张照荷, 陈典, 赵微, 等. 水环境中药物与个人护理品(PPCPs)的环境水平及降解行为研究进展[J]. 岩矿测试, 2023, 42(4): 649−666. doi: 10.15898/j.ykcs.202210260207.
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水环境中药物与个人护理品(PPCPs)的环境水平及降解行为研究进展

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摘要：药物和个人护理品(PPCPs)是一种存在于各种介质中的新污染物，具有生物富集、致癌致畸性，近年来在水环境中被广泛检出，其种类和浓度也有逐渐增多和加重的趋势，加之与人类生活密切相关，可以通过家庭垃圾、医院废水、垃圾填埋场、污水处理厂等方式直接污染地表水，并进一步污染孔隙水、地下水等，致使生态环境和人体健康存在风险。因此，广泛了解 PPCPs 在各种环境介质中的浓度水平对于防范生态健康风险具有重要意义。近年来，对 PPCPs 浓度的调查研究取得了较大进展，自 1976 年美国堪萨斯城首次报道药物以来，各国陆续报道了不同介质中 PPCPs 的存在，弥补了各研究区污染物及浓度的空白，有利于开展综合治理工作。PPCPs 在水环境中常见的降解方式有水解、光解及生物降解，同时在降解过程还会受到 pH、温度、共存离子等影响，而且在各种降解过程中生成的产物也有所不同。污水处理厂因为去除工艺的限制，使得地表水中许多 PPCPs 虽然经过了废水的生物降解环境，但是光降解仍然可能比暴露在阳光下的生物降解更强。其中，抗生素在水环境中主要发生光降解；布洛芬、碘普罗胺、咖啡因等更易发生生物降解；而自然界中 PPCPs 发生水解的概率较低，酯类和酰胺类是其中最常见的易水解的官能团，除此之外，四环素类等因为吸附到沉积物中，也会发生水解反应。目前，对于 PPCPs 浓度水平的研究很多集中在单一水体，而海水、雨水等介质缺乏监测和分析，同时对于降解行为的研究大都没有关注到降解过程和降解产物，使得一些降解产物的高毒性被低估。因此，全面了解各种水环境介质中 PPCPs 浓度可以较为准确、系统地获知各地区 PPCPs 的污染情况，对于 PPCPs 治理与削减工作具有重要的现实意义；而探究 PPCPs 在水环境中的降解行为，有利于了解其在环境中的残留和代谢情况，厘清中间产物和最终产物的性质，以便针对性地对 PPCPs 的环境生态效应进行评估分析，降低风险。

关键词：水环境；药物和个人护理品(PPCPs)；浓度水平；降解行为；影响因素

要点：

(1) PPCPs 在各种水环境中都被检出，其中地表水 PPCPs 的检测相对较高。

(2) PPCPs 在水解、光降解、生物降解过程中受到 pH 值、温度等多种因素影响。

(3)由于污水处理厂技术有限，同样光照条件下，光降解可能比生物降解效果更大。

中图分类号：X52 **文献标识码：**A

收稿日期：2022−10−26；**修回日期：**2022−12−15；**接受日期：**2023−03−29
基金项目：国家自然科学基金项目(41771515)； 中国地质科学院基本科研业务费项目(CSJ-2021-08)； 中国地质调查局地质调查项目(20211414)
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药物和个人护理品(PPCPs)是一类人为使用的化学物质,主要包括各种医药品和日常生活的个人护理品。近年来,人们对 PPCPs 的需求逐渐增加[1],导致其在环境中的浓度也日渐升高。水环境是经济发展和生态环境的重要资源,同时也与人体健康密切相关。由于日常使用,大部分 PPCPs 通过污水处理厂、垃圾填埋场等途径进入水环境中,致使各种水环境介质中 PPCPs 的浓度升高[2-5]。1976 年,美国堪萨斯城首次在处理的废水中检测到氯贝酸,浓度为 0.8~2μg/L[6],此后在不同国家陆续检测到 PPCPs,但是种类和浓度存在一定差别。中国是世界上最大的药品使用消费国,每年使用的 PPCPs 超过 20000t,尤以通过水体传播的抗生素类使用较多[7],其中磺胺类抗生素在水体中检出频率最高,最高浓度可达 1080ng/L[8]。非洲则是以非甾体抗炎药为主[9],常见的有萘普生、布洛芬、双氯芬酸,其中布洛芬浓度最高为 222μg/L。环境中 PPPCs 的种类和浓度不仅在国家之间不同,而且在同一国家的不同地区之间也有所不同。例如,在京杭大运河地区夏季地表水中以磺胺甲恶唑为主,最高浓度为 116ng/L[10];在永定河地区以替米考星为主,浓度为 71.6ng/L[11];在北运河地区则以双氯芬酸为主,3 月份地表水中浓度范围为 831~8095ng/L[12]。另外,在西班牙、非洲及美国等的地表水和污水处理厂中检测到降压降血脂、精神类药物及个人护理品[8-9,13],其中西班牙污水处理厂中咖啡因的浓度最高达 65625ng/L[8]。

PPCPs 在水环境中常见的降解方式有水解、光解及生物降解,且各种降解方式的主要影响因素也不尽相同。Baena-Nogueras 等[14] 对 PPCPs 的降解行为进行研究,认为水溶液 pH 值在化合物的光降解中起重要作用,而降解菌群的种类对生物降解有显著影响。此外,他们还认为,对于大多数化合物来说,水解通常慢于光解及生物降解。另有研究发现一些降解产物的产生甚至比母体更具毒性[15],加之生物富集[16] 及食物链传递作用,使其对生态系统造成危害的同时损害人类健康[17-21]。目前从已有研究中发现水环境中 PPCPs 污染程度普遍较高,因此了解 PPCPs 的环境行为、水环境中的赋存现状及降解行为,对于防治污染、减少生态风险、保护健康方面意义重大。

前人对于 PPCPs 的研究更多集中在单一水体,且降解的研究还不够具体,本文根据现有文献,广泛总结了地表水、地下水、沉积物及雨水、海水中 PPCPs 的赋存现状和浓度水平,重点对 PPCPs 在水环境中降解行为的机理、影响因素等进行综述,阐明降解过程中的中间产物和最终产物,拟为水环境中 PPCPs 的降解转化研究提供理论参考,同时对于探究降解过程中的毒性变化、减少 PPCPs 的污染和降低风险提供科学依据。

