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水体中微界面对 PhACs 环境行为影响的研究进展

但孝香[1,2], 刘建超[1,2], 陆光华[1,2]

(1. 河海大学浅水湖泊综合治理与资源开发教育部重点实验室,江苏 南京 210098;
2. 河海大学环境学院,江苏 南京 210098)

摘要:药物活性化合物(pharmaceuticals, PhACs)作为一种新型的环境污染物,其大量使用导致的环境残留和负面影响引起社会广泛关注。然而 PhACs 在水体中的环境行为不仅与自身特性有关,还受水体纳米颗粒物、胶体、悬浮颗粒物等界面的影响。通过对现有研究的分析,介绍了国内外 PhACs 的污染水平及检测方法,综述了 PhACs 微界面作用的主要影响因素及环境风险,并对后续 PhACs 微界面作用研究进行了展望。

关键词:药物活性化合物;微界面;环境行为
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Effects of micro interface on behavior of pharmaceuticals in water

DAN Xiaoxiang[1,2], **LIU Jianchao**[1,2], **LU Guanghua**[1,2]

(1. *Key Laboratory of Integrated Regulation and Resources Development of Shallow Lakes, Ministry of Education, Hohai University, Nanjing* 210098, *China*;
2. *College of Environment, Hohai University, Nanjing* 210098, *China*)

Abstract: As a new type of environmental pollutants, pharmacologically active compounds (PhACs) have attracted wide attention from the public because of their environmental residue and negative effects. However, the environmental behavior of PhACs in water is not only related to its own characteristics, but also by the interaction of waterborne nanoparticles, colloids, and suspended particulates. Based on the analysis of existing research, the pollution level and detection methods of PhACs at home and abroad were introduced, the main influencing factors and environmental risks of PhACs micro interface interaction were summarized, and the subsequent research on PhACs micro interface effect was prospected.

Key words: PhACs; micro interface; environmental behavior

药物活性化合物(pharmaceuticals, PhACs)作为一种新型环境污染物,主要包括抗生素、抗菌药、消炎止痛药、抗抑郁药、激素等。我国每年有超过 200 万 t 4 000 多种 PhACs 被用于农业、水产养殖业、畜牧业和人类健康维护等方面[1]。大部分 PhACs 使用后并未完全代谢,而是以母体及其代谢产物的形式排出体外,而后直接排入水环境或者进入市政污水处理厂或者农业污水处理设施[1-5]。然而传统的污水处理工艺对大部分药物并不能完全去除,随同污水处理厂尾水进入水环境。因此污水处理厂尾水被认为是 PhACs 进入自然水体环境的主要来源[2-3]。除此之外,养殖废水、制药废水、过期药品处理不当也是天然水体 PhACs 的主要来源[4]。为了准确评估环境中 PhACs 可能产生的生态风险,须建立准确高效的 PhACs 检测方法。表 1 对比了不同国家对 PhACs 的前处理和检测方

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作者简介:但孝香(1992—),女,硕士研究生,研究方向为环境毒理学。E-mail:13655646950@163. com
通信作者:陆光华,教授。E-mail:ghlu@hhu. edu. cn

表 1　国内外 PhACs 的前处理和检测方法

PhACs 种类	样品类型	前处理方法	检测技术	LOQ	LOD	国家
雌激素类	地表水	SPE（Oasis HLB，150 mg）	LC-MS/MS	0.09～3.45 ng/L	0.06～1.25 ng/L	美国[5]
	污泥	PLE（ASE）	HPLC-MS/MS	0.25～375 μg/kg	0.15～175 μg/kg	西班牙[6]
	生物组织	SPE（Strata-X-AW，200 mg）	UPLC-TOF/MS		0.26～16 ng/g	英国[7]
抗生素类	地表水	SPE（Oasis HLB，200 mg）	HPLC-MS	0.06～0.35 μg/L	0.01～0.35 μg/L	比利时[8]
	生活污水	SPE（Waters，150 mg）	SPE-LC-MS/MS	0.2～1.2 ng/L	0.06～0.36 ng/L	法国[9]
	生物组织	PLE（Speed-Extractor-E-916/914）	HPLC-MS	0.18～0.53 ng/g	0.01～0.17 ng/g	韩国[10]
非甾类	生活污水	SPE（Oasis HLB，150 mg）	HPLC-DAD	2.75 μg/L	0.83 μg/L	南非[11]
咖啡因	无脊椎动物	超声萃取（Branson-Digital -Sonifier，model102C），SPE	HPLC-HRMS UPLC-QqQ-LIT	0.06～4.3 ng/g	0.08～2.4 ng/g	西班牙[12]

