标相关性¹⁾

	Table 1 Correlations between DOM optical index values and contributions from each end-member source					
	SUVA ₂₅₄	$S_{275-295}$	S_R	FI	BIX	HIX
含 C 量	0.89 **	0.47	0.03	-0.95 **	-0.89 **	0.93 **
$f_{allo}/\%$	-0.14	-0.40	0.17	0.02	-0.07	0.12
$f_{auto}/\%$	0.14	0.40	-0.17	-0.02	0.07	-0.12

1) 光谱数据来源于文献[17]; ** 表示相关性极显著($P<0.01$)

2.4 和 ATR-FTIR 数据相关性

结合 ATR-FTIR 分析,尽管本研究样本中碳组成主要和多酚类结构有关[1610 cm^{-1} 和1240 cm^{-1} ,图4(a)]——碳骨架仍旧以陆源主导;但 f_{auto} 和脂肪族链烃结构(2930 cm^{-1})显著相关性表明[图4(b)],内源部分基本骨架组成和脂肪族碳有关^[11]. 另外, N/C 代表的内源信息仅反映了 N 和 C 相对变化快慢程度[图4(b)]:虽然微生物对内源部分利用程度较陆源部分高——这和含氮组分可生物利用较高有关;但微生物对脂肪族碳消耗也是另一重要原因^[38]. 根据源负荷率结果(图3),本文定义陆源输入超过70%的样本为“陆源主导型”

样本($N=6$). 这类样本中,陆源负荷率(f_{allo})和多酚类结构显著相关[图4(c)],进一步证明芳香性结构是“陆源主导型”样本的重要组成部分之一.

2.5 和 Py-GC-MS 以及 THM-GC-MS 数据相关性

热解-质谱联用技术是研究天然有机质地球化学特征的重要方法之一^[39]. 和 Py-GC-MS 相比,THM-GC-MS 更为温和,对在热解过程中二次重排的次级分子灵敏度较差;虽然前者可以提供更多关于微生物源信息,但后者有助于提供更为可靠的关于木质素和糖类组分的来源信息. 将热解-质谱分析结果归类出7类主要有机化合物^[17]:包括糖类(CARB),木质素类(LIG),单环芳烃类(MAH),

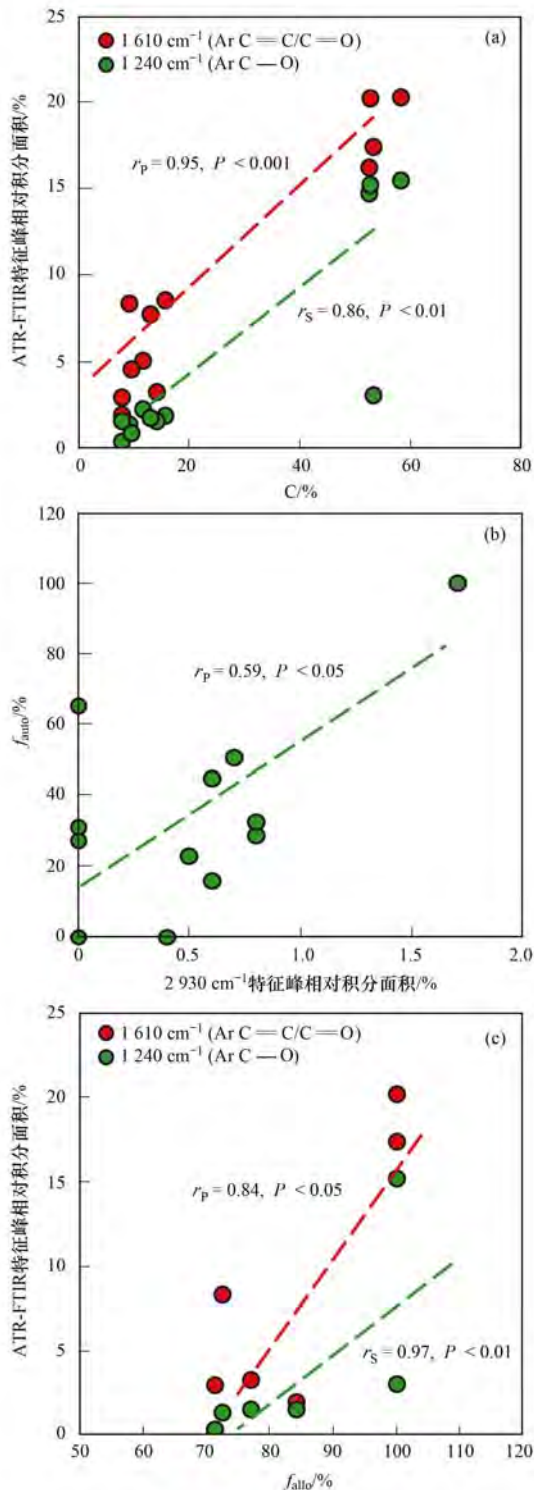


图4 元素分析与 ATR-FTIR 特征峰相关性分析

Fig. 4 Correlations between elemental analysis data and specific peaks of ATR-FTIR

亚甲基链化合物 (MCC); 含氮类 (NCOMP), 多环芳烃类 (PAH), 酚类 (PHEN). 虽然未发现 N/C 比值与各类组分的显著相关性 ($P > 0.05$), 但源负荷 f_{auo} 与 NCOMP 组分显著相关 [图 5(a)], 证明含氮组分是构成 DOM 内源组分主体^[40]. 而 C% 和 LIG 以及 PAH 显著相关 [$P < 0.01$, 图 5(b)], 说明陆生植物木质素及秸秆燃烧产生的黑炭等, 是样本中

