



环境中微塑料研究进展与展望

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摘要 环境微塑料污染正成为整个地球表层生态系统最严重的威胁之一, 受到世界多国政府的严重关切和科技界多学科广泛研究. 本文从地球科学、化学、生物学、管理学等多学科角度, 系统综述了水、土、气、沉积物、生物等环境介质中微塑料的丰度分布和来源、分离与分析方法、陆海空迁移与预测、表面变化与吸附特征、生物吸收积累与生态风险、食物链传递与健康风险、降解与削减等方面的国内外研究进展, 并展望了环境微塑料未来研究方向与关键科学问题, 旨在促进环境微塑料污染的研究与治理.

关键词 微塑料, 环境介质, 环境行为, 生态风险

尽管早在1972年*Science*就报道了新英格兰南部近海水体中存在大量的粒径变幅在0.1~2 mm的聚苯乙烯小球^[1], 但是“微塑料(microplastics)”一词则是在32年后的*Science*上首次提出^[2], 从此微塑料污染成为全球环境界热门话题. 微塑料是指直径小于5 mm的塑料碎屑和颗粒, 可以进一步划分为纳米塑料(1~100 nm)、亚微米塑料(100 nm~1 μm)、微米塑料(1 μm~5 mm)^[3]. 截至

2020年7月19日, 从Web of Science上的文献检索可知, 全球环境微塑料研究文献(SCI论文)已达3254篇, 其中中国学者贡献的文献量占比达到33.9%. 目前, 微塑料研究涉及海、陆、空等环境介质以及生物体和食物等. 在海洋上涵盖了河口、海湾、近海、深海、大洋及其沉积物; 在陆地上覆盖了土壤(农业土壤、城市土壤、湿地土壤、填埋场周边土壤、极地土壤等)、淡水(湖

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泊、河流、水库、冰雪、污水处理厂的污水)及沉积物;在大气上包括了城市、乡村、滨海大气及室内空气;在生物上包含了海洋和陆地的多种动物、植物/作物、微生物以及人体和动物粪便;在食物上涉及盐、矿泉水、啤酒、蔬菜等人类日常食品以及宠物食品。对微塑料的主要研究内容有微塑料的特征及来源、积累与分布、传输与沉降、形貌与性质、表面反应与复合污染、老化与破碎次生、生物膜与生物降解、生物吸收与毒性毒理、生态风险和健康风险、监管与替代技术、分离鉴别与观测方法及分析仪器开发等^[4-8]。本文从地球科学、化学、生物学、管理学等多学科角度,综述了环境微塑料的国内外研究进展,提出未来研究的关键科学问题与方向内容,为促进环境微塑料污染的治理与管控研究提供科学指导。

1 环境中微塑料的丰度、分布和来源

1.1 海洋

全球海水中微塑料的平均浓度从赤道东太平洋的 4.8×10^{-6} 个/ m^3 到瑞典近岸海域的 8.6×10^3 个/ m^3 ,最大差异达9个数量级,其中约45%的研究所报道的微塑料平均浓度在0.01~10个/ m^3 ^[4]。从全球海洋微塑料的分布来看,河口区是陆源微塑料的重要“汇”,尤其是大型河流的河口区通常汇聚了较高丰度的微塑料,因此成为海洋微塑料污染的主要“源”^[9]。例如,珠江三角洲河口区的微塑料入海通量约为390亿个/a和66 t/a^[10]。在靠近人类活动的区域,如沿岸潮滩、海湾、港口、海水养殖区和红树林湿地均发现有微塑料的广泛分布,微塑料的化学成分、形态、颜色、大小等与外海区域相比更具多样性,反映了其更多来源于人类日常生活。外海区域的微塑料主要分布于海水表层,而深海沉积物成为了海洋微塑料的最终归宿^[11]。在全球海洋的最深区域——马里亚纳海沟5108~10908 m表层沉积物中,微塑料含量为200~2200个/L,明显高于其他深海沉积物中的含量^[12],但关于微塑料在外海水层中的沉降机理与深海累积及生态危害仍缺乏研究。大洋区域的微塑料分布主要受到大洋环流和季风等作用的影响^[13],在太平洋、大西洋和印度洋的外海区域已出现多个范围较广的微塑料环流圈^[14],如北太平洋环流中微塑料丰度高达33.42万个/ km^2 ,微塑料大量累积会对当地的海洋生物和生态环境构成巨大威胁。在远离人类活动的南北极地区,大气、冰川、海水、沉积物、海洋生物体等也

都受到了微塑料污染的影响,其污染来源可能与大洋环流、大气传输、海雪运动、海上航运等因素有关^[15]。

1.2 海岸带

海岸带是微塑料的重要聚集区之一。目前,海岸带微塑料的调查研究区域主要涉及岛屿、旅游滩、养殖滩、港湾、自然湿地和河口等^[16,17]。陆源(河流、排污口等)、海源(潮汐、海流等)和海岸带人类活动(旅游、养殖等)是海岸带地区微塑料的三大重要源^[16,17]。此外,海岸带微塑料污染与分布受微域环境(当地人类活动、植被等)影响较大。研究表明,海岸带潮滩沉积物中微塑料的丰度在几个~数万个/kg(干重)不等,呈现高异质性特点。这一方面是由采样点的地理位置、气候、潮汐等差异造成的,另一方面也因分析方法的不同而导致^[18-20]。在海岸带地区,微塑料除了聚集在表层沉积物外,还会随着沉积作用发生纵向迁移,在深至地表以下2 m处,微塑料丰度仍可达几个~数百个/kg(干重)^[21]。海岸带微塑料污染会向滨海环境释放卤化阻燃剂等污染物,或被滨海生物体摄食与富集,为河口、盐沼、红树林和海草床等沿海湿地生态系统带来潜在的风险^[22,23]。

