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## 微/纳米塑料对淡水生物毒性、机理及其影响因素研究进展

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**摘要:** 微/纳米塑料(MNPs)在全球水环境中被检出,其污染问题已引起科学界和公众的普遍关注。MNPs因其物理化学特性可对水环境生物产生不可预知的危害。本文综述了MNPs对不同营养级淡水生物(藻类、水蚤和鱼类)毒理效应的研究进展,阐述了MNPs对淡水生物毒性的作用机理,重点评述了影响MNPs对淡水生物毒性的主要因素,包括直接因素(聚合物类型、元素掺杂、尺寸、颗粒形状和表面特征)和间接因素(单体和添加剂释放、其他污染物及水溶液化学条件),并指出了塑料生态毒理学今后的研究趋势。

**关键词:** 微塑料; 纳米塑料; 淡水生物; 毒性机制; 影响因素

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## Toxicity, Mechanism and Their Impact Factors of Micro/Nano Plastics to Freshwater Organisms: A Review

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**Abstract:** Micro/nano plastics (MNPs) have been detected in the global water environment, which has attracted the widespread concern of the scientific community and the public. Owing to the unique physicochemical properties, MNPs pose unprecedented harm to species in the aquatic environment. This work overviewed the progress of the toxicity of MNPs to freshwater organisms (algae, water fleas, and fish) with different trophic levels and elucidated mechanism in the toxicity, as well as focused on the effects of main direct factors (polymer types, element doping, size, shape, and surface characteristics) and indirect factors (monomers and additives release, other contaminants, and water chemistry conditions) on the toxicity of MNPs to the freshwater organisms. Moreover, we addressed the further trends in this research field.

**Keywords:** microplastics; nanoplastics; freshwater organisms; toxicity mechanism; impact factors

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随着现代人类社会的发展,人们在生产和生活中正过度地使用各种塑料材料,并以每年上百万吨的数量向海洋环境排放着塑料垃圾<sup>[1]</sup>。目前,塑料污染已成为全球亟需解决的环境问题<sup>[2]</sup>。微塑料为颗粒直径在5 mm以下的小颗粒塑料碎片<sup>[3]</sup>,当颗粒直径处在1~100 nm范围,可将微塑料称为纳米塑料<sup>[4]</sup>,其在全球水环境均有检出及分布<sup>[5]</sup>,并已成为塑料污染的首要污染物。微/纳米塑料(MNPs)具有粒径小、比表面积大、疏水性强和难降解等物理化学特性<sup>[6]</sup>,这也引起人们对MNPs的人类健康<sup>[7]</sup>和生态环境<sup>[8]</sup>风险的关注。近年来,国际上发表了大量有关MNPs生态毒性的研究论文,其中,考察MNPs对海洋环境物种的毒理效应的居多,而考察MNPs对淡水生态系统中生物的毒性研究起步较晚,可能与前期MNPs污染调查主要集中在海洋环境有关。此外,MNPs可通过多种途径进入到淡水环境中<sup>[9-10]</sup>,使得从微生物(如细菌和部分藻类)到更复杂的生物体(如水生脊椎动物)有机会暴露于MNPs。因此,建立MNPs生态风险评估程序对解决塑料污染问题具有十分重要的意义。

藻类、水蚤和鱼类是淡水生态系统的重要组成部分,构成了淡水生态系统中由不同营养级生物所形成的食物链,也是污染物进行标准化测试(如ISO、OECD、US EPA)所经常选取的物种。本文整理和总结MNPs对藻类、水蚤和鱼类毒理效应的研究进展,并阐释MNPs对淡水生物毒性的作用机理,着重分析影响MNPs对淡水生物毒性的主要因素,最后指出塑料生态毒理学今后的研究趋势。

## 1 MNPs对淡水生物的毒理效应 (Toxicological effects of MNPs to freshwater organisms)

释放到水环境中的MNPs可经历多种迁移(如沉降<sup>[11]</sup>)和转化(如物理化学作用<sup>[12]</sup>)过程,将以多种形式对水生生物造成潜在的危害。为了实现MNPs生态风险管理,需要评价不同种类、性质及形式MNPs对水生生物的生态毒理效应。遵循van Leeuwen等<sup>[13]</sup>概述的框架,我们进一步对MNPs为代表的塑料污染物生态风险评估程序进行补充,主要包括9个程序(图1):生态危害识别、暴露评估、物理化学性质表征、效应评估、风险表征、风险分类、风险效益分析、风险削减、监测和审查、生态危害识别、暴露评估、物理化学性质表征、效应评估、风险表征、风险分类、风险效益分析、风险削减、监测和审查、生态危害识别、暴露评估、物理化学性质表征、效应评估、风险表征、风险分类、风险效益分析、风险削减、监测和审查。

