

水环境中微塑料的研究现状

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摘要

近年来, 微塑料作为一种新型污染物已成为各国政府和公众关注的热点问题。由于其体积小、比表面积大, 微塑料易成为各种有机污染物的载体, 进而通过食物链威胁人类健康。从微塑料的来源、微塑料富集微生物和动植物所引发的生态效应、微塑料富集多种污染物所引发的联合毒性效应等方面介绍了微塑料对水环境系统的危害。综述了现阶段水环境中微塑料的研究进展, 包括海洋环境、淡水环境以及污水处理厂, 进而提出微塑料领域亟待解决的问题, 以便于进来准确评估微塑料的环境风险。

关键词

微塑料, 水环境, 毒理效应, 生态效应

Research Status of Microplastics in the Water Environment

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Abstract

In recent years, as a new type of pollutant, microplastics have become a hot issue of concern to

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governments and the public. Due to its small size and large specific surface area, MPs are likely to become carriers of various toxins, which in turn threaten human health through the food chain. From the sources of microplastics, the ecological effects caused by the enrichment of micro-plastics in microorganisms, animals and plants, and the combined toxicity effects caused by the enrichment of micro-plastics in multiple pollutants, the harm of microplastics to the water environment system is introduced. The current research progress of microplastics in water environment is reviewed, including marine environment, freshwater environment and sewage treatment plants. Furthermore, the problems that need to be solved in the field of microplastics are put forward so as to accurately assess the environmental risks of microplastics.

Keywords

Microplastics, Water Environment, Toxicological Effect, Ecological Effect

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1. 引言

伴随人们生活节奏的加快,社会生活正向便利化、卫生化发展。为了顺应这种需求,一次性泡沫塑料饭盒、塑料袋、筷子、水杯等开始频繁地进入人们的日常生活。这些使用方便、价格低廉的包装材料的出现给人们的生活带来了诸多便利。但另一方面,这些包装材料在使用后往往被随手丢弃,造成极大环境危害。近年来,由于其在自然环境中的广泛存在,微塑料开始受到社会各界的广泛关注。微塑料在海洋[1] [2],淡水[3] [4],沉积物[3] [5]和陆地环境[6] [7]等自然环境中被发现,甚至在极地地区[8]。最近的研究表明,污水处理厂的出水是微塑料的重要来源[9] [10]。大量的微塑料通过污水处理厂进入水生环境中,并且通过食物链的方式进入人体,威胁人类生命健康。目前,国内外对微塑料的研究大部分集中于海洋环境,对淡水环境中的微塑料的研究相对比较匮乏。因此,对水环境中微塑料的研究现状进行梳理有助于我们更好地理解微塑料的环境影响。

2. 微塑料概述

2.1. 微塑料的定义与分类

微塑料是一种尺寸小于 5 mm 的塑料颗粒和碎片[11]。微塑料可以分为初生微塑料和次生微塑料两大类。初生微塑料是指经过河流、污水处理厂等而排入水环境中的塑料颗粒工业产品,如化妆品等含有的微塑料颗粒或作为工业原料的塑料颗粒和树脂颗粒[12]。这些微塑料可以通过河流,污水处理厂排放,风和地表径流进入淡水和海水环境。次生微塑料是由大型塑料垃圾经过物理、化学和生物相互作用过程造成分裂和体积减小而成的塑料颗粒[13]。次生微塑料的来源包括渔网,工业树脂颗粒,家居用品和其他废弃的塑料碎片[14]。值得注意的是,发现大多数微塑料是次生微塑料,并且随着不同来源的塑料碎片输入量的增加,水中的丰度也会增加,从而导致次生微塑料不断转化。当暴露在环境中时,微塑料更易分解为纳米塑料,而纳米塑料可能具有更高的环境风险。

2.2. 微塑料的来源

微塑料的来源陆地和海洋两个领域[15]。由于海洋中商业捕鱼、船只和其他活动,海洋来源仅占海洋

环境中塑料碎片总量的 20% [1]。陆地来源的微塑料占据总量的 80%，陆地来源主要是个人护理产品、污水处理厂出水、不当处置的塑料和垃圾填埋场的渗滤液等等[16]。一旦将陆地微塑料释放到天然水系统中，大部分将通过河流运到海洋，而其余的将留存在淡水环境中，包括偏远的高山、湖泊等孤立的水系统。