1　常见的 PPCPs 种类及其特性

PPCPs 主要分为两类:一类是各种处方和非处方药物,常见的有抗生素类、激素类、消炎止痛药、降压降血脂类、抗精神类药等;另一类是个人护理品[22],常见的有消毒杀菌剂、合成麝香等。该类物质具有慢性毒性、伪持久性和生物累积性[23]。大部分 PPCPs 在环境中的浓度在 ng/L~μg/L 之间,但是由于大量使用加之常规污水处理工艺无法将其彻底去除,使其在环境中不断累积,在生物体内也不断富集。虽然 PPCPs 含量很低,但其毒性却不容忽视,如磺胺类药物会损伤组织器官,且会引起人体致病菌的耐药性,甚至具有致畸和致癌作用[9];合成麝香对荷尔蒙的分泌有干扰作用,还会导致哮喘、过敏症、偏头痛等疾病[20],长期使用会导致肝肾损坏并诱发癌症等[21]。

常见的 PPCPs 种类及其特征如表 1 所示。

2　水环境中 PPCPs 的环境行为及含量水平

PPCPs 与人类活动密切相关,可以通过不同的途径进入水环境中。未被吸收的药物以母体形式进入污水处理厂,而废弃药品进入到垃圾填埋场,个人护理品则可以通过沐浴、洗漱等途径进入水环境。这些 PPCPs 会通过径流、挥发等途径进入地下水、孔隙水及雨水等环境中,造成了各种水环境系统中不同含量的 PPCPs。

2.1　水环境中 PPCPs 的来源、迁移与归趋

近年来,中国不同地区报道的 PPCPs 已有上百种,主要通过医院、垃圾填埋场、养殖场、工厂废水及生活污水等途径进行环境累积(图 1),并通过污水处理厂及垃圾填埋场的渗滤液进入水环境中,进一步造成地下水、沉积物、孔隙水等污染。

药物的主要使用场所是医院,使用后的药物进入医院废水,导致医院废水中 PPCPs 浓度升高[24]。以布洛芬为例,在希腊市政医院污水处理厂[25] 的检出浓度为 7.0~8.9μg/L,略低于日本某污水处理厂(9±16μg/L)[26],但高于约阿尼纳医院报告的布洛芬浓度(2.05μg/L)[27],因此作者推测布洛芬浓度的差异可能与各国不同的消费率有关。个人护理品主要通过人类的日常洗涤活动排放到下水道系统和地表水中。

表 1　抗生素、激素、消炎止痛药、降压药类等常见 PPCPs 的物理化学特征

Table 1　Physical and chemical characteristics of common PPCPs such as antibiotics, hormones, anti-inflammatory painkillers and antihypertensive drugs.

PPCPs 的常见类别	中文名称	英文名称	缩写	分子式	医学应用	CAS 号
抗生素	磺胺甲噁唑	Sulfamethoxazole	SMX	$C_{10}H_{11}N_3O_3S$	抗菌	723-46-6
	诺氟沙星	Norfloxacin	NOR	$C_{16}H_{18}FN_3O_3$	治疗肠炎痢疾	70458-96-7
	四环素	Tetracycline	TC	$C_{22}H_{24}N_2O_8$	杀菌	60-54-8
	土霉素	Oxytetracycline	OTC	$C_{22}H_{28}N_2O_{11}$	治疗犬、猫的呼吸道、尿道感染	79-57-2
	红霉素	Erythromycin	ERY	$C_{37}H_{67}NO_{13}$	治疗呼吸道感染	114-07-8
激素	地塞米松	Dexamethasone	DEX	$C_{22}H_{29}FO_5$	抗炎、免疫抑制	50-02-2
	雌酮	Estrone	E1	$C_{18}H_{22}O_2$	维持雌性个体的第二生理特征	53-16-7
	乙烯雌酚	Diethylstilbestrol	DES	$C_{18}H_{20}O_2$	治疗雌激素低下症及激素平衡失调引起的功能性出血	56-53-1
消炎止痛药	萘普生	Naproxen	NAP	$C_{14}H_{14}O_3$	止痛解热	22204-53-1
	双氯芬酸	Diclofenac Acid	DIC	CHClNO	治疗风湿性关节炎等	15307-86-5
	布洛芬	Ibuprofen	IBU	$C_{13}H_{18}O_2$	镇痛、抗炎	15687-27-1
降压药	科素亚	Losartan	-	$C_{22}H_{22}ClKN_6O$	降血压	124750-99-8
	缬沙坦	Valsartan	ARB	$C_{24}H_{29}N_5O_3$	降血压	137862-53-4
降血脂药	吉非罗齐	Gemfibrozil	GEM	$C_{15}H_{22}O_3$	调血脂	25812-30-0
	苯扎贝特	Bezafibrate	BZF	CHClNO	调血脂	41859-67-0
β-受体阻断药	阿替洛尔	Atenolol	-	$C_{14}H_{22}N_2O_3$	降压、调整心率	29122-68-7
	美托洛尔	Metoprolol	MPL	$C_{15}H_{25}NO_3$	降压、调整心率	51384-51-1
抗精神病药	卡马西平	Carbamazepine	CBZ	CHN_2O	治疗癫痫、神经性疾病	298-46-4
	可铁宁	Cotinine	-	$C_{10}H_{12}N_2O$	促进神经系统兴奋	486-56-6
驱虫剂	避蚊胺	Diethyltoluamide	DEET	$C_{12}H_{17}NO$	防止蚊虫叮咬	134-62-3
合成麝香	佳乐麝香	Galaxolide	HHCB	$C_{18}H_{26}O$	用于化妆品、调制香料	1222-05-5
	吐纳麝香	Tonalide	AHTN	$C_{18}H_{26}O$	用于化妆品、调制香料	1506-02-1
消毒杀菌剂	三氯生	Triclosan	TCS	$C_{12}H_7Cl_3O_2$	抗菌除臭	3380-34-5
	三氯卡班	Triclocarban	TCC	$C_{13}H_9Cl_3N_2O$	杀菌除臭	101-20-2
除草剂	阿特拉津	Atrazine	ATZ	$C_8H_{14}ClN_5$	除草	1912-24-9

不需要或疗效过期的 PPCPs 通常被丢弃在垃圾填埋场中, 导致垃圾填埋场中 PPCPs 残留物的浓度很高[28]。已有研究证明, 在日本[29]、美国[30]、德国[31] 的垃圾填埋场渗滤液中存在 μg/L~mg/L 量级的咖啡因、避蚊胺等 PPCPs, 在中国广州市郊[32] 和上海市[33] 垃圾填埋场渗滤液中也检测到 PPCPs, 但其种类不同, 其中布洛芬浓度高达 202μg/L。这些 PPCPs 经过雨水等淋洗进入垃圾渗滤液, 对地表水产生污染, 并进一步污染地下水[34-35]。

此外, 养殖场使用的兽药[36]、工厂的废水及生活污水[37] 也主要排放到污水处理厂, 并进一步积聚在沉积物孔隙水中。含有 PPCPs 的地表水最终由河流汇入海洋, 是海水中 PPCPs 重要的来源之一, 并且某些具有挥发性的 PPCPs 又会进入雨水中[38], 随着降雨进一步污染环境。

