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水生生态系统中微塑料对微藻的生态毒理效应研究进展

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摘要: 作为一种新污染物, 微塑料引起的环境问题日益严重, 引起的生物效应和健康风险备受关注。微塑料粒径小, 比表面积大, 易成为各种污染物的载体, 影响水生生物的生长繁殖或沿食物链传递, 从而威胁到水生生态系统的安全。然而微塑料对水生生物的毒性作用机理尚不明确, 因此, 微塑料对水生生态系统的影响在很大程度上仍然是未知的。微藻是水生食物链的基础, 是水生生态系统的基本组成部分, 也是实现多种生态系统功能的关键生物, 了解微塑料对微藻的生态毒性效应有助于评估其生态风险。本文基于已有研究, 通过个体-种群-群落-生态系统等不同尺度综合论述微塑料对微藻的生态毒理效应, 解析微塑料对微藻毒性作用的影响因素, 包括浓度、粒径、形状、表面电荷和添加剂等。在此基础上, 提出当前领域存在的问题和未来研究的重点方向。期望能为今后的微塑料毒性作用研究提供理论基础和数据参考。

关键词: 微塑料; 微藻; 生态毒理效应; 作用机制; 水生生态系统

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Research Progress on Ecotoxicological Effects of Microplastics on Microalgae in Aquatic Ecosystems

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Abstract: As a new type of environmental pollutants, microplastics have caused many environmental problems, including biological effects and health risks, and gradually attracted worldwide attention. Microplastics with small particle sizes and large specific surface areas are easy to become the carriers of various pollutants, affecting the growth and reproduction of aquatic organisms. At the same time, they can be transmitted along the food chain, threatening the safety of aquatic ecosystems. However, the toxic mechanism of microplastics on aquatic organisms is not clear. Therefore, the effects of microplastics on aquatic ecosystems remain largely unknown. Microalgae are the foundation of the aquatic food chain, as well as the basic components of the aquatic ecosystem and the key or-

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ganisms that realize various ecosystem functions. Understanding the impact of microplastics on microalgae is helpful to assess its ecological risks. This paper comprehensively discusses the mechanism of microplastics on microalgae through different scales such as individual, population, community and ecosystem, and further summarizes the influencing factors of the toxicity of microplastics on microalgae, including concentration, particle size, shape, surface charge, and additives. On this basis, the current problems in the field of microplastics are proposed, and the direction and focus of future research are put forward. It is expected to provide a theoretical basis and data reference for future studies on the toxicity of microplastics.

Keywords: microplastics; microalgae; ecotoxicological effects; mechanisms of action; aquatic ecosystems

作为一种新型污染物,微塑料(microplastics, MPs)污染已经成为全球关注的环境问题^[1]。微塑料广泛存在于全球多种介质中,海洋、河流、湖泊、土壤和沉积物,甚至极地地区都检测出微塑料的存在^[2]。通常<5 mm 的塑料颗粒被称为微塑料^[3]。微塑料具有不同的形状,如碎片、薄膜、纤维、泡沫和颗粒^[4]。环境中的微塑料分为初生微塑料和次生微塑料。初生微塑料指的是在工业生产过程中由于特定用途而制备成为微米级的小粒径塑料颗粒,如沐浴露、洗面奶等;次生微塑料则是由环境中的废弃塑料,在物理、化学或生物作用下破碎所形成^[5]。微塑料化学性质稳定、不易分解且分布广泛,对水生生物的影响仍不明朗。一方面,微塑料可以被多种水生生物摄入,对生物体构成直接威胁。研究表明,微塑料一旦进入生物体内,外排将变得十分缓慢,最终会蓄积在生物体的消化系统中,造成其消化道的机械堵塞和损伤,如贻贝(*Mytilus edulis*)消化腺^[6]、鱼类胃部^[7]和藤壶(*Lepas* sp.)肠道^[8]等,影响生物体内的系统平衡和正常代谢。另一方面,由于微塑料具有较大的比表面积和良好的疏水性能,可通过一系列复杂的相互作用吸附水体中的污染物。同时,塑料在生产过程中使用的添加剂也会在微塑料降解时释放到环境中,增加了水生生物受到污染物毒性效应的风险。

与陆地生态系统相比,高分子聚合物在水生生态系统中更容易破碎、降解成较小的塑料碎片,成为微塑料的重要来源^[9]。微塑料及其携带的化学污染物会影响水生生物的生长繁殖,也会随着食物链和食物网向更高级的生物传递,最终富集在人类体内,威胁人类健康^[10]。因此,研究水生生态系统中的微塑料就显得尤为重要。在众多水生生物中,微藻位于食物链的底部,是水生生态系统中重要的初级生产者,可通过光合作用将无机碳转化成有机碳,是水生生物的主要能量来源。微藻具有生长周期短、易

操作、易观察、对有毒物质敏感和无摄食过程等特点。微藻常被用作检测微塑料污染造成环境威胁的指示生物^[11]。吸附着微藻的微塑料和漂浮在水面上的微塑料被浮游动物所捕食^[12],鱼类和其他生物又以这些浮游生物为食。由于捕食作用,微塑料会通过食物链大量进入水生生态系统食物网,对水生生态系统造成巨大的威胁。目前微塑料对微藻的生态毒性效应研究大多停留在细胞和个体水平,对生物种群、群落乃至整个生态系统的研究存在着严重的数据缺口和认识不足。本文从个体、种群和群落,生态系统等尺度论述微塑料对微藻的生态毒理效应,总结微塑料对微藻的毒性作用影响因素,提出目前研究中存在的问题,展望未来的研究方向,以期对微塑料污染的生态毒理效应研究有所裨益。

