

海洋生物中微塑料的赋存特征 及毒性效应研究进展

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摘 要: 微塑料因其性质稳定, 自然条件下难以降解, 并能够在风力和洋流的作用下实现远距离输送, 已成为海洋中广泛存在的污染物, 从表层海水到深海沉积物中均有微塑料被检出。海洋中的微塑料不仅可被生物摄食, 随着食物链的传递危害海洋生态系统健康, 还对环境中的污染物有吸附作用, 并可作为一个新的生态位为微生物提供定殖空间。基于国内外已有的研究成果, 总结了微塑料在典型海洋生物体内的分布规律及其影响因素, 并归纳了微塑料的毒性效应, 诸如对生物体生理机能、氧化应激、免疫应答、神经毒性和繁殖遗传等的毒性, 阐释了微塑料致毒机理, 包括微塑料作为异物入侵生物体后因其颗粒效应所产生的毒性、微塑料产品中添加剂在环境中的释放, 以及由于微塑料对环境中各种污染物质的吸附而产生的复合毒性。最后探讨了微塑料研究方法存在的问题, 指出成熟完善的微塑料研究系统与标准的重要性, 提出未来毒性暴露实验设计需更贴近真实环境, 可为今后微塑料的相关研究提供思路和参考。

关键词: 微塑料; 海洋生物; 赋存特征; 生物毒性; 致毒机理

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海洋塑料污染已经成为全球性的环境问题^[1]。研究表明, 每年有超过 1 200 万 t 塑料垃圾排放进入海洋^[2]。进入海洋的塑料垃圾, 在太阳辐射(光降解、脆化、光氧化)、生物降解、波浪等众多作用下, 逐渐被破碎分解成小的塑料碎片即微塑料^[3]。微塑料同塑料制品一样, 化学性质稳定, 难以降解, 可在环境中长期稳定存在, 已有研究表明, 微塑料可在环境中留存 1 000 年^[4]。此外, 由于微塑料体积小、质量轻, 能够在风力和洋流的作用下实现远距离输送, 扩大了微塑料的污染范围, 已有研究发现, 在人迹罕至的地区, 如深海甚至也有微塑料检出^[5]。

海洋中微塑料持续产生, 却很少能被降解, 这导致海洋中微塑料丰度不断增加, 进而增加了海洋生物的微塑料暴露风险。海洋生物是微塑料通过食物链转移的重要载体。已有研究通过

现场调查对海洋生物消化道内容物进行分析, 发现微塑料可被海洋生物摄入, 并进入具有转移潜力的水生食物链中, 通过食物链对海洋生态环境产生影响甚至威胁人类健康^[6-7]。通过现场调查能够对微塑料生态环境效应获得宏观认识, 但是由于现场调查的环境背景复杂, 对于阐释微塑料的毒性效应有许多不确定性。为探讨微塑料的毒性效应, 许多学者开展了有关微塑料毒性效应研究, 结果发现, 微塑料被海洋生物摄入后, 会引起一系列物理或生化损伤^[8-10]。

微塑料的环境问题引起了研究人员的极大关注, 为了更系统地揭示微塑料的海洋生态毒性效应, 本文通过文献采集, 从宏观现场调查研究着手, 总结不同类型海洋生物对微塑料的响应, 并通过微观暴露实验研究进展的综述, 评价微塑料毒性效应及其机制。以期微塑料海洋生态

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影响评价提供参考。

1 典型海洋生物体内微塑料赋存特征

微塑料是海洋生态系统中普遍存在的污染物,已有研究发现,浮游生物、自游生物、底栖生物均存在微塑料摄入现象^[11]。鉴于相关生物类型报道频次,笔者选择在微塑料研究领域关注度最高的几种典型海洋生物,分析探讨其体内微塑料分布特征及影响因素。