1.3 湖泊、河流和冰雪

近年来,越来越多的研究表明,内陆的湖泊河流和海洋一样面临着严重的微塑料污染问题。湖泊是内陆水体微塑料污染重要的“汇”。相关研究在包括北美五大湖地区、蒙古偏远湖泊、非洲维多利亚湖等世界各区域的湖泊中都发现了微塑料的赋存^[24],而我国学者也在青海湖、太湖、洞庭湖、鄱阳湖、洪湖、乌梁素海等湖泊发现了较高的微塑料丰度^[25-29]。根据采样方法的差异,这些湖泊的微塑料丰度从0.1个/ m^3 到上千个/ m^3 不等,达到甚至超过相同采样方法报道的海洋中微塑料残留水平。河流是陆源微塑料向湖泊、海洋传输的重要通道。多个模型研究对河流微塑料的输海通量进行了估算。长江被认为是全球微塑料输海通量最高的河流,但无论是对长江干流中下游的调查,还是对长江口区域的研究都表明,之前的模型研究可能高估了长江的微塑料输海通量^[30,31],而对韩国NakDong河的研究也显示了相似的结论^[32]。河流上大坝修建而形成的水库中,由于拦截作用,往往存在较高的微塑料污染,需要引起高度重视^[33]。除了湖泊、河流等典型水体外,还有研究报道了养殖池塘和暴雨形成的水塘等特

殊水体的微塑料污染特征^[34,35]。

相对于海洋沉积物, 内陆河湖的沉积物微塑料污染研究也还在起步阶段, 多是集中在河湖岸带沉积物的微塑料污染研究, 但近年来也出现了越来越多对河湖沉积物的微塑料研究^[28,36~38]。针对莱茵河的研究发现, 工业发达区的下游河岸会存在较高的微塑料丰度^[39]; 青海湖的研究也表明旅游活动区的湖岸沉积物微塑料丰度较高^[26]。Li等人^[38]对长江中下游地区18个湖泊沉积物中微塑料丰度和营养水平的分析发现, 沉积物丰度和氮浓度显著正相关, 这也提示了人类活动导致的营养输入和微塑料积累之间的关联。Dong等人^[40]对武汉东湖沉积柱中微塑料的研究也揭示了近年来人类活动增加导致的沉积物微塑料快速上升。

冰雪圈近年来被发现是淡水环境微塑料重要的“汇”。通过大气传输的微塑料会通过降雪进入高山和极低冰冻圈, 并在积雪中积累。研究人员在北极和欧洲高山地区的积雪中发现了最大丰度达到 154×10^3 个/L的微塑料污染^[41]。北极海冰也被发现是微塑料重要的“汇”, 而海冰芯中的微塑料丰度甚至远高于海冰表面, 这些海冰中的微塑料能通过融化作用向海水输出^[42]。最新的研究还表明, 北极冰雪圈表面的微塑料可能会加速冰雪圈的升温和融化^[43]。

1.4 土壤

近年来, 农田、林地等内陆土壤生态系统微塑料污染日益受到关注。目前, 已在水稻田、菜地、果园和林地等土壤中发现微塑料存在, 包括纤维、薄膜、碎片、颗粒和发泡等多种形貌类型, 以及聚乙烯、聚丙烯、聚氯乙烯、聚苯乙烯、聚酯和聚丁烯等多种聚合物成分, 微塑料丰度从几个/kg(干重)到数万个/kg(干重)不等。地表径流、污水灌溉、农业设施(农用地膜等)、肥料施用(污泥、有机肥等), 以及大气沉降等是内陆土壤中微塑料污染的重要来源^[44~46]。微塑料能在土壤环境中长期存在, 并释放增塑剂等污染物, 可能会影响土-气交换、土壤水力特征和土壤团聚体的变化^[47,48], 造成土壤质量的下降, 同时也对土壤动物(蚯蚓、蜗牛、线虫和跳虫等)生长、发育和繁殖造成影响^[49~52], 对小麦、玉米、蔬菜等农作物或烟草、黑麦草等其他陆生植物的发芽率、生长、光合作用或氧化应激反应等方面造成影响^[53,54], 同时也会通过影响土壤微生物群落组成与结构多样性影响植物-微生物相互作用体系^[55], 导致农作物产量下降并影响食品安全。

1.5 大气

大气中微塑料来源多样且复杂, 纺织厂等日常生产活动过程, 衣物服饰、生活设施等日常生活过程, 以及塑料垃圾堆放、填埋或燃烧等过程产生的微塑料都可能成为大气环境中微塑料的来源^[4]。调查结果表明, 大气环境中每日每平方米能沉降数百或数千个微塑料, 主要包含纤维、碎片和薄膜等多种类型, 成分上以天然纤维和合成纤维为主, 尺寸在200~700 μm 的最多, 且沉降通量与季节变化有关^[42,56~61]。微塑料进入到大气环境中后, 可通过风力等作用进行远距离传输, 并能以降雨、沉降等方式进入陆海环境^[43,45,56~58]。有研究表明, 全球每年约有14万吨的道路交通产生的微塑料通过大气沉降至海洋中, 成为陆海微塑料污染不可忽视的“源”^[43,59~61]。此外, 大气环境中微塑料的存在增加了飞禽类等陆生动物对微塑料的吸食概率, 构成包括人类在内的潜在健康风险问题^[62]。