含 C 组分主体. 整体上, f_{allo} 并未显示出与单一热解组分的相关性, 这可能是由于陆源输入的多样性导致. 但在“陆源主导型”样本 ($f_{allo} > 70\%$, $N = 6$) 中 [图 5(c)], f_{allo} 与 LIG 及 PAH 显著相关, 说明高等维管植物及黑炭等在这些样本的贡献比重更为明显. 尽管含氮内源碳组分 (吡咯以及酰胺) 同样与 C% 显著相关 ($P < 0.05$), 但是对于“陆源主导型”DOM, 含碳组分仍主要受陆源碳 (例如木质素) 影响. 另外, THM-GC-MS 解析结果表明, CARB 与 f_{auo} 显著相关 [$P < 0.05$, 图 5(a)]. 样本中 CARB

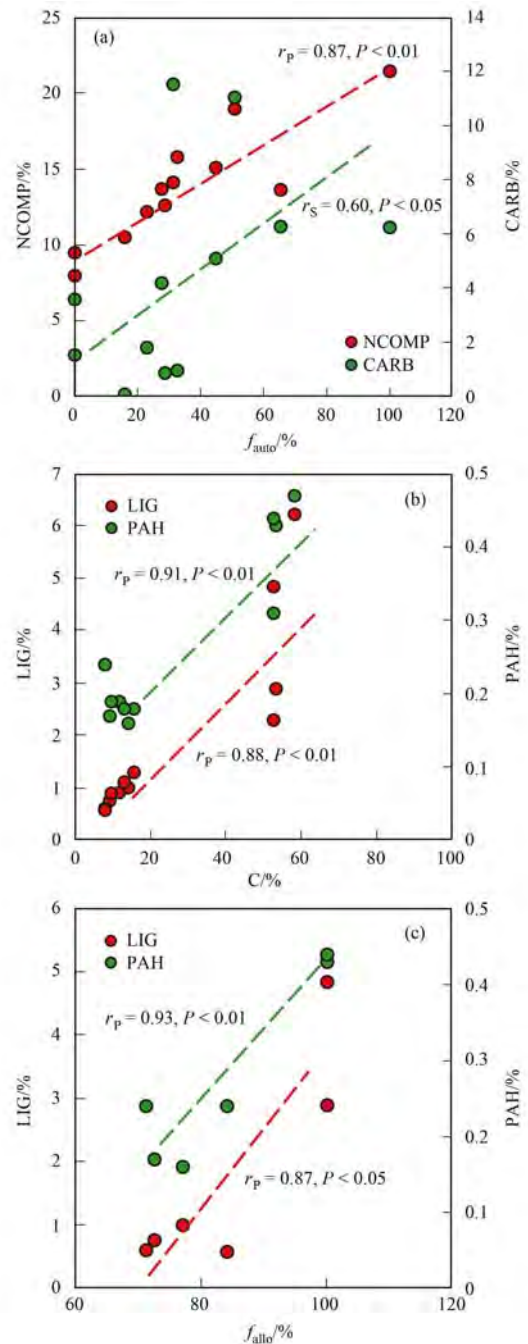


图5 元素分析热解结果的相关性分析

Fig. 5 Correlations between elemental analysis data and main groups of compounds identified by pyrolysis

主要由 C₆-葡萄糖二酸甲酯组成，缺少吡喃类结构；这表明微生物源多糖对内源负荷 f_{auto} 存在贡献；而来自于陆生植物多糖对 f_{auto} 影响不大。

2.6 DOM 源负荷与反应活性关系

DOM 因其丰富的功能基团和活跃的生物地球化学活性，在生态环境系统中扮演着重要角色^[3]。基于 DOM 结构组成及来源评估其环境效应，是 DOM 研究领域先驱 Aiken 的“结构-效应”概念核心之一^[3, 41]。因此，本研究采用操作最为便捷的光漂白试验，计算反应一级动力学指标作为评估库区土壤 DOM 的反应活性基础。动力学过程如图 6 (a) 所示，动力学常数 K_{bleach} 在

0.002 6 ~ 0.008 8 h⁻¹ 之间，库区均值为 (0.005 7 ± 0.002 1) h⁻¹ (表 2)。整个库区土壤 DOM 光漂白平均半衰期和生色团平均稳定时间分别为 (5.9 ± 2.6) d 和 (8.5 ± 3.8) d (表 2)。和其他光漂白试验比较^[42~45]，本研究 K 值较低，这可能是因为本研究光照试验地点位于瑞典北部(北温带)，温度和光照强度均低于已有研究中亚热带野外试验(尤其是夏季)环境。另外，文献[42~45]中光降解时间均未超过 50 h，试验时长更强调光降解的快反应阶段；而本研究时长达 5 d，动力学速率常数实际上反映的是快-慢反应阶段的整体均值。

