

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.5
第40卷 第5期

目次

2016年10~11月期间北京市大气颗粒物污染特征与传输规律	张晗宇,程水源,姚森,王晓琦,张俊峰(1999)
餐饮排放有机颗粒物的质量浓度、化学组成及排放因子特征	王红丽,景盛翱,乔利平(2010)
泰山顶(1534 m)夏季气溶胶粒径分布特征	沈利娟,王红磊,银燕,陈魁,陈景华,施双双(2019)
郑州-新乡冬季PM _{2.5} 中元素浓度特征及其源分析	闫广轩,张朴真,黄海燕,高雅,张靖雯,宋鑫,张佳羽,李怀刚,曹治国,姜继韶,樊静,王跃思,金彩霞(2027)
我国PM _{2.5} 浓度分阶段改善目标情景分析	贺晋瑜,燕丽,王彦超,雷宇,汪旭颖(2036)
安阳市典型工业源PM _{2.5} 排放特征及减排潜力估算	杜小申,燕丽,贺晋瑜,汪旭颖,王克,张瑞芹(2043)
郑州市典型工业炉窑细颗粒物排放特征及清单	赵庆炎,韩士杰,张轶舜,杨留明,张瑞芹,燕启社(2052)
2015年南京市城区挥发性有机物组成特征及大气反应活性	乔月珍,陈凤,赵秋月,刘倩(2062)
兰州市化石燃料燃烧源排放VOCs的臭氧及二次有机气溶胶生成潜势	刘镇,朱玉凡,郭文凯,刘晓,陈强(2069)
12种常见落叶果树BVOCs排放清单和排放特征	李双江,袁相洋,李琦,冯兆忠(2078)
我国典型陆地生态系统水化学离子特征及空间分布	黄丽,张心昱,袁国富,朱治林,唐新斋,孙晓敏(2086)
我国典型区域地表水环境中抗生素污染现状及其生态风险评价	刘昔,王智,王学雷,李珍,杨超,厉恩华,位慧敏(2094)
我国七大流域水体多环芳烃的分布特征及风险评价	范博,王晓南,黄云,李霖,高祥云,李雯雯,刘征涛(2101)
大连海域入海污染源中PFASs的赋存、输入通量和季节特征	陈虹,韩建波,张灿,程嘉熠(2115)
干旱内陆河流域降水稳定同位素的时空特征及环境意义	袁瑞丰,李宗省,蔡玉琴,邹海明(2122)
柳林泉域岩溶地下水区域演化规律及控制因素	黄奇波,覃小群,刘朋雨,程瑞瑞,李腾芳(2132)
崇左响水地区岩溶地下水主要离子特征及控制因素	周巾枚,蒋忠诚,徐光黎,覃小群,黄奇波,张连凯(2143)
三峡水库水体溶解磷与颗粒磷的输移转化特征分析	秦延文,韩超南,郑丙辉,马迎群,杨晨晨,刘志超,张雷,赵艳民(2152)
三峡水库蓄水至175 m后干流沉积物磷蓄积特征及释放潜力	黎睿,潘婵娟,汤显强,肖尚斌,李青云,杨文俊(2160)
不同水期洞庭湖水体中磷分布特征及影响因素	李莹杰,王丽婧,李虹,欧阳美凤(2170)
巢湖十五里河沉积物磷平衡浓度对外源磷的响应及释放风险	李如忠,鲍琴,戴源(2178)
闽江上游溪流沉积物有机磷空间分布及其环境意义分析	徐健,袁旭音,叶宏萌,张晓辉,周慧华,韩年(2186)
生态工程综合治理系统对农业小流域氮磷污染的治理效应	蒋倩文,刘锋,彭英湘,王华,姚燃,李红芳,罗沛,刘新亮,吴金水(2194)
太湖流域河流沉积物重金属分布及污染评估	张杰,郭西亚,曾野,邓建才(2202)
三峡水库支流汝溪河口水体汞的时空变化特征	马尉斌,陈秋禹,尹德良,孙涛,王永敏,王定勇(2211)
多功能型城市人工湿地水体汞分布特征及其量变分析	刘伟豪,王永敏,樊宇飞,吕东威,王定勇(2219)
不同类型城市人工湿地水体汞的分布特征	樊宇飞,刘伟豪,孙涛,苑萌,吕东威,李先源,王永敏,王定勇(2226)
微塑料对河口沉积物抗生素抗性基因的影响	黄福义,杨凯,张子兴,苏建强,朱永官,张娟(2234)
上海市郊道路地表径流多环芳烃污染特征对比及源解析	吴杰,熊丽君,吴健,沙晨燕,唐浩,林匡飞,李大雁,沈城(2240)
异龙湖不同湖区浮游植物群落特征及其与环境因子的关系	王振方,张玮,杨丽,徐玉萍,赵凤斌,王丽卿(2249)
水库热分层期藻类水华与温跃层厌氧成因分析	刘雪晴,黄廷林,李楠,杨尚业,李扬,徐进,王涵玥(2258)
绿狐尾藻对铜绿微囊藻和羊角月牙藻的抑藻效应	毕业亮,吴诗敏,周思宁,吴尚华,宿辉,白志辉,徐圣君(2265)
紫外/亚硫酸钠还原降解三氯乙酰胺的效能	伏芝萱,郭迎庆,楚文海(2271)
UV降解水溶液中拉法辛的影响因素及机制	吕娟,许志伟,王言(2278)
铝代水铁矿协同吸附砷的机制	黄博,郭朝晖,肖细元,彭驰,朱惠文,史磊,阳安迪(2287)
新型材料磁性氧化铁的除氟效能	方文侃,李小娣,方菁,吴德意(2295)
羧基改性阴极对微生物电合成系统产乙酸性能的影响机制	祁家欣,曾翠平,骆海萍,刘广立,张仁铎,卢耀斌(2302)
基于分区供氧与溶解氧调控的低C/N比污水短程硝化反硝化	吴春雷,荣懿,刘晓鹏,史会欣,章武首,金鹏康,马文伟(2310)
不同COD浓度下低基质厌氧氨氧化的启动特征	马艳红,赵智超,安芳娇,黄利,师晓娟,慕浩,陈永志(2317)
15℃SBBR短程硝化快速启动和稳定运行性能	孙艺齐,卞伟,李军,赵青,王文啸,梁东博,吴耀东(2326)
长期低聚磷条件对AO-SBR系统Accumulibacter代谢特性的影响	王少坡,李柱,赵乐丹,于静洁,赵明,郑胜达,孙力平(2333)
厌氧氨氧化颗粒污泥EPS及其对污泥表面特性的影响	杨明明,刘子涵,周杨,祁菁,赵凡,郭劲松,方芳(2341)
HN-AD菌生物强化接触氧化工艺处理猪场沼液	刘向阳,张千,吴恒,李宸,唐健泓,封丽,肖芃颖,赵天涛(2349)
温度对自养型同步脱氮工艺处理猪场废水厌氧消化液性能及微生物群落的影响	黄方玉,邓良伟,杨红男,杨含,肖友乾,王兰(2357)
城市污水处理系统真核微生物群落特性与地域性差异	秦文韬,张冰,孙晨翔,陈湛,文湘华(2368)
三江平原湿地开垦对土壤微生物群落结构的影响	王娜,高婕,魏静,刘颖,庄绪亮,庄国强(2375)
亚高山湖群中真菌群落的分布格局和多样性维持机制	刘晋仙,李鑫,罗正明,王雪,暴家兵,柴宝峰(2382)
生物质炭对双季稻田土壤反硝化功能微生物的影响	刘杰云,邱虎森,王聪,沈健林,吴金水(2394)
地膜覆盖和施肥对菜地CH ₄ 排放的影响	倪雪,江长胜,陈世杰,李晓茜,石孝均,郝庆菊(2404)
亏缺灌溉对冬小麦农田温室气体排放的影响	王晓云,蔡焕杰,李亮,徐家屯,陈慧(2413)
不同施肥模式对热区晚稻田CH ₄ 和N ₂ O排放的影响	田伟,伍延正,汤水荣,胡玉麟,赖倩倩,文冬妮,孟磊,吴川德(2426)
周期性变温对紫色土有机碳矿化的影响	曾蔓蔓,慈恩,樊晶晶,李江文,翁吴璐,李松(2435)
广西高镉异常区水田土壤Cd含量特征及生态风险评价	宋波,王佛鹏,周浪,吴勇,庞瑞,陈同斌(2443)
超富集植物藿香薹(Ageratum conyzoides L.)对镉污染农田的修复潜力	张云霞,宋波,宾娟,周子阳,陈记玲,陈同斌(2453)
种植油菜麦评价多环芳烃污染土壤的农用风险	焦海华,郭佳佳,张婧旻,张晓霞,茹文明,白志辉(2460)
土壤重金属累积对土地利用与景观格局的响应	舒心,李艳,李锋,冯靖仪,沈嘉瑜,史舟(2471)
某区生活垃圾焚烧发电厂周边及厂区内土壤中重金属元素的污染特征及评价	吕占禄,张金良,陆少游,邹天森,刘凯,张晗,谷亚亚(2483)
《环境科学》征订启事(2018)	《环境科学》征稿简则(2042)
信息(2114, 2348, 2393)	