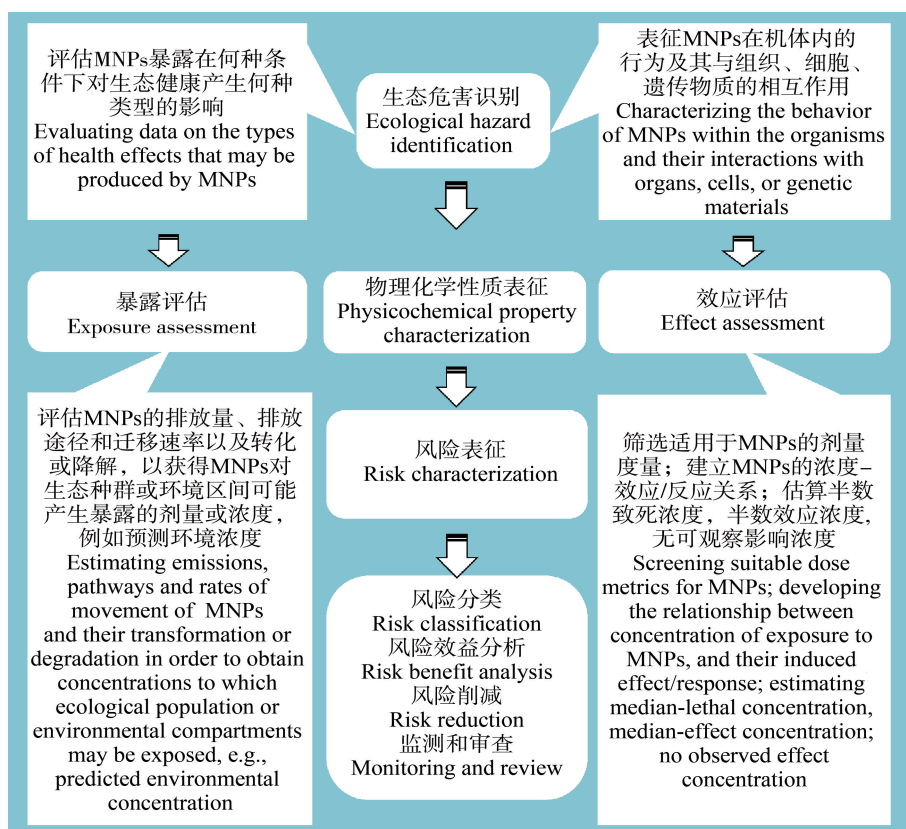


图1 微/纳米塑料(MNPs)的生态风险评估程序

Fig. 1 Programme of ecological risk assessment of micro/nano plastics (MNPs)

险效益分析、风险削减以及监测和审查。在各个评估过程中,MNPs生态毒理学数据可作为其生态风险评估的依据。

### 1.1 MNPs对藻类的毒性

藻类因个体小、繁殖快、对毒物敏感,是评价水生系统中MNPs潜在毒性的常用模式生物<sup>[14]</sup>。目前,关于MNPs对淡水藻类表观毒性作用的研究,主要涉及以下2个方面的内容。

(1)考察MNPs对藻类生长抑制毒性。少量研究表明,MNPs对淡水藻类产生了生长抑制毒性<sup>[15-16]</sup>,例如55 nm和110 nm聚乙烯亚胺-聚苯乙烯MNPs对羊角月牙藻(*Pseudokirchneriella subcapitata*)的72 h生长抑制毒性的50%效应浓度(EC<sub>50</sub>)值分别为0.58 mg·L<sup>-1</sup>和0.54 mg·L<sup>-1</sup><sup>[15]</sup>。然而,大部分研究发现,MNPs对淡水藻类的生长没有显著影响,这可能是由于细胞壁的存在限制了MNPs侵入藻细胞中。

(2)考察MNPs对藻类光合活性的抑制。Bhattacharya等<sup>[17]</sup>发现,20 nm聚苯乙烯MNPs降低了小球藻(*Chlorella* sp.)的光合活性;类似地,Mao等<sup>[18]</sup>发现,100 nm和1 μm聚苯乙烯MNPs降低了蛋白核小球藻(*Chlorella pyrenoidosa*)的光合活性。值得指出的是,藻类光合活性的降低可能与光合成基因表达的下降有关<sup>[19]</sup>。