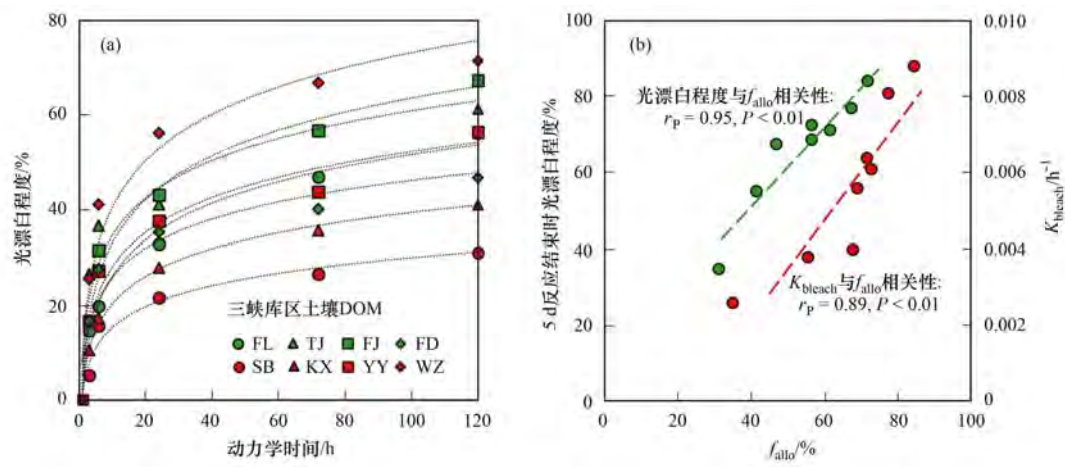


图 6 光漂白动力学过程及相关性分析
Fig. 6 Kinetic process of the photo-bleaching of chromophoric DOM and correlation analysis results

进一步，土壤 DOM 来源组成对其光漂白反应活性影响显著。N/C 比值和 K_{bleach} 之间存在极显著负相关 ($P < 0.01$)。另外， K_{bleach} 和 5 d 光降解反应结束时 CDOM 漂白程度，分别与 f_{allo} 均达到极显著水平 ($P < 0.01$)，相关系数分别为 0.89 和 0.95，说明 DOM 陆源特征越强，其光反应活性越高——这和水体 DOM 光降解特性类似^[46]；这可能与高陆源负荷样本中的较强芳香性结构有关^[46~50]。尽管有研究发现 DOM 光谱斜率 ($S_{275-295}$ 或者 S_R)——即 DOM 分子量大小与光漂白活性有关^[50, 51]；但本研究中，这两个指标与 DOM 反应活性相关性较低，相对独立，这可能与无机离子(例如铁)的干扰有关^[36, 37]。

DOM 的光化学特性在环境系统中十分重要，一方面影响 DOM 参与全球碳循环^[40, 52, 53]；另一方面通过诱导产生自由基，对环境污染物质迁移和转化产生深刻影响^[47, 48]。例如，DOM 介导的甲基汞光解^[48]；改变水环境光场及初级生产力^[49]等。因此，当具有较高光反应活性的陆源土壤 DOM 通过径流、渗滤等过程进入相邻水体，其环境生态效值得

更多关注和研究^[54, 55]。对库区土壤 DOM 而言，N/C 比值及衍生的端元负荷率，可以作为较方便指标，快速简单判断 DOM 光化学反应活性。

表 2 光漂白一级动力学常数计算¹⁾

Table 2 Calculations for the first-order kinetic parameters			
土壤 DOM 样本	$K_{\text{bleach}}/\text{h}^{-1}$	半衰期 $t_{1/2}/\text{d}$	生色团稳定时间/ d
FL	0.006 1	4. 7	6. 8
SB	0.002 6	11. 1	16. 0
TJ	0.006 4	4. 5	6. 5
KX	0.003 8	7. 6	11. 0
FJ	0.008 1	3. 6	5. 1
YY	0.005 6	5. 2	7. 4
FD	0.004 0	7. 2	10. 4
WZ	0.008 8	3. 3	4. 7
库区平均值	0.005 7 ± 0.002 1	5. 9 ± 2. 6	8. 5 ± 3. 8

1) 根据一级动力学模型 [公式 (8)] : $K_{\text{bleach}} = -\ln [a (355) _t / a (355) _0]$; $t_{1/2} = \ln 2 / K_{\text{bleach}}$; 生色团稳定时间 (平均滞留时间) = $1 / K$

3 结论

(1) 与其他高级分析技术溯源结果基本一致，N/C 值和双端元线性混合模型值均表明土壤 DOM 具有“陆源”和“内源”的双重特性。

(2) 元素分析的结果在分子水平上具有合理性. 与光谱分析(例如紫外-可见光谱、荧光光谱)类似, 元素分析和源估算模型, 仅仅反映的是 DOM 结构和来源在特定面相上的信息, 只能证明库区土壤 DOM 属于“混合型来源”, 却无法提供分辨率更高的来源信息, 例如区分微生物和藻类对内源输入的影响; 特定分子组分(例如黑炭、木质素)的贡献等.

(3) N/C 元素比值及源负荷分别和光漂白动力学过程极显著相关, 可用以预测 DOM 的光化学反应活性.

(4) 另外, 本研究对采用 N/C 比值及端元混合模型的应用提出两点建议: ①在 DOM 的环境效应研究中, 例如不同来源 DOM 介导的光化学过程、生物可利用性、重金属结合、水生环境毒理学等, 由于 DOM 溯源精度要求不高, 分析简单、判读直观, 可直接采用; ②在研究 DOM 本身生物地球化学特性, 例如源解析、演化等, 通过和其他分析技术联用, 对结果进行多重比较, 有助于提高单一方法解析的分辨率.