大连海域入海污染源中 PFASs 的赋存、输入通量和季节特征

陈虹, 韩建波*, 张灿*, 程嘉熠

(国家海洋环境监测中心, 国家海洋局近岸海域生态环境重点实验室, 大连 116023)

摘要: 本文对大连海域入海河流和入海排污口中 19 种 PFASs 和 2 种 PFOS 新型替代品 Cl-PFESAs 进行了分析, 估算其入海通量, 并分析了季节变化特征。结果表明, 研究区域入海河流中总 PFASs 的含量范围为 $9.85 \sim 757 \text{ ng} \cdot \text{L}^{-1}$ (浓度中位数为 $74.7 \text{ ng} \cdot \text{L}^{-1}$), 与国内外其他河流相比, 大连海域入海河流中总 PFASs 的含量处于中等或较低水平; 入海排污口中总 PFASs 的含量范围为 $9.19 \sim 801 \text{ ng} \cdot \text{L}^{-1}$ (浓度中位数为 $29.5 \text{ ng} \cdot \text{L}^{-1}$)。入海河流和入海排污口中 PFASs 的主要贡献要素为 PFOS 和 PFOA, 其中入海河流、市政污水和污水处理厂出水中总 PFASs 含量未发现明显的季节差异特征, 但工业废水中冬季含量显著高于夏季。计算结果显示, 大连海域总 PFASs 入海通量约 $123 \text{ g} \cdot \text{d}^{-1}$ ($44.7 \text{ kg} \cdot \text{a}^{-1}$), 入海河流和入海排污口的贡献相当。全氟/多氟醚类磺酸化合物 (Cl-PFESAs) 检出率较低, 其中 8:2Cl-PFESA 均为检出。

关键词: 多氟/全氟化合物 (PFASs); 输入通量; 来源; 组成; 季节特征

中图分类号: X55 文献标识码: A 文章编号: 0250-3301(2019)05-2115-07 DOI: 10.13227/j.hjkk.201810132

Occurrence, Input, and Seasonal Variations of Poly-and Perfluoroalkyl Substances (PFASs) in Rivers and Drain Outlets from the Dalian Coastal Area, China

CHEN Hong, HAN Jian-bo*, ZHANG Can*, CHENG Jia-yi

(Key Laboratory of Coastal Ecology and Environment of State Oceanic Administration, National Marine Environmental Monitoring Center, Dalian 116023, China)

Abstract: Concentrations of 19 PFASs (poly-and perfluoroalkyl substances) in riverwater, coastal wastewater, and effluents from wastewater treatment plants (WWTPs) directly discharged into the Dalian coastal area were measured and their inputs were calculated accordingly. For riverwater samples, the total PFAS concentration ranged from 9.85 to $757 \text{ ng} \cdot \text{L}^{-1}$, with a median of $74.7 \text{ ng} \cdot \text{L}^{-1}$. For drain outlets, the total PFAS concentration in wastewater ranged from 9.19 to $801 \text{ ng} \cdot \text{L}^{-1}$, with a median of $29.5 \text{ ng} \cdot \text{L}^{-1}$. PFOS and PFOA were the dominant contributors for the PFASs in both riverwater and wastewater samples in this study. The total PFASs concentration in the industrial wastewater samples collected during the winter were found to be significantly higher than those collected in the summer. However, no seasonal variation was found for other samples. The total PFAS input into the Dalian coastal area was calculated to be $44.7 \text{ kg} \cdot \text{a}^{-1}$. The detection frequencies of Cl-PFESAs were low, and no 8:2Cl-PFESA was detected in all collected samples.

Key words: poly-and perfluoroalkyl substances (PFASs); input; source; composition; season variation

多氟/全氟化合物 (poly-and perfluoroalkyl substances, PFASs) 是近年来国际上较为关注的一类新型污染物, 此类物质具有良好的疏水疏油性、表面活性和热/化学稳定性, 从而被广泛用于工业生产和生活消费的各个领域^[1,2], 如生产纺织品、皮革制品、纸张、地毯等表面防污处理剂, 泡沫灭火剂、纸质食品包装材料和粘锅等, 是 20 世纪最重要的化工产品之一。PFASs 种类繁多, 其中全氟羧酸类 (perfluoroalkyl carboxylic acids, PFCAs) 和全氟磺酸类 (perfluoroalkane sulfonic acids, PFASs) 是环境中研究较为集中的两类物质, 分别以全氟辛烷羧酸 (PFOS) 和全氟辛烷磺酸 (PFOA) 为代表物质。目前, 由于此类物质, 特别是长碳链的 PFASs, 在包括南北极和其他边远地区的各类环境

介质、生物体和非职业暴露人体中均有所检出^[3-8], 同时研究发现其具有较高的生物累积性和多种毒性^[9,10], PFOS 及其相关物质 (PFOSF) 于 2009 年被新增进入《关于持久性有机污染物的斯德哥尔摩公约》名单^[11], 在国际公约的框架下开展全球 PFOS 及其相关物质的管控。对于 PFOA 的管控也进入了发达国家的进程, 如 2006 年美国环保署与 PFASs 八大生产商达成协议^[12], 于 2015 年前淘汰含有 PFOA 的相关产品的生产和使用; 2014 年,

收稿日期: 2018-10-19; 修订日期: 2018-11-16

基金项目: 国家自然科学基金项目 (41876128); 国家重点研发计划项目 (2017YFA0604902)

作者简介: 陈虹 (1982 ~), 女, 博士, 副研究员, 主要研究方向为污染物调查和环境行为, E-mail: hchen@nmemc.org.cn

* 通信作者, E-mail: jbhan@nmemc.org.cn; zhangcan@nmemc.org.cn

欧洲化学品管理局将 PFOA 及碳链长度为 11 ~ 14 的全氟烷基羧酸类物质增列进入高关注度污染物候选名单, 随后欧盟颁布实施了一个从 2014 年 10 月起禁止生产和使用 PFOA 相关产品的决议^[13,14]等. 近年来我国政府也开始重视 PFASs 的污染问题, 2016 年已将 PFOS 的削减淘汰纳入我国《“十三五”生态环境保护规划》^[15] 范围内, 计划于 2020 年基本淘汰 PFOS 及其相关物质, 同时要求强化对拟禁止污染物替代品的研究.