1 微塑料对微藻个体的生态毒理效应 (Ecotoxicological effects of microplastics on individual microalgae)

微塑料对微藻细胞个体的毒性机理十分复杂,且仍有许多未能明确的部分。以下将尝试从物理损伤和生理生化损伤(光合系统、氧化应激和胞外聚合物)方面加以阐述。

1.1 物理损伤(Physical damage)

微塑料对微藻细胞的物理损伤主要在于吸附和内化。一方面,微塑料由于体积小,比表面积大,易于吸附微藻细胞。Mao 等^[13]研究发现,聚苯乙烯(polystyrene, PS)会对蛋白核小球藻细胞造成物理损伤,包括细胞膜受损和类囊体扭曲。Lagarde 等^[14]发现当微藻定植在聚丙烯(polypropylene, PP)上时,聚合聚丙烯密度平均值($1.19 \text{ g} \cdot \text{cm}^{-3}$)大于原始聚丙烯的密度($0.90 \text{ g} \cdot \text{cm}^{-3}$)。异质聚集改变了微藻的密度和垂直分布状态,使微藻发生沉降进入深水弱光区,降低微藻的生长速率^[15]。此外,微塑料的吸附会导致物理堵塞,影响细胞中的空气流动速率,限制细胞与环境间物质和能量转移,使细胞内的有害代谢物

难以分解^[16]。不仅如此,微藻的运动方式还会被附着在鞭毛上的微塑料影响^[17]。

另一方面,微塑料还可能内化进入微藻细胞^[18]。Chen 等^[19]将微藻分别暴露于不同直径的 PS 微珠中,处理 72 h 后发现,2 种细胞中均发现了 1.0 μm 和 2.0 μm PS 微珠,而 3.0、4.0 和 5.0 μm 的 PS 微珠则未在细胞内发现。结果证明了微藻中微塑料具有尺寸依赖性的颗粒内化。微塑料内化会对微藻细胞内部结构和功能造成不利影响,如蛋白核不清晰、类囊体变形和细胞膜受损等。由于微藻细胞壁的屏障作用,大粒径的微塑料往往难以穿透^[20]。目前环境中的微塑料有逐渐变小的趋势^[21],而微塑料内化的机理尚不明确,因此仍需更多的实验来验证微塑料能否进入微藻细胞。

1.2 生理生化损伤(Physiological and biochemical damage)

1.2.1 光合系统损伤

微塑料已被证明会影响微藻细胞光合作用^[22]。具体表现为光合反应效率下降^[23]和光合色素含量(如叶绿素)降低^[24]。研究表明,可变荧光(F_v)和最大荧光(F_m)之间的比率(F_v/F_m)是光系统 II (PS II) 电子传输活性的指标^[25]。微塑料可通过影响电子供体部位、光系统 II 的反应中心(负责能量转换)和电子传递链而阻碍光合作用。Wu 等^[26]发现微藻暴露于微塑料中时, F_v/F_m 显著降低。这可能归因于微塑料中断了 PS II 反应中心的受体 Q_A 和 Q_B 之间的光电子传输,从而形成更多处于还原状态的 Q_A ,减少了微藻的光合效率。Ansari 等^[27]发现高浓度的微塑料暴露使微藻光合效率(F_v/F_m)降低。随着时间延长,光合效率逐渐恢复。深层次研究表明,微藻光合效率的降低与参与光合成基因表达的下降有关^[24]。

另外,Sendra 等^[28]发现 PS 微塑料会降低叶绿素浓度。Wang 等^[29]观察到 25 ~ 200 $\text{mg} \cdot \text{L}^{-1}$ 的聚氯乙烯(polyvinylchloride, PVC)使硅藻的叶绿素 a 含量下降。Zheng 等^[30]发现在不同浓度的 PVC、PS 和聚乙烯(polyethylene, PE)微塑料作用下,铜绿微囊藻的叶绿素 a 含量在 48 h 后显著降低。原因可能是微塑料导致细胞内活性氧的积累,破坏了细胞结构并抑制了叶绿素合成。然而也有研究得出了不同的结果。Sjollema 等^[31]证明不同粒径的 PS 和 PS-COOH 颗粒对微藻光合作用没有负面影响。出现不同结果的原因可能与微藻所处的生长时期和光照条件有

关。当微藻处于指数生长期时,能够通过代谢过程的自我调节克服微塑料胁迫带来的负面效应。另外,当实验中光照过剩时,即使大部分光被微塑料的遮蔽效应所阻挡,剩余的光也能够满足微藻基本光合作用的需要。因此,在弱光条件下,微塑料对于微藻光合作用的影响还有待进一步研究。

1.2.2 氧化应激和抗氧化酶活性降低

氧化应激是指当生物体受到环境应激时,细胞内高活性分子物质的浓度瞬间或缓慢升高,破坏细胞代谢和调节,导致细胞损伤的生理现象。当环境中存在有毒污染物时,会刺激微藻细胞产生活性氧簇(reactive oxygen species, ROS),如超氧阴离子($\cdot\text{O}_2^-$)和过氧化氢(H_2O_2)等。低水平的 ROS 可以调节细胞中许多生理生化反应,但在高浓度下对生物体有明显毒性^[32]。研究表明,ROS 诱导的氧化应激是微塑料对微藻细胞的主要致死机制(图 1)^[33]。ROS 的过度积累会氧化脂质,导致细胞膜损伤^[23]。此时生物体内会产生抗氧化酶,如超氧化物歧化酶(SOD)、过氧化氢酶(CAT)、过氧化物酶(POD)、谷胱甘肽过氧化物酶(GPx)和谷胱甘肽-S-转移酶(GST)等,通过分解产生的 ROS 以减轻污染物对生物体的潜在毒性。氧化应激是微藻应对外界污染时的典型反应^[34]。