2 环境介质中微塑料的分离与分析

2.1 环境介质中微塑料的分离方法

不同环境介质中微塑料的分离步骤基本类似, 均包括采样、预处理、浮选、过滤和消解。水体中的微塑料常使用拖网采集, 土壤和沉积物中微塑料采用金属器皿收集, 大气微塑料样品多用气泵抽取或沉降收集, 水生生物中的微塑料样品多使用浮游生物网采集^[63,64]。采集到的样品需先去除大的碎屑, 或用筛网初筛预处理。之后的密度浮选是分离微塑料的关键, 建议选择饱和NaCl溶液浮选低密度微塑料, 饱和NaBr、ZnCl₂或NaI溶液则更适合高密度微塑料, 也有研究使用钨酸钠或与上述溶液混合, 以实现分离效率和成本的优化^[65~67]。有研究提出电磁等分离方法, 但不常使用^[64]。浮选后的上清液需要使用滤膜进一步筛分, 常用醋酸纤维素膜、硝酸纤维素膜、尼龙滤膜、聚四氟乙烯膜和玻璃膜^[67,68], 其孔径在0.45~20 μm 之间, 需根据样品类型和微塑料目标尺寸来加以选择。对于相对复杂的样品(特别是活性污泥样品), 需要在浮选前后添加消解程序, 常使用30% H₂O₂溶液, 其对不同类型微塑料影响甚微^[66,67], 也有使用NaOH和KOH溶液来消解食品和生物样品^[64]。有使用脂肪酶或蛋白酶去除脂类和蛋白质等有机物, 但试剂价格昂贵^[66]。这些不同的分离处理方法各有利弊, 需根据样品特性和检测微塑料的目标和特征, 在实际中优化组合来实现效率最大化^[64]。

2.2 微塑料的分析、鉴定与表征方法

目前,有关环境和生物样品微塑料的分析鉴定主要包括目视法、光谱法和热分析等方法.目视法主要借助放大镜或显微镜等辅助工具根据微塑料外观特征做主观鉴别^[69,70].光谱法主要通过获得微塑料官能团信息进行聚合物成分鉴定^[71,72],常见方法包括快速大面积拉曼光谱成像、衰减全反射傅里叶红外光谱成像和焦平面阵列红外光谱成像等^[73-76].拉曼成像理论上可以鉴定亚微米级的微塑料,但该方法最大的挑战是容易受环境和生物样品中许多发射荧光物质的干扰.焦平面阵列红外光谱成像可识别数个微米的塑料颗粒.这两种方法如果和颗粒自动计数分析软件结合,可以对滤膜上已进行良好前处理的微塑料实现快速鉴定和定量.衰减全反射傅里叶红外光谱成像则可达到1~2 μm的空间分辨率.对亚微米和纳米级的微塑料,则需要原子力显微镜-红外光谱联用的纳米红外光谱成像系统来鉴别,该方法还可以获取塑料颗粒表面的力学、热学等性质^[77],这对微塑料的溯源具有重要价值.利用上述方法检测土壤和生物等复杂介质中的微塑料都存在效率低下的问题.除了光谱学鉴定和定量方法之外,热重-傅里叶红外光谱-气相色谱/质谱联用系统(TGA-FTIR-GC/MS)在分析复杂样品中微塑料的类型和总质量及其中的添加剂方面具有一定的可行性^[78,79],但该方法无法对微塑料颗粒进行计数.近年来,核磁共振氢谱(¹H NMR)、凝胶渗透色谱(GPC)等新型分析方法在微塑料聚合物鉴定和风化引起的改性结构表征研究中得到应用^[80].此外,微塑料表面微形貌分析是研究微塑料化学性质与环境行为的重要基础.对于微塑料表面微形貌分析,目前应用较多的方法是扫描电子显微镜-能谱(SEM-EDS)、原子力显微镜(AFM)等成像仪器^[76,81],微塑料比表面积和孔隙度等性质分析方法包括BET比表面积测试法和压汞仪测试法等^[82].在今后相当长一段时间,土壤、沉积物、自然水体及生物组织中数个微米、亚微米和纳米级塑料颗粒的鉴定和快速定量方法及其标准化是环境微塑料领域最关键的方法学挑战.然而,需要重视与关注有关环境中亚微米或更小粒径的微塑料鉴别与微分析方法研究^[83].

3 微塑料的陆海空迁移与预测

微塑料可以通过陆源排放、海洋活动、大气沉降等多种方式进入海洋^[84,85],对环境微塑料迁移过程的

预测,需要在明确边界条件(陆源、海源、大气沉降)下微塑料负荷的基础上,研究微塑料在陆地-海洋-大气之间不同环境介质中的迁移运输过程.