当大型塑料进入海洋环境中，就会开始发生降解。降解过程是一种大大降低聚合物平均分子量的化学过程。由于塑料的机械特性取决于其平均分子量，因此任何明显的降解程度都不可避免地会使材料变弱。大量被降解的塑料变得很脆，在处理时会分解成粉状碎片。

微塑料的降解过程根据机理不同分为：生物降解、光降解、热氧化降解(适合的温度、速度缓慢)、热降解(高温下)、水解[1]。当塑料聚合物暴露在海洋环境中，太阳光中的紫外线辐射引发光氧化降解。一旦启动，聚合物在一段时间内开始热氧化降解，而无需进一步暴露于紫外线辐射。只要环境中有氧气，自动催化降解反应就可以进行。与光诱导氧化相比，其他类型的降解过程要慢几个数量级。尽管包括塑料在内的所有生物材料都会在海洋环境中生物降解，但与光诱导的塑料氧化降解相比，即使在底栖沉积物中，该过程的速度也要慢几个数量级[1]。

综上，尽管不同降解过程降解效率不同，但是塑料在海洋环境中仍会被分解为微塑料，甚至纳米级塑料，从而导致海洋环境中微塑料浓度急剧上升。

3. 微塑料研究现状

3.1. 微塑料在海洋环境中的研究现状

20世纪70年代初，研究人员首次在海洋环境中发现小型塑料颗粒[17] [18]。自此之后，微塑料研究的目标是多种多样的。由表1可以看出，大多数研究致力于微塑料在海洋环境中的空间分布(丰度，质量，类型和大小) [19] [20] [21]。部分研究的目的是证实实验地点是否存在微塑料[22]，比较不同的采样和分类方法[23]，并估算微塑料与塑料或浮游动物的比例[24]。少数研究分析了微塑料丰度[25]，分散和降解速率随时间变化[26]。

近年来，微塑料在海洋环境中的生态影响受到越来越多地关注[27] [28]。微塑料可以作为持久性有机污染物和重金属的载体。当海洋生物摄食后，不仅对海洋生物的健康造成影响，而且通过食物链中对人类健康造成威胁。

Table 1. Classes of plastics that are commonly encountered in the marine environment

表 1. 海洋环境中微塑料研究的主要目标

目标	沉积物(44)	表层水(30)	水柱(7)	合计 ^a (68)
方法	2	2	—	3
有/无	4	2	1	5
空间分布	25	22	5	45
时间变化	3	6	1	9
分散过程	1	—	—	1
物理性质和破碎过程	4	2	—	6
污染物	12	3	1	13

^a-某些研究有多个目标，因此总和可能会超出每列中的研究总数。

3.2. 微塑料在淡水环境中的研究现状

与海洋环境相比，淡水环境中微塑料的研究有限[29]，并且分布高度不均一[30]。表2总结了有关天然淡水中微塑料含量的一些相关研究。在过去的几年中，研究人员已经在各大洲各类淡水系统中发现微

塑料。例如: 洛杉矶盆地[31], 圣劳伦斯河[32], 五大湖[33] [34], 奥地利多瑙河[35], 莱茵河[36]以及中国长江[3]。淡水系统中微塑料的丰度变化很大, 从几乎没有到每立方米几百万个。这种重大差异是由采样位置, 人类活动, 固有自然条件和采样方法等关键因素导致的[14]。

Table 2. Studies on microplastics contamination in natural fresh water systems**表 2.** 天然水体中微塑料的研究

地理位置	平均含量 ^a	最大含量 ^a	文献
洛杉矶河, 圣盖博河, 土狼溪	—	$1.29 \times 10^4 \text{ p/m}^3$	Moore 等人[31]
奥地利多瑙河	0.317 p/m^3	141.7 p/m^3	Lechner 等人[35]
莱茵河	$8.93 \times 10^5 \text{ p/km}^2$	$3.9 \times 10^6 \text{ p/km}^2$	Mani 等人[39]
荷兰河三角洲和阿姆斯特丹运河	$1 \times 10^5 \text{ p/m}^3$	$1.87 \times 10^5 \text{ p/m}^3$	Leslie 等人[40]
大巴黎	30 p/m^3	106 p/m^3	Dris 等人[41]
中国三峡大坝	$8.47 \times 10^6 \text{ p/km}^2$	$1.36 \times 10^7 \text{ p/km}^2$	Zhang 等人[42]
长江入海口	$4.14 \times 10^3 \text{ p/m}^3$	$1.02 \times 10^4 \text{ p/m}^3$	Zhao 等人[43]
中国太湖	—	$6.8 \times 10^6 \text{ p/km}^2$	Su 等人[4]
美国 29 个大湖支流	4.2 p/m^3	32 p/m^3	Baldwin 等人[44]

