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水体中药物残留物的分布、检测和毒性评价

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摘要:针对水体新兴微污染物之一的药物残留物,介绍了其在世界主要国家水体中的分布情况,总结了分析检测方法和生态毒性评价方面的研究进展,并提出了导致目前污水处理厂药物残留物处理效率较低的 2 个原因:一是在立法层面上,现行的污染物排放标准没有针对药物残留物的明确要求;二是在技术层面上,适用高级水处理技术的发展还不完善。基于预防性原则,建议对污水处理厂进行必要的升级改造,提高传统污水处理厂的处理效果,阻断药物残留物进入自然水体的途径。

关键词:新兴微污染物;药物残留物;生态毒性评价
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Occurrence, Detection and Toxicity Assessment of Pharmaceutical Residues in Water and Wastewater

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Abstract: This paper collects data from worldwide research groups and aims to critically review and analyse the advances of knowledge development in the area of occurrence, detection, and toxicity assessment of pharmaceutical residues from around the globe and to recommend the research needs in this research area. In addition, this paper puts forward suggestions regarding future research needs and challenges in terms of toxicity assessment and relevant legislation. To date, no regulatory guidelines for WWTPs regarding the discharging limits of pharmaceuticals have been established, which may be caused by two reasons. Firstly, the long-term and chronic influence of drugs in the environment lacks scientific and firm conclusion. Secondly, the emission limit of these drugs is difficult to decide, which not only depends on their harm to the environment but also the economic conditions of available treatment techniques. However, based on the precautionary principle, to prevent the entry of pharmaceutical compounds into the aquatic environment via WWTPs is necessary.

Key words: emerging micropollutants; pharmaceutical residues; toxicity assessment

自 20 世纪 90 年代以来,随着环境技术的进步和人们环保意识的增强,水体新兴微污染物(Emerging micropollutants)在自然环境中的存在越来越受到科研人员的重视[1-2]。水体新兴微污染物种类繁多,药物残留物(Pharmaceutical residues)是其中主要的一类。尽管药物残留物在自然水体中的质量浓度很低,一般为纳克或微克级,但是它们在自然界的迁移转化仍然可能对生态环境和人类健康造成严重的危害。因此,对于药物残留物在自然水体的存在需要引起人们足够的重视。一方

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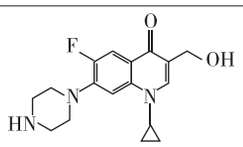
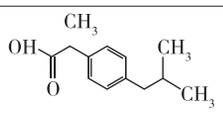
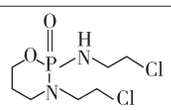
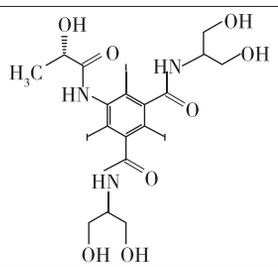
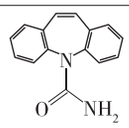
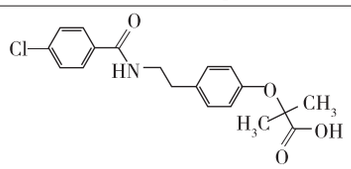
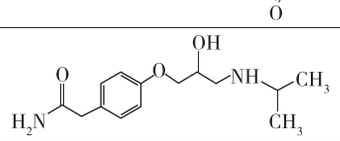
面对水体中药物残留物的种类以及在世界范围内的分布情况进行介绍,同时,综述了药物残留物的分析检测方法以及药物残留物的生态毒性评价方面的研究进展,并对相关立法方面的工作也进行了介绍。期望能够帮助人们更好地理解药物残留物在水体中的分布和迁移转化规律,提高对这种水体新兴微污染物的认识水平。

1 水体中药物残留物的种类和分布情况

近年来,由于抗生素、消炎止痛药物、β受体阻断剂以及X射线造影剂的广泛使用,在水体中不断检出各种药物残留物,目前已有数十种药物残留物在多种水体样品中被检出,包括污水处理厂的进出水、地表水、地下水,甚至饮用水。表1列出了常见的水体中检出的药物残留物的种类,表2则给出了世界范围内药物残留物在水体中被检出的情况以及质量浓度水平。