3.1 陆海迁移过程与预测模型

陆源输入是海洋微塑料的重要来源,包括污水处理厂、海岸垃圾和河流径流,其中河流是微塑料向海洋环境输送的重要途径,将全球88%~95%的微塑料负荷输送到海洋河口附近^[86].潮滩是陆海连接的纽带,在海洋动力条件作用下,陆源与海源微塑料集中在潮滩海域(包括河口)进行迁移.现今已有的河口水动力模型虽然可以实现微塑料在近岸河口区域的迁移模拟,但是只考虑了河流输入和污水排放,没有考虑人类活动和陆地相互作用的影响.van Wijnen等人^[59]使用GRE-Mis模型模拟了全球河流向沿海的每年输入量,并考虑了汽车轮胎磨损、洗衣纤维、五氯苯酚等人类活动的影响,结果显示世界各地河流微塑料的输入量随区域变化,并与废水管理密切相关.目前在淡水环境中发现的微塑料主要来源包括合成纺织品、个人护理产品、工业原料以及塑料废物的不当处理^[87,88].陆地微塑料除了保留在土壤中还会被地下水雨渗透进入淡水环境,之后以污泥和废水排放的形式进入海洋^[89].淡水微塑料与生物和非生物成分相互作用,导致夹带、沉降、生物结垢、降解等反应过程,这些过程在海洋环境中同样发生.目前在模型设置中,仍然存在很多未知过程,例如陆地微塑料如何进入河流、河流里塑料的碎片化、降解反应以及滞留性^[90].未来提高模型预测的准确性需要更多的实证研究,包括污水处理厂的微塑料移除率、河流中微塑料的降解和保留、河流中大塑料向微塑料的转化率以及影响该转化率的因素,大塑料在河流中的停留时间以及在陆地上降解的大型塑料进入河流的微塑料含量.

3.2 海洋迁移过程与预测模型

微塑料在海洋环境中受海洋动力过程以及自身物理性质的影响,其在海洋中的运动过程主要有漂浮、悬浮和沉降-再悬浮.影响微塑料在海洋中传输的因素很多,涵盖物理、化学和生物等多重过程^[91].根据微塑料的物理性质,将微塑料在海洋中的运动形式分为漂浮、悬浮和沉降3种,通过将漂浮、沉降、生物附着、降解等过程参数化,建立数值模型,实现微塑料在海洋中的迁移预测.近年来水动力模型、质点示踪以及泥

沙输运模型的长足发展为海洋微塑料的迁移预测提供了关键技术。目前已有大量研究对微塑料的漂浮过程进行了模拟预测, 结果与观测数据比较吻合^[13]。但是关于微塑料的悬浮和沉降过程的模拟预测还很少, 主要受观测手段的限制, 对塑料颗粒在海表以下的垂直迁移和沉降过程所知甚少。并且因缺乏充分的观测数据, 悬浮和沉降模型中的关键参数难以确定, 尤其是微塑料的密度、降解状态以及生物膜厚度, 这些直接影响沉降过程和微塑料的输运路径。Jalón-Rojas等人^[92]开发了TrackMPD模型来模拟微塑料, 考虑了微塑料性质(密度、大小、性质)的影响, 结果显示沉降速度对微塑料的运移路径和归宿至关重要, 并且受微塑料的性质影响。但该模型只考虑了规则形状的球体和圆柱体微塑料, 对于不规则形状的碎片、薄膜、纤维等形状尚未考虑。因此, 需要在实际观测和实验模拟的基础上进一步量化微塑料的性质参数, 结合观测和实测数据, 全面考虑降解、再悬浮-埋藏、生物附着、动物摄食等行为过程, 才能准确描述不同水层和海底沉积物中微塑料的分布, 实现对微塑料海洋迁移过程的准确预测。

3.3 大气迁移、沉降与预测模型

除了陆地和海洋环境外, 大气也是环境微塑料存在的重要介质。大气的远距离输运可以将微塑料输运至海洋表层上空甚至更远区域^[41,58,93]。大气微塑料在远距离传输过程中受气象要素, 如风、湍流、降水、湿度等因素影响, 发生干/湿沉降进入陆地或海洋环境中^[41,56]。但目前对微塑料经大气传输进入陆海环境的“源-路径-汇”的过程与通量尚不清楚, 仅有少量对大气微塑料的输运路径的研究^[94]。拉格朗日大气模型(如PYSPLIT、LAGRANTO、FLEXPART等模型)可以用于大气微塑料的来源和迁移路径的模拟^[95], 但由于描述和表征大气微塑料的相关参数尚不清楚, 大气颗粒的夹带、沉积和滞留过程以及大气的沉降速率未知, 这为大气微塑料迁移的精准模拟与预测带来了挑战。未来需进一步明确大气微塑料迁移的动力过程, 同时考虑微塑料粒径、形貌以及气象条件的影响, 精准预测大气微塑料的迁移-沉降过程。

4 环境微塑料的表面变化和吸附特征

4.1 微塑料的表面特征与变化

环境中的微塑料会因生物或非生物作用使其表面

微形貌发生变化。非生物过程包括热风化、化学风化、机械磨损和光降解。不同风化途径下微塑料的表面微形貌特征具有差异, 一般地, 物理性机械磨损多会导致微塑料表面出现划痕、裂缝和破碎等^[96]; 光热等物理化学作用会导致微塑料表面凹凸不平或粉化^[97]; 而生物降解作用多会导致微塑料表面出现凹陷或孔洞等^[98]。然而, 真实环境中微塑料的微形貌变化是多种环境因素共同作用的结果^[99]。微塑料表面形貌的变化通常会引起微塑料比表面积和孔隙度增大、分子链断裂、形成含氧或含氮等官能团, 产生极性基团, 增加亲水性, 以及改变表面电荷等微塑料理化性质的变化, 进而影响微塑料表面微生物和污染物的吸附特征^[100-102]。因此, 环境微塑料表面变化及其环境风险研究应受到关注。