由于 PFASs 管控日益严格, 而该类物质由于在实际使用中因性能突出而难以或缺, 因此包括中国在内的各个国家均加强该类物质替代品的开发和生产. 其中作为 PFOS 新型替代品的全氟/多氟醚类磺酸化合物 (per-and polyfluoroalkyl ether sulfonates, PFAESs) 通过在碳链中加入一个或多个醚基而被认为更易于生物降解^[16], 从而取代传统全氟磺酸类和羧酸类物质的应用, 该类物质于 2013 年被首次报道. PFAESs 在中国具有一定的特殊性, 中国作为世界上唯一有记录的 PFAESs 生产使用国 (前年产量为 20 ~ 30 t·a⁻¹^[17]), 其在我国污水处理厂污水污泥^[17,18]、地表水^[19]和鱼类^[20]中均有所检出, 同时该类物质已在北极生物体中有所检出^[21].

海洋作为污染物最终的汇, 承载着陆海双重的污染压力, 其中入海河流和入海排污口的污染物排放是海洋环境中重要的污染源. 为了解我国海洋环境中此类污染物的污染来源和季节特征, 本研究以大连海域为研究范围, 以传统 PFASs 和 PFOS 新型替代品 Cl-PFESAs 为目标化合物, 对进入大连海域的入海河流河水和入海排污口污水中此类污染物的污染特征进行研究, 并估算了入海通量, 分析了该区域重要的输入路径, 以期评价 PFASs 在我国海洋环境中的生态风险、以及该类污染物治理措施的制定等提供基础数据和理论依据.

1 材料与方法

1.1 样品采集

本研究选择大连周边海域为研究范围. 采集了进入大连海域各类污染源的水样, 具体包括 6 条河流河水样品、6 个入海排污口污水样品和 4 个污水处理厂污水直排口的出水样品, 各类污染源的位置见图 1. 为了解 PFASs 污染的季节变化特征, 分别于 2015 年 11 月 (枯水期) 和 2016 年 7 月 (丰水期) 采集各类样品, 采样容器为不锈钢材质. 各站位采集 1.25L 的水样, 且采样日当天确保连续两天未有降雨活动. 对于入海河流样品的采集, 采集时间避开潮流的影响.

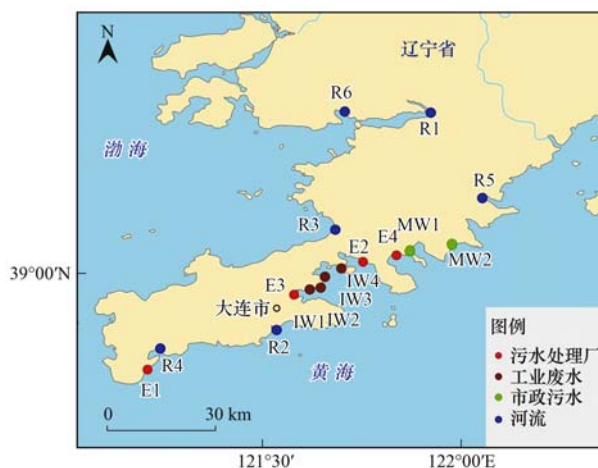


图 1 大连入海污染源位置分布示意

Fig. 1 Sampling sites (rivers and drain outlets) in this study

1.2 样品前处理与分析

1.2.1 主要仪器与试剂

主要试剂: 21 种 PFASs 标准物质及相关的内标化合物采购于 Wellington 实验室 (Guelph, ON, Canada), 具体各化合物的信息见表 1. HPLC 纯度的甲醇和乙腈来自于 Sigma 公司. 固相萃取柱采购自 Waters 公司 (200 mg, Milford, MA).

主要仪器: 液相色谱-质谱/质谱联用仪 (HPLC-MS/MS, Agilent 1200, Agilent 6410 Triple Quadrupole mass spectrometer); 固相萃取仪 (Waters Corp., Milford, MA).

1.2.2 样品前处理

样品前处理和分析方法与本课题组已发表文章的相关方法基本一致^[22,23]. 1 000 mL 水样过玻璃纤维滤膜 (1.6 μm ; Whatman, Florham Park, NJ) 后加入 2 ng 内标. 样品采用固相萃取的方法进行前处理, 萃取柱为 Oasis HLB SPE cartridges (200 mg, Milford, MA). 萃取柱先采用 10 mL 甲醇和 10 mL 干净的 Milli-Q 水预处理, 洗脱液为 4 mL 甲醇和 4 mL 含有 0.1% 的氢氧化铵甲醇溶液. 萃取液采用氮吹法吹干并复溶至 1 mL 进行测定.

1.2.3 样品分析

萃取液中 PFASs 采用 HPLC-MS/MS 进行分析, 流动相为 10 mmol·L⁻¹ 醋酸铵溶液和甲醇溶液, 流速为 250 $\mu\text{L} \cdot \text{min}^{-1}$. 流动相起始于 40% 甲醇, 保留 3 min, 17 min 内线性提高至 90% 甲醇, 再在 10 min 内提高至 100% 甲醇溶液, 保留 6 min. 进样量为 10 μL . 采用的液相小柱为 Agilent Eclipse Plus C18 column (2.1 $\times$ 100 mm, 3.5 μm , Agilent, Palo Alto, CA), 并采用 (ESI)-MS/MS 模式. 其他仪器信息见表 2.

表 1 PFASs 目标化合物的名称及缩写
Table 1 Names and abbreviations of the studied PFASs

类别	缩略名	化合物
PFCAs(perfluoroalkyl carboxylates)	PFBA	perfluorobutanoate
	PFPeA	perfluoropentanoate
	PFHxA	perfluorohexanoate
	PFHpA	perfluoroheptanoate
	PFOA	perfluorooctanoate
	PFNA	perfluorononanoate
	PFDA	perfluorodecanoate
	PFUnDA	perfluoroundecanoate
	PFDoDA	perfluorododecanoate
	PFTriDA	perfluorotridecanoate
	PFTeDA	perfluorotetradecanoate
	PFHxDA	perfluorohexadecanoate
	PFOcDA	perfluorooctadecanoate
PFSAs(perfluoroalkyl sulfonates)	PFBS	perfluorobutane sulfonate
	PFHxS	perfluorohexane sulfonate
	PFOS	perfluorooctane sulfonate
	PFDS	perfluorodecane sulfonate
Precursors	FOSA	perfluorooctane sulfoneamide
	FOSAA	perfluorooctane sulfonamidoacetate
Cl-PFESAs	6:2Cl-PFESA	6:2clorinated polyfluoroalkyl ether sulfonic acid
	8:2Cl-PFESA	8:2clorinated polyfluoroalkyl ether sulfonic acid

表 2 PFASs 仪器分析测试参数及其方法检出限 (MLQ) 和回收率结果
Table 2 Parameters for instrumental analysis, method limit of quantification (MLQ), and extraction process recovery for each measured compound