注：LOQ：定量限；LOD：检测限；ASE：加速溶剂萃取；SPE：固相萃取；PLE：加压流体萃取。

法。从表 1 看出，目前 PhACs 的分析检测手段主要依赖于高效液相色谱-质谱联用（HPLC-MS）和气相色谱-质谱联用技术（GC-MS）。

对于极性强、不易挥发的物质（如双氯芬酸、大环内酯类抗生素、阿司匹林等）一般采用 HPLC-MS 检测。

近年来，PhACs 先后在污水、地表水、地下水、甚至自来水中都有检出。表 2 对比了国内外不同环境介质中检测到的 PhACs 种类及浓度。十几个国家的地表水中累计检测出 80 多种 PhACs，浓度最高达到 μg/L 水平[13-14]。对我国河流、湖泊水体中 158 种药物及个人护理品进行的调查研究结果表明，检出频率较高的前 10 种污染物都是抗生素类 PhACs[15]。总体而言，磺胺类检出率高，浓度达到 1 390 ng/L；而氟喹诺酮类、大环内酯类、四环素类和 β 内酰胺类抗生素在中国地表水中最高质量浓度分别达到了 6 800 ng/L[16]、3 700 ng/L[17]、1 000 ng/L[18] 和 4 500 ng/L[19]。目前 PhACs 监测方法标准没有统一，瞬时采样不能反映真实的连续情况，PhACs 污染水平在各类水体中呈现出较大的空间和时间上的差异性。虽然 PhACs 的半衰期不长，但由于频繁地使用并进入水环境，导致其形成“假持续”现象。此外 PhACs 是针对生物疾病而设计，具有特殊的药理、生理功能，短期内并不一定会凸显其危害性，但这些污染物往往以复杂的混合物形式存在，易产生协同作用，长期暴露可能对非靶生物的新陈代谢产生明显影响，从而影响非靶生物体正常的生理生化功能，对生态系统安全和人类健康构成潜在威胁。我国对 PhACs 类污染物的排放没有制定相应的法规，目前欧盟也只对雌二醇、炔雌醇和双氯芬酸制定了相应的排放阈值（分别为 0.4 ng/L、0.035 ng/L 和 100 ng/L）。

表 2　国内外不同环境介质中检测到的 PhACs 种类及浓度

环境介质	地区	PhACs 种类及浓度
地表水[20-21]	中国	抗生素类（ND～940 ng/L）、激素类（ND～558 ng/L）
	法国	抗生素类（ND～40 ng/L）、咖啡因（ND～6 ng/L）、激素类（0.6～4 ng/L）
	日本	抗癫痫类（ND～200 ng/L）、非甾类（ND～18 ng/L）
地下水[22-23]	中国	抗生素类（<10 ng/L）
	美国	抗生素类（46～678 ng/L）、咖啡因（18～290 ng/L）、抗癫痫类（30～420 ng/L）
	德国	抗生素类（ND～110 ng/L）、非甾类（5～590 ng/L）
胶体[24]	中国	抗生素类（10～27 414 ng/g）、激素类（ND～6 ng/L）、抗炎解热类（ND～10 ng/g）
悬浮颗粒物[24]	中国	非甾类（ND～80 ng/L）、抗生素（<LOQ～180 ng/g）
	加拿大	激素（5～149 ng/g）、非甾类（124～145 ng/g）
沉积物[25]	法罗群岛	非甾类（ND～260 ng/kg）、抗炎解热类（<0.1～850 ng/kg）
	法国	咖啡因（ND～29 ng/g）、抗生素类（30～660 ng/kg）