4.2 微塑料表面生物膜与生物多样性

环境中的微塑料因具有比表面积高、表面风化产生丰富的官能团等特点, 极易被微生物快速附着定殖于其表面, 并形成动态变化的生物膜^[98,103]。研究表明, 微塑料表面生物膜的微生物群落组成及多样性与周围环境及某些天然基质表面的微生物显著不同, 可形成“塑料圈(plastisphere)”所特有生态位^[98,104]。同时, 微塑料表面生物膜的微生物群落结构与多样性还与塑料类型, 以及地理位置、温度和季节等环境因素有关^[4,105,106]。微塑料与其表面的生物膜间存在密切的相互作用, 一方面, 微塑料为微生物的生存提供了独特的栖息地, 可作为微生物(包括病原菌和抗生素抗性基因)的载体, 促进其在全球环境中的迁移^[105]; 另一方面, 生物膜的形成可改变微塑料的密度、疏水性、化学官能团、粗糙度等一系列理化性质和表面形貌, 甚至在一定程度上参与了微生物对微塑料的生物降解, 进而影响微塑料在环境中的迁移与归趋^[106-108]。

4.3 微塑料表面的病原菌与抗性基因

微塑料是重要的微生物生境, 也是致病菌和耐药性细菌的重要载体^[109]。在淡水河流、河口海岸及海水环境中, 与微塑料周围水体中的浮游细菌相比较, 微塑料可选择性地富集抗生素、抗生素抗性基因(antibiotic resistance genes, ARGs)、病原菌和耐药菌^[109]。微塑料表面附着病原菌可随着微塑料在多种环境介质中迁移扩散, 从而改变其自然分布的范围, 加速了生物的传播与入侵^[4]。近年来, 在北海、波罗的海、北大西洋的塑料颗粒上检出的丰度较高的人类潜在致病菌弧菌属

(*Vibrio* spp.)就印证了这一假说^[98]。国内外学者已经在水体和土壤等多种环境介质中的微塑料表面检出了大量抗生素抗性基因的存在^[110,111]，例如，聚乙烯微塑料可显著富集*sull*，*sulA/folP-01*，*tetA*，*tetC*，*tetX*和*ermE*等ARGs的丰度，并富集*sulA/folP-01*和*tetA*等周围水体中没有的ARGs^[109]。微塑料表面对ARGs的选择性富集与微塑料的材质、水体以及盐度等因素相关。大量致病细菌耐药菌进入环境后可能诱发微生物间的基因交流，在微生物分子遗传学层面引发可移动遗传元件介导的病原菌致病基因与抗性基因的水平转移，造成抗生素抗性基因的不可控传播及耐药致病菌的大面积爆发，甚至引发生态灾难^[112]。

4.4 微塑料对污染物的吸附与释放机制

微塑料自身的疏水特性可使其吸附(或富集)环境中疏水性有机污染物^[113]，在大量的环境微塑料样品中已检测出多氯联苯(PCBs)、多环芳烃(PAHs)和有机氯农药等污染物^[114]。在某些情况下，PCBs在微塑料上的浓度甚至可达到其在水中浓度的 $10^5\sim 10^6$ 倍^[115]。疏水性有机化学物质在塑料聚合物上的吸附常符合双模态聚合物吸附模型，包括吸附和分配两种机制^[116]。吸附取决于聚合物与化学物质之间的亲和力，而两者之间的静电和疏水等作用力是微塑料和污染物之间相互作用的主要机制，除此之外二者相互作用还包括p-p键、H键、表面络合作用等^[115]。

微塑料与环境污染物的相互作用受到自然环境中塑料自身性质(如颗粒大小、比表面积、晶体结构等)和有机污染物理化性质(如疏水性、解离状态以及空间构型等)的影响^[117]。一般情况下，二者间相互作用随微塑料粒径减小、比表面积增加、污染物疏水性增加而增强。另外，玻璃态聚合物(如聚苯乙烯、聚氯乙烯等)通常具有较高度度的分子交联和密度，其吸附性能不及空间结构松散的橡胶态聚合物(如低密度聚乙烯)，但是由于分子内部扩散的吸附机制，较容易出现解吸迟滞现象^[118]。除从环境中吸附有机污染物外，微塑料还能够向环境中释放小分子单体或添加剂，如阻燃剂、塑化剂和着色剂等^[119]。研究表明，如果塑料薄膜不从土壤中回收，土壤中酞酸酯的浓度可从 2 mg kg^{-1} 上升至 $5.5\sim 6.6\text{ mg kg}^{-1}$ ^[120]。

4.5 微塑料与污染物的相互作用及效应

环境中微塑料能被多种营养级的生物摄入，其上

所吸附的污染物也被携带进入到生物体内^[121,122]。尽管微塑料自身对生物体的危害相对有限，但是所携带污染物在生物体内如被释放，可对生物体产生毒性^[123]。微塑料颗粒上所携带的污染物也可以沿着食物链在各种营养级上传递^[124]。微塑料对污染物的“载体”效应受微塑料性质及污染物种类的影响^[118,125]。微塑料对有机污染物生物富集的影响取决于生物体对微塑料负载的有机污染物的吸收效率以及生物体对有机污染物的代谢过程。Diepens和Koelmans^[126]利用MICROWEB模型对微塑料影响下疏水性有机污染物的生物富集进行了理论计算，结果发现由于吸附态的有机污染物生物可利用性有限，微塑料的存在会抑制有机污染物的生物富集和食物链传递，然而对于容易代谢的污染物如某些PAHs物质而言，这种生物可利用性的降低同时降低了污染物在系统中的降解和代谢，增加其环境持久性，长远来看反而增加PAHs的生物累积及食物链放大。