2.2　不同水环境中 PPCPs 的含量水平

由图 1 可知, PPCPs 大部分都被排放到水体中, 在地表水、地下水、沉积物等介质都检测出 PPCPs, 但不同国家的污染程度有所差别。在中国, 珠江水系有 95 种 PPCPs 被检出, 辽河水系检出 PPCPs 的种类有 48 种[39-43], 其中尤以抗生素类 PPCPs 为主, 而在国外地区, 水环境中抗生素类 PPCPs 的含量远小于中国。以各国的检出情况为例, 水环境中抗生素类 PPCPs 的含量见表 2。

由表 2 可知, 磺胺甲恶唑是水环境介质中分布最为广泛的一类 PPCPs, 这类抗生素的亲水性较强, 在人类呼吸道疾病和禽畜养殖方面应用广泛, 因此在水环境中浓度也较高[58]。地下水中 PPCPs 主要是通过生活污水、医院和养殖场废水下渗产生的, 而且极性越大的化合物越易渗透至地下水中[59]。沉积物中除了磺胺类抗生素, 喹诺酮类抗生素也占一定比例, 由于其自身具有较多官能团, 且在水产养殖中使用较多, 加之具有较强的吸附能力, 所以更易吸附在沉积物中[58]。孔隙水中 PPCPs 浓度相对较低, 雨水中 PPCPs 报道相对较少, 含量也都＜10ng/L, 主要是由于某些化合物所具有的挥发性被检出, 报道较多的是阿特拉津, 在、密西西比州、长江河口处均有检出[60-61]。海洋被许多学者认为是污染物的重要汇,

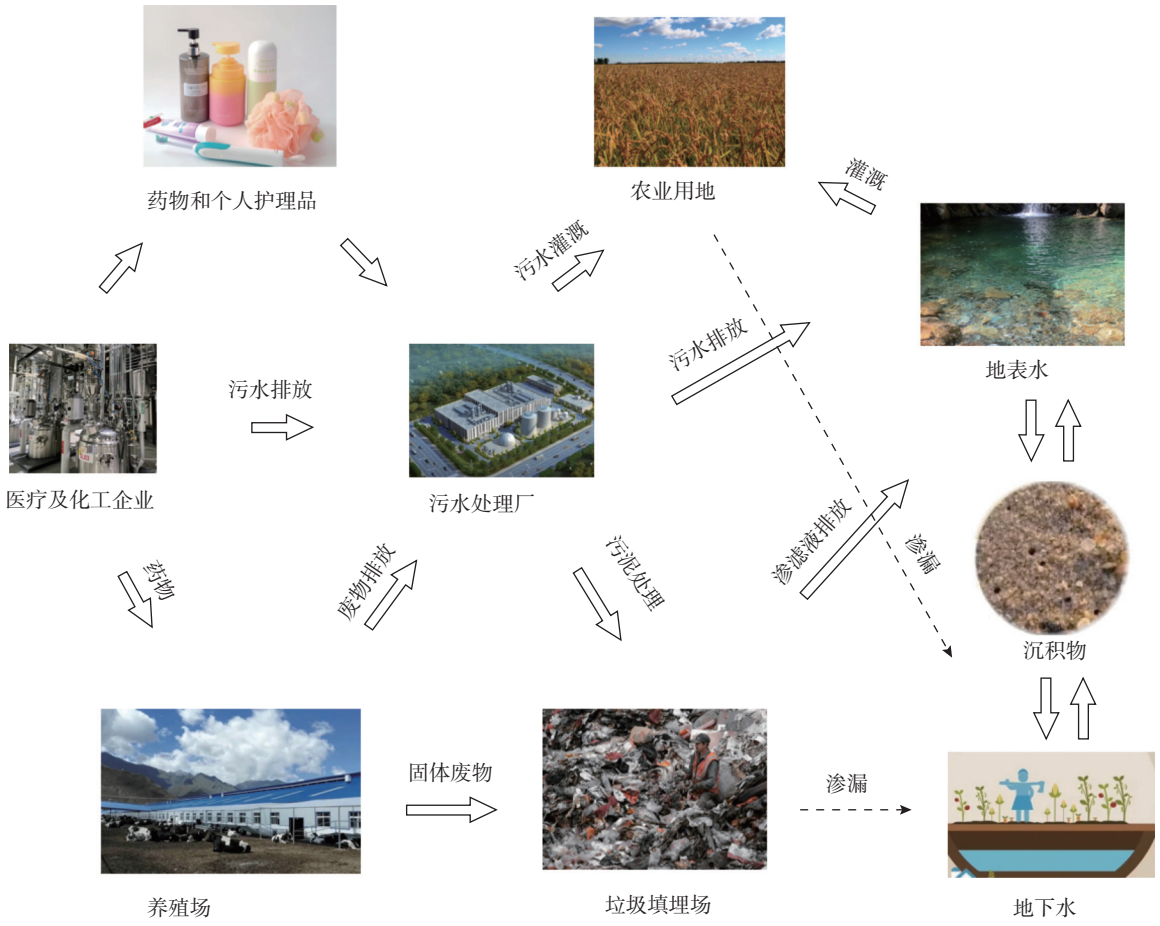


图1　水环境中 PPCPs 的来源与迁移归趋

Fig. 1　Source and migration fate of PPCPs in water environment.

研究发现在海水中检测到 20 多种抗生素，浓度高达 μg/L[62]。其中咖啡因是海水中检测最为广泛的 PPCPs。

3　PPCPs 在水环境中的降解行为

理解 PPCPs 在环境中的状态是研究其分布情况和环境水平的关键，因此有必要对 PPCPs 在水环境中的降解方式进行分析，以此来探究水体中 PPCPs 的水解、光降解及生物降解[63]，帮助人们进一步了解 PPCPs 的降解原理及其行为。

3.1　水解

水解是 PPCPs 在水环境中消除或浓度降低的一种重要途径，其实质是亲核取代反应，即由亲核基团（氢氧根离子或水分子）进攻化合物（RX）中的亲电子基团，并取代之相连的带负电趋势的强吸电子基团（X）。水解反应可以用方程式表示[63-64]：

$$RX+H_2O=ROH+HX$$

如青霉素 G 和阿莫西林的水解就是侧链对 β-内酰胺羰基的分子内亲核攻击，C—N 键断裂开环从而发生降解（图 2、图 3[65]）。

对 PPCPs 水解的研究主要考虑 pH 的影响，不同的酸碱度与目标化合物会产生不同的反应，对其水解速率及水解产物都存在一定影响。Volmer 等[66]发现磺胺类和大环内酯类抗生素在 pH=7 的环境下活性较低且水解缓慢，而 β-内酰胺类抗生素几乎在任何 pH 条件下降解速率都很快[67]；Paesen 等[68]发现泰乐菌素 A 在酸性条件下可水解成泰乐菌素 B，而在中性和碱性条件下，则可产生泰乐菌素 A 丁间醇醛和一些极性的分解产物[69]。一般情况下，温度越高，化合物水解越快[64]，这是由于化合物的水解过程属于热反应，活化能又主要来源于分子之间的碰撞。Białk-Bielińska 等[70]的实验证明在 pH=4.0 和 70℃ 的条件下，磺胺类药物水解最高的水解速率为 41%，而当环境条件改变为 20℃ 时，水解速率大大减少。