综上所述,不同毒性指标反映出藻类对MNPs敏感性不同。因此,筛选敏感的毒性指标来评估MNPs对淡水藻类毒性仍是本领域重要的研究内容之一。

### 1.2 MNPs对水蚤的毒性

在生态毒理学研究中,水蚤也是最常用的非靶标受试生物之一。为了全面评估MNPs生态风险,考察其对水蚤的毒理效应是必不可少的一环。目前针对MNPs水蚤毒性的研究主要集中于以下3个方面。

(1)急性毒性作用。Eltemsah和Bøhn<sup>[20]</sup>研究发现,聚苯乙烯MNPs(6 μm)暴露48 h后对大型蚤(*Daphnia magna*)无急性毒性,但暴露120 h后引起水蚤致死;Rehse等<sup>[21]</sup>发现1 μm聚乙烯MNPs暴露96 h对大型蚤产生急性毒性,并确定了96 h-EC<sub>50</sub>值为57.43 mg·L<sup>-1</sup>;Liu等<sup>[22]</sup>研究发现,聚苯乙烯MNPs(75 nm)对蚤状蚤(*Daphnia pulex*)的48 h 50%致死浓度(LC<sub>50</sub>)值为76.69 mg·L<sup>-1</sup>。

(2)慢性毒性作用。据报道,MNPs对水蚤存在明显的慢性毒性<sup>[16,22-23]</sup>。例如,Cui等<sup>[23]</sup>发现,聚苯

乙烯MNPs(52 nm)抑制了蚤形蚤(*Daphnia galeata*)的繁殖并诱导其胚胎发育异常。Zhang等<sup>[24]</sup>认为,聚苯乙烯MNPs(75 nm)诱导蚤状蚤生长缓慢、生殖能力减弱及生殖方式改变(由无性向有性转变)。Bosker等<sup>[25]</sup>的研究表明,在暴露于1~5 μm MNPs 29 d后,大型蚤的种群数量明显减少。

(3)吸收与生物富集。大型蚤对聚苯乙烯MNPs(6 μm)在20 颗粒·mL<sup>-1</sup>和2 000 颗粒·mL<sup>-1</sup>的浓度下生物富集因子分别为0.034±0.005和0.026±0.006<sup>[26]</sup>。Scherer等<sup>[27]</sup>的研究表明,大型蚤以浓度依赖的方式摄入聚苯乙烯MNPs,摄入量达到6 180 颗粒·h<sup>-1</sup>,在所研究的水生生物中最高。此外,Chae等<sup>[28]</sup>通过实验研究认为,MNPs(51 nm)能够富集在大型蚤的肠道内,并可从大型蚤转移到较高营养级的中华青鳉(*Oryzias sinensis*)中,说明MNPs可沿食物链向更高营养级转移,但是否存在生物放大作用还有待进一步研究。

### 1.3 MNPs对鱼类的毒性

鱼类是水生食物链中最顶端的生物,同时具有较高的生态和经济价值,被广泛用于污染物的生态风险评价。因此,有关MNPs对淡水鱼类毒理学效应的研究备受关注,主要集中在考察MNPs对鱼类早期发育阶段生理特征的影响及生物分布和富集。例如,Malafaia等<sup>[29]</sup>观察到,低浓度的聚乙烯MNPs(38.26 μm±15.64 μm)对斑马鱼(*Danio rerio*)胚胎和幼鱼有危害效应,并对胚胎的孵化率产生负面效应,同时引起了鱼体不同形态指标的显著变化。Lei等<sup>[30]</sup>揭示了5种不同类型MNPs(~70 μm)对斑马鱼肠道产生损伤,包括绒毛破裂和肠细胞分裂。Parenti等<sup>[31]</sup>还发现,斑马鱼胚胎可摄入0.5 μm聚苯乙烯MNPs,且颗粒可富集在鱼体的消化道,并可通过肠上皮迁移到其他组织。Qiang和Cheng<sup>[32]</sup>的研究表明,1 μm聚苯乙烯MNPs可引起斑马鱼幼鱼游动距离和活动速度的降低。