注：ND 表示未检出。

近年来，我国对水环境中 PhACs 的残留、环境行为和归宿进行了初步研究。但水环境中 PhACs 并不是单独存在的，它们在水体中的环境行为不仅与其他有机污染物直接相关，还受到水体纳米颗粒物、胶体、悬浮颗粒物等环境介质的影响与控制。这些不同性质和不同尺寸的颗粒物构成的水/颗粒物微界面体系是污染物进行物理、化学和生物转化的重要载体和场所，决定着污染物的环境行为与生态效应。现有研究显示，目前大部分 PhACs 的分析都集中在液相中，缺少沉积物、悬浮物，尤其是胶体等固相中的浓度分析。本文分别从水环境界面污染特征、影响因素、环境风险及 PhACs 管理方法 4 个方面对现有研究进行了总结，讨论了现有研究存在的问题，并对今后的研究进行了展望。

1　PhACs 在微界面结合特性及赋存状态

水体微界面是水环境中普遍存在的实体，如自然水体中的悬浮颗粒物（suspended particulate matter，SPM）、腐殖质、矿物微粒、细菌、病毒、无机和有机胶体，人工生态系统的滤料、吸附剂、活性污泥等。这些具有一定粒度的颗粒物对河流中碳和营养物的迁移扮演着重要的角色[26]。微界面的活性反应基团与周围水溶液可以发生几乎所有的物理、化学反应，如络合、氧化等。除此之外，天然水体中

颗粒物间的聚集、絮凝、溶胶,人工设施中活性污泥的生物氧化、膜与纤维过滤、滤料层等也都涉及微界面反应过程。目前,PhACs 在水体中的分布研究主要集中在水/悬浮颗粒物、水/沉积物等二维构相中,忽略了纳米颗粒物、胶体等典型环境微界面的存在,不能反映水体 PhACs 污染的真实风险水平[27]。

1.1 沉积物对 PhACs 的吸附

沉积物是非常复杂的体系,包括金属氧化物、黏土矿物和有机质等,对环境中的 PhACs、无机阳离子和重金属都具有很强的吸附能力,因此是很多 PhACs 的最终归宿[28]。国内外不同地区的水体沉积物中都有不同浓度 PhACs 的检出,其质量比一般在几十 μg/kg 左右[29]。不同沉积物组分对 PhACs 的吸附机理不同,如铁铝硅氧化物类沉积物与水接触后形成大量的表面羟基,易与抗生素类 PhACs 中羧基、氨基和酮基官能团发生相互作用,从而被氧化物吸附。黏土类沉积物与 PhACs 相互作用的主要机制是离子交换作用和氢键作用等[30]。而类固醇类 PhACs 吸附特性受沉积物粒径的显著影响,低质量浓度(1 ng/L)固醇类 PhACs 优先吸附于黏土类沉积物中,直径介于 0.87 ~1.43 μm,高质量浓度(500 μg/L) PhACs 主要吸附于泥沙类沉积物,直径介于 8.1 ~17.7 μm。此外,沉积物与阳离子吸附强度明显高于阴离子,且阴离子吸附大都是可逆的,而中性离子的吸附则忽略不计[31]。