目标物	内标	母离子	子离子	碎裂电压 /V	碰撞能量 /V	MLQ /ng·L ⁻¹	回收率 /%
PFBA	[¹³ C ₄] PFBA	212.7	168.7	65	5	0.22	56.9 ± 9.2
PFPeA	[¹³ C ₂] PFHxA	262.7	218.7	70	5	0.16	72.8 ± 4.5
PFHxA		312.7	268.7	65	5	0.15	83.5 ± 3.9
PFHpA	[¹³ C ₄] PFOA	362.7	318.7	75	5	0.05	88.7 ± 3.4
PFOA		412.7	368.7	75	5	0.05	92.5 ± 4.5
PFNA	[¹³ C ₅] PFNA	462.7	418.7	80	5	0.05	70.9 ± 3.8
PFDA	[¹³ C ₂] PFDA	512.7	468.7	75	5	0.05	60.4 ± 12.3
PFUnDA	[¹³ C ₂] PFUnDA	562.7	518.7	85	5	0.05	73.8 ± 9.5
PFDoDA	[¹³ C ₂] PFDoA	612.7	568.7	95	5	0.05	90.8 ± 5.9
PFTriDA		662.7	618.7	100	5	0.08	85.2 ± 5.8
PFTeDA		712.7	668.7	105	5	0.08	73.8 ± 4.5
PFHxDA		812.7	768.7	120	9	0.08	66.8 ± 8.2
PFOcDA		912.7	868.7	100	9	0.08	50.9 ± 9.8
PFBS		298.7	98.7	130	29	0.12	118 ± 8.6
PFHxS	[¹⁸ O ₂] PFHxS	398.7	98.7	170	37	0.04	93.8 ± 3.0
PFOS	[¹³ C ₄] PFOS	498.7	98.7	200	40	0.04	93.4 ± 4.8
PFDS		598.7	98.7	205	40	0.04	89.3 ± 7.9
FOSA	[¹³ C ₄] PFOS	497.7	77.7	155	40	0.05	81.0 ± 1.6
FOSAA		557.7	499.7	135	17	0.08	89.5 ± 9.2
6:2Cl-PFESA	[¹³ C ₄] PFOS	530.9	350.9	70	24	0.21	95.2 ± 5.9
8:2Cl-PFESA		630.9	450.9	70	24	0.22	90.6 ± 9.8

1.2.4 质量保证与质量控制(QA/QC)

样品浓度的测定采用内标法，各物质标准曲线的 r^2 均超过 0.99。回收率实验是通过在 1 000 mL 干净水中加入 2 ng 标准物质，回收率结果见表 2，各类污染物的回收率在 50.3% ~

110% 范围内。

2 结果与讨论

2.1 入海河流中 PFASs 总体污染水平与组成
大连周边海域的入海河流中总 PFASs 的含量

及其组成见图 2 和表 3. 各类 PFASs 单体的检出率为 50% ~ 100%, 其中碳链长度为 7 ~ 10 的 PFCAs 和碳链长度为 6 ~ 8 的 PFSA 在各个河流中均全部检出, 而碳链长度为 16 和 18 的 PFHxDA 和 PFOcDA 检出率最小(50%). 本研究采样河流河水中总 PFASs 的含量在 $9.85 \sim 757 \text{ ng} \cdot \text{L}^{-1}$ 范围内, 其浓度中位数为 $74.7 \text{ ng} \cdot \text{L}^{-1}$. 总 PFASs 含量最高值比最低值高出约 2 个数量级左右, 说明河水中 PFASs 含量存在明显的区域分布特征. 在丰水期和枯水期采集的河水样品中, 含量最高和最低的河流均分别为 R5(龙口河)和 R4(旅顺龙河). 与韩国入

海河口、日本东京湾流域和我国环渤海入海河流等国内外其他河流中总 PFASs 含量相比^[22,24-26], 大连周边海域入海河流中此类污染物的含量处于中等或较低水平.

本研究所开展的河水中各类 PFAS 单体含量如表 3 所示, 根据各类单体在总 PFASs 含量中所占比例计算结果显示, 河水中的 PFASs 主要由 PFOS(平均占比为 18.0%)、PFOA(平均占比为 17.2%)和 PFHxS(平均占比为 16.2%)所组成. 此结果与以前报道的结果类似^[22], PFOA 和 PFOS 是河流中 PFASs 的主要组成单体.

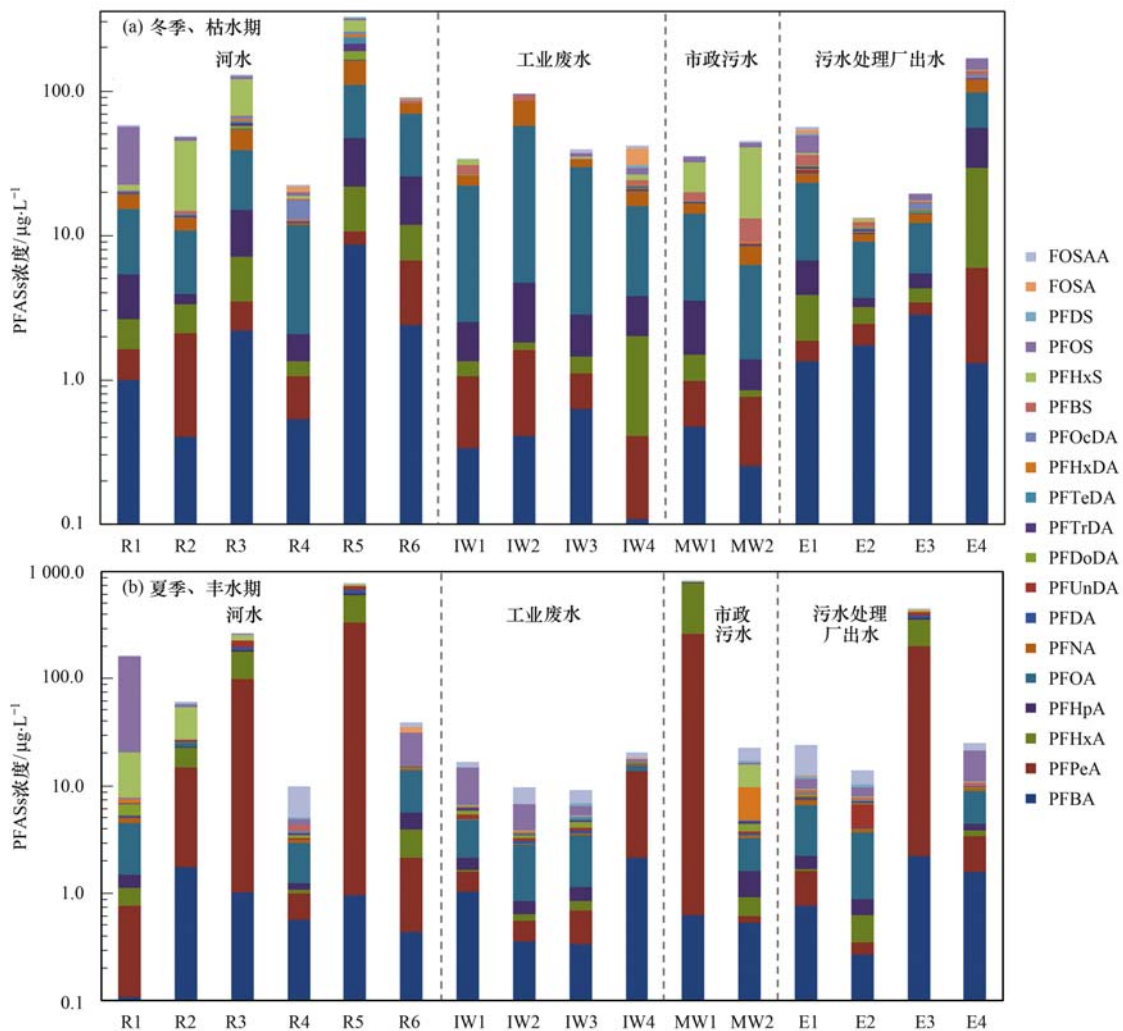


图 2 不同季节各类入海污染源中总 PFASs 含量及其组成

Fig. 2 Concentrations and composition profiles of the analyzed PFASs in rivers and drain outlets around the Dalian coastal area

2.2 入海排污口中 PFASs 总体污染水平与组成

大连周边海域的入海排污口污水分为市政污水、工业废水和污水处理厂出水 3 种类型, 各类污水中总 PFASs 的含量及其组成见图 2 和表 3. 污水中部分 PFASs 单体检出率较河水中小(检出率范围为 35.0% ~ 100%), 检出率最小的物质为碳链长度较长的 PFOcDA. 在各污水中全部检出的物质也相