此外,Ding等<sup>[33]</sup>观察到,聚苯乙烯MNPs(100 nm)可富集在罗非鱼(*Oreochromis niloticus*)的多个组织中,包括肠道、鳍、肝脏和头部,其中肠道富集的量最大。Elizalde-Velázquez等<sup>[26]</sup>确定了,黑头软口鲮(*Pimephales promelas*)对聚苯乙烯MNPs(6 μm)在20 颗粒·mL<sup>-1</sup>和2 000 颗粒·mL<sup>-1</sup>的浓度下生物富集因子分别为0.094±0.037和0.205±0.051,显著高于大型蚤的生物富集因子值。可见,吸收、富集和代谢作用将有助于进一步理解MNPs对鱼类的毒理效应,

但定量研究鱼类对 MNPs 的吸收、富集和代谢完整过程仍有大量工作要做。

综上,目前关于 MNPs 生态毒理效应的研究主要是在细胞和个体水平,如何将 MNPs 对细胞和个体水平效应外推到对生物种群、群落甚至整个生态系统的效应是本领域重大挑战之一。

## 2 MNPs 对淡水生物毒性的作用机理 (Toxicity mechanism of MNPs to freshwater organisms)

MNPs 对淡水生物毒理效应的研究方兴未艾,然而 MNPs 确切的毒性作用机理尚未完全阐明。值得注意的是, MNPs 对不同种类的淡水生物的毒性作用机理不同,加之 MNPs 对某一特定淡水生物的毒性效应并不一定通过单一机理来实现,而是通过多种机理共同作用于生物体。因此,需要开展既有深度又有广度的机理性研究工作。MNPs 对淡水藻类、水蚤和鱼类的主要致毒机理概述如下。

### 2.1 MNPs 对藻类的毒性作用机理

目前针对 MNPs 对淡水藻类的毒理学研究还十分有限,且致毒机理研究不够完善。现有研究结果显示, MNPs 对微藻毒性的致毒机理,主要有表面效应<sup>[17]</sup>、细胞膜毒性<sup>[34]</sup>和细胞内活性氧物种(ROS)引起的氧化应激反应<sup>[17]</sup>等。MNPs 对淡水绿藻毒性,还可能存在遮蔽效应、机械损伤及遗传毒性等作用机理,但这些致毒机理有待进一步阐明。

### 2.2 MNPs 对水蚤的毒性作用机理

水环境中 MNPs 较易于被水蚤摄入体内,并主要富集在肠道中,而更小尺寸乃至纳米级 MNPs 的颗粒可能会转移到肝脏和循环系统,从而导致较强的毒理效应。MNPs 对水蚤产生的活动抑制主要是由于肠道的阻塞作用引起的<sup>[35]</sup>。MNPs 对水蚤的毒理效应不仅体现在个体水平上,在组织、细胞水平及物质代谢、合成等方面也可能产生负面的影响<sup>[36-38]</sup>。Liu 等<sup>[39]</sup>研究发现, MNPs 可被摄入蚤状溞体内,高浓度水平的 MNPs 可影响水蚤的热休克蛋白和能量系统,随即影响其生长和繁殖。纳米尺寸的 MNPs 可诱导水蚤体内产生过量的 ROS,并激发下游路径,最终抑制机体生长、发育及繁殖<sup>[40]</sup>。

### 2.3 MNPs 对鱼类的毒性机理

淡水中的鱼类会误食 MNPs,亦可排泄 MNPs<sup>[41]</sup>。肠道是 MNPs 主要存在的场所和进入循环系统的通道<sup>[42]</sup>。由于 MNPs 难降解,一旦被鱼类摄入体内,其在肠道的停留时间较长,从而导致鱼类摄食量下降,进而引发机体的炎症效应,使其吸收与

储备能量的能力下降。MNPs(5 mm ~ 100 nm)对鱼的毒性作用方式与机理主要包括:消化和排泄系统损伤<sup>[30,43]</sup>、肠道炎症<sup>[43-44]</sup>、微生物菌群失调<sup>[43]</sup>、行为、感知和神经肌肉功能失调<sup>[33,45-47]</sup>、循环和呼吸系统效应<sup>[48-49]</sup>、免疫系统效应<sup>[48,50-51]</sup>、氧化应激效应<sup>[43,52]</sup>、干扰葡萄糖代谢<sup>[53]</sup>、DNA 损伤<sup>[54]</sup>及生殖损伤<sup>[55-56]</sup>。