参考文献:

- [1] Kalbitz K, Solinger S, Park J H, *et al.* Controls on the dynamics of dissolved organic matter in soils: A review[J]. *Soil Science*, 2000, **165**(4): 277-304.
- [2] Jansen B, Kalbitz K, McDowell W H. Dissolved organic matter: linking soils and aquatic systems[J]. *Vadose Zone Journal*, 2014, **13**(7), doi: 10.2136/vzj2014.05.0051.
- [3] Aiken G R, Hsu-Kim H, Ryan J N. Influence of dissolved organic matter on the environmental fate of metals, nanoparticles, and colloids[J]. *Environmental Science & Technology*, 2011, **45**(8): 3196-3201.
- [4] Tranvik L J, Downing J A, Cotner J B, *et al.* Lakes and reservoirs as regulators of carbon cycling and climate[J]. *Limnology and Oceanography*, 2009, **54**(6): 2298-2314.
- [5] Bolan B S, Adriano D C, Kunhikrishnan A, *et al.* Dissolved organic matter: biogeochemistry, dynamics, and environmental significance in soils[J]. *Advances in Agronomy*, 2011, **110**: 1-75.
- [6] 何伟, 白泽琳, 李一龙, 等. 溶解性有机质特性分析与来源解析的研究进展[J]. *环境科学学报*, 2016, **36**(2): 359-372.
He W, Bai Z L, Li Y L, *et al.* Advances in the characteristics analysis and source identification of the dissolved organic matter[J]. *Acta Scientiae Circumstantiae*, 2016, **36**(2): 359-372.
- [7] Ye C, Li S Y, Zhang Y L, *et al.* Assessing soil heavy metal pollution in the water-level-fluctuation zone of the Three Gorges Reservoir, China[J]. *Journal of Hazardous Materials*, 2011, **191**(1-3): 366-372.
- [8] Bing H J, Zhou J, Wu Y H, *et al.* Current state, sources, and potential risk of heavy metals in sediments of Three Gorges Reservoir, China[J]. *Environmental Pollution*, 2016, **214**: 485-496.
- [9] Liu J, Jiang T, Huang R, *et al.* A simulation study of inorganic sulfur cycling in the water level fluctuation zone of the Three Gorges Reservoir, China and the implications for mercury methylation[J]. *Chemosphere*, 2017, **166**: 31-40.
- [10] Rice J A, MacCarthy P. Statistical evaluation of the elemental composition of humic substances[J]. *Organic Geochemistry*, 1991, **17**(5): 635-648.
- [11] Sun L, Perdue E M, Meyer J L, *et al.* Use of elemental composition to predict bioavailability of dissolved organic matter in a Georgia river[J]. *Limnology and Oceanography*, 1997, **42**(4): 714-721.
- [12] Tan F C, Strain P M. Organic carbon isotope ratios in recent sediments in the St Lawrence Estuary and the Gulf of St Lawrence[J]. *Estuarine and Coastal Marine Science*, 1979, **8**(3): 213-225.
- [13] Perdue E M, Koprivnjak J F. Using the C/N ratio to estimate terrigenous inputs of organic matter to aquatic environments[J]. *Estuarine, Coastal and Shelf Science*, 2007, **73**(1-2): 65-72.
- [14] Leenheer J A, Croué J P. Peer reviewed: characterizing aquatic dissolved organic matter; understanding the unknown structures is key to better treatment of drinking water[J]. *Environmental Science & Technology*, 2003, **37**(1): 18A-26A.
- [15] Mopper K, Stubbins A, Ritchie J D, *et al.* Advanced instrumental approaches for characterization of marine dissolved organic matter: extraction techniques, mass spectrometry, and nuclear magnetic resonance spectroscopy[J]. *Chemical Reviews*, 2007, **107**(2): 419-442.
- [16] Li W T, Chen S Y, Xu Z X, *et al.* Characterization of dissolved organic matter in municipal wastewater using fluorescence PARAFAC analysis and chromatography multi-excitation/emission scan: a comparative study[J]. *Environmental Science & Technology*, 2014, **48**(5): 2603-2609.
- [17] Jiang T, Kaal J, Liang J, *et al.* Composition of dissolved organic matter (DOM) from periodically submerged soils in the Three Gorges Reservoir areas as determined by elemental and optical analysis, infrared spectroscopy, pyrolysis-GC-MS and thermally assisted hydrolysis and methylation[J]. *Science of the Total Environment*, 2017, **603-604**: 461-471.
- [18] Stubbins A, Lapierre J F, Berggren M, *et al.* What's in an EEM? Molecular signatures associated with dissolved organic fluorescence in boreal Canada[J]. *Environmental Science & Technology*, 2014, **48**(18): 10598-10606.
- [19] 李璐璐, 江韬, 闫金龙, 等. 三峡库区典型消落带土壤及沉积物中溶解性有机质 (DOM) 的紫外-可见光谱特征[J]. *环境科学*, 2014, **35**(3): 933-941.
Li L L, Jiang T, Yan J L, *et al.* Ultraviolet-visible (UV-Vis) spectral characteristics of dissolved organic matter (DOM) in soils and sediments of typical water-level fluctuation zones of Three Gorges Reservoir areas[J]. *Environmental Science*, 2014, **35**(3): 933-941.
- [20] 高洁, 江韬, 李璐璐, 等. 三峡库区消落带土壤中溶解性有机质 (DOM) 吸收及荧光光谱特征[J]. *环境科学*, 2015, **36**(1): 151-162.
Gao J, Jiang T, Li L L, *et al.* Ultraviolet-visible (UV-Vis) and fluorescence spectral characteristics of dissolved organic matter (DOM) in soils of water-level fluctuation zones of the Three Gorges Reservoir region[J]. *Environmental Science*, 2015, **36**(1): 151-162.
- [21] 王齐磊, 江韬, 赵铮, 等. 三峡库区典型农业小流域土壤溶解性有机质的紫外-可见及荧光特征[J]. *环境科学*, 2015, **36**(3): 879-887.
Wang Q L, Jiang T, Zhao Z, *et al.* Ultraviolet-visible (UV-Vis)