1.1 浮游动物

浮游动物是微塑料进入食物链的切入点,表1为几种典型海洋生物微塑料赋存特征^[1,12,14-25],ZHENG等^[12]通过对渤海海域浮游动物体内微塑料丰度调查发现,每个浮游动物体内微塑料丰度8月(夏季)时为0.117个,11月(秋季)时为0.056个,浮游动物体内微塑料丰度呈现季节差异变化。SUN等^[1]通过调查黄海水域浮游动物体内微塑料赋存情况,发现浮游动物体内微塑料平均丰度为 (12.24 ± 25.70) 个 $\cdot m^{-3}$ 。目前,在相关研究中,有关浮游动物体内微塑料丰度的统计单位不尽相同(如:个 $\cdot m^{-2}$ 、个 $\cdot m^{-3}$ 、个 $\cdot g^{-1}$ 、个 $\cdot 生物体^{-1}$ 等),这给微塑料数据分析对比带来一定困难^[13]。

一般而言,浮游动物体内微塑料赋存特征与环境中的微塑料丰度密切相关。FRIAS等^[26]在葡萄牙沿岸调查浮游动物体内微塑料丰度,结果显示,微塑料在不同站位浮游动物体内差异较为显著,这种差异可能与人为活动有关。其中在Aveiro与Lisboa站位浮游动物体内微塑料检出率分别达到66%与91%,这两个站位对应区域恰好人口密度较高。而在自然公园Vicentina和实施净滩计划的Algarve海滩,微塑料检出率均不及50%,这说明陆源控制对降低浮游动物体内微塑料丰度起到了一定作用。除了受暴露环境中微塑料丰度的影响,浮游动物的分布密度、捕食方

式都会影响微塑料在浮游动物体内的赋存情况^[14]。SUN等^[14]调查了东海10个浮游动物类群中微塑料的生物累积浓度,结果显示,每个生物体内微塑料丰度为0.13~0.35个。微塑料的赋存情况还受浮游动物摄食方式的影响,呈现杂食动物>食肉动物>食草动物的趋势。COLE等^[7]发现大西洋东北地区常见的浮游动物中有13个浮游动物类群会摄入聚苯乙烯微塑料,其吸收量随着类群、生命阶段和微塑料尺寸的变化而变化。

1.2 鱼类

在海洋生物的调查,有关鱼类摄食微塑料的报道逐年增加^[27]。SEQUEIRA等^[28]汇总了近年来的研究,分析了24个国家捕获的198种鱼,其中60%的鱼类器官中含有微塑料。虽然肉食性鱼类比杂食性鱼类体内微塑料丰度更高,但是在大部分研究中,纤维和碎片是鱼体内微塑料的常见形态。如表1所示,NIE等^[24]通过对南沙群岛周围采集的鱼样进行调查发现,鱼样中每个生物体内微塑料的平均丰度为3.1个,微塑料形态以纤维为主,多为透明或者蓝色。PETERS等^[22]调查了德克萨斯州墨西哥湾沿岸的6种共计1381条海洋鱼样,其中有42.4%存在微塑料摄入情况,被检出的鱼样中每个生物体内微塑料的平均丰度为1.93个,且以纤维状(86.4%)为主。ZHANG等^[29]通过现场采样调查发现,鱼类和沉积物中不同类型的微塑料丰度百分比之间存在显著的正相关关系。

除了环境差异,鱼的种间差异也是造成鱼体内微塑料赋存特征存在差异的一个极重要因素。JABEEN等^[30]对中国21种海水鱼和6种淡水鱼体内的微塑料丰度进行了调查,发现所有鱼样都存在摄入微型或中型塑料的情况,海洋底栖鱼类中微塑料的平均丰度显著高于淡水底栖鱼类。

表1 海洋生物微塑料赋存特征
Tab.1 Occurrence characteristics of microplastics in marine organism