## 3 MNPs 对淡水生物毒性的主要影响因素 (Main factors of affecting the toxicity of MNPs to freshwater organisms)

甄别 MNPs 淡水水生毒理效应及致毒机理的主要影响因素(图 2),是完善 MNPs 生态风险评估体系的重要环节。近年来,国内外的学者分别从 MNPs 基本的物理化学性质、共存物质和水溶液化学条件 3 个方面进行了研究。其中,基本的物理化学性质(如聚合物类型、元素掺杂、尺寸、表面特征及颗粒形状)是影响 MNPs 生态毒性的直接因素,而共存物质(如单体和添加剂释放、其他污染物)与水溶液化学条件(pH、盐度和溶解性有机质)是影响 MNPs 与生物体间相互作用的间接因素。

### 3.1 聚合物类型

聚合物(即母体结构)类型包括元素成分和化学结构,是所有物质的一种内在特征。因此,化学组成是了解 MNPs 生物效应的一个重要参数。MNPs 有多种聚合物类型<sup>[57]</sup>,从不可降解的聚乙烯、聚丙烯、聚氯乙烯、聚苯乙烯和聚对苯二甲酸乙二酯,到可降解的聚乳酸、聚羟基丁酸酯和聚丁二酸丁二酯。目前,研究表明,不同聚合物类型的 MNPs 对淡水生物产生了不同的毒性效应。例如, Lagarde 等<sup>[19]</sup>的研究表明,聚丙烯对淡水藻类莱茵衣藻(*Chlamydomonas reinhardtii*)的生长存在抑制作用,但高密度的聚乙烯并未产生生长抑制毒性。Renzi 等<sup>[58]</sup>的研究结果表明,不同类型 MNPs 对大型溞的毒性大小顺序依次为:聚氯乙烯(含表面活性剂)>聚乙烯(含表面活性剂)>聚丙烯(含表面活性剂)>聚乙烯。

### 3.2 元素掺杂

新型 MNPs(尤其是金属元素掺杂 MNPs)的研究与应用日益受到关注<sup>[59]</sup>。Zhang 等<sup>[60]</sup>研究发现,铁氧化物掺杂氨基化 MNPs(1 μm)在水中的稳定性高于铁氧化物掺杂羧基化 MNPs(1 μm),且铁氧化物掺杂氨基化 MNPs 对蛋白核小球藻和大型溞的急性毒性强于铁氧化物掺杂羧基化 MNPs 和非掺杂 MNPs。该研究还发现,铁氧化物掺杂 MNPs 可部分溶解于水中,但毒性作用主要由颗粒本身所引起而

非其溶解部分<sup>[60]</sup>。在低效应浓度下,藻细胞对铁氧化物掺杂氨基化 MNPs 的摄取量高于铁氧化物掺杂羧基化 MNPs。此外,铁氧化物掺杂氨基化 MNPs 被大量吸附在大型溞体表的触角、甲壳和壳刺,而铁

氧化物掺杂羧基化 MNPs 主要被积累在大型溞消化道内部。研究还表明,铁氧化物掺杂 MNPs 对蛋白核小球藻和大型溞的毒性作用机制与颗粒物诱导的氧化损伤效应无关<sup>[60]</sup>。