a—数据经过标准化以确保一致性;

b—湿式过氧化物氧化。

陆地上存在很多微塑料的来源。其中, 污水处理厂是微塑料的主要来源之一。尽管污水处理厂可以去除高达 95% 的微塑料, 而第三级处理可以去除 90% 以上的直径大于 10 毫米的细小颗粒, 但是仍有大量的微塑料通过污水处理厂排入天然水中。**表 3** 列出了污水处理厂中微塑料研究的主要结果。Mason 等人[37]研究了 17 个污水处理厂的污水样本, 预测美国市政污水处理厂的微塑料平均排放量为每天 130 亿片。Cheung 和 Fok [38]估计中国大陆每年向水生环境排放 209.7 万亿微塑料(306.9 吨), 其中 80% 以上来自污水处理厂的废水的排放。由于全球已排放大量已处理和未处理废水, 并且仅仅处理了 60% 的市政废水, 大量的微塑料将通过污水处理厂的排放进入环境。此外, 地表径流, 大气沉降和废物处理等其他来源也导致流入水环境的微塑料流量增加。

Table 3. Microplastics detected in waste water treatment plants**表 3.** 污水处理厂中微塑料的研究

地理位置	平均丰度 ^a	最大丰度 ^a	文献
美国 17 个污水厂出水	50 p/m^3	159 p/m^3	Mason 等人[37]
美国东湾市政公用事业区的污水处理厂	—	169 p/m^3	Dyachenko 等人[45]
Violinmaking 污水处理厂, 芬兰	—	进水: $9 \times 10^5 \text{ p/m}^3$ 出水: $3.5 \times 10^3 \text{ p/m}^3$	Talvitie 等人[46]
污水处理厂, 克莱德河, 格拉斯哥	进水: $1.57 \times 10^4 \text{ p/m}^3$ 出水: 250 p/m^3	—	Murphy 等人[10]
德国下萨克森州 12 个污水处理厂的出水	—	$9 \times 10^3 \text{ p/m}^3$	Mintenig 等人[47]
圣彼得堡污水处理厂	进水: $1.6 \times 10^5 \text{ p/m}^{3b}$ 出水: $7 \times 10^3 \text{ p/m}^{3b}$	—	Talvitie [48]
荷兰 7 个污水处理厂	进水: $7.3 \times 10^4 \text{ p/m}^3$ 出水: $5.2 \times 10^4 \text{ p/m}^3$	进水: $5.66 \times 10^5 \text{ p/m}^3$ 出水: $9.4 \times 10^4 \text{ p/m}^3$	Leslie 等人[40]

a—数据经过标准化以确保一致性;

b—湿式过氧化物氧化。

2017年9月,一家非营利性新闻机构Orb Media发布了一份报告,声称饮用水中存在微塑料。这项研究对五大洲的159个饮用水样本进行了测试,发现其中83%的样本受到微塑料碎片污染。由于微塑料可以直接进入人体,这些发现引发了公众对饮用水和食品安全的担忧。

4. 微塑料的环境影响

目前,人们对微塑料的关注集中于对生物和人类的潜在危害。微塑料对自然环境的影响大致分为物理、化学和生物影响。这些影响的发现集中于海洋环境,为淡水环境提供一定的参考。

4.1. 物理影响

物理影响主要包括缠绕和摄入效应。Laist [49]进行的研究表明,有200多种海洋物种受到塑料碎片的缠结和摄入。尽管尚不确定物理作用会对生物产生多大影响,但是与摄入效应相比较,我们容易发现与大型动物有关的缠绕效应。缠绕可能对水生生物造成严重影响;它们甚至可能因溺水,窒息或饥饿而致死[50]。目前没有关于淡水体内缠绕行为发生的报道。而海洋生物缠绕行为的发生为淡水环境提供了明确的指示。

