

环境中的微塑料:赋存、检测及其危害

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摘要:近年来,由个人护理品及废旧塑料直接或间接产生的微塑料不断地在各种环境介质中被检出,且微塑料会对生态系统产生各种危害,因此对微塑料的研究受到越来越广泛的关注。阐述了微塑料在水体、沉积物、沙滩和生物体中的赋存情况,介绍了微塑料的采集与分离方法,以及定性定量分析方法。指出微塑料对环境及生物体产生的危害,提出现阶段研究存在的主要问题,并对今后的研究方向进行了展望。

关键词:微塑料;赋存;检测方法;环境危害

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Microplastics in the Environment: Occurrence, Detection and Harm

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Abstract: In recent years, microplastics, which are directly or indirectly produced by personal care products and waste plastics, are constantly detected in various environmental media, and microplastics will cause various hazards to the ecosystem, so the research on microplastics has attracted more and more attention. The occurrence of microplastics in water, sediment, beach and organism was described. The collection and separation methods, as well as the qualitative and quantitative analysis methods of microplastics were introduced. Finally, the harm of microplastics to the environment and organism, as well as the main problems existing in the research at the present stage are pointed out, and the future research direction is prospected.

Key words: Microplastic; Occurrence; Detection method; Environmental hazard

自1907年酚醛塑料的专利申请以来,塑料真正意义上成为了大范围应用的工业产品,多年以来,塑料产品种类不断丰富,应用领域不断扩展,制品产量逐年增加,根据欧洲的研究,全球塑料制品产量在2016年达到3.35亿t,而中国生产了其中的29%^[1]。由于塑料难以降解,能够在环境中持久存在,在水解、光降解、机械磨损以及生物降解等外力作用下,塑料能够形成细小的颗粒,直径<5mm的塑料颗粒被称为微塑料^[2]。除此之外,个人护理品中添加的去角质塑料微珠也是微塑料的来源之一^[3]。微塑料同样性质稳定且难以降解,可以随着河流、海洋、大气远距离地迁移^[4],由于

微塑料尺寸很小,容易被微生物吞食,从而对生态系统造成危害。因此,联合国环境规划署已在2014年将微塑料列入十大新兴污染物表单^[5]。

近年来,随着人们对微塑料关注度的不断提升,关于微塑料在环境中的赋存研究越来越多,其已经在水体^[6-7]、沉积物^[8-11]以及海洋生物^[12-13]等大量环境及生物样品中被检出。由于微塑料的尺寸及表面特征因素复杂多变,因此,如何对环境中的微塑料进行定性定量是研究难点之一。现对已有环境中微塑料的检测方法进行总结对比,阐明各个检测分析方法的优缺点,并总结了微塑料危害的研究进展,探究微塑料对环境的主要危害路

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径,为今后的研究提供参考。

1 微塑料在环境中的赋存

1.1 微塑料在水体中的赋存

近年来,由于塑料的大规模使用,海洋中的微塑料也随之快速增长,1974年,大西洋海域中的微

塑料丰度仅为 $6.06 \times 10^{-5} \sim 8.32 \times 10^{-3}$ 个/ m^3 ^[14], 而到2017年,路易斯安那海岸的海洋中微塑料丰度已达到 $5.0 \sim 18.4$ 个/ m^3 ^[15]。当前,关于海洋中微塑料赋存情况的研究已经涵盖太平洋^[16]、北冰洋^[17]、大西洋^[18]及印度洋^[19]等主要海域,其部分研究总结见表1。

表1 海洋中微塑料的研究

海域	微塑料尺寸/mm	微塑料丰度/(个· m^{-3})	参考文献
中国北黄海	<0.5	545 ± 282	[20]
长江入海口	0.5~5	$4\ 137.3 \pm 2\ 461.5$ (入海口) 0.167 ± 0.138 (海水)	[21]
南非东南海岸线	0.08~5	$257.9 \pm 53.36 \sim 3\ 308 \pm 1\ 449$	[22]
大西洋	<1	$6.06 \times 10^{-5} \sim 8.32 \times 10^{-3}$	[14]
太平洋东北部	<0.25	2.46 ± 2.43	[23]
北极中央盆地	1~2	0.7	[24]