5 微塑料的生物吸收、积累和生态风险

5.1 海洋生物积累与生态风险

微塑料可以通过多种途径进入生物体，最常见的是微塑料通过动物摄食进入消化道，例如，目前已在加拿大沿海、美国查尔斯顿港，我国渤海、黄海、东海、南海等海域不同浮游动物类群体内被检出^[127-129]。除此之外，微塑料还可以通过生物体表组织的间隙以揉合或渗入的方式进入生物体，或者黏附在生物的组织表面。例如，有研究表明微塑料可以通过揉合方式进入贻贝的足丝、通过胚孔进入斑马鱼的胚胎及黏附在贻贝的足等非消化器官的表面等^[130,131]。

进入到生物体的微塑料会通过多种方式在生物体内进行转运。例如，微塑料可以进入鱼类的鳃部血管，随血液循环转运到肝脏等部位，甚至进入性腺而后传递给子代；微塑料还可以进入贻贝的血淋巴循环系统^[132]，随血淋巴转运到其他部位。

微塑料在生物体通过转运后可以在多种器官进行积累。一般而言，消化道是微塑料在动物体内最主要的积累器官，同时研究表明鳃也是部分动物易于积累微塑料的部位。有报道指出在动物的肝脏、脑，甚至肌肉组织等也积累了微塑料。其中，室内暴露采用尺寸极小的荧光微塑料甚至纳米塑料能给出在上述器官积累的较为信服的证据，而在野外样品发现肝脏和肌肉中积累微塑料的报道还有待进一步验证^[133]。微塑料可以通

过多种途径进入生物体并通过多种方式在生物体内转运,在生物体的不同器官和组织积累,表明这些器官或组织都将是微塑料潜在的作用靶器官.因此,今后对微塑料的生态风险研究必须在深入探究微塑料进入生物体的途径、转运方式和作用靶标的基础上进行综合分析和评估.

生物对微塑料的积累能影响生物体营养摄食、生长、发育、繁殖和生存率等,可能在生态系统层面上进一步影响次级生产力,降低粪便沉降率并进而影响生物泵^[134],改变不同水层中的捕食者与被捕食者之间的耦合关系^[135].

5.2 土壤生物积累与生态风险

微塑料在陆地生态系统分布,可通过土壤动植物的吸收和积累而诱发生态风险^[136].土壤线虫、跳虫、蚯蚓和蜗牛等土壤动物均能摄入不同尺寸的微塑料,通过荧光或染色方法可清楚追踪其在体内的分布^[52,137].微塑料会使线虫的成活率、体长和繁殖率明显下降,并导致肠道损伤和氧化应激基因表达升高^[52],甚至产生跨代的毒性^[137].在黏壤土中对白符跳暴露聚氯乙烯微塑料,能引起其肠道微生物群落变化^[138].蚯蚓能选择性摄入小尺寸微塑料,表现出氧化胁迫,并影响能量代谢^[139].研究发现蜗牛摄入土壤中的聚对苯二甲酸乙二醇酯微纤维后,能利用其特有的齿舌和肠道来加速微塑料消解^[50].微塑料对植物的影响还少有报道,但最近有研究表明微塑料可延缓蚕豆种子发芽和生长,诱发遗传毒性^[140].另一项研究发现,0.2 μm的聚苯乙烯微球能通过质外体空间进入生菜根部,分布于维管组织和细胞间隙,并能迁移到茎叶部位^[54],其关联的生态和健康风险应受到关注.

5.3 淡水生物积累与生态风险

微塑料同样会被淡水生物摄入和积累.实验室研究表明,金鱼可以在食物存在或食物包裹的情况下摄入微塑料,同时造成消化道的损伤,不同类型的微塑料在金鱼体内还存在滞留时间的差异^[141].基于野外采样调查的结果同样发现了淡水鱼体内的微塑料积累.目前多个野外研究表明,野生淡水鱼体内的微塑料检出率从10%以下到100%不等,鱼体内的微塑料丰度从0.1个/条~20个/条不等,但大多小于3个/条^[142].除了鱼类以外,淡水浮游动物、淡水双壳类、底栖大型无脊椎动物等淡水生物类群也可以摄入微塑料并在体内积

累^[143,144].Hu等人^[145]还在蝌蚪体内发现了微塑料的积累.值得注意的是,在蝌蚪、底栖动物等体内发现的微塑料丰度并不低于前面提到的淡水鱼类微塑料积累的水平.这意味着单位体重下,小型淡水生物的微塑料丰度可能会高于鱼类等大型淡水生物,这可能预示着更高的生态风险.事实上,对于淡水底栖动物的研究发现,微塑料会在较长时间尺度上对淡水底栖动物的群落结构造成影响^[146],还有可能会影响淡水底栖动物群落在氮循环方面的功能^[147].对浮游动物来说,微塑料暴露会对其生长、后代数量、行为等产生不利影响^[148,149].另外,虽然藻类不会摄入微塑料,但一些研究显示,微塑料的存在可以对淡水藻类的生长、生理指标产生胁迫^[149-151].