3.2　光降解

PPCPs 在水中发生的光降解，其机理主要就在于分子吸收光能变成激发态从而引发各种反应[71]。光降解可分为直接光解和间接光解过程，具有吸光

表 2　水环境中抗生素类 PPCPs 在地表水、地下水、沉积物、孔隙水、海水、雨水中的检出情况

Table 2　Detection of antibiotic PPCPs in surface water, groundwater, sediment, pore water, seawater and rainwater.

水环境介质	PPCPs 化合物	PPCPs 检出含量（ng/L）	水环境	数据来源
地表水	磺胺甲恶唑	ND~57.76	中国上海市青浦区	[44]
		28.34	中国上海黄浦江	[45]
		＜MDL~934	斯里兰卡	[46]
		0.7~16	意大利米兰	[47]
		77.7(最大浓度)	密西西比河国家河和娱乐河	[13]
	氧氟沙星	114	中国黄河	[42]
		0	中国黄浦江	[45]
	诺氟沙星	152	中国黄河	[42]
		0	中国黄浦江	[45]
	红霉素	34	中国黄河	[42]
		0~722.04	中国天津	[48]
	罗红霉素	53	中国黄河	[42]
		3.63	中国黄浦江	[45]
	四环素	113.89	中国黄浦江	[45]
		0~9.74	天津	[48]
地下水	醋磺胺甲恶唑	ND~91	中国北运河	[49]
	磺胺二甲基嘧啶	ND~969.7	中国北运河	[49]
	磺胺甲恶唑	ND~14.2	中国北运河	[49]
		1110	美国	[50]
		23.40	西班牙	[51]
	磺胺嘧啶	11.62	西班牙	[51]
		29.9	哈尔滨	[52]
	环丙沙星	4~9.68	中国江汉平原	[53]
		0.82	哈尔滨	[52]
	四环素	2.26~9.51	中国江汉平原	[53]
	罗红霉素	1.47~13.8	中国江汉平原	[53]
	诺氟沙星	4.74~52.6	中国江汉平原	[53]
	土霉素	1.1~7.24	中国江汉平原	[53]
	林可霉素	0.32	美国	[50]
沉积物	磺胺甲恶唑	1. 27~688.59	中国上海市青浦区	[44]
		0~11.3	中国太湖	[54]
	磺胺嘧啶	0~0.41	中国太湖	[54]
	土霉素	0~8.73	中国太湖	[54]
	环丙沙星	0~15.33	中国太湖	[54]
	氧氟沙星	0.9~18.27	中国太湖	[54]
	罗红霉素	0.15~3.96	中国太湖	[54]
孔隙水	红霉素	29.9	中国白洋淀	[55]
	林可霉素	20.2	中国白洋淀	[55]
	土霉素	47.8	中国太湖	[56]
	氧氟沙星	33.6	中国太湖	[56]
雨水	环丙沙星	10.3	美国明尼苏达州	[38]
	恩诺沙星	2.97	美国明尼苏达州	[38]
海水	磺胺甲恶唑	42	波罗的海	[57]
		11	希腊爱琴海	[57]
		7.2	意大利威尼斯	[57]
	克拉霉素	14	波罗的海	[57]
		16	希腊爱琴海	[57]
		8.5	意大利威尼斯	[57]

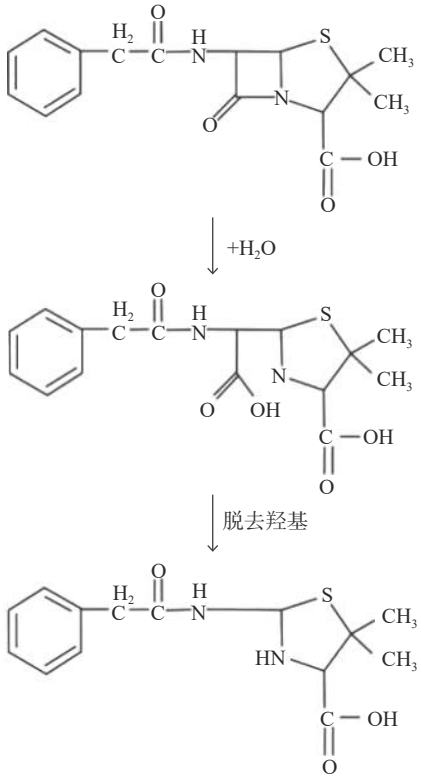


图2　青霉素 G 通过侧链对 β-内酰胺羰基的分子内亲核攻击产生的水解过程(据高雪泉，2016[65] 修改)

Fig. 2　Hydrolysis process resulting from the intramolecular nucleophilic attack of the β-lactam carbonyl group by the side chain of penicillin G. Modified from Gao (2016)[65].

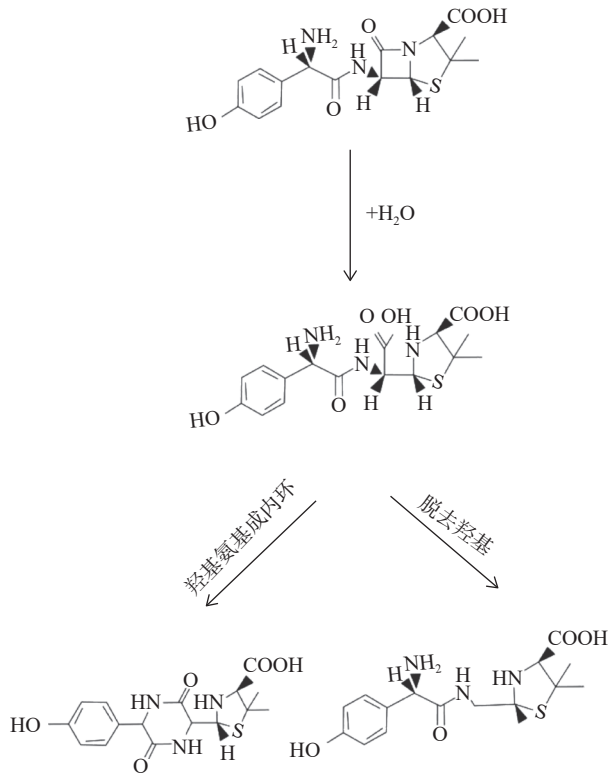


图3　阿莫西林通过侧链对 β-内酰胺羰基的分子内亲核攻击产生的水解过程(据高雪泉[65]，2016 修改)

Fig. 3　Hydrolysis process resulting from the intramolecular nucleophilic attack of the β-lactam carbonyl group by the side chain of amoxicillin. Modified from Gao (2016)[65].