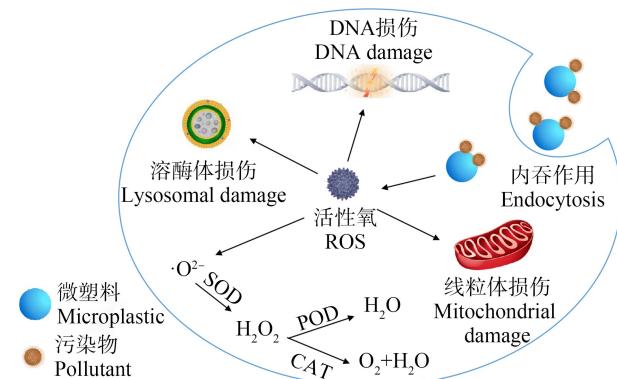


图 1 微塑料导致的氧化应激对微藻细胞的毒性作用

Fig. 1 Toxic effects of oxidative stress induced by microplastics on microalgae cells

一般来说,微藻抗氧化酶的活性在短期接触微塑料期间会增加,在长期接触后会下降^[35]。在正常生长条件下,微藻细胞的氧化和抗氧化系统处于平衡状态,细胞内 ROS 处于稳定状态。当微塑料的摄入和积累程度超过阈值时,微藻细胞的抗氧化酶系统不能保持 ROS 产生和消除的动态平衡,导致酶活

性受到抑制,抗氧化酶系统发生严重的氧化损伤,引发细胞凋亡^[36]。Bhattacharya 等^[17]将小球藻和栅藻暴露于纳米塑料中,发现 2 种微藻均摄入了纳米塑料,导致细胞内 ROS 的生成;Xiao 等^[24]发现 PS 微塑料暴露显著增加了裸藻(*Euglena gracilis*)细胞内 ROS 含量,并抑制了色素的生成。目前关于微塑料诱导 ROS 产生的原理、ROS 与微藻损伤之间关系的研究仍较少。

1.2.3 调控相关基因表达和胞外聚合物(extracellular polymer substances, EPS)变化

微塑料会影响微藻细胞中部分基因的表达。Lagarde 等^[14]发现,高密度聚乙烯(HDPE)提高了莱茵衣藻中参与糖合成途径基因的表达。Xiao 等^[24]证明将裸藻暴露于 5 μm PS 微塑料后,*CTR1* 基因的表达显著下降,该基因被证明与植物生长有关^[37]。同时,与长链脂肪酸合成相关的 *KCS* 基因显著上调,该基因的过度表达可能导致更高浓度胞外聚合物 EPS 的分泌。

EPS 是一种存在于细胞表面的多糖胶体物质,主要成分包括多糖、蛋白质(即酶和结构蛋白)、核酸(DNA)和脂质。能够形成保护层以抵御污染物的危害^[38]。在微塑料的应激作用下,微藻会产生并释放 EPS。EPS 具有净负表面电荷,能够通过静电作用吸附微塑料颗粒,促进微藻-微塑料异质聚集体的形成^[39]。异质聚集体的形成会导致微藻细胞表面结构改变,如细胞膜增厚、细胞壁破损等。分泌的 EPS 会在微塑料表面形成了一层新的结构,称为生态冠状结构(eco-corona),其会改变微塑料的表面电荷和聚集性,起到物理屏蔽的作用^[40]。研究表明,不同微藻产生的 EPS 的大小、含量和形态不同。Cunha 等^[41]考察了淡水微囊藻和海水微囊藻生成 EPS 的大小和产量,发现海水微囊藻产生 EPS 的数量更多。另外值得注意的是,EPS 具有吸附和聚集水环境中微塑料的巨大潜力。Grassi 等^[42]发现海洋硅藻释放 EPS 能够减缓 PS-COOH 在海水中的聚集速率,促使微塑料更多地与微藻聚集。微藻生物处理有望成为解决淡水和海洋环境中微塑料污染的一种高效方法。

2 微塑料对微藻种群和群落的生态毒理效应 (Ecotoxicological effects of microplastics on microalgal populations and communities)

当微塑料对微藻个体毒性作用足够强烈时,就

会对微藻种群及周围群落产生影响。表 1 中归纳了微塑料对微藻种群生态毒理效应的研究,效应终点集中于生长抑制率、光合作用和氧化损伤等方面。

首先,微塑料对微藻种群的影响与其本身的理化性质有关,如浓度、粒径等。例如 Gambardella 等^[43]的研究表明,11~13 μm 和 20~25 μm PE 对三角褐指藻生长没有抑制作用。Sjollema 等^[31]测定 PS 对杜氏盐藻的生长影响,发现小粒径(0.05 μm)、高浓度(250 mg·L⁻¹)条件下对微藻种群的抑制作用最明显。类似的,Wu 等^[26]研究了 PVC 和 PP 暴露对微藻种群光合系统的影响,发现 PVC 和 PP 浓度越高,蛋白核小球藻光合作用活性越低。Hitchcock^[44]测试了微藻群落对低、中、高浓度微塑料的响应。结果表明,高浓度微塑料显著改变了微藻群落的结构。相反,Lagarde 等^[14]对低浓度、大粒径聚丙乙烯(400 mg·L⁻¹,400~1 000 μm)和莱茵衣藻之间的相互作用进行了研究,发现莱茵衣藻的生长并未受影响。显然,浓度越高、粒径越小,对微藻种群和群落的抑制作用更显著。