- and fluorescence spectral characteristics of soil dissolved organic matter (DOM) in typical agricultural watershed of Three Gorges Reservoir region [J]. *Environmental Science*, 2015, **36** (3): 879-887.
- [22] Zhang Y L, Du J Z, Ding X P, *et al.* Comparison study of sedimentary humic substances isolated from contrasting coastal marine environments by chemical and spectroscopic analysis[J]. *Environmental Earth Sciences*, 2016, **75** (5): 378, doi: 10.1007/s12665-016-5263-8.
- [23] Kaal J, Wagner S, Jaffé R. Molecular properties of ultrafiltered dissolved organic matter and dissolved black carbon in headwater streams as determined by pyrolysis-GC-MS [J]. *Journal of Analytical and Applied Pyrolysis*, 2016, **118**: 181-191.
- [24] Sparks D L. *Environmental soil chemistry* (2nd ed.) [M]. San Diego, US: Academic Press, 2003. 86-87.
- [25] Zhang Y L, Qin B Q, Chen W M, *et al.* A preliminary study of chromophoric dissolved organic matter (CDOM) in Lake Taihu, a shallow subtropical lake in China [J]. *CLEAN—Soil, Air, Water*, 2005, **33** (4): 315-323.
- [26] Zhang Y L, Van Dijk M A, Liu M L, *et al.* The contribution of phytoplankton degradation to chromophoric dissolved organic matter (CDOM) in eutrophic shallow lakes: field and experimental evidence [J]. *Water Research*, 2009, **43** (18): 4685-4697.
- [27] Ghabbour E A, Davies G, MacCarthy P. The principles of humic substances; an introduction to the first principle [A]. In: Ghabbour E A, Davies G (Eds.). *Humic Substances: Structures, Models and Functions* [M]. Gateshead, UK: Royal Society of Chemistry, 2001.
- [28] Zsolnay Á. Dissolved organic matter: artefacts, definitions, and functions [J]. *Geoderma*, 2003, **113** (3-4): 187-209.
- [29] Kothawala D N, Roehm C, Blodau C, *et al.* Selective adsorption of dissolved organic matter to mineral soils [J]. *Geoderma*, 2012, **189-190**: 334-342.
- [30] Ohno T, Bro R. Dissolved organic matter characterization using multiway spectral decomposition of fluorescence landscapes [J]. *Soil Science Society of America Journal*, 2006, **70** (6): 2028-2037.
- [31] Perdue E M, Benner R. Marine organic matter [A]. In: Senesi N, Xing B S, Huang P M (Eds.). *Biophysico-Chemical Processes Involving Natural Nonliving Organic Matter in Environmental Systems* [M]. Hoboken, New Jersey, US: John Wiley & Sons, 2009.
- [32] Coble P G, Lead J, Baker A, *et al.* *Cambridge environmental chemistry series: Aquatic organic matter fluorescence* [M]. Cambridge, UK: Cambridge University Press, 2014.
- [33] Fellman J B, Hood E, Spencer R G M. Fluorescence spectroscopy opens new windows into dissolved organic matter dynamics in freshwater ecosystems: a review [J]. *Limnology and Oceanography*, 2010, **55** (6): 2452-2462.
- [34] Findlay S E G, Sinsabaugh R L. *Aquatic ecosystems: interactivity of dissolved organic matter* [M]. San Diego: Academic Press, 2003.
- [35] Dittmar T, Stubbins A. Dissolved organic matter in aquatic systems [J]. *Treatise on Geochemistry*, 2014, **12**: 125-156.
- [36] Xiao Y H, Sara-Aho T, Hartikainen H, *et al.* Contribution of ferric iron to light absorption by chromophoric dissolved organic matter [J]. *Limnology and Oceanography*, 2013, **58** (2): 653-662.
- [37] Poulin B A, Ryan J N, Aiken G R. Effects of iron on optical properties of dissolved organic matter [J]. *Environmental Science & Technology*, 2014, **48** (17): 10098-10106.
- [38] Sleighter R L, Cory R M, Kaplan L A, *et al.* A coupled geochemical and biogeochemical approach to characterize the bioreactivity of dissolved organic matter from a headwater stream [J]. *Journal of Geophysical Research: Biogeosciences*, 2014, **119** (8): 1520-1537.
- [39] Bianchi T S, Canuel E A. *Chemical biomarkers in aquatic ecosystems* [M]. Princeton, New Jersey, US: Princeton University Press, 2011.
- [40] Romankevich E A. *Geochemistry of organic matter in the ocean* [M]. Berlin, Heidelberg: Springer, 1984.
- [41] Weishaar J L, Aiken G R, Bergamaschi B A, *et al.* Evaluation of specific ultraviolet absorbance as an indicator of the chemical composition and reactivity of dissolved organic carbon [J]. *Environmental Science & Technology*, 2003, **37** (20): 4702-4708.
- [42] 冯胜, 张运林, 秦伯强. 太湖梅梁湾有色可溶性有机物的光化学降解 [J]. *中国环境科学*, 2006, **26** (4): 404-408.
- Feng S, Zhang Y L, Qin B Q. Photochemical degradation of chromophoric dissolved organic matter in Meiliang Bay of Lake Taihu [J]. *China Environmental Science*, 2006, **26** (4): 404-408.
- [43] 高洁, 江韬, 闫金龙, 等. 天然日光辐照下两江交汇处溶解性有机质 (DOM) 光漂白过程: 以涪江-嘉陵江为例 [J]. *环境科学*, 2014, **35** (9): 3397-3407.
- Gao J, Jiang T, Yan J L, *et al.* Photobleaching of dissolved organic matter (DOM) from confluence of two rivers under natural solar radiation: A case study of Fujiang River-Jialingjiang River [J]. *Environmental Science*, 2014, **35** (9): 3397-3407.
- [44] 郭卫东, 程远月. 天然日光辐照下河口区 CDOM 的光化学降解 [J]. *环境科学*, 2008, **29** (6): 1463-1468.
- Guo W D, Cheng Y Y. Photodegradation of chromophoric dissolved organic matter from Jiulong River estuary under natural solar radiation [J]. *Environmental Science*, 2008, **29** (6): 1463-1468.
- [45] Zhang Y L, Liu M L, Qin B Q, *et al.* Photochemical degradation of chromophoric-dissolved organic matter exposed to simulated UV-B and natural solar radiation [J]. *Hydrobiologia*, 2009, **627** (1): 159-168.
- [46] Obernosterer I, Benner R. Competition between biological and photochemical processes in the mineralization of dissolved organic carbon [J]. *Limnology and Oceanography*, 2004, **49** (1): 117-124.
- [47] Fimmen R L, Cory R M, Chin Y P, *et al.* Probing the oxidation-reduction properties of terrestrially and microbially derived dissolved organic matter [J]. *Geochimica et Cosmochimica Acta*, 2007, **71** (12): 3003-3015.
- [48] O'Driscoll N J, Siciliano S D, Peak D, *et al.* The influence of forestry activity on the structure of dissolved organic matter in lakes: implications for mercury photoreactions [J]. *Science of the Total Environment*, 2006, **366** (2-3): 880-893.
- [49] Sulzberger B, Durisch-Kaiser E. Chemical characterization of dissolved organic matter (DOM): a prerequisite for understanding UV-induced changes of DOM absorption properties and bioavailability [J]. *Aquatic Sciences*, 2009, **71** (2): 104-126.
- [50] Hansen A M, Kraus T E C, Pellerin B A, *et al.* Optical properties of dissolved organic matter (DOM): effects of biological and photolytic degradation [J]. *Limnology and Oceanography*, 2016, **61** (3): 1015-1032.
- [51] Helms J R, Stubbins A, Ritchie J D, *et al.* Absorption spectral