基团的 PPCPs 可吸收光能直接进行降解。如阿替洛尔经过阳光照射后，能够吸收光子达到激发态，激发态分子内部键的断裂或重组从而形成降解产物(图 4[72])；不具备吸光基团的 PPCPs 化合物需要接受其他物质吸收光子获得能量，从而发生间接光降解反应。如阿昔洛韦是加入催化剂吸收光能，发生电子跃迁，生成电子-空穴对，从而对表面污染物进行氧化还原，或氧化吸附的氢氧根，生成强氧化性的氢氧自由基(图 5[13,73])。

影响水环境中 PPCPs 发生光降解的因素有很多，主要包括水的 pH 值、溶解性有机质、共存离子等。通常认为水环境中较高的 pH 值会产生较快的光降解速率，因为许多 PPCPs 的分子中含有酸碱解离基团，在水溶液中容易电离产生多种解离形态，而影响 PPCPs 电离的原因就是溶液 pH 的改变[74]。Yuan 等[75] 发现阿莫西林在 pH=7.5 时的降解速率大于 pH=5 时；廖伟等[76] 也发现在一定时间内三氯生光降解速率随着初始 pH 的增加呈现增加的趋势。共存离子的存在会对污染物的光降解产生或促进或抑制的双重作用。DOM 既可通过光敏化污染物产生 ROS 促进其光解，也可淬灭 ROS 或激发态分子抑制其光解[77]。崔馨[78] 研究发现，pH 为 7.0 时，加入 Ca(Ⅱ)、Mg(Ⅱ)、Zn(Ⅱ)和 Cu(Ⅱ)能加快土霉素的光降解速率，而且离子的含量越多，土霉素的光解速率越大。

3.3　生物降解

生物降解是指微生物在好氧或缺氧条件下，通过一系列生化反应改变 PPCPs 的化学结构，最终达到去除的目的。目前，关于 PPCPs 的生物降解研究主要针对污水处理系统、天然地表水和实验室模拟系统 3 个方面[79]。对于污水处理厂主要是通过二级处理的生物降解去除 PPCPs[80]。

如酮基布洛芬的生物降解，是在好氧条件下被部分矿化，沿着联苯、联苯醚的途径进行(图 6[80])；对于咖啡因的生物降解，主要是通过脱甲基过程来进行(图 7[81])。

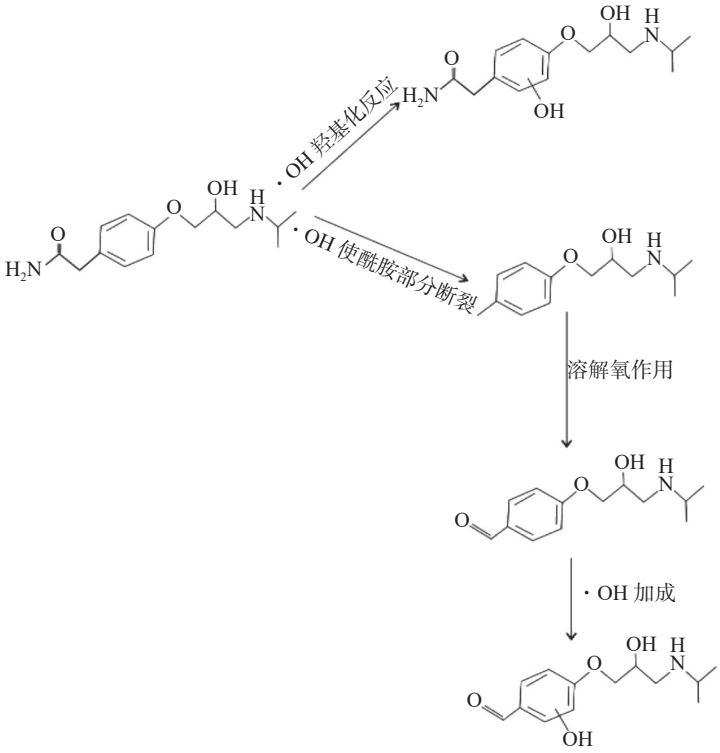


图4　阿替洛尔直接吸收光能引起内部键断裂进行的光降解过程(据季跃飞，2014[72] 修改)

Fig. 4　Photodegradation process in which atenolol directly absorbs light energy and causes internal bond breakage. Modified from Ji (2014)[72].

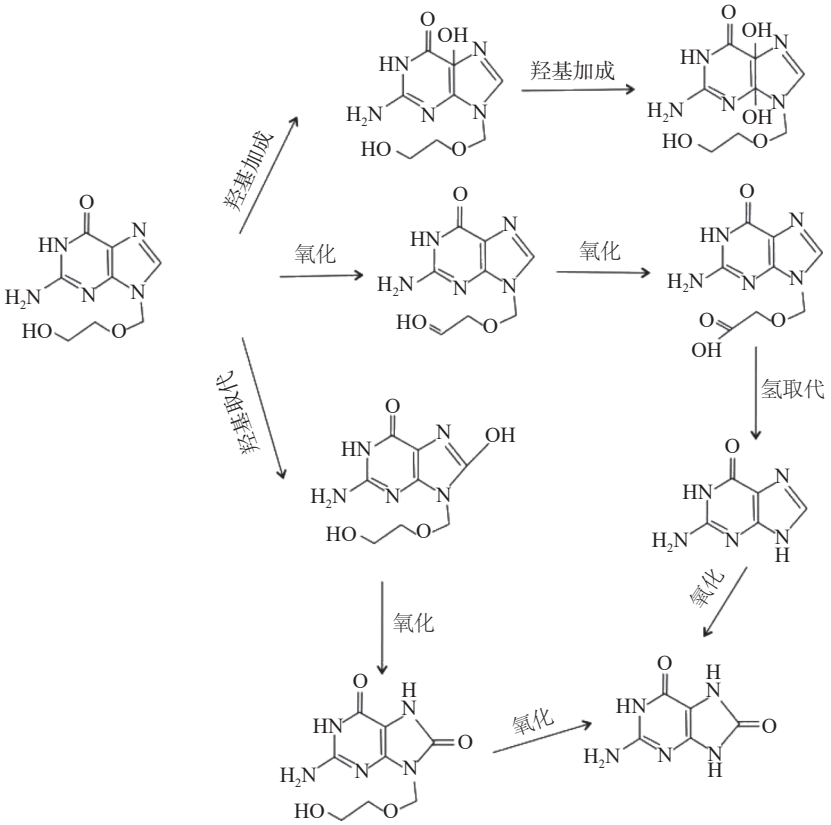


图5　阿昔洛韦通过加入催化剂获得能量形成电子跃迁产生间接光降解的过程(据 Elliott 等，2017[13]；安继斌，2011[73] 修改)

Fig. 5　The process of indirect photodegradation of acyclovir by obtaining energy through the addition of catalysts to form electronic transition. Modified from Elliott, et al (2017)[13] and An (2011)[73].