1.2 微塑料在沉积物及沙滩中的赋存

大多数微塑料的密度与水近似或小于水,因此,一般情况下,微塑料会漂浮在水面上或悬浮在水中,也有一些密度较大的微塑料容易沉入沉积物中或滞留在沙滩上^[25-26]。当前关于微塑料的研究有95%以上是关于海洋水域中的微塑料^[12],因此,关于沉积物中微塑料的研究也多集中在海洋沉积物中。Güven等^[27]研究发现,在地中海东北部的海域沉积物中,直径<5mm的微塑料赋存丰度约为 $(18.6 \pm 17.9) \times 10^3$ 个/ m^3 。Claudia等^[28]研究发现,在大西洋北海海域南部,直径为0.011~0.5mm的微塑料丰度约为2.8~1 188.8个/kg。Zobkov等^[29]发现,在波罗的海东南部区域,直径为0.1~0.335mm的微塑料丰度约为 34 ± 10 个/kg。而关于沙滩中微塑料的研究,Isobe等^[30]研究表明,在中国的珠海、北海、香港及澳门海岸线的沙滩中,微塑料的赋存丰度约为 97.5 ± 157.4 个/ m^2 。Eo等^[31]研究发现,在韩国海岸线的沙滩中,直径为1~5mm的微塑料颗粒赋存丰度约为0~2 088个/ m^2 ,Lo等^[32]发现,在中国香港的西部沙滩中,微塑料的赋存丰度约为0.58~2 116个/kg。Korez^[33]等研究发现,在斯洛文尼亚海滩中,直径<5mm的微塑料赋存丰度约为 0.5 ± 0.5 个/kg。当以“个/kg”作为单位时,可见沉积物中微塑料的赋存丰度比沙滩中要多,这可能是由于沉积物长时间作为海洋下沉物质的汇总聚集地导致的^[34]。

1.3 微塑料在生物中的赋存

由于微塑料尺寸小、密度小,易混杂于漂浮在水里的食物中而被滤食动物或鸟类误食,从而富集在低等生物体内^[35-36],通过食物链的转移,最终到达高等动物甚至人类的体内。人们已经在大量的生物样品中发现了微塑料,包括贝类、东方牡蛎、鱼类以及大型蚤^[12-13,37-40]。

2 微塑料的检测方法

2.1 微塑料的采集与分离

目前,对于含有微塑料的土壤、水体、空气和沉积物样品,其采样方法众多,大致可以分为直接挑选法、大体积采样法、散装采样法和体积缩减采样法^[41]。直接挑选法是基于微塑料的用途、颜色、硬度以及形状等特性,通过肉眼直接从环境样品中挑选微塑料颗粒。此法适用于沉积物及沙滩中的微塑料采样,且采集的微塑料粒径一般为2~5mm^[42],该法简单高效,但若微塑料粒径较小,与环境污染物质混合在一起,或者需要采集空气样品中的悬浮微塑料时,直接挑选法则会受到很大限制^[43]。大体积采样法主要应用于水样中微塑料的采集,一般将固定开口与固定孔径的筛网固定于流动的水中或者在静水中以一定的速度拖行,通过水流速度或者拖行速度与开口的直径计算过水体积,结合微塑料的定量结果得到微塑料的赋存浓度。散装采样法指的是将所有环境样品无损失地采集,带回实验室做进一步处理,此法多用于采集沉积物

及沙滩样品中难以用肉眼识别的微塑料。体积缩减采样法指的是在采集样品时,经过现场原位的过滤筛分,只保留自己感兴趣的部分样品带回实验室进一步分析,此法适用于既要大体积采样又要带回实验室进一步分析的情况。