6 微塑料的食物链传递与健康风险

6.1 陆地动物摄食与健康风险

食物链富集传递是微塑料暴露的重要途径.已知微塑料能在海洋环境中沿着从浮游植物到浮游动物,再到哺乳动物的食物链富集传递^[152].陆地动物,如啮齿类和禽类都可以通过误食或者食物链摄食等途径使微塑料进入消化道,并进一步进入到血液、肌肉、肝脏等器官和组织中,从而危害身体健康^[153].但目前关于微塑料被陆地动物摄食及其沿食物链传递的研究仍非常有限.Huerta Lwanga等人^[154]首次报道了家庭花园中的微塑料可通过土壤-蚯蚓-鸡的食物链进行传递,从土壤到蚓粪、鸡粪和鸡砂囊的微塑料富集系数分别为12.7、105和5.1.鸡砂囊可作为人类的食材而被人体摄入,从而对人体健康产生潜在影响.最新研究发现,人类粪便样品中也有微塑料检出,平均浓度为20个/10 g^[155],表明陆地食物链中可能已经广泛存在微塑料的污染.另外,大气中的微塑料可能通过呼吸摄入进入呼吸系统,这些都会带来微塑料的人体健康风险.未来有必要对食物链中的不同营养级进行微塑料污染特征调查,并进一步开展微塑料对人体健康风险的研究.

6.2 植物吸收传输与健康风险

有关研究已证实土壤中微塑料不仅可通过食物链传递、富集,带来潜在的环境健康风险,也可影响土壤作物的生长发育^[156].而对土壤中微塑料能否直接进入作物则需引起重视.李连祯等人^[157]在营养液水培条件下发现绿叶蔬菜——生菜能吸收和积累聚苯乙烯塑料

微球(0.2 μm), 并能将其运输到可被直接食用的茎叶之中。Jiang等人^[140]则报道了水培条件下聚苯乙烯微球(0.1 μm)可以被蚕豆根系吸收和积累, 干扰营养物质运输而产生遗传毒性。Sun等人^[158]通过激光共聚焦显微镜观察到聚苯乙烯微球(<0.1 μm)在拟南芥的根内部有分布。近来也有报道不同粒径的纳米塑料和微塑料颗粒能积累在水芹(*Lepidium sativum*)种子的种皮^[159]。目前相关研究还处于初步探索阶段, 仅局限于对现象描述, 而对其吸收途径、传输过程与内在机制及其关键控制因素尚不清楚并有待深入探讨。通过废水水培试验和模拟废水灌溉的沙土培养试验, Li等人^[54]发现尺寸在亚微米级甚至是微米级的聚苯乙烯和聚甲基丙烯酸酯塑料颗粒都可以穿透小麦和生菜根系进入植物体, 并能在蒸腾拉力的作用下, 通过导管系统随水流和营养流进入作物地上部可食用部位。同时, 他们还发现塑料颗粒进入植物体的另一种通道与机制: 在植物新生侧根边缘存在狭小的缝隙, 微米级塑料颗粒可以通过该通道跨过屏障, 进入根部木质部导管并进一步传输到茎叶组织。

7 环境微塑料的降解与削减

7.1 环境中微塑料的物化破碎与生物降解

塑料进入环境后, 在物理(机械磨损、土壤翻耕、水体扰动、波浪击打、风力搬运)、化学(紫外光辐射、冻融循环)和生物(植物根系生长、动物摄食与排泄、微生物降解)过程的作用下发生风化、裂解、降解, 进而形成塑料碎片或微塑料^[160]。微生物作为自然界强大的分解者, 几乎可降解所有已知的天然化合物及大部分人工合成物质。目前对环境中(微)塑料降解菌的研究主要集中在陆地环境, 有关近海、深海远洋以及各种特殊极端环境中(微)塑料降解菌的报道仍非常有限^[161]。在陆地环境中已报道的塑料降解菌包含了30多个属的细菌和真菌, 包括芽孢杆菌属、葡萄球菌属、假单胞菌属、无色菌属、寡养单胞菌属、红球菌属, 以及丝状真菌(曲霉菌)和酵母菌等^[161,162]; 其分离来源包括土壤、垃圾填埋场、堆肥以及动物肠道等^[163]; 可降解的主要塑料聚合物类型包括聚乙烯、聚对苯二甲酸乙二醇酯、聚苯乙烯、聚氯乙烯、聚丙烯和聚氨酯^[164,165]。除了单一细菌或真菌菌株, 微生物菌群和生物膜也可有效降解环境中的微塑料^[163,166]。关于微塑料的微生物降解机制, 研究表明微生物可通过分泌水解

酶、酯酶、脂肪酶、蛋白酶K、角质酶、脲酶、氧化酶等多种胞外酶来降解塑料大分子^[167]。

7.2 环境中微塑料的风险削减策略与技术

源头预防是控制和削减微塑料环境风险的最佳选择^[168-170]。微塑料体积小(nm~mm), 一旦进入环境则几乎难以回收, 这就要求针对环境微塑料的不同来源, 利用全生命周期方式加强塑料全过程管理, 消除微塑料的潜在风险^[171]。具体来讲, 在法律制度方面, 通过新建、修订和完善相关法律法规, 为塑料污染防治提供法律依据; 在经济政策方面, 鼓励废旧塑料资源化和循环利用, 设定材料和产品标准提高再生塑料质量, 通过限制生产、禁止使用、产品替代以及税收调节等政策从源头减少塑料使用, 探索利用生产者责任延伸制促进塑料垃圾回收, 减少塑料垃圾进入环境^[172]; 在技术创新方面, 提升产品设计延长塑料制品的使用周期, 研发环境友好型的替代材料, 减少对塑料原材料的使用^[89]; 在科学研究方面, 揭示微塑料的环境行为和生态效应, 评估微塑料的生态风险和人体健康危害, 提供塑料危害的直接证据; 在宣传教育方面, 提升公众意识, 转变消费模式, 发展公民科学, 倡导全民参与环境塑料垃圾(微塑料)污染防治。