4.2. 化学影响

化学影响主要体现在微塑料的成分和特性。首先,塑料是一类高分子聚合物,会引起某些健康影响。例如,对生物降解有抗性的聚苯乙烯(PS)可以在鱼的胃中积聚[17],并通过血液循环转移。在其生产工程中会添加各种添加剂,以改善物理性能,例如颜色,阻燃性和硬度。最常见的添加剂是增塑剂,用于改善可塑性或粘度。例如,聚氯乙烯(PVC)必须具有增塑剂,例如邻苯二甲酸酯和双酚A,以使热降解和光降解最小化[15]。其他添加剂包括着色剂和阻燃剂,这些化学物质会通过生物累积过程在人体中积累,其中一些众所周知是破坏内分泌的化合物。有研究证实,人体中存在双酚A,多溴联苯醚,四溴双酚A和邻苯二甲酸酯等添加剂[51]。此外,某些重金属化合物(例如铬,镉和铅)通常用于生产着色剂、稳定剂和增塑剂[52],它们可以从塑料碎片中释放到水系统中,并进一步进入食物链,从而导致生物体内毒素的生物蓄积。其次,微塑料是疏水性有机污染物的载体[53] [54] [55]。微塑料具有较大的比表面积和疏水性,导致其表面吸附的污染物的能力较强[56]。环境中已经存在大量的多氯联苯(PCBs)、二氯二苯基三氯乙烷(DDT)等持久性有机污染物,当微塑料和这些污染物相遇时,正好聚集形成一个有机污染球体。众所周知,PCBs具有致癌性,致突变性和致畸性[15]。DDT可以导致不良的神经系统影响和免疫缺陷[57]。此外,微塑料还可以吸附水中的润滑油和重金属[58] [59]。在被摄入后,吸附在微塑料表面的污染物会在低pH和中性温度条件下释放出来,对生物和人类造成健康威胁。

4.3. 生物影响

生物影响主要表现两个方面。第一个是在地理位置上转移微生物的能力[60],微生物可以迅速在微塑料的表面聚集,并随着微塑料的移动而移动[61]。McCormick等人[62]对伊利诺伊州芝加哥市一条河流中收集的微塑料进行了高通量测序分析。他们发现一些附属的类群是可塑性分解的生物和病原体。研究结果表明,微塑料可以在水生态系统中转移细菌。第二个附着在微塑料表面上的生物膜引起的塑料性质发生变化。首先,微塑料的密度会增加[63],使较轻的微塑料沉入水底和底栖地带。而且生物膜可以改变微塑料的表面性质,并使其表面的疏水性降低[64]。这些发现可能为有关持久性有机污染物吸附的研究提供一些思路。附着的生物膜是否能够增强或减弱微塑料与水污染物之间的相互作用仍是未知的。

5. 结论与展望

目前,国内外对微塑料的研究主要集中于海洋环境中,但对淡水环境中微塑料的研究呈逐年增加的

趋势。微塑料污染及其生态效应已成为全球环境研究的热点。虽然已有学者在微塑料的样品采集、预处理、定量和定性分析方面做了广泛的研究, 但其毒性及生态效应等问题需要解决。总体而言, 环境样品中微塑料分析在以下三个方面需要加强和完善:

① 建立微塑料的样品采集和预处理标准方法。由于采样方法不同, 很多研究结果浓度单位表示截然不同, 难以横向比较不同地区的微塑料污染程度。另外, 不同分析方法在样品预处理过程的回收率亦有所差异, 导致相同样品以不同方法分析获得的结果偏差较大。

② 目前微塑料分析技术包括 SEM、Pyr-GC-MS、FT-IR 等, 但这些方法只能分析一种或几种参数。针对上述方法多具有破坏性, 环境样品中微塑料含量有限的现状, 开发复杂基地的低样品量、多参数分析方法迫在眉睫。

③ POPs、多环芳烃、农药等有机污染物易富集在微塑料表面, 而其复合毒理效应尚可未知。同时微塑料类型、成分、粒径大小以及其表面结合痕量污染物的影响因素, 研发微塑料结合其他痕量污染物后的测定方法未来会成为微塑料分析方法的研究方向。

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