对于上述4种采样方法所得的微塑料样品,实验室分离都是必不可少的步骤,而微塑料分离一直是研究难点。一方面由于微塑料体积较小,当与环境样品混合时,难以将其与其他干扰物区分开来;另一方面,由于样品的后续研究需求不同,导致需要不同的前处理方法。当前,主要分离方法有密度分离法、过滤筛分法、视觉挑选法以及化学物理分离法。密度分离法指的是利用塑料制品的密度与环境样品不同,而将微塑料分离出来。一般塑料制品的密度为 $0.8 \sim 1.4 \text{ g/cm}^3$ ^[44],而沙子或沉积物的密度约为 2.65 g/cm^3 ^[41],在不同密度的溶液中,微塑料与环境样品得以分离。已有的实验利用NaCl溶液、自来水和海水成功分离塑料样品与环境样品^[43,45-47]。过滤筛分法一般是对已经过密度分离所得的含有微塑料的溶液样品或散装法采样带回的水体样品进行过滤处理,此法一般有真空泵协助^[48]。视觉挑选法可以直接用肉眼或者借助显微镜,将微塑料样品分离^[49-53]。大部分经过大体积采样的海水样品,其网尾的微塑料样品都要经过视觉挑选分离^[14,54-56]。化学物理分离法指的是采用消解去除环境干扰样品,从而保留微塑料样品。常用的消解溶液有酸、碱、过氧化氢以及酶等^[57-59],已有的研究表明,酶法消解对于微塑料的破坏与分解较小,具有良好的应用前景^[60]。

2.2 微塑料的定性定量分析

微塑料的定性定量分析方法包括目视法和光电学法等。

目视法是基于微塑料的颜色、材质以及用途等特质对其进行分离,由于肉眼识别微塑料的尺寸范围一般为 $1 \sim 5 \text{ mm}$,具有较大限制,且在识别透明微塑料颗粒时容易与环境样品混淆。文献[61-62]对肉眼识别微塑料颗粒时应该执行的标准做出了规定:(1)区别微生物及细胞;(2)区别植物细胞和细干草;(3)微塑料材质较硬且有韧性;(4)微塑料颗粒颜色明亮且不突变;(5)白色或透明的颗粒在计数时则需要加倍小心;(6)微塑料没有金属光泽。除此之外,肉眼识别微塑料还常常需要借助显微镜,已有的研究已经利用体式显微镜、偏光

显微镜和双目镜观察到了微塑料并进行了定量及毒性分析^[63-65]。虽然此方法的偶然性较大,但是由于其简单高效的特性被广泛应用。

光电学法鉴定微塑料主要包括扫描电镜法、傅立叶红外光谱法、近红外光谱法以及拉曼或微拉曼光谱法。扫描电镜法的原理是利用聚焦得非常细的高能电子束在试样上扫描,激发出二次电子以及各种物理信息。通过对这些信息的接受、放大和显示成像,对测试试样进行表面形貌的观察。已有研究利用扫描电子显微镜观察到微塑料的多孔、碎裂以及风化特征^[66]。傅立叶红外光谱是一种广泛使用的红外光谱,不仅可以鉴定材料的聚合物成分,还能对所观测的聚合物进行计数,利用傅立叶红外光谱能够大大降低微塑料的定性定量的假阳性结果^[67]。但是傅立叶红外光谱仪的价格较高,在一定程度上限制了其应用的发展。近红外光谱与傅立叶红外光谱类似,都是基于红外光谱的鉴定手段,Jesse等^[68]已经通过近红外光谱成功鉴定了微塑料。拉曼及微拉曼光谱法能够通过将不同聚合物在受到激光束照射时反射的不同频率的光谱与标准聚合物的光谱进行比对来鉴定微塑料的材质,同时能够排除一部分微塑料鉴定的假阳性。当前的研究已经证明,拉曼光谱在微塑料的材料识别与鉴定中具有较好的性能^[69-71]。

3 微塑料的危害

3.1 微塑料单体的危害

由于微塑料的尺寸小、密度小、易浮于水面、颜色鲜艳、在环境中大量存在,导致其很容易被低营养级生物误食,随之会在食物链中由低营养级向高营养级迁移^[35-36]。微塑料在被摄入动物体内的初始阶段,多存在于消化系统,已有研究表明,微塑料在贻贝以及印度洋盘尾鱼的鳃、肠道、消化道以及胃中均有检出^[13,72]。Terepocki等^[73]发现在沙滩上死去的海鸟胃肠道中有大量微塑料存在,这些微塑料对其食道产生的磨损可能最终导致了海鸟的死亡。除了海鸟,海洋鱼类的消化系统也会遭到微塑料磨损而造成损害^[13,73-74]。Schuyler等^[75]证明了暴露于微塑料中可能会导致龟等生长缓慢的动物消化缓慢和营养不良。Pedro等^[76-77]研究发现,当暴露于 $1 \sim 5 \mu\text{m}$ 的微塑料中时,幼鱼的生长可能会受到抑制。除此之外,双壳类贻贝在接触微塑料时会出现摄食活性下降,细胞毒性、解体吞噬活