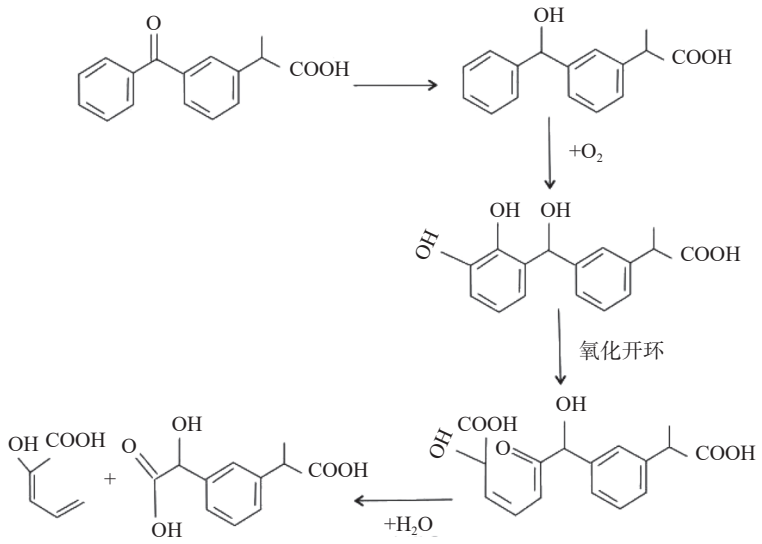


图6　酮基布洛芬在好氧条件下矿化的生物降解过程(据 Quintana 等，2015[80] 修改)

Fig. 6　Biodegradation of ketoibuprofen mineralized under aerobic conditions. Modified from Quintana, et al (2015)[80].

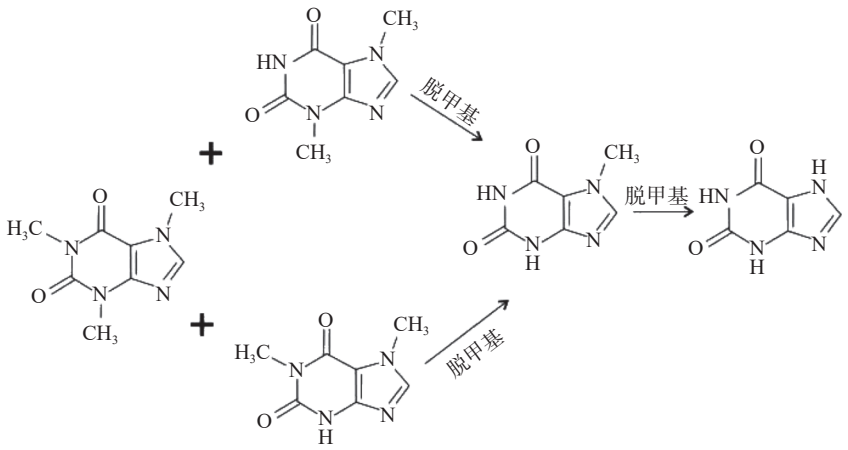


图7　咖啡因通过脱甲基过程的生物降解过程(据杨雪莹等，2019[81] 修改)

Fig. 7　Biodegradation of caffeine through the demethylation process. Modified from Yang, et al (2019)[81].

环境的 pH 值和温度影响微生物对营养物质的吸收、生长和代谢，从而改变微生物的生长生活状态，进而影响生物降解[82]。张欣阳等[83] 研究了 pH 值对降解菌降解四环素的影响，发现当 pH 为 7 时，降解菌对四环素的降解最强。Liao 等[84] 发现当温度达到 45℃ 时，微生物群对磺胺的去除率可达 89.5%，但是在温度降至 5℃ 时，去除率仅为 13%[85]。降解菌株的种类也会对生物降解产生一定影响，del Carmen Molinna 等[86] 通过实验发现沙雷氏菌和假单胞菌可使萘普生彻底降解，而革兰氏阳性菌株对萘普生的降解只有 30%。另外，对于污水处理厂的生物降解，不同生物反应器活性污泥中微生物的多样性、污泥絮凝体的大小也会使 PPCPs 的降解效率有所不同[79]。

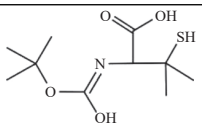
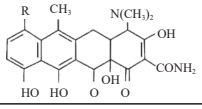
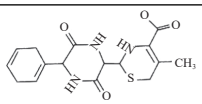
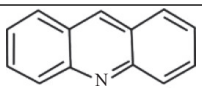
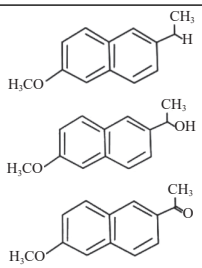
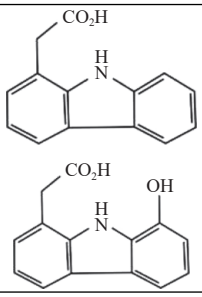
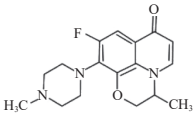
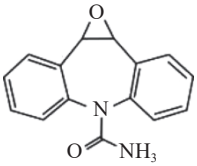
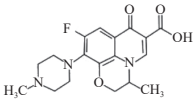
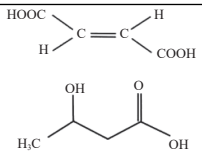
不同 PPCPs 的降解机制及影响因素都会有所差别，pH 和温度是发生降解的主要影响因素。现就主要 PPCPs 的降解情况进行汇总，见表 3。

4　结语及展望

本文对 PPCPs 在地表水、地下水、沉积物、孔隙水、海水、雨水中的含量进行综合分析，自 1976 年 PPCPs 首次在污水处理厂检出后，陆续在全球范围内开始检出。中国作为 PPCPs 使用大国，在钱塘江、珠江、北京等地区的河流中均检测到不低的含量，且以磺胺类抗生素、布洛芬、卡马西平等为主，其中磺胺甲恶唑是环境中分布最广泛且检测次数最多的 PPCPs。另外，在国外地区如西班牙、美国等地

表 3　水环境中 PPCPs 常见化合物的降解类型、影响和因素及降解产物

Table 3　Types, effects, factors, and degradation products of common PPCPs in the water environment.