样品种类 Sample	地点 Location	微塑料丰度/(个·生物体 ⁻¹) Microplastic level	检出率 Detection rate	参考文献 Reference
浮游动物 Zooplankton	中国渤海 Bohai Sea	8月: 0.117, 11月: 0.056	No	[12]
	中国黄海 Yellow Sea	(12.24 ± 25.70) 个·m ⁻³	No	[1]
	中国东海 East China Sea	0.13	No	[14]
	中国东海 East China Sea	0.35	No	[14]
	法国大西洋沿岸 French Atlantic coast	0.61 ± 0.56	No	[15]
	法国大西洋沿岸 French Atlantic coast	2.1 ± 1.7	No	[15]
	土耳其海岸 Turkish coast	0.69	48%	[16]
	英国海岸 United Kingdom coast	1.1 ~ 6.4	No	[17]
贝类 Mussel	法国海峡海岸线 Channel coastlines(France)	0.76 ± 0.40	No	[18]
	法国海峡海岸线 Channel coastlines(France)	2.46 ± 1.16	No	[18]
	英国西南部 South west of England	1.43 ~ 7.64	88.5%	[19]
	地中海 Mediterranean Sea	1.7 ~ 2.0	46.25%	[20]
	韩国沿海 Korean coast	1.21 ± 0.68	No	[21]
	韩国沿海 Korean coast	2.19 ± 1.20	No	[21]
	德克萨斯州墨西哥湾沿岸 Texas Gulf coast	1.93	42.4%	[22]
	北雅加达的沿海水域 Coastal waters in North Jakarta	1.97	75%	[23]
鱼类 Fish	中国南海 South China Sea	3.1	No	[24]
	南非沿海 Agulhas Bank, South Africa	2.8~4.6	86.67%	[25]
	地中海 Mediterranean Sea	1.5~1.9	No	[20]

注:No表示没有数据

Note: No means no data

1.3 贝类

微塑料不仅存在于水环境中,对浮游动物、鱼类等水生生物造成影响,同时会因其富集于沉积物,增加底栖生物的暴露风险。VAN等^[31]在法国-比利时-荷兰海岸线的6个地点,采集了两种食性不同的海洋无脊椎动物:紫壳菜蛤(*Mytilus edulis*,滤食性动物)和沙蠋(*Arenicola marina*,食碎屑动物),在所有采集到的生物中都有微塑料检出,两者微塑料平均丰度分别为(0.2 ± 0.3)

个·g⁻¹和(1.2 ± 2.8)个·g⁻¹。贝类可以作为海洋微塑料污染的指示生物^[21]。DIGKA等^[20]采集了地中海希腊海域4种高度商业化的海洋物种(紫贻贝 *Mytilus galloprovincialis*、沙丁鱼 *Sardina pilchardus*、绯小鲷 *Pagellus erythrinus*、须羊鱼 *Mullus barbatus*),调查其体内的微塑料丰度,发现紫贻贝平均每个生物体内微塑料的丰度为1.7 ~ 2.0个。CHO等^[21]以滤食性双壳类动物(牡蛎 *Ostrea gigas*、贻贝 *Mytilus edulis* 和菲律

宾帘蛤 *Ruditapes philippinarum*) 为指示生物,对韩国沿海微塑料污染情况进行了调查,结果显示,牡蛎和贻贝平均每个生物体内微塑料的丰度为 (1.21 ± 0.68) 个,菲律宾帘蛤平均每个生物体内微塑料的丰度为 (2.19 ± 1.20) 个。

影响贝类体内微塑料丰度的原因有多方面。研究表明,与野生贻贝相比,在养殖的贻贝中能检测出更多的微塑料^[15]。这与贝类生长环境不无关系,由于在养殖过程中大量使用塑料容器、网、管、绳索等,这些塑料制品都增加了贝类摄食微塑料的可能性^[32]。但是也有学者持不同观点,如 PHUONG 等^[15] 研究认为,贝类体内的微塑料赋存特征主要来自种间差异,采样点、季节、养殖模式(野生或养殖)对其影响不明显。

2 微塑料毒性效应

大量的现场采样数据已表明微塑料会被海洋生物摄食,为了进一步研究摄入微塑料对海洋生物造成的影响,学者们通过一系列毒理暴露实验考察其毒性。已有研究表明,生物体暴露于微塑料可能影响其生长生理机能,诱导抗氧化体系,免疫、神经异常表达,甚至产生繁殖遗传毒性^[3]。