性和溶菌酶活性增加等状况^[78-79]。

3.2 微塑料吸附有机污染物的危害

微塑料被称为水环境中的PM_{2.5},除了其本身的物理特性给摄入微塑料的生物带来诸如食道堵塞与消化道磨损等危害以外,微塑料中还存在大量的工业添加剂如增塑剂、染料、阻燃剂等,由于其较大的比表面积,会导致这些工业添加剂在环境及生物体内被释放出来^[80],微塑料中诸如溴代阻燃剂、双酚A以及增塑剂的释放导致的生长抑制以及繁殖能力下降等已经有所报道^[64,81-82]。同时,比表面积大、不规则或多孔的特性导致微塑料具有吸附重金属、持久性有机污染物、抗生素等环境污染物的特性。因此,微塑料释放的污染物危害可能远大于微塑料本身。已有研究证明,海水中的微塑料可以吸附滴滴涕、邻苯二甲酸二酯、菲以及有害微生物群等污染物^[83-84]。而吸附的环境污染物在模拟胃液中的释放速度大于其在海水中的释放速度,可能会导致其危害到生物体的健康^[84]。

4 总结与展望

4.1 微塑料研究中存在的问题

微塑料研究中仍然存在诸多问题,在微塑料的环境赋存研究中,一方面由于微塑料的来源多种多样,无论是来源于废旧塑料还是个人护理品,都会随着大气、河流以及土壤迁移,微塑料在水体、沉积物、沙滩、生物中均被发现,表明微塑料污染问题已十分紧迫,这导致很难实现对其进行有效管控;另一方面,微塑料的丰度单位尚未统一,这导致对同样的研究很难实现横向比较。在微塑料的采集与定性定量中,最为重要的问题即是对微塑料的定义,多大尺寸的塑料可以算是微塑料至今未有定论,虽然大多数情况下认为1~5 mm为微塑料颗粒尺寸,但是当前已有的研究中微塑料颗粒的尺寸介于几微米与十几毫米之间,微塑料尺寸的定义间接决定了微塑料采集时的筛网及滤网尺寸,这又会决定微塑料最终的丰度。除此之外,微塑料采集过程中的质控也是一个亟待解决的问题,筛网、拖绳、衣物及容器等掉落的颗粒对采集结果产生的影响需要进行控制。而在微塑料的定性定量方面,基于红外光谱的定性定量结果已经十分有效,但是限于其成本高昂,仍然有很多研究是基于目视法进行定性定量,这导致了微塑料的定性定量研究中出现了大量的假阳性结果。

在微塑料的危害方面,微塑料单体的物理危害、微塑料含有的添加剂以及其上吸附的有机污染物都会对生态系统产生极大的危害,但是到底哪种危害更为严重,这些危害在生态系统受到伤害时的贡献程度依然是未知的。最后,微塑料会在环境中发生迁移,因此其污染并不是单个国家管理不善导致的,解决微塑料污染需要多国协同合作。

4.2 微塑料研究的展望

今后关于微塑料的研究要关注政策管控中微塑料的直接与间接来源、各个途径迁移的贡献量以及各个国家的协同合作管理,同时国际之间的研究应当确定统一的赋存浓度单位,便于各个区域及各个时间点研究的纵、横向比较。微塑料的采集方面,要统一微塑料的尺寸,使用统一的筛网及滤网孔径,使得采集的微塑料粒径统一。当前的定性定量方法已经相对完善,但是如何开发更为廉价高效的方法也是今后的重点研究方向。在微塑料的危害方面,如何将微塑料单体的危害与其添加剂及吸附污染物的释放危害做比较?微塑料到底能吸附多少污染物?这些污染物与环境本体中的污染物浓度水平相比如何?而微塑料的危害又处于什么程度?这些都是亟待研究的问题,也是近期的主要研究方向。

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