1.2 SPM 对 PhACs 的吸附

SPM 指颗粒直径在 0.45 μm 以上,以悬浮态存在于水体中的颗粒物,含有较高比例的微生物和藻类等活性有机组分[32]。SPM 在国内外河流平均质量浓度范围为 29.8 ~100 mg/L[33-34],其在水体中广泛存在,并对水体 PhACs 的吸附起着重要作用[35]。世界各大水体中都有 SPM 吸附 PhACs 的研究报告,总体结果显示 SPM 吸附 PhACs 水平低于水体溶解水平,质量比范围为 6.4 ~149 ng/g[35-37]。SPM 的微观形状不规则,各个单体可以聚集成絮状、链状、分枝状等,其表面凹凸不平且具有孔隙结构,使 SPM 能够充分地与 PhACs 接触,并且能够大量吸附 PhACs,进而影响 PhACs 的环境归趋[38]。同时,SPM 对 PhACs 吸附与 PhACs 辛醇-水分配系数 K_{ow} 密切相关,随 K_{ow} 值增加,PhACs 疏水性增强,因而在 SPM 上吸附量增加[37]。

1.3 胶体对 PhACs 的吸附

天然水体中胶体物质通常是粒径介于 1 nm ~ 1 μm 的无机和有机非均相颗粒混合物,包括氢氧化铁、铝硅酸盐、表面活性剂等;此外,工程纳米材料、微塑料等纳米颗粒物不断进入水环境,使胶体微界面表面效应更加复杂[39]。胶体的物质组成决定了其具有体积小、比表面大、表面点位密集、吸附位点多、成分复杂等特点,可通过共价键合、静电吸附、表面络合等作用对 N/P 循环、络合沉降及污染物的分布、转化等环境行为产生重要影响[40-41]。

胶体是水环境中多种污染物重要的“汇”,其对 PhACs 的贡献率可达 30% ~40%[3, 42],而对激素类 PhACs 的贡献率达到 60% 以上,远高于 SPM 对激素类 PhACs 30% 的吸附贡献率;而且胶体与 PhACs 的标准化吸附系数 K_{coc} 比沉积物要高 1 ~2 个数量级[43]。我国不同水体胶体对 PhACs 的吸附结果显示,长江下游水体胶体中 PhACs 的总质量浓度范围为2 419 ~5 065 ng/L[44],珠江流域抗生素类 PhACs 在胶体中平均质量浓度范围分别为 23.2 ~108 ng/L[45]。而内陆湖泊白洋淀中抗生素类 PhACs 在胶体中平均质量比 1 381 ng/g(干重)[46],与上述自然水体相比,污水处理厂尾水胶体中 PhACs 质量浓度较低,为 0.03 ~147.5 ng/L[47],占比在 36% 以下[42]。相较于市政污水,自然水体是多种 PhACs 的重要归宿[48]。

2 环境因素对微界面作用的影响

2.1 离子强度

离子强度是衡量溶液中阴阳离子产生电场的程度,与溶液浓度和元素化合价密切相关。其通过改变胶体表面的双电层厚度、促进离子交换等影响微界面对 PhACs 的吸附[49-50]。王东升等[51]研究了不同离子浓度(0.01、0.03、0.05、0.08、0.10 mol/L $CaCl_2$ 溶液)对抗生素类 PhACs 在土壤胶体中的吸附影响,结果表明,随离子强度增加,PhACs 吸附量呈降低趋势,而 Ca^{2+} 离子与 PhACs 对土壤胶体吸附点位竞争机制是 PhACs 吸附量降低的主要原因。水体胶体相中含有丰富的 Ca、Mg、Na、K 等微量元素,质量比高达 193.34 g/kg[46, 52-53],而这些离子对 PhACs 的胶体吸附形成竞争性,从而影响胶体对药物的吸附量[46]。同时,不同价态离子的竞争性吸附能力存在差异,其价态越高,竞争能力越强:M^+ (Na^+、K^+、NH_4^+) < M^{2+} (Ca^{2+}、Mg^{2+}、Zn^{2+}) < M^{3+} (Al^{3+})[54]。

2.2 溶解有机物

溶解有机物(dissolved organic matter, DOM)是指水中能通过 0.45 μm 滤膜的有机物组分,主要成分为腐殖质,是以醌和多元酚为芳香核心的多聚物,其芳香核心主要有羧基、羰基、多肽等,并通过—O—、=CH-等键相连,其在水体中普遍存在[55]。河流及湖泊自然水体中含有大量的 DOM,其含量约占总有机物的 25%[56],而城市污水中 DOM 含量更