PPCPs 常见化合物	降解类型	水环境中降解行为影响因素	降解产物	参考文献
青霉素	水降解	金属离子		[87]
四环素	水降解	pH		[69]
头孢拉定	水降解	pH		[88]
卡马西平	光降解	pH, 共存离子		[89]
萘普生	光降解	pH, 温度		[71, 90]
双氯芬酸	光降解	pH=8		[90]
氧氟沙星	生物降解	pH=4.5, 25℃		[91]
卡马西平	生物降解	pH, 温度		[92]
碘普罗胺	生物降解	pH=4.5, 25℃		[91]
双氯芬酸	生物降解	菌株种类		[93]

PPCPs 也有广泛的存在。雨水和海水中都检测出 PPCPs, 且分别以咖啡因和阿特拉津检出最为广泛。与地表水、地下水、沉积物环境相比, 雨水中 PPCPs 含量相对较低。研究发现 PPCPs 检出浓度和分布区

域与人类活动及经济发达程度密切相关，人口密度大、经济发达地区 PPCPs 的含量相对较大。PPCPs 的降解方式主要有水解、光降解和生物降解，不同的 PPCPs 会发生不同的降解行为，同时也会有一种或多种降解方式。总体来说，光降解和生物降解要比水解更为普遍，且光照条件相同时，光降解的效果大于生物降解。对于影响因素，pH 和温度是影响 PPCPs 降解的主要因素，除此之外的共存离子、初始浓度等也会对其产生影响。更为重要的是，不同的降解行为或影响因素会产生不同的降解产物。

未来对于 PPCPs 的研究工作应更多地聚焦在之前研究较少的雨水、海水等水环境，使体系更为完备。且水环境中 PPCPs 含量很低，对检测技术及仪器要求比较严格，现有分析技术和仪器条件需要不断改进，建立更加全面、系统的检测体系。同时，基于目前的研究，主要集中在 PPCPs 自身的迁移转化及毒性效应，对于降解产物的毒性效应等有待进一步研究。应深入开展水环境中 PPCPs 代谢产物的行为、迁移转化及毒性效应研究工作，为水环境污染去除提供依据。

Environmental Levels and Degradation Behavior of Pharmaceuticals and Personal Care Products (PPCPs) in the Water Environment

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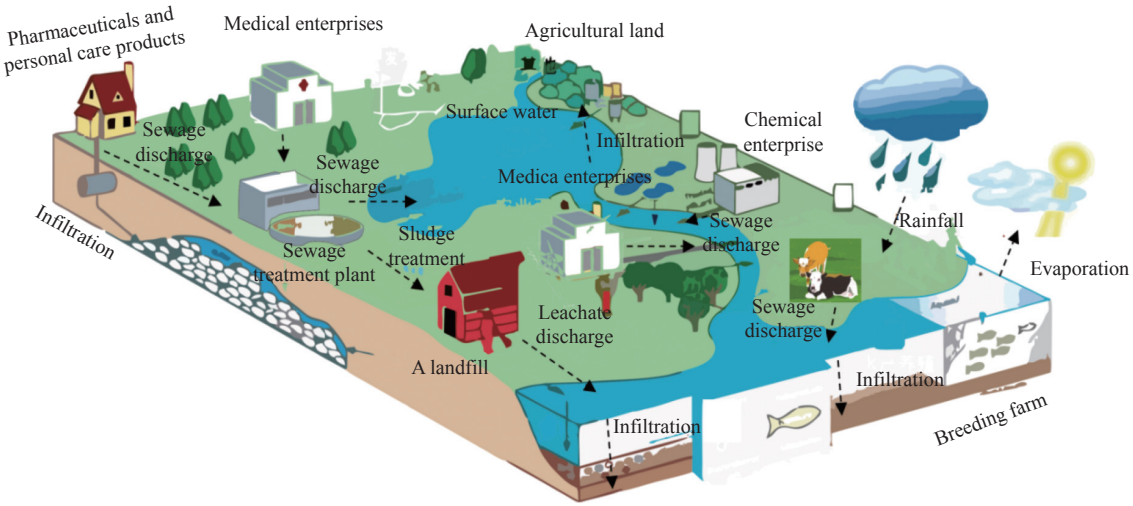
HIGHLIGHTS

(1) PPCPs have been detected in various water environments, among which the detection of PPCPs in surface water is relatively higher.

(2) The hydrolysis, photodegradation and biodegradation of PPCPs are affected by many factors such as pH value and temperature.

(3) Due to the limited technology of sewage treatment plants, photodegradation may be more effective than biodegradation under the same light conditions.



ABSTRACT

Pharmaceuticals and personal care products (PPCPs) are a class of chemicals used by humans for daily life. PPCPs are closely related to people's production and life, and are even used every day worldwide. PPCP-like compounds were first detected in treated wastewater in Kansas City, USA in 1976 (concentrations of 0.8-2μg/L[6]), and subsequently detected in various countries. The mass production and use of PPCPs have led to increasing concentrations in the environment. PPCPs can induce microorganisms to produce resistance genes because of their persistence and bioaccumulation, thus changing the structure and community of microorganisms in the ecosystem. At the same time, they are accumulated at the top of the food chain or food web[17-21], destroying the balance of the ecosystem. In addition, PPCPs also have chronic toxicity, teratogenicity and carcinogenicity. For example, sulfonamides will damage tissues and organs and cause drug resistance of pathogenic bacteria[9]. Synthetic musk interferes with the secretion of hormones and can also lead to asthma, allergies, migraines and other diseases[20]. Long-term use will lead to liver and kidney damage and induce cancer[21], causing irreversible damage to human health.

PPCPs are mainly accumulated in the environment through hospitals, landfills, farms, factory wastewater and domestic sewage, and enter the water environment through various pathways. After the production of PPCPs, some are used by humans, some are directly generated in the production of waste, and some are used by animals in livestock farms. The solid or liquid waste generated in the above three ways will enter the sewage treatment plant or landfill. Then through sewage, landfill leachate directly into the surface water, through further infiltration into the sediment, pore water, groundwater, ocean and other environments, in addition to the surface water through evaporation and precipitation can also return to the water environment. The above environmental behaviors will cause harm to the ecological environment, ecosystem, and humans.