- slopes and slope ratios as indicators of molecular weight, source, and photobleaching of chromophoric dissolved organic matter[J]. *Limnology and Oceanography*, 2008, **53**(3): 955-969.
- [52] Cory R M, Crump B C, Dobkowski J A, *et al.* Surface exposure to sunlight stimulates CO₂ release from permafrost soil carbon in the Arctic[J]. *Proceedings of the National Academy of Sciences of the United States of America*, 2013, **110**(9): 3429-3434.
- [53] Cory R M, Ward C P, Crump B C, *et al.* Sunlight controls water column processing of carbon in arctic fresh waters[J]. *Science*, 2014, **345**(6199): 925-928.
- [54] Stanley E H, Powers S M, Lottig N R, *et al.* Contemporary changes in dissolved organic carbon (DOC) in human-dominated rivers: is there a role for DOC management? [J]. *Freshwater Biology*, 2012, **57**(S1): 26-42.
- [55] Solomon C T, Jones S E, Weidel B C, *et al.* Ecosystem consequences of changing inputs of terrestrial dissolved organic matter to lakes: current knowledge and future challenges[J]. *Ecosystems*, 2015, **18**(3): 376-389.

《环境科学》再获“百种中国杰出学术期刊”称号

2018年11月1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17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。



CONTENTS

Concurrent Measurement of Wet and Bulk Deposition of Trace Metals in Urban Beijing	ZHANG Guo-zhong, PAN Yue-peng, TIAN Shi-li, <i>et al.</i> (2493)
Concentration and Ecological Risk Assessment of Heavy Metals in PM _{2.5} Collected in Urban and Suburban Areas of Beijing	XU Jing, LI Xing-ru, ZHANG Lan, <i>et al.</i> (2501)
Secondary Aerosol Formation in Urban Shanghai: Insights into the Roles of Photochemical Oxidation and Aqueous-Phase Reaction	GAO Jie, QIAO Li-ping, LOU Sheng-rong, <i>et al.</i> (2510)
Secondary Inorganic Pollution Characteristics During Heavy Pollution Episodes of 2017 in Tianjin	XU Hong, XIAO Zhi-mei, CHEN Kui, <i>et al.</i> (2519)
Characterization of PM ₁₀ and PM _{2.5} Source Profiles for Emissions from Nonmetal Mineral Products Manufacturing Processes	ZHAO Xue-yan, YU Gao-feng, WANG Xin-wu, <i>et al.</i> (2526)
Characteristics of Component Particle Size Distributions of Particulate Matter Emitted from a Waste Incineration Plant	YU Zhuo-jun, WU Jian-hui, ZHANG Yu-fen, <i>et al.</i> (2533)
Characteristics and Source Apportionment of Carbon Components in Road Dust PM _{2.5} and PM ₁₀ During Spring in Tianjin Derived by Using the Quadrat Sampling Method	MA Yan, JI Ya-qin, GUO Ji-liang, <i>et al.</i> (2540)
Urban Aerosol Hygroscopicity During Haze Weather	YANG Su-ying, TIAN Zhi-jie, ZHANG Tie-ning, <i>et al.</i> (2546)
Atmospheric Pollution Characteristics and Inhalation Exposure Risk of Nitrated Polycyclic Aromatic Hydrocarbons in PM _{2.5} at the Ningdong Energy and Chemical Industry Base, Northwest China	LIU Pan-liang, JU Yuan-li, MAO Xiao-xuan, <i>et al.</i> (2556)
Health Benefit Evaluation for PM ₁₀ and PM _{2.5} Pollution Control in Zhengzhou, China, 2014-2016	HAN Shi-jie, WANG Jia, YAN Qi-she, <i>et al.</i> (2565)
Spatial-temporal Distribution of Aerosol Optical Depth and Its Main Influence Types in China During 1990-2017	LIU Ying, LIN Ai-wen, QIN Wen-min, <i>et al.</i> (2572)
Research on the Pollution Characteristics and Causality of Haze-sand Air Pollution in Beijing in Spring	WANG Yao-ting, LI Qing-chun, ZHENG Zuo-fang, <i>et al.</i> (2582)
Vessel Emission Inventories and Emission Characteristics for Inland Rivers in Jiangsu Province	XU Wen-wen, YIN Cheng-qi, XU Xue-ji, <i>et al.</i> (2595)