微塑料摄入会对生物生长生理机能产生影响。WELDEN 等^[33] 研究了挪威海螯虾 (*Nephrops norvegicus*) 长时间暴露于高浓度聚乙烯纤维产生的毒性效应。通过监测摄食率、体质量和营养状况等指标,发现暴露于高浓度微塑料环境中,可能会减少其对营养物质的利用率。WRIGHT 等^[34] 将沙蠋暴露于未增塑聚氯乙烯 (unplasticized polyvinyl chloride, uPVC), 由于吸收和积累聚氯乙烯,沙蠋能量储量显著减少。动物行为也常被用作生理机能评价指标,相关报道记录了微塑料暴露下可能导致滩跳虾 (*Platorchestia smithi*) 弹跳高度^[35] 和旧金山湾卤虫 (*Artemia franciscana*) 游泳速度的下降^[36], 甚至有研究发现模糊网纹溞 (*Ceriodaphnia dubia*) 因微塑料团聚而丧失游泳能力^[37]。

微塑料对生物生长指标产生显著的影响。一方面,可能是由消化功能障碍导致的。一个普遍的观点认为,微塑料摄入会产生假性饱腹感,进而减少摄食量^[38]。WATTS 等^[39] 的研究证实了这一观点,当投喂微塑料污染处理的食物

(0.3% ~ 1%) 时,欧洲绿蟹 (*Carcinus maenas*) 的摄食量从 $0.33 \text{ g} \cdot \text{d}^{-1}$ 降至 $0.03 \text{ g} \cdot \text{d}^{-1}$ 。另一方面,可能是由于能量调配导致。原本用于生长的能量用于基因表达、细胞信号调控、氧化应激和免疫应答,从而影响生物生长^[40]。

已有不少研究将氧化应激作为生物标志物,评估微塑料摄入是否产生毒性效应。如 PAUL-PONT 等^[41] 的研究表明,7 d 的微塑料暴露史会使贻贝体内的活性氧 (reactive oxygen species, ROS) 含量增加,且在停止暴露后回归正常水平。说明在微塑料诱导下生物体产生了氧化损伤。研究虽未测得 ROS 含量水平的变化(或因 ROS 高活性造成),但结果显示,氧化应激酶如超氧化物歧化酶 (superoxide dismutase, SOD)、过氧化氢酶 (catalase, CAT)、谷胱甘肽还原酶 (glutathione reductase, GR) 均呈现高表达水平,这同样表明,微塑料的摄入会引起氧化应激反应^[42]。免疫应答也是学者们关注的毒性效应之一。VON MOOS 等^[8] 的研究结果表明,暴露于微塑料的贻贝 6 h 后形成粒细胞瘤,引起溶酶体膜不稳定的强烈免疫反应,反应随着暴露时间的增加而显著增强。由此可见微塑料能够被细胞吸收并引发生物体对毒性的应激反应。

与其他有机污染物一样,微塑料不仅对暴露生物自身具有毒性效应,大量的研究证实,微塑料暴露可能影响其繁殖能力甚至产生遗传毒性,对后代产生深远的影响^[43]。

3 微塑料毒性产生的因素

有关微塑料毒性的研究,大部分以塑料作为暴露源,采用综合评价的视角探讨微塑料的毒性效应,如上所述,各种类型的微塑料可能会产生诸如影响生理机能、激发抗氧化体系、影响免疫或神经甚至产生遗传毒性的毒性效应。与单一污染物的毒性效应不同,微塑料产生毒性的因素可能来自多方面。

3.1 微塑料作为异物入侵

研究表明,当微塑料尺寸大于 $150 \mu\text{m}$ 时,微塑料虽然不会被肠道吸收,但是有可能粘附在肠粘膜层,并与肠的上皮细胞接触,这有可能会导致局部的免疫反应。当尺寸小于 $150 \mu\text{m}$ 时就可能被吸收,产生进一步的毒性效应^[44]。

关于颗粒本身产生的毒性效应,已发表的大

部分文章都是聚焦于球形塑料的研究,对不规则塑料的毒性探究相对较少,事实上环境中大部分的次生塑料是非球状的不规则形态^[45],而非球形的次生塑料的毒性可能与球形塑料有所不同。研究表明,大型溞(*Daphnia magna*)能够摄取塑料微珠(10 ~ 106 μm)和不规则形状的微塑料,但不规则形状微塑料的急性抑制作用更为明显^[46]。