其次,微塑料对不同生长时期微藻种群的影响有明显差异。微藻的生长周期可分为适应期、对数增长期、稳定期和衰亡期 4 个阶段。在不同的生长时期,外界污染胁迫对微藻种群的影响程度不同。Mao 等^[13]研究 PS 微塑料和蛋白核小球藻相互作用时发现,在适应期和对数增长期早期,蛋白核小球藻种群受到明显的抑制作用,包括生长活性降低和细胞表面结构改变。随着时间的延长,微塑料的不利影响会逐渐减轻甚至消失。类似的,孙炎等^[45]考察了聚苯乙烯微塑料对东海原甲藻生长的影响,具体表现为先抑制、后促进。PS 微塑料会抑制处于稳定期和衰亡期东海原甲藻的生长。由此可见,处于对数增长期末期的和稳定期的微藻细胞对于外界胁迫有着更强的适应与恢复能力,随着时间推移到稳定期后期和衰亡期后,微塑料抑制效应逐渐变大^[46]。Guo 等^[47]证明,PE 和 PVC 微塑料在 4 d 时不会影响三角褐指藻种群的生长,但到 9 d 时,生长抑制率明显提高。目前对于微藻种群研究大多以短期暴露试验为主,缺乏长期(168~240 h)试验的研究。试验结果可能会放大微塑料的生态毒理效应。在某些条件下微塑料能够促进微藻的生长,原因可能是特定的微藻种群能以微塑料作为基质进行生长繁殖。

表1 微塑料对微藻的生态毒理效应
Table 1 Ecotoxicological effects of microplastics on microalgae

测试物种 Test species	分类 Classification	物种环境 Species environment	Microplastics			影响机制 Effect mechanism	参考文献 References	
			Polymer	种类 Species	粒径 /μm	浓度 (mg·L ⁻¹)		
中肋骨条藻 <i>Skeletonema costatum</i>	硅藻 Diatom	海水 Saltwater	PVC	1	0~2 000	96 h	抑制藻细胞生长,叶绿素含量和光合速率降低 Inhibition on the algae growth; chlorophyll content and photosynthesis decrease	[16]
球等鞭金藻 <i>Isochrysis galbana</i>	金藻 Chrysophyta	海水 Saltwater	PE	2~6	25	72 h	对微藻生长无明显影响 No effect on the algae growth	[55]
朱氏四片藻 <i>Tetraselmis chuii</i>	绿藻 Chlorophyta	海水 Saltwater	PE	1~5	0.75~48	96 h	抑制藻细胞生长,叶绿素含量降低 Inhibition on the algae growth; chlorophyll content decrease	[56]
杜氏盐藻 <i>Dunaliella tertiolecta</i>	绿藻 Chlorophyta	海水 Saltwater	PS	0.05~6	25 & 250	72 h	对微藻生长有显著抑制作用,对光合作用无影响 Significant inhibition on the algae growth with no effects on photosynthesis	[31]
米氏凯伦藻 <i>Karenia mikimotoi</i>	甲藻 Dinophyta	海水 Saltwater	PS	1	10	13 d	抑制藻细胞生长 Inhibition on the algae growth	[57]
大溪地金藻 <i>Tisochrysis lutea</i>	金藻 Chrysophyta	海水 Saltwater	PS	2	0.04	720 h	对微藻生长无明显影响 No effect on the algae growth	[58]
东海原甲藻 <i>Prorocentrum donghaiense</i>	甲藻 Dinophyta	海水 Saltwater	PS	0.1~1	10	19 d	微塑料对微藻生长的影响表现先抑制、后促进 The effect of microplastics on the growth of microalgae is first inhibited and then promoted	[45]
三角褐指藻 <i>Phaeodactylum tricornutum</i>	硅藻 Diatom	淡水 Freshwater	PE	150	50~100	4 d & 9 d	短期暴露下对微藻生长无明显影响; 长期暴露抑制藻生长并诱导脂质积累 Microalgal growth was not significantly affected by short-term exposure; long-term exposure inhibits algal growth and induces lipid accumulation	[47]
青岛大扁藻 <i>Platymonas helgolandica</i>	绿藻 Chlorophyta	淡水 Freshwater	PVC	250			微塑料被微藻内化,抑制微藻生长 Microplastics are internalized by microalgae, inhibiting the growth of microalgae	[19]