高,约占到总有机物的 40%[57]。胶体态颗粒物中有机质含量达 49% ~71%,胶体分子量越小,有机质 C/N 值增加,有机质活性越高[58]。在土壤中,PhACs 的吸附分配系数与 DOM 的浓度呈正相关关系,高浓度 DOM 能促进有机物的吸附,减弱其在土壤中的迁移能力[59]。而在水体胶体中,增加 DOM 可以减缓胶体中卡巴呋喃、雄烯二酮和睾酮的光解速率,增加它们在环境中的持久性[60-61]。此外,DOM 还具有一定的光化学活性,不仅可以在吸收光子后将能量传递给 PhACs[62],还可以在光的照射下产生 · OH 等活性中间体,然后活性中间体与 PhACs 发生反应,影响 PhACs 环境行为[63]。

2.3 表面活性剂

表面活性剂是一大类有机化合物,具有很强的表面活性,能使液体的表面张力显著下降,作为乳化剂、洗涤剂、渗透剂、分散剂、表面改性剂等数十种功能产品而应用于日常生活和工农业生产领域。表面活性剂进入环境介质后,通过降低沉积物/水之间的界面张力,增加疏水性有机物(hydrophobic organic contaminants, HOCs)在水相中的溶解度,同时促进 HOCs 从沉积物上的解吸并再次吸附在表面活性剂的单体上,进而影响 HOCs 的生物可利用性[64]。非离子表面活性剂能够吸附在水体胶体表面,产生位阻效应;而阴离子表面活性剂可提高胶体的 Zeta 电位绝对值,使胶体静电效应和位阻效应同时增强[65]。对于疏水性 PhACs 来说,表面活性剂能降低其界面张力,增加 PhACs 的水溶解度和生物有效性,从而影响其在水环境中的迁移转化过程及环境行为[66-67]。

2.4 水动力作用

水动力作用是影响 PhACs 在水体微界面分配的重要因素。流速、水流紊动强度、水力停留时间(hydraulic retention time, HRT)等水动力因素会通过改变水体微界面运动状态及水体理化性质对 PhACs 的迁移转化过程产生影响[68]。研究发现,当 HRT 为 45.9 h 时,雌醇(E1)、雌二醇(E2)、炔雌醇(E3)的降解速率分别为 46.2%、44.6%、0.0%,当水力停留时间为 137.5 h 时,其降解速率分别为 84.3%、59.2%、40.0%。当 HRT 增大时,水体中胶体浓度增加,胶体对 PhACs 吸附量变大,从而抑制 PhACs 降解速率[69]。此外,流速的增大会减小边界层厚度,增大水体溶解氧含量、氧化还原电位等参数,使 PhACs 在水体里的扩散由分子扩散转为紊动扩散,从而增强 PhACs 在水/SPM 界面的交换量,对 PhACs 在水/SPM 两相间的分配产生影响[30]。

3 PhACs 微界面结合体风险评价

根据当前水体污染水平及实验室生态风险评估数据,虽然 PhACs 引起水生生物急性毒性风险概率较低,但慢性毒性风险不容忽视,将威胁生态环境及人体健康[1]。尤其是 PhACs 长期暴露对高等水生生物的慢性毒性风险有待深入研究[70]。PhACs 长期暴露可以干扰生物体内分泌物的合成、代谢、结合等过程,影响其生长、发育等行为,还可能引起水生生物免疫功能抑制和癌症等病变的发生[71-72]。PhACs 在水生生物代谢、抗氧化、神经、生殖等系统产生毒害作用已经被证实,但大多集中于实验室模拟水体 PhACs 暴露研究,而对天然水体中胶体等微界面存在对此类 PhACs 生态风险评价的研究鲜有报道[73]。