Atmospheric Nitrogen Dioxide, Nitric Acid, Nitrate Nitrogen Concentrations, and Wet and Dry Deposition Rates in a Double Rice Region in Subtropical China	OUYANG Xiu-qin, WANG Bo, SHEN Jian-lin, <i>et al.</i> (2607)
Characteristics of Stable Isotopes in Precipitation and Moisture Sources in the Headwaters of the Yangtze River	WANG Shao-yong, WANG Qiao-li, WU Jin-kui, <i>et al.</i> (2615)
Historical Trends of Atmospheric Trace Metal Pollution in Northern Guizhou Province as Reconstructed from Alpine Lake Sediments	LIANG Meng-yao, LIU En-feng, ZHANG En-lou, <i>et al.</i> (2624)
Distribution Characteristics of Microplastics in Qingdao Coastal Beaches	LUO Ya-dan, LIN Qian-hui, JIA Fang-li, <i>et al.</i> (2631)
Pollution Characteristics of Microplastics in Migratory Bird Habitats Located Within Poyang Lake Wetlands	LIU Shu-li, JIAN Min-fei, ZHOU Long-yin, <i>et al.</i> (2639)
Use of the Nitrogen/Carbon Ratio (N/C) and Two End-Member Sources Mixing Model to Identify the Origins of Dissolved Organic Matter from Soils in the Water-Level Fluctuation Zones of the Three Gorges Reservoir	JIANG Tao, JOERI Kaal, LIANG Jian, <i>et al.</i> (2647)
Effects of Photosynthesis of Submerged Aquatic Plants on CDOM in a Karst Water System: A Case Study from Xueyu Cave, Chongqing, China	FAN Jia-xin, JIANG Yong-jun, HE Qiu-fang, <i>et al.</i> (2657)
Indicators of Groundwater Evolution Processes Based on Hydrochemistry and Environmental Isotopes: A Case Study of the Dongyuan Drinking Water Source Area in Ji'nan City	ZHANG Ya, SU Chun-li, MA Yan-hua, <i>et al.</i> (2667)
Water Quality Analysis and Health Risk Assessment for Groundwater at Xiangshui, Chongzuo	ZHOU Jin-mei, JIANG Zhong-cheng, XU Guang-li, <i>et al.</i> (2675)
Chemical Characteristics of Groundwater and Material Sources Analysis in Buckwheat Field, Yunnan Province	ZHANG Yong, GUO Chun-qing, ZHU Yan-guang, <i>et al.</i> (2686)
C and N Transport Flux and Associated Changes of Water Quality Parameters from a Multiscale Subtropical Watershed in the Poyang Lake Area	LU Yao, GAO Yang, JIA Jun-jie, <i>et al.</i> (2696)
Pollutant Transport Analysis and Source Apportionment of the Entire Non-point Source Pollution Process in Combined Sewer Systems	FANG Jin-xiu, XIE Wen-xia, ZHU Yu-xi, <i>et al.</i> (2705)
Nitrogen Removal Efficiencies from Road Runoff by Dry Grass Swales with a Shallow Substrate Layer	DUAN Jin-kai, LI Tian, ZHANG Jia-wei (2715)
Migration Characteristics of Manganese During Rainfall Events and Its Impacts on Water Quality in a Drinking Water Source Reservoir	DENG Li-fan, HUANG Ting-lin, LI Nan, <i>et al.</i> (2722)
Potential for Phosphorus Uptake by Bed Sediments and Its Response to Carbon Additions in the Shiwuli River, Chaohu Lake Basin	LI Ru-zhong, BAO Qin, ZHANG Rui-gang, <i>et al.</i> (2730)
Sources and Distribution of Phosphorus in Sediments of the Jinpen Reservoir	MAO Xue-jing, HUANG Ting-lin, LI Nan, <i>et al.</i> (2738)
Water Quality Characteristics and Distribution of Bacterial Communities During Thermal Stratification in the Miyun Reservoir	WANG Yu-bing, WANG Xiao-yan, PANG Shu-jiang, <i>et al.</i> (2745)
Relationship Between the Vertical Distribution of Nutrients and Bacterial Community Structures in Sediment Interstitial Waters of Stratified Reservoirs with Different Water Temperatures	WANG Shen, ZHANG Si-si, XU You, <i>et al.</i> (2753)
Accumulation Characteristics and Release Regularity of Nutrients in Sediments of a Surface-flow Constructed Wetland After Long-term Operation	ZHU Yi-meng, JIANG Cui-ling, ZHU Li-qin, <i>et al.</i> (2764)
Application of Goethite Modified Biochar for Arsenic Removal from Aqueous Solution	ZHU Si-hang, ZHAO Jing-jing, YIN Ying-jie, <i>et al.</i> (2773)