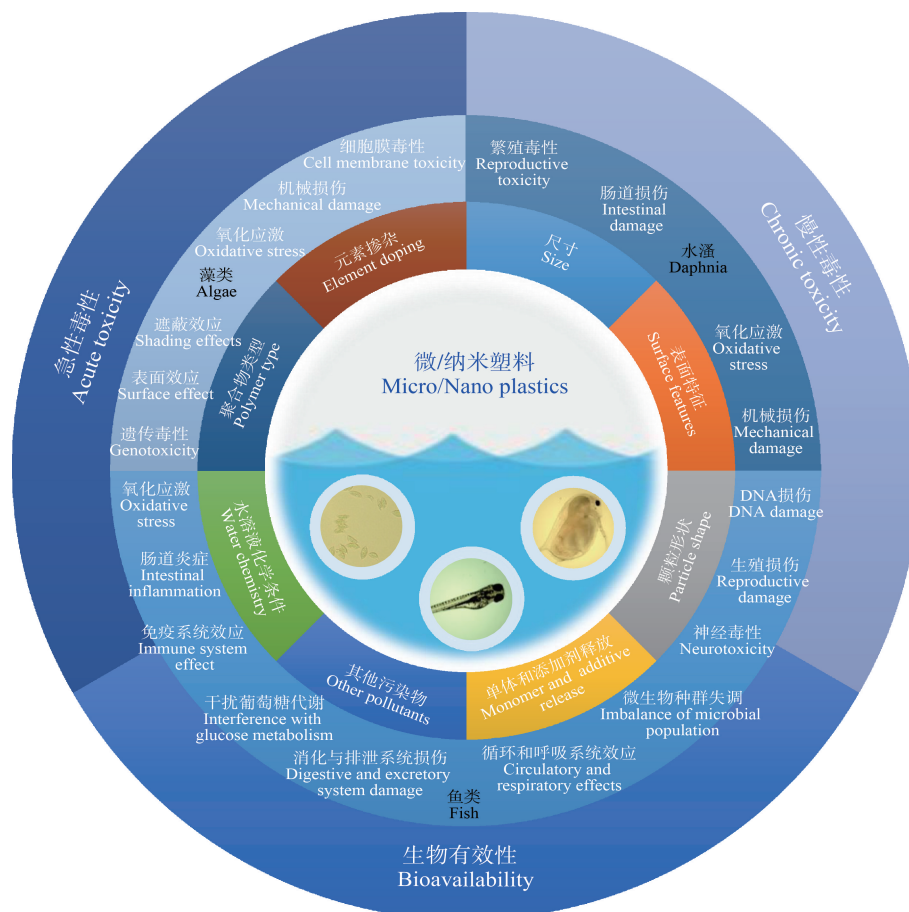


图2 微/纳米塑料对淡水生物表现毒性和致毒机理的主要影响因素示意图

Fig. 2 Schematic diagram of the main factors affecting the apparent toxicity and toxicity mechanism of micro/nano plastics

### 3.3 尺寸

尺寸大小是 MNPs 最显著的特征,它在影响 MNPs 最终特性方面至关重要。尺寸大小也是 MNPs 进入生物体并产生毒理效应的关键因素之一。学者们普遍认识到纳米塑料对淡水生物的毒理效应强于微塑料。

例如,在同等浓度( $250 \text{ mg} \cdot \text{L}^{-1}$ )条件下,50 nm 的聚苯乙烯 MNPs 比 0.5  $\mu\text{m}$  和 6  $\mu\text{m}$  的聚苯乙烯 MNPs 降低藻细胞密度的效果更为显著<sup>[61]</sup>。粒径大小是影响大型溞摄入和积累 MNPs 的重要因素之一。Scherer 等<sup>[27]</sup>发现,大型溞可摄入 1  $\mu\text{m}$  和 10  $\mu\text{m}$  聚苯乙烯 MNPs,但无法摄入 90  $\mu\text{m}$  聚苯乙烯 MNPs。Rist 等<sup>[62]</sup>研究了 2  $\mu\text{m}$  和 100 nm 聚苯乙烯

MNPs 对大型溞摄食率的影响,发现 100 nm 聚苯乙烯 MNPs 暴露下大型溞的摄食率比 2  $\mu\text{m}$  聚苯乙烯 MNPs 暴露下大型溞的摄食率降低了 21%,表明纳米尺寸比微米尺寸的 MNPs 对大型溞的毒性作用更强。类似的,Rehse 等<sup>[21]</sup>考察了 2 种粒径(1  $\mu\text{m}$  和 100  $\mu\text{m}$ )聚乙烯 MNPs 对大型溞的毒理效应,结果表明,大型溞可摄入 1  $\mu\text{m}$  聚乙烯颗粒,而无法摄入 100  $\mu\text{m}$  聚乙烯颗粒,且 100  $\mu\text{m}$  聚乙烯颗粒对大型溞无明显毒性作用。

Yang 等<sup>[63]</sup>发现,70 nm MNPs 对金鱼(*Carassius auratus*)幼鱼的毒理效应高于 50  $\mu\text{m}$  MNPs。尺寸越小的 MNPs 更易于穿越生物屏障,渗入组织并富集在器官上。同时,尺寸越小的 MNPs 具有越高的比

表面积,提高了其反应性进而提高了颗粒的生物活性。然而,最新研究显示,5  $\mu\text{m}$  和 70 ~ 90  $\mu\text{m}$  MNPs 在红罗非鱼体内产生的氧化应激效应比 300 nm 更强,意味着 MNPs 对红罗非鱼的毒性效应与尺寸呈负相关,可能的原因是由于摄入的生物碎片调节了 MNPs 的生物有效性,从而增加其毒理学潜力<sup>[64]</sup>。