续表1

测试物种 Test species	分类 Classification	物种环境 Species environment	Microplastics				影响机制 Effect mechanism	参考文献 References
			Polymer	种类 Species	粒径 /μm	浓度 /(mg·L ⁻¹)		
			Size /μm	Concentration /(mg·L ⁻¹)				
蛋白核小球藻 <i>C. pyrenoidosa</i>	Chlorophyta	淡水 Freshwater	PS	1	10 ~ 100	720 h	抑制微藻生长和光合作用， 对微藻细胞膜造成物理损伤 [13]	
近头状尖胞藻 <i>Raphidocelis subcapitata</i>	Chlorophyta	淡水 Freshwater	PE	63 ~ 75	130	120 h	Inhibits microalgal growth and photosynthesis, causing physical damage to microalgal cell membranes [59]	
莱茵衣藻 <i>Chlamydomonas reinhardtii</i>	Chlorophyta	淡水 Freshwater	PS	0.3 ~ 0.6	100	10 h	促进微藻生长 Promote microalgae growth [23]	
斜生栅藻 <i>Scenedesmus obliquus</i>	Chlorophyta	淡水 Freshwater	PS	0.05 ~ 0.1	1	96 h	抑制藻细胞生长、蛋白质合成及光合作用 Inhibition on the algae growth, protein synthesis and photosynthesis [60]	
富油栅藻 <i>Actodesmus obliquus</i>	Chlorophyta	淡水 Freshwater	HDPE PVC PP	100 250	0 ~ 250	504 h	对微藻生长无明显影响, 细胞内 ROS、SOD 均上升 It has no obvious effect on the growth of microalgae, and both intracellular ROS and SOD increase [27]	
水华微囊藻 <i>Microcystis flos-aquae</i>	Cyanobacteria	淡水 Freshwater	PP	0.6	0 ~ 55	264 h	抑制藻细胞生长 Inhibition on the algae growth [46]	
铜绿微囊藻 <i>Microcystis aeruginosa</i>	Cyanobacteria	淡水 Freshwater	PS	20 ~ 350	66.7	504 h	对微藻生长无明显影响 It has no obvious effect on the growth of microalgae [61]	

注: PS 表示聚苯乙烯; PP 表示聚丙烯; PVC 表示聚氯乙烯; HDPE 表示高密度聚乙烯; 下同。
Note: PS stands for polystyrene; PP stands for polypropylene; PE stands for polyethylene; PVC stands for polyvinyl chloride; HDPE stands for high-density polyethylene; the same below.

最后,微塑料除了对微藻种群直接的生长抑制外,还可以通过干扰种群调节机制影响微藻^[48]。微塑料对种群的影响有2种机制,一是自下而上的调节,基于生长速率和营养限制,二是自上而下的调节,基于捕食者对丰度的调节^[49]。如微塑料可以通过吸附水环境中的基本营养物质,如维生素B12^[50]。通过降低营养物质的可用性或吸收来破坏种群调节机制,从而通过自下而上的调节减少微藻的生长。不仅如此,微塑料还可能会改变微藻与初级消费者之间的相互作用。初级消费者往往难以分辨尺度相近的微塑料颗粒和微藻细胞^[51],对微塑料优先摄入会减少对于微藻的捕食。同时,浮游动物极易受到微塑料毒性的影响^[52]。微塑料对浮游动物的影响会进一步降低浮游动物的滤食效率^[53],导致微藻的相对丰度发生变化,通过自上而下的调节导致微藻种群数量增加^[48]。微藻增加会导致赤潮,水华发生频率增高^[54]。

种群是动态的,易受到多种环境因素的影响。分析微塑料对于种群和群落响应的干扰机制显得尤为困难。更为关键的是,由于微塑料对微藻个体的生态毒理效应具有物种差异性,其对不同微藻种群间的生态毒理效应也有所不同。微塑料对生物种群和群落的效应是本领域重大挑战之一,接下来需要更多从宏观角度开展研究。

3 微塑料对水生生态系统的生态毒理效应 (Eco-toxicological effects of microplastics on aquatic ecosystems)

微塑料粒径小,化学性质稳定,可通过多种途径进入水生生物体内,并在其组织和器官中蓄积和转移^[62]。由于微塑料的生物传递性,微藻可以携带着微塑料被高营养级生物(如初级消费者)所捕食,营养级间的转移会导致大量微塑料进入水生食物网中,并被水生生物群所同化^[63],从而对生物体内系统平衡和正常代谢造成危害(表2)。Bhattacharya等^[17]发现PS微球会特异性吸附在绿藻的表面,导致扇贝类对绿藻表面的微塑料的吸收能力增强。Cedervall等^[64]的研究表明,微塑料颗粒能够从微藻转移至浮游动物,并最终被鱼类所吸收。同样,Mattsson等^[65]证明了PS微塑料颗粒在斜生栅藻-大型蚤-鲫鱼3个营养级生物中的传递效应,并影响鲫鱼的行为方式和脂质代谢。Chae等^[66]将暴露于荧光PS微塑料中的莱茵衣藻喂食大型蚤,再用大型蚤喂食青鳉。而后在大型蚤的肠道和青鳉的消化系统中检测

到了微塑料,并发现微塑料在青鳉的肠腔中被内化。值得注意的是,微塑料中添加的化学物质也会沿着食物链向不同营养级传播。Batel等^[67]在实验室中使用丰年虾和斑马鱼组成的简易食物链,发现微塑料(1~20 μm PE颗粒)和其携带的化学物质(苯并芘)可能在丰年虾中积累,然后转移到斑马鱼身上。

尽管有越来越多的研究表明微塑料存在生物富集和生物放大效应,但只有有限的证据表明其在不同食物链中的迁移、传递和富集过程^[68]。在未来研究中,我们应集中于水生生态系统中不同营养级的典型种群和群落,阐明微塑料在各级生物体内的累积效应和危害,进一步明晰复杂食物网中微塑料摄取机制和途径^[69]。进一步研究表明,微藻也会影响微塑料在水环境中分布状态。如前所述,微藻与其他微生物对微塑料的定植产生聚合物,导致微塑料密度增加。下沉的微藻-微塑料聚集体和温盐循环会影响微塑料在水生环境中的运输和生物利用度^[70]。这些聚集体会随着海洋残骸垂直运输到水环境底部。随着微塑料在水生环境中自上而下迁移^[58],会导致其在从地表水到底栖沉积物的水生环境中广泛垂直分布,从而破坏和干扰生态系统平衡^[71]。在海洋环境中,有机聚集体(所谓的海洋雪)可以捕获微塑料并将具有浮力的微塑料运输到深海,最终提高它们在深海动物群中的生物利用度^[72]。