大部分 PhACs 具有潜在的基因毒性,这意味着它们可以直接破坏 DNA 或者产生活性物质(如亲电基团或自由基)破坏 DNA。实验表明,黑头呆鱼(Pimephalespromelas)分别在黄体酮(P4)-粉粒颗粒物(1.36 m^2/g)、P4-黏粒颗粒物(19.9 m^2/g)水生体系中暴露 7 d 后,黄体酮(P4)-粉粒颗粒物体系显著降低了黑头呆鱼卵黄蛋白原和雄激素受体的基因表达[74]。Duong 等[73]的研究同样表明而雌激素(E1、E2、BPA)-SPM 体系对雄性青鳉鱼具有同样的诱导效应,可显著增加雄性青鳉鱼的卵黄蛋白原水平。从环境介质粒径来看,粒径越小,介质对激素类 PhACs 吸附能力越强[26],从而加强 PhACs 在水生生物体内的累积和内分泌干扰效应[73],且尺寸效应在高等水生生物鱼体内表现得更为明显[75]。水体中碳纳米管、富勒烯等纳米级微界面能够改变水生生物(如:摇蚊幼虫)对 PhACs 的吸收途径,通过体外吸附和体内解吸过程增加 PhACs 在生物体内的生物累积风险[76-77]。同时,胶体微界面的存在还能增强菲、芘等污染物在大型蚤体内的被动扩散过程,从而增加其细胞毒性[78]。因此,需开展和运用多种可靠的模型进行环境暴露预测,加强 PhACs 对人体暴露和生物累积的研究,建立基于人体健康和生态环境安全的 PhACs 风险评价基准[79-80]。

4 PhACs 管理方法

针对当前 PhACs 管理过程中存在的问题,需要加强环境管理和控制技术开发,结合我国 PhACs 生产和使用特点,开展生态环境中 PhACs 的分布和迁移转化规律研究,识别高风险 PhACs 母体及其降解产物,判断其引起健康风险的主要途径,进而开发新型的控制技术。对于医院的药物管理,应做到以下

几点:①加强基层医院药库管理,②建立药物网络管理平台,③提升药物管理人员素质[81]。对于养殖业兽药管理,则应做到:①广泛宣传畜禽健康养殖知识和药物残留对人类健康的危害,②加强兽药生产经营管理,③加强饲料生产管理,④加强兽药残留监控[82]。另外,要积极开展科普宣传,提高全民对此类污染物的认知,减少不必要的药物使用,科学处置废弃药品和生活护理品,同时加强对过期 PhACs 的收集处理,降低 PhACs 进入环境的可能性。

5 展 望

a. 我国对水环境中 PhACs 污染特征的监测数据积累较少,并且缺乏统一的监测和检测标准,数据可比性差,有必要进一步推进 PhACs 相关监测和检测标准体系建设,为此类污染物的监测和控制提供基础技术和规范依据。

b. 目前大部分有关 PhACs 污染研究只涉及水溶液,缺乏一个整体性的环境监测分析体系。应将 PhACs 在水环境中沉积物、悬浮物和胶体中的含量分析纳入在内,更加准确地了解 PhACs 的去向和环境影响。

c. 大部分 PhACs 呈现低浓度下的慢性作用,多种污染物及介质共存的复合毒性作用更是不可忽视,因此基于 PhACs 低浓度、复合污染的特征,研究 PhACs 及其代谢产物的毒性效应和作用机制,是正确认识其健康风险和修订水质标准的基础。

d. PhACs 在不同水环境中的污染特征和人口数量、生活水平、用药习惯、畜牧养殖密集程度等因素息息相关,并存在较大差异。这些因素一定程度上决定了 PhACs 区域污染水平,因此必须有针对性地加强重要流域水环境中持续性 PhACs 的监测研究,并通过建立信息网络实现主要污染物的动态监测和风险预警,更加直观地反应水体中 PhACs 的污染状况。

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