### 3.4 表面特征

除了尺寸,表面特征也是决定 MNPs 毒性效应的重要因素。工程化 MNPs 特别是球型颗粒的表面可被功能化的官能团所修饰<sup>[65]</sup>,常见的有氨基化和羧基官能团。此外,在紫外辐射、机械磨损、水解和生物降解的作用下,不同官能团(如氨基和羧基)也可被引入到 MNPs 的表面<sup>[66]</sup>。一般而言,进入水环境后,表面修饰后的颗粒具有较好分散性,同时氨基化 MNPs 表面携带正电荷,而羧基化 MNPs 表面携带负电荷。目前的研究显示,带正电荷的 MNPs 比带负电的 MNPs 对藻类具有较高的相互作用<sup>[67]</sup>和毒性<sup>[77]</sup>。这可能是由于带正电荷的 MNPs 与藻细胞膜的磷脂双分子层有高的亲和力,有利于藻细胞通过内吞作用对 MNPs 进行摄取并引起毒性作用<sup>[68]</sup>。

### 3.5 形状

MNPs 具有多种形状,如球状、纤维和碎片等。研究证实,MNPs 对淡水生物的毒理效应与颗粒形状密切相关。Qiao 等<sup>[69]</sup>发现,斑马鱼以形状依赖的方式在肠道内富集聚苯乙烯 MNPs(15  $\mu\text{m}$ ),对 3 种不同形状 MNPs 富集量的大小顺序依次为:纤维(8.0  $\mu\text{g}\cdot\text{mg}^{-1}$ )>碎片(1.7  $\mu\text{g}\cdot\text{mg}^{-1}$ )>球形颗粒(0.5  $\mu\text{g}\cdot\text{mg}^{-1}$ )。Frydkjær 等<sup>[70]</sup>采用形状规则的聚乙烯颗粒和不规则的聚乙烯碎片作为实验材料,对比研究这 2 种形状的 MNPs 对大型蚤的毒性效应,发现大型蚤可摄入 2 种不同形状的 MNPs,但发现不规则的聚乙烯碎片在大型蚤肠道内停留时间会更长,并且导致大型蚤的活动受抑制率也更高。Ogonowski 等<sup>[71]</sup>的研究也表明,形状不规则的次级 MNPs 对大型蚤的毒性作用比规则的初级 MNPs 强,且导致大型蚤的死亡率也更高。

### 3.6 单体和添加剂释放

一些用于合成塑料的有毒单体<sup>[72]</sup>,如氯乙烯、苯乙烯和双酚等,在聚合过程中仍以残留形式存在,这些残留单体在其使用寿命内释放到水环境中。此外,酯键的水解也促进了这种浸出过程。因此,伴有单体浸出的 MNPs 毒理学效应亦需要重视。

在塑料生产过程中,为改善塑料性能和提升其

耐热性,通常添加多种类型的添加剂<sup>[73]</sup>,包括增塑剂、抗氧化剂、阻燃剂、着色剂和填料等,这些添加剂的主要成分通常包含邻苯二甲酸盐、多溴联苯醚、双酚 A 和重金属等有毒有害物质<sup>[74-75]</sup>,它们具有生殖毒性、致突变性和致癌性<sup>[76]</sup>。释放到水环境中的 MNPs,在老化、破碎过程中经过化学降解及生物降解多种作用下,经历长时间的浸泡会导致单体和添加剂浸出<sup>[77]</sup>,进而对水生生物产生毒害作用。另外,很多研究选用带荧光添加剂的 MNPs 以揭示其生物分布等特征。然而,研究结果显示<sup>[78]</sup>,荧光添加剂随着水溶液 pH 和浸出时间的增加,其浸出量也随之增加,并可降低藻类的光合量子产率。文献资料所获得的毒性数据很可能与实验材料(塑料基质)中的“添加剂”有关,而并非聚合物本身的“各种毒性”<sup>[79]</sup>。总体而言,关于 MNPs 中添加剂的释放对淡水生物毒性数据仍相对匮乏。