表1 水体中检出的常见药物的分类以及代表性药物的分子结构

Table 1 List of common pharmaceutical residues

药物种类	代表性药物	典型药物的分子结构
抗生素	阿莫西林(Amoxicillin),环丙沙星(Ciprofloxacin),克拉霉素(Clarithromycin)	
消炎止痛药	布洛芬(Ibuprofen),双氯芬酸(Diclofenac),萘普生(Naproxen)	
细胞抑制剂	环磷酰胺(Cyclophosphamide),异环磷酰胺(Ifosfamide)	
X射线造影剂	泛影酸(Diatrizoate),碘帕醇(Iopamidol),碘普罗胺(Iopromide)	
抗痉挛药	卡马西平(Carbamazepin)	
调血脂药	苯扎贝特(Bezafibrate)	
β受体阻断剂	阿替洛尔(Atenolol)	

在表1所列出的药物种类中,消炎止痛类药物是检出最频繁的一类,其最高检出质量浓度甚至达到数十μg/L(例如日本)。此外,数种消炎药(例如布洛芬、萘普生以及双氯芬酸)在地表水中的检出质量浓度也都达到了数百ng/L的级别。除了消炎药,卡马西平和苯扎贝特也是检出质量浓度较高的药物之一。

表 2 世界范围内药物残留物的检出情况

Table 2 The worldwide occurrence of pharmaceuticals in the aquatic environment

国家	样品	检出药品数目	浓度最高的 3 种药品				参考文献
			名称	平均检出质量浓度 (ng/L)			
				进水	出水	其他	
英国	3 个污水处理厂的进出水;1 条下游河流	5	卡马西平	1 237～1 833	637～950	150～350	[7]
			普萘洛尔	334～1 090	62～135	25～60	
			双氯芬酸	397～981	78～176	20～50	
	5 个污水处理厂的进出水;1 条下游河流	10	布洛芬	—	4 201	1 105	[8]
			双氯芬酸	—	599	154	
			甲灭酸	—	273	86	
德国	49 个污水处理厂出水	25	苯扎贝特	—	2 200	350	[9]
			卡马西平	—	2 100	250	
			双氯芬酸	—	810	150	
	105 个水井	8	泛影酸	—	—	1 100	[10]
			卡马西平	—	—	900	
			磺胺甲恶唑	—	—	410	
加拿大	1 条河流	14	金霉素	—	—	192	[11]
			莫能菌素	—	—	44	
			强力霉素	—	—	7.8	
	8 个污水处理厂出水	14	磺胺甲恶唑	—	243	—	[12]
			四环素	—	151	—	
			红霉素	—	80	—	
美国	139 条地表水	41	咖啡因	—	—	81～100	[13]
			甲氧苄氨嘧啶	—	—	13～150	
			红霉素	—	—	100	
	19 个饮用水水源	15	氨甲丙二酯	8.2～73	5.7～42	5.2～40	[14]
			苯妥英	5.1～29	6.2～19	3.6～16	
			卡马西平	4.1～51	6～18	6.8～10	
中国	3 条河流	7	水杨酸	—	—	15.6～79.2	[15]
			布洛芬	—	—	7.1～75.2	
			双氯芬酸	—	—	4.6～52.4	
	8 个污水处理厂进出水	14	氧氟沙星	440～3 100	150～1 200	—	[16]
			诺氟沙星	51～310	9.4～130	—	
			磺胺嘧啶	380～2 000	120～560	—	
日本	5 个污水	17	阿司匹林	400～20 000	30～120	—	[17]
			避蚊胺	20～2 000	15～900	—	
			克罗米通	400～2 000	200～1 000	—	