4 微塑料对微藻毒性作用的主要影响因素 (Main factors affecting the toxicity of microplastics to microalgae)

微塑料的生态毒性作用较为复杂,微塑料在微藻细胞上的物理吸附是毒性机制的最初原因^[43]。微塑料的吸附量和毒性取决于微塑料性质(浓度、粒径、形状、表面电荷及添加剂)^[76]和微藻的种类和特征^[41]。

4.1 浓度(Concentration)

微塑料对微藻生长有抑制作用,并且抑制率与微塑料浓度和暴露时间呈正相关^[77]。Li等^[23]分别将莱茵衣藻暴露于5、25、50和100 mg·L⁻¹ PS微塑料中,发现100 mg·L⁻¹时生长抑制率最高。Venâncio等^[78]考察了聚甲基丙烯酸甲酯(PMMA)对4种海洋微藻的毒性影响,结果表明微藻细胞生长抑制率随PMMA浓度升高而升高。Zhang等^[16]将中肋骨条藻暴露于PVC中,证明高浓度下微塑料颗粒可通过对微藻的吸附和聚集减少微藻对营养物质的吸收、降低光合效率(PS II)。然而也有研究发现,微塑料可作为微藻生长的基质,促进微藻的生长^[59]。

表 2 微塑料(MPs)通过食物网转移:营养级类别、物种、微塑料种类和粒径、浓度、暴露时间和影响
Table 2 Microplastics (MPs) transfer through the foodweb: Trophic level category, species, type and size of MPs, concentration, exposure time and effect

营养级类别 Trophic level	物种 Species	种类 & 粒径 Material & size	浓度/(mg·L ⁻¹) Concentration/(mg·L ⁻¹)	暴露时间 Exposed time	影响 Effect	参考文献 References
初级生产者 Primary producer	<i>Scenedesmus</i> sp.	纳米塑料(NPs)				
初级消费者 Primary consumer	大型蚤 <i>Daphnia magna</i>	Nano plastics (NPs) (24 ~ 27 nm)		72 h	证明微塑料能够在 3 个营养级间迁移, 严重影响鱼类的行为和脂质代谢 [73]	
次级消费者 Secondary consumer	黑鲷 <i>Carassius carassius</i>				Three level trophic web experiment demonstrated trophic transfer, severe effects on both behaviour and lipid metabolism in fish [74]	
初级生产者 Primary producer	<i>Scenedesmus obliquus</i>				微塑料降低了微藻生长速率和叶绿素浓度, 改变了微藻和大型蚤种群的生活史 [74]	
初级消费者 Primary consumer	大型蚤 <i>Daphnia magna</i>	PS-NPs	0.22 ~ 150	21 d	Microplastics reduce microalgal growth rate and chlorophyll concentration, altering the life history of microalgal and <i>Daphnia</i> populations [66]	
初级生产者 Primary producer	<i>Chlamydomonas reinhardtii</i>				微塑料可在 4 个营养级中迁移; 对微藻和大型蚤无明显毒性; 对鱼的肝组织、脂质代谢、胚胎有明显毒性 [75]	
初级消费者 Primary consumer	大型蚤 <i>Daphnia magna</i>	PS-NPs	50	48 h, 72 h, 7 d	Four level trophic transfer and individual impact; no significant toxicity for the microalga or <i>D. magna</i> ; toxicity on liver tissue, lipid metabolism, and embryos of fish [66]	
次级消费者 Secondary consumer	中华青鳉 <i>Oryzias sinensis</i>					
三级消费者 Tertiary consumer	纵纹鱲 <i>Zacco temminckii</i>					
初级生产者 Primary producer	蛋白核小球藻 <i>Chlorella pyrenoidosa</i>	PS-MPs (700 nm)	0.01 ~ 15 20	96 h	污染物对微藻和中华圆田螺的急性毒性在微塑料存在下显著增加 Acute toxicity of pollutants significantly increased in the presence of MPs for the microalgae and the snail [67]	
初级消费者 Primary consumer	中华圆田螺 <i>Cipangopaludian cathayensis</i>				小粒径(1 ~ 20 μm)的微塑料颗粒和其携带的污染物在丰年虾中积累, 随后转移到斑马鱼上; 污染物在鱼的肠道中解吸, 而后转移到肝脏中 Small (1 ~ 20 μm) microplastic particles accumulated in <i>Artemia</i> nauplii and were subsequently transferred to zebrafish; contaminants are desorbed in the gut of the fish and then transferred to the liver [67]	
次级消费者 Secondary consumer	丰年虾 <i>Artemia</i>	PE-MPs (1 ~ 20 μm)		48 h		
次级消费者 Secondary consumer	斑马鱼 Zebrafish					