Effects and Mechanisms of Methyl Orange Removal from Aqueous Solutions by Modified Rice Shell Biochar	SHI Yue-yue, SHAN Riu, YUAN Hao-ran (2783)
Performance and Membrane Fouling Properties in an Anaerobic Membrane Bioreactor for Salty Wastewater	YAN Huan-xi, XU Zhen-yu, JIN Chun-ji, <i>et al.</i> (2793)
Pollution Characteristics and Enhanced Removal of Organic Phosphorus in Effluent from a Wastewater Treatment Plant	WANG Xiao-dong, WANG Zi-wen, CHEN Ming-fei, <i>et al.</i> (2800)
Effects of Alkalinity on Partial Nitrification in a Zeolite Sequencing Batch Reactor	WANG Rui-xin, CHEN Jing, WANG Xiao-jun, <i>et al.</i> (2807)
Effects of the Physical Structure of Activated Sludge on Respiration Processes	GUO Yao, LI Zhi-hua, YANG Cheng-jian, <i>et al.</i> (2813)
Performance of an Aerobic Granular Reactor Treating Biogas Slurry from Pig Farm	LIAO Jie, YE Jia-qi, ZENG Zhi-chao, <i>et al.</i> (2821)
Spatial-temporal Characteristics and Driving Factors of Greenhouse Gas Emissions from Rivers in a Rapidly Urbanizing Area	LIU Ting-ting, WANG Xiao-feng, YUAN Xing-zhong, <i>et al.</i> (2827)
Influences of Biochar on Pollutant Removal Efficiencies and Nitrous Oxide Emissions in a Subsurface Flow Constructed Wetland	DENG Chao-ren, LIANG Yin-kun, HUANG Lei, <i>et al.</i> (2840)
Effects of the Veterinary Antibiotic Sulfamethazine on N ₂ O Emissions and the Associated Microbiological Mechanism in a Rice Field	WU Jie, LI Zhi-lin, XU Jia-ying, <i>et al.</i> (2847)
Effects of Different Levels of Nitrogen Fertilization on Soil Respiration Rates and Soil Biochemical Properties in an Alfalfa Grassland	HU Wei, ZHANG Ya-hong, LI Peng, <i>et al.</i> (2858)
Spatial Distribution and Risk Assessment of Heavy Metals in Soils from a Typical Urbanized Area	HE Bo, ZHAO Hui, WANG Tie-yu, <i>et al.</i> (2869)
Accumulation of Heavy Metals in Agricultural Soils and Crops from an Area with a High Geochemical Background of Cadmium, Southwestern China	LIU Yi-zhang, XIAO Tang-fu, XIONG Yan, <i>et al.</i> (2877)
Spatial Distribution Characteristics and Source Apportionment of Soil Heavy Metals in Chinese Wolfberry Land Based on GIS and the Receptor Model	BAI Yi-ru, ZHANG Xing, ZHAO Yun-peng, <i>et al.</i> (2885)
Spatial Distribution and Pollution Assessment of As at a Small Scale in Agricultural Soils of the Karst Region	WANG Hua, LIU Xiu-ming, LIU Fang, <i>et al.</i> (2895)
Soil Aggregate Stability and Its Stoichiometric Characteristics in <i>Robinia pseudoacacia</i> Forest within Different Vegetation Zones on the Loess Plateau, China	QU Qing, XU Hong-wei, WU Xuan, <i>et al.</i> (2904)
Straw Returning Plus Nitrogen Fertilizer Affects the Soil Microbial Community and Organic Carbon Mineralization in Karst Farmland	XU Xue-chi, SU Yi-rong, WANG Gui-hong, <i>et al.</i> (2912)
Effects of Biochar Application and Ageing on the Adsorption of Antibiotics in Purple Soil	YIN Wen-min, GUAN Zhuo, LIU Chen, <i>et al.</i> (2920)
Ammonia Oxidation in a Neutral Purple Soil Measured by the ¹³ C-DNA-SIP Method	LIU Tian-lin, WANG Zhi-hui, YAN Xiao-juan, <i>et al.</i> (2930)
Effects of Silver Nanoparticles and Silver Ions on Soil Nitrification Microorganisms and Ammonoxidation	WU Ling-li, ZHANG Xu, SHU Kun-hui, <i>et al.</i> (2939)
Insight into the Process of Mn-ANAMMOX in Soils of Agricultural Drainage Ditches	CHEN Shi, LI Zheng-kui, QIN Yun-bin, <i>et al.</i> (2948)
Effects of Different Concentrations of Tetracycline in Sludge on Ammonia Oxidizers During Vermicomposting	WU Ying, HUANG Kui, XIA Hui, <i>et al.</i> (2954)