对河水较少, 主要为碳链长度为 8 和 9 的 PFCAs 类物质(PFOA 和 PFDA). 从表 3 可以看出, 本研究采样污水中总 PFASs 的含量在 $9.19 \sim 801 \text{ ng} \cdot \text{L}^{-1}$ 范围内, 其浓度中位数为 $29.5 \text{ ng} \cdot \text{L}^{-1}$. 与我国环渤海区域相比^[22], 大连周边海域入海排污口中 PFASs 含量相对较低(环渤海入海排污口中总 PFASs 含量范围为 $13.1 \sim 7522 \text{ ng} \cdot \text{L}^{-1}$), 但其中污水处理厂出

表 3 入海河流和排污口中各类 PFASs 的浓度范围、中位数和检出率

化合物	入海河流 (n = 12)			入海排污口 (n = 20)		
	范围/ng·L ⁻¹	中位数/ng·L ⁻¹	检出率/%	范围/ng·L ⁻¹	中位数/ng·L ⁻¹	检出率/%
PFBA	< MLQ ~ 8. 61	0. 99	91. 7	< MLQ~2. 83	0. 63	95. 0
PFPeA	0. 43 ~ 330	1. 71	100. 0	< MLQ ~ 257	0. 58	90. 0
PFHxA	< MLQ ~ 265	2. 75	91. 7	< MLQ ~ 505	0. 32	75. 0
PFHpA	0. 17 ~ 25. 7	2. 27	100. 0	< MLQ ~ 26. 1	0. 91	95. 0
PFOA	1. 13 ~ 62. 7	7. 56	100. 0	1. 29 ~ 52. 3	4. 67	100. 0
PFNA	0. 16 ~ 51. 9	0. 63	100. 0	0. 05 ~ 28. 3	1. 01	100. 0
PFDA	< MLQ ~ 45. 5	0. 32	91. 7	< MLQ ~ 19. 2	0. 18	90. 0
PFUnDA	< MLQ ~ 53. 5	0. 10	75. 0	< MLQ ~ 28. 3	0. 18	65. 0
PFDODA	< MLQ ~ 22. 9	0. 19	83. 3	< MLQ ~ 0. 64	0. 19	85. 0
PFTriDA	< MLQ ~ 23. 9	0. 12	75. 0	< MLQ ~ 0. 69	0. 14	70. 0
PFTeDA	< MLQ ~ 21. 4	0. 11	58. 3	< MLQ ~ 0. 68	0. 15	75. 0
PFHxDA	< MLQ ~ 10. 4	0. 31	50. 0	< MLQ ~ 4. 78	0. 10	60. 0
PFOcDA	< MLQ ~ 11. 0	0. 06	50. 0	< MLQ ~ 7. 40	0. 04	35. 0
PFBS	< MLQ ~ 3. 65	0. 51	91. 7	< MLQ ~ 8. 25	0. 62	70. 0
PFHxS	0. 07 ~ 52. 9	19. 36	100. 0	< MLQ ~ 27. 3	0. 77	90. 0
PFOS	0. 50 ~ 138	3. 69	100. 0	< MLQ ~ 28. 1	2. 45	90. 0
PFDS	< MLQ ~ 5. 31	0. 14	83. 3	< MLQ ~ 1. 28	0. 12	60. 0
FOSA	< MLQ ~ 3. 84	0. 12	83. 3	< MLQ ~ 9. 67	0. 08	60. 0
FOSAA	< MLQ ~ 4. 70	1. 59	91. 7	< MLQ ~ 11. 1	2. 30	75. 0
总 PFASs	9. 85 ~ 757	74. 7	100	9. 19 ~ 801	29. 5	100

水中总 PFASs 含量高于部分其他旅游城市(日照市污水处理厂出水中总 PFASs 含量范围为 50. 04 ~ 105. 64 ng·L⁻¹)^[27]. 在大连入海排污口样品中, 夏季采样的 1 个市政污水和 1 个污水处理厂出水样品含量较高, 分别为 801 ng·L⁻¹ 和 444 ng·L⁻¹ 这可能是由于夏季雨水冲刷导致大量 PFASs 进入市政污水和污水处理厂进水系统并引起 PFASs 含量的显著提高.

污水中各类 PFAS 单体含量结果(表 3)显示, 与入海河流中 PFASs 主要组成单体类似, 入海污水中 PFASs 也主要由 PFOA(平均占比为 25. 8%) 和 PFOS(平均占比为 12. 0%) 所组成. 此结果与本课题组已经报道的环渤海入海排污口的结果不同^[22], 对于环渤海入海排污口来说, PFOA 和 PFBS 是主要的单体. 造成不同的原因主要是环渤海区域存在明显的氟化工园区导致 PFBS 的大量排放, 而大连所在区域并不存在直接的工业污染源.

2.3 大连海域污染源中 PFASs 季节变化特征和入海通量

为了解入海河流和排污口中 PFASs 含量的季节变化特征, 对丰水期和枯水期总 PFASs 含量进行了对比, 结果见图 3, 同时对不同类型不同季节总 PFASs 含量进行了显著性检验 (Mann-Whitney U test). 结果表明, 河流、市政污水和污水处理厂出水中总 PFASs 含量均没有显著差异 ($P > 0. 05$), 但对于工业废水来说, 冬季含量显著高于夏季. 对于

工业废水的季节特征, 可能与其产业生产周期等有关, 仍需进一步研究.

大连海域 PFASs 入海通量见表 4, 该区域总 PFASs 入海通量约 123 g·d⁻¹ (44. 7 kg·a⁻¹), 约占环渤海入海通量的 0. 05%. 其中入海河流和入海排污口的贡献相当; 在各类单体中, PFPeA、PFHxA、PFOA 和 PFOS 是主要的贡献物质.

2.4 PFOS 新型替代品 (Cl-PFESAs) 的赋存

本研究选择两类典型的 PFOS 新型替代品多氟烷基醚类物质, 分别是 6: 2Cl-PFESA 和 8: 2Cl-PFESA, 定量研究了其在入海河流和入海排污口中的含量, 具体结果见图 4. 结果显示, 在两

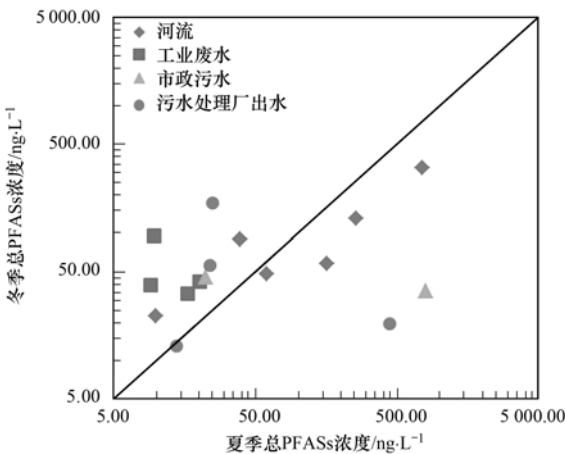


图 3 各类污染源中总 PFASs 含量的季节变化
Fig. 3 Comparison of the total PFAS concentrations in rivers and drain outlets around the Dalian coastal area between low and high water periods

个季节入海河流和入海排污口共计 32 个样品中, 仅 2 个样品的 6:2Cl-PFESA 含量高于 MLQ(分别为 $0.71\text{ ng}\cdot\text{L}^{-1}$ 和 $0.22\text{ ng}\cdot\text{L}^{-1}$), 其余 30 个样品均低于 MLQ; 所有样品中的 8:2Cl-PFESA 含量均低于 MLQ. 与其他区域相比^[23], 大连海域入海污染源中 Cl-PFESAs 含量处于较低水平.