8 环境中微塑料的研究展望

微塑料污染作为一个新兴的全球环境问题, 在研究与治理上, 尤其在真实环境及微塑料实际含量水平下, 仍有诸多具有挑战性的科学、技术与管理问题, 有待回答与解决。

(1) 方法学: 对亚微米和微米级微塑料(<20 μm)乃至纳米级微塑料的分析方法有待突破。由于环境中微塑料的丰度、生物可利用性和生物毒性等与其尺寸大小密切相关, 近年来, 对小粒级微塑料尤其是亚微米和纳米级塑料分离和鉴定技术的突破一直是国际上在微塑料方法学方面努力的目标^[173]。

(2) 环境行为: 微塑料在多介质环境中的分布、迁移、输运及通量的大尺度综合研究。目前, 国际上对局域、单介质环境中的微塑料调查数据已有较多的积累。如何结合对现有数据的分析, 同时组织开展多介质跨区域的大规模调查和模拟是今后在微塑料环境行为研究方面需要着重思考的问题^[174]。未来还需要着重考虑环境中微塑料的次生过程、生物降解与添加剂释放规律, 微塑料表面性质改变、生物膜形成与生物多样性

变化, 化学污染物、生物致病菌与微塑料表面反应及复合污染, 复合污染物共输移、归趋、风险及预测等。

(3) 生态效应: 构建环境微塑料生态毒理学的研究方法、综合监测、量化表征和微塑料对生态系统的长期影响评估体系。当前, 微塑料的室内生态毒性研究场景与真实环境相去甚远, 并且采用的是经典的可溶性污染物的生态毒理学实验方法。鉴于微塑料颗粒态独特的理化特性, 亟须构建环境微塑料室内生态毒理学的专门方法。由于环境条件的复杂性, 在真实环境中很难甄别微塑料在短时间对单个物种的影响。因此, 选取污

染热点区域开展在真实环境及实际含量水平下微塑料对生物生态系统的长期影响与生态风险评估尤为重要。

(4) 健康风险: 探究微塑料进入人体的多种途径, 量化评估微塑料的健康风险与危害性。微塑料在人类生存的环境中无处不在。已有研究表明, 微塑料不仅可以通过食品和饮用水等进入人体^[175], 而且可以通过呼吸途径^[176]及食物链进入人体^[54]。因此, 今后必须加强微塑料进入人体的途径、风险及危害研究, 全面评估人类对微塑料的年摄入量。在综合利用微塑料生态毒性数据和环境暴露组学信息的基础上, 系统评估微塑料对不同人群的健康风险。

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Summary for “环境中微塑料研究进展与展望”

Research progresses and prospects of microplastics in the environment

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The term “microplastics” (MPs) refers to fine plastics less than 5 mm in size and includes primary sources from the original production of small-sized particles and secondary sources from the degradation or fragmentation of large plastics. MPs have been widely detected in marine (estuaries, bays, coastal zones, deep seas, ocean waters and sediments), soils (farmlands, urban soils, wetlands, landfill and polar areas), freshwater (lakes, rivers, reservoirs, snow and ice, and sewage treatment plants) and sediments, atmosphere (outdoor and indoor airs), living organisms (plants, animals, microorganisms, human and pet faeces), and foods (table salts, drinking waters, beers, vegetables and pet foods). Besides, MPs could be acted as the vector for many environmental pollutants, pathogens and even antibiotic resistance genes (ARGs). Moreover, MPs can be taken up by various terrestrial and aquatic organisms and transfer along the food chain at various trophic levels. Thus, environmental MP pollution is becoming one of the most serious threats to the Earth’s surface ecosystems which has attracted serious concern and extensive research by many governments and the scientific community worldwide. Up to now, comprehensive studies and reports on the latest multidisciplinary research progress on microplastics in multiple environmental media remain limited. From the perspectives of earth sciences, chemistry, biology, and management, this article systematically reviews the research progress on the abundance, distribution and sources of microplastics in the waters, soils, atmosphere, sediments and organisms; the separation and analytical methods of microplastics in multiple environmental media; the migration and prediction of microplastics in terrestrial, marine and atmospheric environments; the surface changes and biofilm formation on microplastics and their adsorption characterization of environmental pollutants, pathogens and ARGs; the biological uptake, accumulation and ecological risks of MPs; the food chain transfer and health risks of MPs; the physico-chemical fragmentation and biodegradation of MPs in the environment and their risk reduction strategies and techniques. Finally, the key scientific issues and future research directions of environmental microplastics are also proposed in this review, such as methodology breakthroughs in separation and identification of submicron and nanoscale microplastics; comprehensive study on the distribution, migration, transport and flux of microplastics in environmental multi-media at cross-regional and global scale; comprehensive monitoring, quantitative characterization and long-term evaluating the impacts of environmental microplastics on ecosystems; and the systematic assessment of human health risks of microplastics to different populations.

microplastics, environmental media, environmental behavior, ecological risks

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