PPCPs exist in surface water, groundwater, sediment, and other environmental media, but the pollution degree varies in different countries. In recent years, a large concentration of PPCPs has been detected in various water environmental media, and sulfonamides, antibiotics, ibuprofen, carbamazepine and DEET are widely distributed in the environment, among which sulfamethoxazole has the highest detection frequency and the highest concentration can reach 1080ng/L[8]. China is the world's largest consumer of drugs, with more than 20000t PPCPs used annually, which have been widely detected in surface water, groundwater, soil and sediments, among which antibiotics transmitted through water bodies are used more[7] than others. In addition, PPCPs are also detected in water environmental media in the United States[50], Europe[57], and Africa[9], and the study found that the concentration of PPCPs is positively correlated with the degree of economic development. In China, the highest concentration of sulfamethoxazole is detected in the sediments of the Qingpu District of Shanghai, with a concentration of 688.59ng/L[44], while the highest concentration of sulfamethoxazole in other countries is detected in groundwater of the United States, with a concentration of 1110ng/L[50]. The concentration of PPCPs in pore water and seawater is relatively low, and caffeine is the most widely detected PPCP in seawater. Some compounds have been detected in rainwater because of their volatility. Atrazine has been reported in Mississippi and at the mouth of the Yangtze River[60-61]. The presence of ofloxacin and ciprofloxacin has also been detected in Minnesota, USA[38]. PPCPs in groundwater are mainly produced through the infiltration of domestic sewage, hospital and aquaculture wastewater, and compounds with greater polarity are more likely to penetrate into groundwater[59]. Antibiotics such as lincomycin and erythromycin have been detected in groundwater in North America, Jianghan Plain of China[53,50] and Harbin[52]. Carbamazepine is one of the most commonly detected drugs in sediments, and it has been reported in the Haihe River and Baiyang Lake[55], with the highest concentration of 14.7ng/g, and also in the sediments of the Taihu Lake Basin[54], the concentrations of ciprofloxacin and ofloxacin are relatively high, 15.33ng/g and 18.27ng/g respectively. The ocean is considered by many to be an important sink of pollutants. Studies have found that more

than 20 kinds of antibiotics with concentrations as high as μg/L have been detected in seawater[62]. Among them, caffeine has been widely detected in the Aegean and Baltic Sea. Besides caffeine, sulfamethoxazole and clarithromycin also have a high detection frequency[57]. PPCPs were also detected in pore water and rainwater. The pore water samples of Baiyangdian Lake[55] mainly contain erythromycin and caffeine, but their concentrations are much lower than those of surface water in the same area. In Taihu Lake[56], the concentrations of oxytetracycline and ofloxacin are found, but the concentrations of surface water are lower than those of pore water. Therefore, the different physical and chemical conditions of environmental substrates in different study areas are considered to be the cause. There are relatively few reports of PPCPs in rainwater, and the content of PPCPS is less than 10ng/L.

PPCPs will degrade after entering water, and different degradation processes have their own degradation mechanisms. The degradation behavior of PPCPs in water mainly includes hydrolysis, photodegradation and biodegradation. Hydrolysis is an important way to eliminate or reduce the concentration of PPCPs in a water environment. Its essence is nucleophilic substitution reaction, that is, the nucleophilic group (hydroxide ion or water molecule) attacks the electrophilic group in the compound (RX), and replaces the associated strong electron-withdrawing group (X) with a negative electric tendency. For example, the hydrolysis of penicillin G and amoxicillin is the intramolecular nucleophilic attack of the side chain on the β-lactam carbonyl group, and the C-N bond is broken causing degradation. Degradation can be divided into direct photolysis and indirect photolysis processes. PPCPs with light-absorbing groups can be directly degraded by absorbing light energy. PPCPs without light-absorbing groups need to absorb photons through other substances to obtain energy, so that indirect photodegradation occurs. For example, atenolol is a degradation process that directly absorbs light energy, while acyclovir is an indirect photodegradation process by adding a catalyst. Biodegradation means that microorganisms change the chemical structure of PPCPs through a series of biochemical reactions under aerobic or anoxic conditions, and finally achieve the purpose of removal. At present, studies on the biodegradation of PPCPs mainly focus on three aspects: sewage treatment system, natural surface water and laboratory simulation system[79]. For sewage treatment plants, PPCPs are mainly removed through biodegradation of secondary treatment[80].

The degradation of PPCPs is affected by various factors, among which pH and temperature are the main influencing factors. The study on hydrolysis of PPCPs mainly considers the influence of pH on PPCPs. Different pH and target compounds will have different reactions, which have certain effects on the hydrolysis rate and hydrolysis products. In addition, temperature will also affect hydrolysis. In general, the higher the temperature, the faster the hydrolysis of a compound[61], because the hydrolysis process of a compound is a thermal reaction, and the activation energy mainly comes from the collision between molecules. The mechanism of photodegradation of PPCPs in water mainly lies in the molecular absorption of light energy into an excited state, which triggers various reactions[71]. There are many factors affecting the photodegradation of PPCPs in a water environment, mainly including pH of water and co-existing ions. It is generally believed that the higher pH in a water environment, the faster the photodegradation rate. Because many PPCP molecules contain acid-base dissociative groups, they are easily ionized in aqueous solution to produce a variety of dissociative forms, and the reason for affecting the ionization of PPCPs is the change of solution pH[74]. The presence of co-existing ions can either promote or inhibit the photodegradation of pollutants. The pH and temperature of the environment will affect the absorption, growth and metabolism of nutrients by microorganisms, thus changing the growth and living state of microorganisms, and then affecting biodegradation[82]. In addition, different compounds have different sensitivity to pH and temperature in the process of biodegradation. Also, the types of degraded strains have a certain impact on degradation. In general, photodegradation and biodegradation are more common than hydrolysis. In surface water, many PPCPs have avoided the strict biodegradation environment of wastewater treatment, and photochemistry may have a greater effect than the biodegradation under sunlight, in which antibiotics are mainly photodegraded in the water

environment; ibuprofen, iopromide and caffeine are more prone to biodegradation; esters and amides are the most common functional groups that are easily hydrolyzed in PPCPs[63], and tetracycline can undergo hydrolysis reactions due to adsorption into sediments. The factors affecting the degradation of PPCPs include pH, temperature, co-existing ions and dissolved organic matter, among which pH and temperature are the main factors affecting the degradation. Exploring the fate of PPCPs in the environment is the key to studying their distribution and environmental level, so it is necessary to analyze the degradation mode of PPCPs in a water environment to help further understand the degradation principle and behavior of PPCPs.

Future research on PPCPs should be more in-depth and detailed. More emphasis will be placed on the water environment such as rain and sea water, which has been studied less before, to make the system more complete. The current research mainly focuses on the migration, transformation and toxic effects of PPCPs, and the toxic effects of degradation products need to be studied further. It is necessary to study the behavior, migration, transformation and toxic effects of PPCPs metabolites in the water environment, so as to provide basis for water environment pollution removal. In addition, the content of PPCPs in the water environment is very low, and the testing technology and instrument requirements are relatively strict. The existing analysis technology and instrument conditions need to be continuously improved to establish a more comprehensive and systematic testing system.

KEY WORDS: water environment; pharmaceuticals and personal care products (PPCPs); concentration level; degradation behavior; influencing factors

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