污水处理厂是药物残留物进入自然水体的一个重要环节。造成这种局面的主要原因在于大部分药物残留物都超出了传统污水处理工艺的处理能力。例如在意大利,6 个采用活性污泥工艺的污水处理厂对卡马西平、克拉霉素、红霉素等药物残留物没有任何去除效果[3]。此外,虽然某些药物残留物能够被污水处理厂部分去除,例如布洛芬和萘普生,但是它们在出水中的检出质量浓度仍然很高[4]。污泥吸附被认为是这些药物残留物部分去除的主要原因[5-6]。

2 环境中痕量药物残留物的分析检测技术

可靠的污染物检测技术是了解药物残留物在水体中存在和自然转化的关键。药物残留物在水体中是微量存在的,因此需要合适的样品预处理技术和具有较高灵敏度的检测仪器。

药物残留物水样的预处理和分析检测是一个非常耗时耗力的过程。固相萃取技术(Solid phase ex-

traction，SPE）是最经常使用的水样预处理方法[18]。SPE操作过程简单，并且具有较高的样品回收率。样品预处理的目的主要有以下2点：①去除或部分去除共存物质的干扰；②富集水样中的痕量化合物，提高其在检测仪器中的灵敏度。目前，Oasis HLB，Strata-X和Isolute ENV+是被频繁采用的固相萃取柱[19-21]。药物的回收率取决于SPE吸附剂和药物本身的物理化学性质。例如，如果化合物的K_{ow}值<-1.0，则其在硅系吸附剂或聚合物吸附剂上的吸附能力较弱；而如果化合物的$K_{ow}>1.0$，其在这些吸附剂上则具有较好的吸附效果[22]。水样中的共存有机物对SPE的萃取效果同样有干扰，例如天然有机物。水样中的共存有机物还是干扰后续仪器检测的一个重要因素。通过调节萃取过程中的溶液pH可以改变目标污染物的存在形态，同时通过选用合适的洗涤溶剂，可以减少共存物质的干扰。此外，采样误差和不合理的实验设计都是影响样品检测结果准确性的重要因素[23]。因此，建立一个被广泛认可的样品采集和分析方法对于分析新兴微污染物的存在和演化很有必要。

固相萃取之后，萃取液通常通过气质联用仪（GC-MS/MS）或者液质联用仪（LC-MS/MS）进行分析检测。药物大部分都是非挥发性化合物[24]，因而LC-MS/MS更经常被用来分析检测该类样品。

3 生态毒性评价方面的进展

对药物残留物进行生态毒理学实验可以帮助人们了解水体新兴微污染物对水生态系统和人类健康的潜在危害性。近年来科研人员已在此方面做了大量的工作[15, 25-29]，其中，药物在环境中的预测浓度（Predicted environmental concentrations，PEC）与其对环境无影响的预测浓度（Predicted no-effect concentration，PNEC）的比值PEC/PNEC，可以被用来评估某一种药物残留物对环境危害作用的大小[30]。如果PEC/PNEC>1，意味着这种药物残留物对人体具有潜在的危害作用。PNEC的数值可以通过对某些生物的生态毒理实验来获得[31-33]。尽管有一些关于药物残留物无害的报道[26, 34]，但是，接触药物残留物的长期和慢性作用仍然不能被忽视，比如某些药物对生物内分泌系统的干扰[35-36]。而且，布洛芬和萘普生在污水处理厂下游的野生鱼类的检出，更说明了这些微污染物具有生物累积效应，因而对食物链也存在潜在的影响[37]。

4 结 论

药物残留物对生态系统和人类健康具有潜在的危害，目前已经有数十种药物残留物在世界范围内的各种水体中被检出，其质量浓度范围在数十ng/L至数百μg/L。传统污水处理工艺对痕量药物残留物的去除效果有限，因此，采用新型污水处理工艺对阻断药物残留物进入自然水体意义重大。到目前为止，对于提高污水处理厂的出水标准，尤其是增加对新兴水体微污染物的检出要求，还没有实质性进展。其原因主要有两方面：一是对于接触这些药物残留物的长期影响缺乏有力的科学依据；二是对于这些新兴水体微污染物的排放标准很难确定。但是基于预防性原则，对污水处理厂进行升级改造，提高传统污水处理厂的处理效果，阻断药物残留物进入自然水体的途径，是非常必要的。

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