不仅仅球形与非球形能导致毒性的差异。塑料的尺寸也是微塑料毒性的一个重要影响因素。随着环境中纳米级微塑料的检出,近年来陆续有学者开始关注纳米尺寸微塑料的毒性效应。由于纳米塑料具有独特的纳米尺度物理化学性质,使得它能够通过影响细胞功能的生物屏障进行生物积累。如 BESSELING 等^[47]研究发现,纳米尺度的聚苯乙烯能够抑制斜生栅藻(*Scenedesmus obliquus*)种群的生长并降低其叶绿素浓度,同时受试大型溞不仅体积缩小,而且下一代的畸形率上升到 68%。BERGAMI 等^[48]研究发现,纳米尺度的聚苯乙烯系塑料能够影响卤虫幼体的食物摄取(进食)、行为(运动)和生理(多次蜕皮)。也有报道指出,纳米级微塑料对鱼类先天免疫系统有影响,研究概述了鱼类先天免疫系统的细胞成分对聚苯乙烯和聚碳酸酯纳米颗粒/聚集体的应激反应,表明鱼类对聚苯乙烯和聚碳酸酯纳米颗粒的应激反应可能干扰鱼类种群的抗病性^[49]。更有学者研究发现,纳米级聚苯乙烯塑料会从主要生产者淡水藻类到最终食肉性鱼类转移^[50]。可见纳米级微塑料不仅可能对水生生物生化、行为和组织学变化产生不利影响,并且可以通过水生食物链实现转移。

3.2 微塑料添加剂释放

一件塑料制品可能添加了数百种添加剂,包括各种抗氧化剂、阻燃剂、塑化剂、着色剂以及各种产品副产物等,大部分这些物质可能是以范德华力等弱结合形式与高分子聚合物相结合^[51]。因此当体系环境改变时,部分弱结合的有机物就有可能被释放。LITHNER 等^[52]系统地探讨了 26 种塑料制品在去离子水中浸泡后,其水相对水蚤的急性毒性。结果表明,所有来自增塑聚氯乙烯(plasticized polyvinyl chloride)和环氧树脂(epoxy)产品的渗滤液都是有毒的(48 h EC_{50} 2 ~ 235 $\text{g} \cdot \text{L}^{-1}$)。聚丙烯(polypropylene, PP)、丙

烯腈-丁二烯-苯乙烯(acrylonitrile-butadiene-styrene, ABS)和硬质聚氯乙烯(rigid polyvinyl chloride)产品的渗滤液均未显示毒性。

ZIMMERMANN 等^[51]以水蚤为研究对象,就微塑料毒性是源自塑料颗粒本身的损害还是添加剂的毒性这一致毒机理进行了探讨。结果表明,不同类型塑料的致毒机理有所不同,在该研究中,塑料添加剂是聚氯乙烯(polyvinyl chloride, PVC)毒性的主要驱动因素,而聚氨酯(polyurethane, PUR)和聚乳酸(poly(lactic acid), PLA)微塑料的毒性是由颗粒效应所引起的。

3.3 复合毒性

除上述微塑料自身的毒性效应外,环境中微塑料因其比表面积大的特性,使其在自然水体中易于吸附各种有毒化学物质、抗生素、重金属等^[53]。因此研究微塑料毒性的产生因素时,其复合毒性效应不容忽视。

QIAO 等^[54]研究了微塑料和天然有机物对斑马鱼(*Danio rerio*)中铜(Cu)的积累和毒性的联合影响,研究结果表明,微塑料和天然有机物共同作用会增加肝脏和肠道中 Cu 的积累。同时, BESSELING 等^[55]研究发现,低浓度的聚苯乙烯(polystyrene, PS)也会增加多氯联苯(polychlorinated biphenyls, PCBs)的生物积累。微塑料复合毒性污染引起了学者的广泛关注,如 SYBERG 等^[56]报道了微塑料增强了三氯生(triclosan, TCS)的毒性效应,MA 等^[57]研究发现,微塑料会增强非在水蚤体内的生物积累。