另有研究表明,培养基中存在低浓度微塑料时,对微藻的抑制程度更明显。Fu 等^[20]证明 PVC 在高浓度($\geq 100 \text{ mg}\cdot\text{L}^{-1}$)下对小球藻的抑制作用比低浓度($10 \text{ mg}\cdot\text{L}^{-1}$)时小。Guo 等^[47]发现 PVC 在 $50 \text{ g}\cdot\text{L}^{-1}$ 时对三角褐指藻表现出生长促进,而在 $0.05 \text{ g}\cdot\text{L}^{-1}$ 时表现出显著抑制(37%)。原因可能是低浓度微塑料会发生漂浮并大量分散在介质中,创造更大的接触表面积,导致微藻与微塑料吸附程度增大;当为高浓度时,大多数微塑料会聚集并在底部沉淀。微塑料的聚集会随着静置时间的增加而加剧^[20]。由于产生了更多的颗粒聚集和沉降,导致实验环境中微塑料暴露量减少,抑制作用降低。因此,未来在实验中应合理控制微塑料颗粒的沉降。

4.2 粒径、形状(Particle size, shape)

粒径是微塑料的重要特征,也是其进入微藻细胞并产生毒理效应的关键因素。微藻更容易受到小粒径微塑料的影响^[79]。随着细胞粒径/微塑料粒径比的减小,微塑料的相对粒径增大,负面效应减小^[80]。Guo 等^[47]的研究表明 $150 \sim 250 \mu\text{m}$ 的微塑料不会抑制微藻生长,而粒径为 $50 \sim 74 \text{ nm}$ 的微塑料对微藻生长有抑制作用^[81]。Lagarde 等^[14]将微藻暴露在粒径 $>400 \mu\text{m}$ 的 PP 和 HDPE 中,发现微藻的生长没有受到影响且参与应激反应的基因在其接触面上没有过度表达。类似的,Zhang 等^[16]考察了 2 种粒径 PVC 的毒性作用,发现 $1 \mu\text{m}$ PVC 颗粒对微藻细胞生长有影响,而更大的颗粒(1 mm)则没有。粒径小的微塑料通常在生物体内停留时间更久,并能迁移至其他组织,造成细胞及分子水平的毒害效应。而大粒径的微塑料往往会被细胞壁的孔隙所限制^[55]。不仅如此,粒径大小能够控制微塑料中添加剂的释放^[82]。随着粒径的减小,微塑料的比表面积增加,能够加速添加剂释放到环境中。

形状也是影响微塑料性质的关键因素。在水环境中塑料颗粒形状大多不规则,通常以碎片、纤维、泡沫和薄膜的形式存在。研究表明,微塑料对微藻的毒理效应与颗粒形状密切相关,非球形颗粒如纤维对微藻生长有刺激作用,而球形颗粒则有抑制作用^[83]。目前在大多数实验中使用的均为球形微塑料,这可能会影响实验结果的准确性^[84]。进一步的研究表明,微塑料表面粗糙度与细胞内化具有相关性。与更光滑的微塑料颗粒相比,粗糙微塑料颗粒更难被细胞所内化^[85]。正如 Kooi 和 Koelmans^[86]所指出,环境中的微塑料是塑料碎片的复杂混合物,可

以将其视为具有不同尺寸、形状和密度的颗粒的连续概率分布的集合。目前关于微塑料形状对微藻毒性的机理尚不明确,未来还需更多关注形状的影响。

4.3 表面电荷(Surface charge)

工程化微塑料的表面可被功能化官能团所修饰,常见的有氨基和羧基官能团。修饰后微塑料的表面电荷对于预测它们在水生生态系统中的毒性效应至关重要,因为其会影响微藻稳定性、聚集和沉积^[87]。Zhang 等^[88]考察了带正电荷微塑料($\text{NH}_2\text{-MPs}$)和负电荷微塑料(COOH-MPs)对微藻的吸附能力,发现正电荷 $\text{NH}_2\text{-MPs}$ 对微藻细胞表现出很高的亲和力;类似的,Nolte 等^[89]研究了近头状尖胞藻对不同官能团的聚苯乙烯纳米颗粒的吸附作用,发现带正电的微塑料颗粒吸附在细胞壁上的能力强于带负电的微塑料。Liu 等^[90]验证了具有表面电荷的聚苯乙烯颗粒对斜生栅藻的生态毒性效应,结果表明正电荷微塑料比负电荷的微塑料抑制能力更高,原因在于其能够与微藻细胞膜上的磷脂双分子层紧密结合,促进污染物通过内吞作用被细胞摄入。进一步研究表明,细胞壁中存在阴离子纤维素、羧基和磷酸基团^[91],会排斥带负电的微塑料。由于大多数微塑料是不透明的,微塑料的大量吸附会产生遮光效应,影响微藻细胞的光合作用。吸附作用不仅与微塑料的物理化学特性有关,还取决于微藻的形态和生化特性^[17]。

4.4 添加剂(Additive)

塑料制造过程涉及多种化学物质添加剂(如邻苯二甲酸盐、多溴联苯醚和双酚 A 等)^[92-93]。大多数添加剂不与塑料共价结合,它们可以迁移到微塑料表面,在生物或非生物因素(如风化力、光氧化或热氧化)影响下破碎或降解后释放到环境中^[94]。添加剂与微塑料的吸附能力和毒性息息相关^[95]。比如,不同颜色微塑料添加剂的成分不同,而颜色在污染物吸附中起着重要作用^[96]。据报道,相比于白色,黑色微塑料能够吸附更多的污染物^[97]。目前尚缺乏对微塑料颜色的研究。另一方面,Capolupo 等^[98]研究了微塑料(PP、聚对苯二甲酸乙二醇酯(polyethylene glycol terephthalate, PET)、PS 和 PVC)中添加剂渗滤液对中肋骨条藻的毒性影响。结果表明,除 PET 外,所有塑料类型对微藻都具有生长抑制作用。Luo 等^[99]使用荧光标记微塑料中的添加剂,发现随着添加剂浸出量增加,微藻光合效率降低。然而也有不同的研究成果,Chae 等^[80]将盐藻分别暴露于 0 、