表 4 大连海域各类 PFASs 的入海通量估算结果/ $\text{g}\cdot\text{d}^{-1}$

化合物	输入通量		总和
	入海河流	入海排污口	
PFBA	0.79	0.71	1.51
PFPeA	11.6	16.6	28.2
PFHxA	9.79	13.6	23.4
PFHpA	3.86	2.28	6.14
PFOA	10.4	5.99	16.4
PFNA	3.75	2.29	6.04
PFDA	1.26	1.64	2.91
PFUnDA	2.52	2.39	4.91
PFDoDA	0.62	0.11	0.74
PFTriDA	0.60	0.10	0.70
PFTeDA	0.52	0.13	0.66
PFHxDA	0.37	0.23	0.60
PFOcDA	0.37	0.37	0.75
PFBS	0.76	1.07	1.83
PFHxS	6.75	2.44	9.19
PFOS	12.1	2.73	14.8
PFDS	0.22	0.14	0.36
FOSA	0.72	0.29	1.01
FOSAA	1.04	1.44	2.48
总 PFASs	68.0	54.6	123

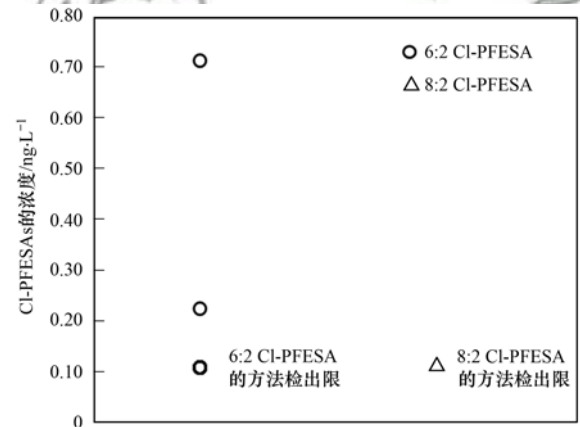


图 4 PFOS 替代品 Cl-PFESAs 在大连海域入海污染源中的含量
Fig. 4 Concentrations of Cl-PFESAs as PFOS novel alternatives in rivers and drain outlets around the Dalian coastal area

3 结论

(1)大连海域入海河流中总 PFASs 的含量范围为 $9.85 \sim 757\text{ ng}\cdot\text{L}^{-1}$, 其浓度中位数为 $74.7\text{ ng}\cdot\text{L}^{-1}$; 与国内外其他河流中总 PFASs 含量相比, 本研究区域 PFASs 的含量处于中等或较低水平; 大连海域入海排污口中总 PFASs 的含量在 $9.19 \sim 801$

$\text{ng}\cdot\text{L}^{-1}$ 范围内, 其浓度中位数为 $29.5\text{ ng}\cdot\text{L}^{-1}$.

(2)本研究区域入海河流和排污口中 PFOA 和 PFOS 是 PFASs 的主要组成单体.

(3)本研究区域入海河流、市政污水和污水处理厂出水中总 PFASs 含量未发现明显的季节差异特征, 但对于工业废水来说, 冬季含量显著高于夏季.

(4)大连海域总 PFASs 入海通量约 $123\text{ g}\cdot\text{d}^{-1}$ ($44.7\text{ kg}\cdot\text{a}^{-1}$), 约占环渤海入海通量的 0.05%, 其中入海河流和入海排污口的贡献相当.

(5)本研究区域 PFOS 新型替代品 Cl-PFESAs 含量较低, 其中 8:2Cl-PFESA 均未检出.

参考文献:

[1] Buck R C, Franklin J, Berger U, *et al.* Perfluoroalkyl and polyfluoroalkyl substances in the environment: terminology, classification, and origins [J]. Integrated Environmental Assessment and Management, 2011, 7(4): 513-541.

[2] Bowman J S. Fluorotechnology is critical to modern life; the fluoroCouncil counterpoint to the madrid statement [J]. Environmental Health Perspective, 2015, 123(5): A112-A113.

[3] Benskin J P, Phillips V, St. Louis V L, *et al.* Source elucidation of perfluorinated carboxylic acids in remote Alpine Lake sediment cores[J]. Environmental Science & Technology, 2011, 45(17): 7188-7194.

[4] Butt C M, Berger U, Bossi R, *et al.* Levels and trends of poly- and perfluorinated compounds in the Arctic environment [J]. Science of the Total Environment, 2010, 408(15): 2936-2965.

[5] Campo J, Lorenzo M, Pérez F, *et al.* Analysis of the presence of perfluoroalkyl substances in water, sediment and biota of the Jucar River (E Spain). Sources, partitioning and relationships with water physical characteristics[J]. Environmental Research, 2016, 147: 503-512.

[6] Castiglioni S, Valsecchi S, Polesello S, *et al.* Sources and fate of perfluorinated compounds in the aqueous environment and in drinking water of a highly urbanized and industrialized area in Italy[J]. Journal of Hazardous Materials, 2015, 282: 51-60.

[7] Kärman A, Ericson I, van Bavel B, *et al.* Exposure of perfluorinated chemicals through lactation: levels of matched human milk and serum and a temporal trend, 1996-2004, in Sweden[J]. Environmental Health Perspective, 2006, 115(2): 226-230.

[8] Giesy J P, Kannan K. Global distribution of perfluorooctane sulfonate in wildlife[J]. Environmental Science & Technology, 2001, 35(7): 1339-1342.

[9] Lau C, Anitole K, Hodes C, *et al.* Perfluoroalkyl acids: a review of monitoring and toxicological findings[J]. Toxicological Sciences, 2007, 99(2): 366-394.

[10] 孟娣, 王潇, 王赛赛, 等. 水体中典型重金属和全氟化合物对水生生物的联合毒性[J]. 生态毒理学报, 2018, 13(2): 13-22.

[11] Meng D, Wang X, Wang S S, *et al.* Review on combined toxicity of typical heavy metals and perfluorinated compounds in water environment on aquatic organisms[J]. Asian Journal of Ecotoxicology, 2018, 13(2): 13-22.

[11] UNEP. SC-4/17: Listing of perfluorooctane sulfonic acid, its salts and perfluorooctane sulfonyl fluoride, COP-4; Stockholm