另外,微塑料的疏水表面为微生物定殖形成生物膜提供了理想的生态位。微塑料表面能够形成生物膜。生物膜是一种复杂的群落,包括细菌、古生菌、藻类、病毒、真菌和原生生物^[58]。生物膜是一种复杂的吸附系统,一些潜在的病原体 and 有毒藻类被吸附于附着生物膜的塑料微粒上也可能导致额外的毒性。RICHARD 等^[58]研究发现,微塑料表面生物膜可以促进水环境中的重金属在塑料碎片上积累。QI 等^[59]的研究结果表明,生物膜不仅增强了 Pb(II)在微塑料上的吸附能力,而且增强了 Pb(II)和微塑料的联合毒性。

4 小结

微塑料在海洋环境中的分布、环境效应及对海洋生物的影响是近年来的研究热点^[60],也是环

境科学领域相对较新的研究。本文首先探讨了典型海洋生物体内微塑料的赋存特征,并对其影响因素进行介绍。众多研究团队进行了微塑料调查,研究区域与研究对象也日益扩大,为丰富科学认识提供了大量基础数据。但是,由于微塑料评估调查缺乏统一的标准,不同研究小组之间差异很大,核算单位也未统一,这些都为数据之间的比较带来了困难。另外,本文还对微塑料的毒性及其致毒机理进行了探讨。整体而言,微塑料毒性效应的研究在近几年取得了突破性进展,但研究体系尚不完善,缺乏成熟完善的研究系统与标准。毒性暴露实验方法千差万别,不具有普遍性,使用的微塑料浓度、粒径等没有科学合理的参考标准,对小尺寸、低浓度、长时间暴露的研究相对较少。今后研究应强化微塑料,特别是纳米微塑料检测及毒性评价手段。另外,毒性暴露实验设计也应更贴近真实环境,对海洋微塑料及其吸附水体中的污染物可以通过生态系统的食物链传递进行研究。海洋微塑料添加剂的生态影响、毒性效应、迁移转化路径和停留时间及其在生态水平上的影响,也将是未来的研究方向。

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Research progress on occurrence characteristic and toxicity of microplastics in marine organisms

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Abstract: Plastic products are light, tough, resilient, inexpensive, corrosion-resistant and easy to work with, and have been extensively used in industry, agriculture and daily lives. These plastic debris are discarded and enter the ocean as a result of many different land- and sea-based activities. Microplastics (MPs), defined as plastic fragments ranging from a few micrometers to five millimeters in any dimension, play a key role in the world's marine litter problem. They originate from two sources, manufactured products (such as abrasive micro-beads in face scrubber cosmetic, toothpastes and antifouling of boats) that contain microplastics (primary microplastics) and fragments released from larger plastic debris through photooxidation, mechanical action and biodegradation (secondary microplastics). The presence of microplastics in the marine environment may be distributed globally by way of currents and winds. Various studies have shown that MPs are now distributed in all oceans, occurring on shorelines, sediments, surface waters even in remote locations (i. e. Arctic) and at all depths. Once entering into ocean, microplastics may pose serious hazards to marine organisms, including phytoplanktons, zooplanktons, clams, mussels, crabs and fishes. Microplastics not only can cause physical harm to marine organisms by contact, uptake and ingestion, but also can provide the marine organisms with a potential pathway for exposure to organic pollutants, metals and pathogens adsorbed from the ambient environment or to chemicals leached by themselves. Microplastics may also pose risks to human health, because they may be transferred through the food chain and can facilitate the food web transfer of incorporated/ adsorbed toxic chemicals. Therefore, the effects of microplastics on the marine environment have become major concerns, marine ecological issues caused by microplastics are now at the forefront of marine ecology and environmental research. Based on the existing research results, this paper summarized the distribution of microplastics in typical marine organisms and its influencing factors. In addition, the toxic effects of microplastics, such as physiological function, oxidative stress, immune response, neurotoxicity and even reproductive genetic toxicity, were summarized. This paper also explained the toxic mechanism of microplastics, including the particle effect of microplastics as foreign bodies into the organism, the leaching of microplastics additives, and the combined toxicity of microplastics and environmental pollutants caused by the adsorption effect of microplastics. At the end of the paper, the problems of microplastics research methods were discussed, the importance of mature and perfect microplastics research system and standards was pointed out and the suggestion that design of future toxicity exposure experiments need to be closer to the real environment was proposed, providing ideas and references for future research on microplastics.

Keywords: microplastics; marine biota; occurrence; toxicity; toxic mechanism