5、10、15 和 20 mg·L⁻¹ 4 种添加剂渗滤液(BPA、DE-HP、DBP 和 UV-326)中,确认从微塑料中浸出的微量化学物质可诱导微藻生长。Kim 等^[100]发现 100 ~ 2 000 mg·kg⁻¹ 邻苯二甲酸酯(DEHP)略微提高莱茵衣藻的生物量和叶绿素含量。出现相反结果的原因可能是由于微塑料中的添加剂常为有机化合物,且以低浓度释放时,可用作微藻的碳源,刺激微藻的生长^[101~102]。

目前微塑料毒性实验中所测得的数据很可能与微塑料中的添加剂有关,而并非微塑料本身的毒性^[103]。另外值得注意的是,在水生生态系统中水流会稀释添加剂渗滤液,导致实验室中的研究结果可能高估了环境中添加剂的毒性。尽管如此,微塑料仍可作为添加剂的载体加速其向生物体迁移,并逐级传递至更高营养级生物体内。这一部分研究仍存在很大空缺^[104]。

5 总结与展望(Conclusion and prospect)

本文回顾和总结了微塑料对微藻的生态毒理效应研究进展,阐释了微塑料对微藻个体、种群和群落、生态系统的毒理效应机制,分析了微塑料毒性效

应的影响因素(图 2)。尽管目前关于微塑料生态毒性效应研究取得了积极的进展,但由于微塑料具有分布广、可迁移传递、易富集其他污染物等特点,已有的研究方向尚存在一定的局限性,还有很多问题亟待阐明。未来的研究可针对以下几方面问题进行深入与拓展。

(1)健全微塑料检测的标准和体系。微塑料研究中存在实验计量单位与监测时丰度单位不同(g·L⁻¹、mg·L⁻¹、颗·m⁻²、颗·m⁻³)以及粒径划分不一致等问题,由于单位不统一难以进行换算比较,因此需统一不同单位间的换算关系,以便于进行环境管理。

(2)完善微塑料毒性的标准测定方法。大部分微塑料毒性效应研究中缺乏实验材料的纯度、粒径分布和添加剂种类的说明,文献中所报道的微塑料毒性很大程度是塑料添加剂引起的,且实际环境中的微塑料大多含有添加剂。并且大部分关于微塑料生态毒性的研究均没有描述分散体系中微塑料颗粒物的稳定性。由于微米级微塑料容易沉淀,导致暴露体系中微塑料浓度分布不均。在未来的研究中应予以足够的重视,这样才能更准确地评估实际环境中微塑料的生态毒理效应。

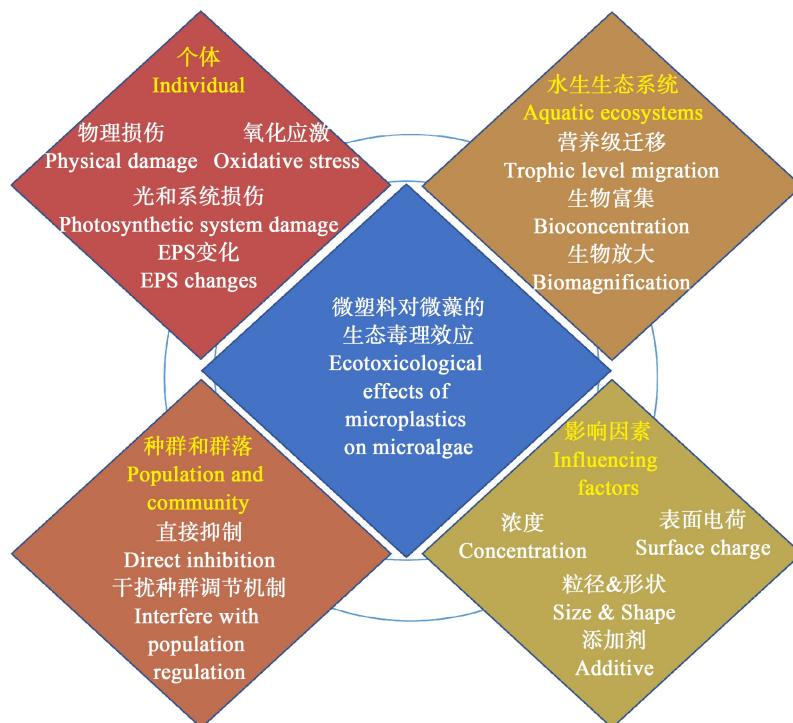


图 2 微塑料对微藻的生态毒理效应示意图

注:EPS 表示胞外聚合物。

Fig. 2 Schematic diagram of the ecotoxicological effects of microplastics on microalgae

Note: EPS stands for extracellular polymer substances.

(3)深入微塑料及污染物复合毒理效应和机制的研究。先前的研究中往往仅关注微塑料与某种污染物的吸附行为和联合暴露后的毒性作用,然而实际环境中污染物众多,应关注微塑料和污染物的系统性研究,明晰微塑料与污染物共存时的环境行为。

(4)明确微塑料及其携带污染物是否在不同营养级上存在生物放大与富集效应。考虑到大部分进入体内的微塑料最终都会排出体外,因此微塑料颗粒本身不存在生物浓缩的现象,而微塑料中吸附的污染物可能会在食物链中传递。微塑料的载体作用在水生生态系统中的影响可能会超过其自身的毒理效应。未来仍需进一步研究。

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