- convention on persistent organic pollutants [R]. United Nations Environment Programme, 2009.
- [12] U. S. EPA. Global PFOA Stewardship [EB/OL]. <http://www.epa.gov/oppt/pfoa>, 2006.
- [13] ECHA. ANNEX XV PROPOSAL FOR A RESTRICTION-Perfluorooctanoic acid (PFOA), PFOA salts and PFOA-related substances, Version 1.0 [R]. Helsinki, Finland; ECHA European Chemicals Agency. <http://echa.europa.eu/documents/10162/e9cddee6-3164-473d-b590-8fe9caa50e7>, 2014-10-17/2015-06-02.
- [14] Heydebreck F, Tang J H, Xie Z Y, *et al.* Alternative and legacy perfluoroalkyl substances; differences between European and Chinese river/estuary systems [J]. *Environmental Science & Technology*, 2015, **49**(14): 8386-8395.
- [15] 国务院. 国务院关于印发“十三五”生态环境保护规划的通知 [R]. http://www.gov.cn/zhengce/content/2016-12/05/content_5143290.htm, 2016-11-24.
- [16] Strynar M, Dagnino S, McMahon R, *et al.* Identification of Novel Perfluoroalkyl ether carboxylic acids (PFECAs) and sulfonic acids (PFESAs) in natural waters using accurate mass time-of-flight mass spectrometry (TOFMS) [J]. *Environmental Science & Technology*, 2015, **49**(19): 11622-11630.
- [17] Wang S W, Huang J, Yang Y, *et al.* First report of a Chinese PFOS alternative overlooked for 30 years: its toxicity, persistence, and presence in the environment [J]. *Environmental Science & Technology*, 2013, **47**(18): 10163-10170.
- [18] Ruan T, Lin Y F, Wang T, *et al.* Identification of novel polyfluorinated ether sulfonates as PFOS alternatives in municipal sewage sludge in China [J]. *Environmental Science & Technology*, 2015, **49**(11): 6519-6527.
- [19] Wang T, Vestergren R, Herzke D, *et al.* Levels, isomer profiles, and estimated riverine mass discharges of perfluoroalkyl acids and fluorinated alternatives at the mouths of Chinese rivers [J]. *Environmental Science & Technology*, 2016, **50**(21): 11584-11592.
- [20] Shi Y L, Vestergren R, Zhou Z, *et al.* Tissue distribution and whole body burden of the chlorinated polyfluoroalkyl ether sulfonic acid F-53B in Crucian Carp (*Carassius carassius*): evidence for a highly bioaccumulative contaminant of emerging concern [J]. *Environmental Science & Technology*, 2015, **49**(24): 14156-14165.
- [21] Gebbink W A, Bossi R, Rig  t F F, *et al.* Observation of emerging per-and polyfluoroalkyl substances (PFASs) in Greenland marine mammals [J]. *Chemosphere*, 2016, **144**: 2384-2391.
- [22] Chen H, Wang X M, Zhang C, *et al.* Occurrence and inputs of perfluoroalkyl substances (PFASs) from rivers and drain outlets to the Bohai Sea, China [J]. *Environmental Pollution*, 2017, **221**: 234-243.
- [23] Chen H, Han J B, Zhang C, *et al.* Occurrence and seasonal variations of per-and polyfluoroalkyl substances (PFASs) including fluorinated alternatives in rivers, drain outlets and the receiving Bohai Sea of China [J]. *Environmental Pollution*, 2017, **231**: 1223-1231.
- [24] Naile J E, Khim J S, Wang T Y, *et al.* Perfluorinated compounds in water, sediment, soil and biota from estuarine and coastal areas of Korea [J]. *Environmental Pollution*, 2010, **158**(5): 1237-1244.
- [25] Zushi Y, Ye F, Motegi M, *et al.* Spatially detailed survey on pollution by multiple perfluorinated compounds in the Tokyo bay basin of Japan [J]. *Environmental Science & Technology*, 2011, **45**(7): 2887-2893.
- [26] 王世亮, 张丽萍, 张鑫, 等. 泗河水体及污水厂出水中全氟烷基酸类化合物及其前体物空间分布特征 [J]. *环境科学学报*, 2018, **38**(4): 1459-1557.
- Wang S L, Zhang L P, Zhang X, *et al.* Characteristics of spatial distribution of perfluoroalkyl acids (PFAAs) and their precursors in the water samples from the Sihe River and the effluents of wastewater treatment plants [J]. *Acta Scientiae Circumstantiae*, 2018, **38**(4): 1549-1557.
- [27] 王世亮, 孙建树, 杨月伟, 等. 典型旅游城市河流水体及污水厂出水中全氟烷基酸类化合物的空间分布及其前体物的转化 [J]. *环境科学*, 2018, **39**(12): 5494-5502.
- Wang S L, Sun J S, Yang Y W, *et al.* Spatial distribution of perfluoroalkyl acids and transformation of their precursors in river water samples and effluents of wastewater treatment plants in a typical tourism city [J]. *Environmental Science*, 2018, **39**(12): 5494-5502.