### 3.7 其他污染物

MNPs 具有憎水性和较大比表面积<sup>[57,80-81]</sup>,扮演着多重载体角色<sup>[81]</sup>。当进入水环境中,MNPs 会吸附共存的持久性有机污染物(如多氯联苯<sup>[82]</sup>、多环芳烃<sup>[83]</sup>和滴滴涕<sup>[84]</sup>)、药物及个人护理品(如抗生素<sup>[85]</sup>、毒品<sup>[86]</sup>)、天然有机大分子(腐殖酸<sup>[87-88]</sup>)及重金属(如 Au<sup>[89]</sup>、Ni<sup>[90]</sup>)等,从而产生联合毒性。共存污染物可引起 MNPs 对淡水生物的毒性改变。例如,Au 离子的存在加剧了聚苯乙烯 MNPs(50、200 和 500 nm)对斑马鱼胚胎的毒性作用<sup>[89]</sup>,这与 Au 离子与聚苯乙烯 MNPs 协同产生 ROS 和炎症反应有关,并造成线粒体损伤进而引起二者的协同效应。MNPs 的聚合物类型、成分、粒径大小、表面结构、老化性能以及共存污染物类型均可影响表面结合污染物的能力<sup>[91-93]</sup>,进而影响联合毒性作用。此外,MNPs 还可与工程纳米粒子(如纳米 Ag<sup>[94]</sup>)对淡水生物产生联合毒性。近期有研究证实<sup>[95]</sup>,携带病原菌的 MNPs 可改变鱼体胃肠道和肺部的微生物群落结构,最终导致炎症反应和氧化应激。目前,MNPs 与共存污染物的复合污染问题已成为领域研究的前沿热点。

### 3.8 水溶液化学条件

在淡水环境中,水溶液化学条件例如 pH<sup>[96]</sup>、无机离子<sup>[12,96]</sup>和溶解性有机质<sup>[96-97]</sup>对 MNPs 分散、团聚及毒性有一定的影响。例如,Zhang 等<sup>[96]</sup>研究发现,二价阳离子( $\text{Ca}^{2+}$  和  $\text{Mg}^{2+}$ )与溶解性有机质共存增加了聚苯乙烯 MNPs(50 ~ 100 nm)在水中的团聚程度,这主要归因于二价阳离子与溶解性有机质发

生了吸附架桥作用,表面改性和 pH 是影响 MNPs 在水中长期稳定性的主要因素。Zhang 等<sup>[96]</sup>通过毒性测试观察到,水溶液化学条件越复杂,氨基化和羧基化 MNPs(50 ~ 100 nm)对大型溞的急性毒性就越强。

### 3.9 其他影响因素

除了上述几种影响因素外,实验暴露条件(如暴露途径<sup>[98]</sup>、时间<sup>[99]</sup>、浓度<sup>[99]</sup>及介质条件<sup>[67]</sup>等)、温度<sup>[100]</sup>,甚至气候变化<sup>[101]</sup>都会影响 MNPs 对淡水生物的毒性效应。因此,探究 MNPs 对淡水生物的毒性作用时,需要综合考虑多种因素的影响。

## 4 结论与展望 (Conclusion and prospect)

本文回顾和总结了 MNPs 对淡水生物(即藻类、水蚤和鱼类)毒理效应的研究进展,归纳了不同因素对 MNPs 水生生物毒性的影响,探讨了 MNPs 对淡水生物毒性的作用机理。尽管目前关于 MNPs 对淡水生物毒理学方面研究取得了积极的进展,人们对 MNPs 毒性效应及机理也有了一定的认识,但仍需对以下问题进一步深入研究。

(1) 现有针对 MNPs 的水生毒性测试及机理研究,大多基于高浓度颗粒的急性毒性暴露。虽然在世界各地淡水水体中 MNPs 检出率较高,但其平均丰度普遍较低。因此,亟待加强低剂量 MNPs 长期暴露,对淡水生物早期生命阶段、繁育能力和基因变异的长期多世代影响研究。

(2) 现有针对塑料生态毒性的研究,多集中选用微塑球或微塑珠的初级塑料颗粒。然而,环境中检出的往往是废弃塑料经过物理、化学和生物转化后的塑料颗粒,且这些颗粒具有不规则的形状。据报道,在我国的淡水环境中, MNPs 的形态以纤维状为主<sup>[102]</sup>。与微塑球颗粒相比,不规则形状的塑料颗粒对淡水生物毒性研究仍十分有限,且毒性机理尚不明确。因此,下一步需加强研究不同形状 MNPs(尤其是纤维状)对淡水水生生物的毒理效应、暴露途径及毒性机理。

(3) 对于目前的 MNPs 毒理学研究而言,其质量往往是给予剂量的唯一度量。然而,研究证实具有相同化学组成的 MNPs 可表现出完全不同的毒性作用,这与 MNPs 物理化学性质(如尺寸大小)密切相关。因此,其他物化性质参数(如颗粒数目、表面积等)可能更适用于表征 MNPs 的给予剂量。因而亟需构建 MNPs 的性质-毒性效应关系,比较传统浓度-效应关系,其对丰富 MNPs 生态效应评估框架有

重要意义。

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