CONTENTS

Pollution Characteristics and Regional Transport of Atmospheric Particulate Matter in Beijing from October to November, 2016	ZHANG Han-yu, CHENG Shui-yuan, YAO Sen, <i>et al.</i> (1999)
Chemical Compositions, Mass Concentrations, and Emission Factors of Particulate Organic Matters Emitted from Catering	WANG Hong-li, JING Sheng-ao, QIAO Li-ping (2010)
Size Distributions of Aerosol During the Summer at the Summit of Mountain Taishan (1534 m) in Central East China	SHEN Li-juan, WANG Hong-lei, YIN Yan, <i>et al.</i> (2019)
Concentration Characteristics and Source Analysis of PM _{2.5} During Wintertime in Zhengzhou-Xinxiang	YAN Guang-xuan, ZHANG Pu-zhen, HUANG Hai-yan, <i>et al.</i> (2027)
Scenario Analysis of PM _{2.5} Concentration Targets and Milestones in China	HE Jin-yu, YAN Li, WANG Yan-chao, <i>et al.</i> (2036)
PM _{2.5} Emission Characteristics and Estimation of Emission Reduction Potential from Typical Industrial Sources in Anyang	DU Xiao-shen, YAN Li, HE Jin-yu, <i>et al.</i> (2043)
Emission Characteristics and List of Inorganic Elements in Fine Particles of Typical Industrial Kilns in Zhengzhou City	ZHAO Qing-yan, HAN Shi-jie, ZHANG Yi-shun, <i>et al.</i> (2052)
Composition and Atmospheric Reactivity of Ambient Volatile Organic Compounds(VOCs) in the Urban Area of Nanjing, China	QIAO Yue-zhen, CHEN Feng, ZHAO Qiu-yue, <i>et al.</i> (2062)
Formation Potential of Ozone and Secondary Organic Aerosol of VOCs from Fossil Fuel Combustion in Lanzhou City	LIU Zhen, ZHU Yu-fan, GUO Wen-kai, <i>et al.</i> (2069)
Inventory and Characteristics of Biogenic Volatile Organic Compounds (BVOCs) for 12 Deciduous Fruit Trees	LI Shuang-jiang, YUAN Xiang-yang, LI Qi, <i>et al.</i> (2078)
Ion Concentrations and Their Spatial Variability in Underground Water and Surface Water in Typical Terrestrial Ecosystems in China	HUANG Li, ZHANG Xin-yu, YUAN Guo-fu, <i>et al.</i> (2086)
Status of Antibiotic Contamination and Ecological Risks Assessment of Several Typical Chinese Surface-Water Environments	LIU Xi, WANG Zhi, WANG Xue-lei, <i>et al.</i> (2094)
Distribution and Risk Assessment of Polycyclic Aromatic Hydrocarbons in Water Bodies in Seven Basins of China	FAN Bo, WANG Xiao-nan, HUANG Yun, <i>et al.</i> (2101)
Occurrence, Input, and Seasonal Variations of Poly- and Perfluoroalkyl Substances (PFASs) in Rivers and Drain Outlets from the Dalian Coastal Area, China	CHEN Hong, HAN Jian-bo, ZHANG Can, <i>et al.</i> (2115)
Space-time Characteristics and Environmental Significance of Stable Isotopes in Precipitation at an Arid Inland River Basin	YUAN Rui-feng, LI Zong-xing, CAI Yu-qin, <i>et al.</i> (2122)
Regional Evolution and Control Factors of Karst Groundwater in Liulin Spring Catchment	HUNAG Qi-bo, QIN Xiao-qun, LIU Peng-yu, <i>et al.</i> (2132)
Major Ionic Characteristics and Controlling Factors of Karst Groundwater at Xiangshui, Chongzuo	ZHOU Jin-mei, JIANG Zhong-cheng, XU Guang-li, <i>et al.</i> (2143)
Analysis of Transport and Transformation Characteristics Between Dissolved Phosphorus and Particulate Phosphorus in Water of the Three Gorges Reservoir	QIN Yan-wen, HAN Chao-nan, ZHENG Bing-hui, <i>et al.</i> (2152)
Vertical Distribution Profiles and Release Potential of Mainstream Column Sediments in the Three Gorges Reservoir After Impoundment to 175 m	LI Rui, PAN Chan-juan, TANG Xian-qiang, <i>et al.</i> (2160)
Distribution Characteristics and Influencing Factors of Phosphorus in the Dongting Lake at Different Water Periods	LI Ying-jie, WANG Li-jing, LI Hong, <i>et al.</i> (2170)
Effects of Exogenous Carbon Addition on Equilibrium Phosphate Concentration and Risk of Phosphorus Release from Sediments in the Shiwuli River, Chaohu Lake Basin	LI Ru-zhong, BAO Qin, DAI Yuan (2178)
Spatial Distribution of Organic Phosphorus in Sediment and Its Environmental Implication in the Upper Stream of Minjiang River	XU Jian, YUAN Xu-yin, YE Hong-meng, <i>et al.</i> (2186)
Nitrogen and Phosphorus Removal by Integrated Ecological Engineering Treatment System in a Small Agricultural Watershed	JIANG Qian-wen, LIU Feng, PENG Ying-xiang, <i>et al.</i> (2194)
Spatial Distribution and Pollution Assessment of Heavy Metals in River Sediments from Lake Taihu Basin	ZHANG Jie, GUO Xi-ya, ZENG Ye, <i>et al.</i> (2202)
Temporal and Spatial Variation of Mercury in the Water of the Ruxi River Estuary, a Typical Tributary of the Three Gorges Reservoir Area	MA Wei-bin, CHEN Qiu-yu, YIN De-liang, <i>et al.</i> (2211)
Mercury Distribution Characteristics and Its Mass Balance in a Multifunctional Urban Wetland	LIU Wei-hao, WANG Yong-min, FAN Yu-fei, <i>et al.</i> (2219)
Distribution Characteristics of Mercury in Different Urban Constructed Wetlands	FAN Yu-fei, LIU Wei-hao, SUN Tao, <i>et al.</i> (2226)
Effects of Microplastics on Antibiotic Resistance Genes in Estuarine Sediments	HUANG Fu-yi, YANG Kai, ZHANG Zi-xing, <i>et al.</i> (2234)
Comparison and Source Apportionment of PAHs Pollution of Runoff from Roads in Suburb and Urban Areas of Shanghai	WU Jie, XIONG Li-jun, WU Jian, <i>et al.</i> (2240)
Characteristics of Phytoplankton Community and Its Relationship with Environmental Factors in Different Regions of Yilong Lake, Yunnan Province, China	WANG Zhen-fang, ZHANG Wei, YANG Li, <i>et al.</i> (2249)
Algal Bloom and Mechanism of Hypoxia in the Metalimnion of the Lijiahe Reservoir During Thermal Stratification	LIU Xue-qing, HUANG Ting-lin, LI Nan, <i>et al.</i> (2258)
Allelopathic Effects and Allelochemicals of <i>Myriophyllum elatinoides</i> on <i>Microcystis aeruginosa</i> and <i>Selenastrum capricornutum</i>	BI Ye-liang, WU Shi-min, ZHOU Si-ning, <i>et al.</i> (2265)
Removal Efficiency of Trichloroacetamide by UV/Sodium Sulfite	FU Zhi-xuan, GUO Ying-qing, CHU Wen-hai (2271)
Influencing Factors and Transformation Mechanism of Venlafaxine Degradation by UV	LÜ Juan, XU Zhi-wei, WANG Yan (2278)
Mechanism of Synergistic Adsorption of Arsenic and Cadmium by Aluminium-substituted Ferrihydrites	HUANG Bo, GUO Zhao-hui, XIAO Xi-yuan, <i>et al.</i> (2287)
Fluoride Removal Efficiency of Novel Material: Magnetite Core/Zirconia Shell Nanocomposite	FANG Wen-can, LI Xiao-di, FANG Jing, <i>et al.</i> (2295)
Impact Mechanisms of Carboxyl Group Modified Cathode on Acetate Production in Microbial Electrosynthesis Systems	QI Jia-xin, ZENG Cui-ping, LUO Hai-ping, <i>et al.</i> (2302)
Partial Nitrification and Denitrification of Low C/N Ratio Sewage Based on Zoning Oxygen and Dissolved Oxygen Control	WU Chun-lei, RONG Yi, LIU Xiao-peng, <i>et al.</i> (2310)
Start-up Performance of Low-substrate Anaerobic Ammonium Oxidation Under Different COD Concentrations	MA Yan-hong, ZHAO Zhi-chao, AN Fang-jiao, <i>et al.</i> (2317)
Partial Nitrification Fast Start-up and Stable Performance of 15°C SBBR	SUN Yi-qi, BIAN Wei, LI Jun, <i>et al.</i> (2326)
Effects of Long-term Poly-P Deficiency on the Metabolic Properties of <i>Accumulibacter</i> in AO-SBR System	WANG Shao-po, LI Zhu, ZHAO Le-dan, <i>et al.</i> (2333)
Extracellular Polymeric Substances of ANAMMOX Granular Sludge and Its Effects on Sludge Surface Characteristics	YANG Ming-ming, LIU Zi-han, ZHOU Yang, <i>et al.</i> (2341)
Treatment of Piggery Biogas Slurry by Enhanced Biological Contact Oxidation with HN-AD Bacteria	LIU Xiang-yang, ZHANG Qian, WU Heng, <i>et al.</i> (2349)
Effect of Different Temperatures on the Performance of Autotrophic Nitrogen Removal and Microbial Community from Swine Wastewater	HUANG Fang-yu, DENG Liang-wei, YANG Hong-nan, <i>et al.</i> (2357)
Characteristics and Regional Heterogeneity of Eukaryotic Microbial Community in Wastewater Treatment Plants	QIN Wen-tao, ZHANG Bing, SUN Chen-xiang, <i>et al.</i> (2368)
Effects of Wetland Reclamation on Soil Microbial Community Structure in the Sanjiang Plain	WANG Na, GAO Jie, WEI Jing, <i>et al.</i> (2375)
Distribution Pattern and Diversity Maintenance Mechanisms of Fungal Community in Subalpine Lakes	LIU Jin-xian, LI Cui, LUO Zheng-ming, <i>et al.</i> (2382)
Influence of Biochar Amendment on Soil Denitrifying Microorganisms in Double Rice Cropping System	LIU Jie-yun, QIU Hu-sen, WANG Cong, <i>et al.</i> (2394)
Effects of Plastic Film Mulching and Nitrogen Fertilizer Application on CH ₄ Emissions from a Vegetable Field	NI Xue, JIANG Chang-sheng, CHEN Shi-jie, <i>et al.</i> (2404)
Effects of Water Deficit on Greenhouse Gas Emission in Wheat Field in Different Periods	WANG Xiao-yun, CAI Huan-jie, LI Liang, <i>et al.</i> (2413)
Effects of Different Fertilization Modes on Greenhouse Gas Emission Characteristics of Paddy Fields in Hot Areas	TIAN Wei, WU Yan-zheng, TANG Shui-rong, <i>et al.</i> (2426)
Effects of Cyclical Temperature Fluctuations on Organic Carbon Mineralization in Purple Soil	ZENG Man-man, CI En, FAN Jing-jing, <i>et al.</i> (2435)
Cd Content Characteristics and Ecological Risk Assessment of Paddy Soil in High Cadmium Anomaly Area of Guangxi	SONG Bo, WANG Fo-peng, ZHOU Lang, <i>et al.</i> (2443)
Remediation Potential of <i>Ageratum conyzoides</i> L. on Cadmium Contaminated Farmland	ZHANG Yun-xia, SONG Bo, BIN Juan, <i>et al.</i> (2453)
Evaluation of the Potential Agricultural Risks of Polycyclic Aromatic Hydrocarbon Contaminated Soil by Planting <i>Lactuca sativa</i> L.	JIAO Hai-hua, GUO Jia-jia, ZHANG Jing-min, <i>et al.</i> (2460)
Impacts of Land Use and Landscape Patterns on Heavy Metal Accumulation in Soil	SHU Xin, LI Yan, LI Feng, <i>et al.</i> (2471)
Pollution Characteristics and Evaluation of Heavy Metal Pollution in Surface Soil Around a Municipal Solid Waste Incineration Power Plant	LÜ Zhan-lu, ZHANG Jin-liang, LU Shao-you, <i>et al.</i> (2483)