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浮游生物对持久性有机污染物迁移和转化影响的研究进展

刘溱[1]，赵妍[1,2,*]，吕梦晨[1]，唐学玺[1,2]

1. 中国海洋大学海洋生命学院,青岛 266003
2. 青岛海洋科技中心海洋生态与环境科学功能实验室,青岛 266003

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摘要: 持久性有机污染物(persistent organic pollutants, POPs)被持续排放到自然环境中,严重危害环境安全和生命健康。海洋、河流等水环境是 POPs 重要的“汇”,作为水生食物链的起点,浮游生物在水生生态系统的物质循环和能量流动中扮演着重要的角色,其对 POPs 的吸附、吸收、转化及运输,在很大程度上影响了 POPs 的环境行为。本文将浮游生物对 POPs 迁移和转化的可能影响进行了总结,综合分析了浮游植物和浮游动物对 POPs 的吸附-吸收和生物富集/放大过程及影响以上过程的生物和环境因素,从脱卤代谢、氧化代谢和微生物联合代谢 3 个方面阐述了浮游生物对 POPs 的降解及转化机制,最后讨论了浮游生物的生物泵作用对 POPs 垂直迁移的影响。本文能够为水生生物影响 POPs 迁移和转化的研究提供重要参考。

关键词: 持久性有机污染物;浮游生物;生物富集;生物代谢;生物泵
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Research Progress on Effects of Plankton on Transport and Transformation of Persistent Organic Pollutants

Liu Zhen[1], Zhao Yan[1,2,*], Lv Mengchen[1], Tang Xuexi[1,2]

1. College of Marine Life Sciences, Ocean University of China, Qingdao 266003, China
2. Functional Laboratory of Marine Ecology and Environmental Science, Qingdao Marine Science and Technology Center, Qingdao 266003, China

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Abstract: Persistent organic pollutants (POPs) are continuously released into the natural environments, causing severe threats to the environmental safety and health. As the entrance of the aquatic food chain, plankton play an important role in the material cycle and energy flow of aquatic ecosystems, and their adsorption, uptake, transformation and transportation of POPs could greatly affect the environmental behavior of POPs. This paper summarizes the possible effects of plankton on the transportation and transformation of POPs in aquatic environments, comprehensively analyzes the adsorption-absorption and bioconcentration/amplification processes of POPs by phytoplankton and zooplankton, as well as the biological and environmental factors affecting the above processes in aquatic

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第一作者:刘溱(1999—),男,硕士研究生,研究方向为海洋生态学,E-mail: 1120694670@qq.com
* **通信作者**(Corresponding author), E-mail: zhaoyan@ouc.edu.cn

environments. Furthermore, the degradation and transformation mechanisms of POPs by plankton were discussed in terms of dehalogenation metabolism, oxidative metabolism, and microbial co-metabolism. Finally, the biological pump effect of plankton on the vertical transport of POPs was discussed. This paper provides important references for the research about the influence of aquatic organisms on the migration and transformation of POPs.

Keywords: persistent organic pollutants; plankton; bioaccumulation; biological metabolism; biological pump

持久性有机污染物(persistent organic pollutants, POPs)通常指生物降解半衰期、生物富集系数和毒性符合一定规则的有机化合物,有数千种之多,它们具有生物毒性、难降解性、易生物浓缩性、远距离迁移等特点,会在长时间跨度上持续危害自然环境与人类健康安全[1]。《斯德哥尔摩公约》(简称 POPs 公约)对部分 POPs 的使用和排放进行了进一步限定,包括其生物降解性、生物富集性、迁移性和在极地水体中的浓度符合一定规则,并需要协议国一致同意采取控制措施。目前,研究较多的 POPs 主要包括多溴联苯醚(polybrominated diphenyl ethers, PBDEs)[2]、多环芳烃(polycyclic aromatic hydrocarbons, PAHs)[3]、多氯联苯(polychlorinated biphenyls, PCBs)[4]和全氟化合物(perfluoroalkyl substances, PFASs)[5]等。

环境中存在的 POPs 有 2 种主要来源:工业来源和自然来源[6-7]。前者主要指人类工业活动产生的 POPs 向环境中排放,例如 PBDEs 和 PCBs 均属于商用卤代阻燃剂,由于缺乏紧密的化学键相连,常在使用过程中从产品中逸出;而自然来源则包括自然灾害、生物质代谢、环境化学作用等,例如自然环境中的 PAHs 可能源于石油渗漏、植物残渣、森林和草原火灾等自然因素[8]。POPs 的环境影响和最终归宿是多种过程相互作用的结果,包括物理迁移、多媒介间分配和生物地球化学循环[9]。

海洋、河流等水环境是 POPs 重要的“汇”[10]。全球范围内的水环境,包括近海[11]、远洋[12]、极地[13]、深海[14]和海底沉积物[15],都报道了 POPs 的发现与分布。尽管有些被列入《斯德哥尔摩公约》的 POPs 在部分国家和地区已经停止生产,但它们仍然可能长期存在于水环境中。Lohmann 等[16]认为每年约为 40 t 和 1 t 的 PBDEs 分别通过大气沉降和干沉降输入大西洋,按照这个比例估算全球海域则分别为 135 t 和 3.5 t。PCBs 自 20 世纪 80 年代已经停产,但仍有约 10% 的 PCBs 会持续活跃于环境中[17]。在重工业区和港口附近的海域通常会检测到海水和沉积物中积累高浓度的 PAHs[18]。浮游生物是生活在表层水体中且缺乏自主游泳能力的微小生物的总称,其中既有担任初级生产者的浮游植物,也有以浮游植物为食的浮游动物,它们之间相互作用、相互联系,共同组成了水生食物网的基础[19],在维持自然环境健康和生态系统平衡以及影响气候调节方面发挥着重要作用[20]。POPs 通过陆源输入和水-气分配进入水体中后,庞大的浮游生物群落通过自身的富集和转化,以及沿食物链的累积,将对 POPs 在水环境中的命运造成显著影响[21]。目前,已有大量研究展开了浮游生物对 POPs 环境行为影响的研究,因此,本文针对世界范围内污染严重、重点关注的多种 POPs,系统论述浮游生物对典型 POPs 的富集,累积和转化模式,以及浮游生物对 POPs 在水环境中迁移和转化的具体影响,为进一步加深 POPs 在水环境中环境行为的研究提供理论基础。

1　POPs 在自然环境和浮游生物间的分配方式(Distribution of POPs between natural environment and plankton)

由于具有蒸气压低和强疏水性的特点,进入水环境中的 POPs 容易被颗粒物质和生物体吸附。水体中 POPs 的环境行为会受到浮游生物群落的显著影响,由于自身理化性质的差异,它们以不同的吸附速度附着在浮游生物体表,继而扩散到生物体内,并沿食物链向上传递。浮游生物能够通过多种方式和途径富集环境中的 POPs,参与 POPs 在水生生态系统中从源到汇的变化过程,并最终影响 POPs 在自然界的环境行为。

1.1　浮游生物对 POPs 的富集作用

浮游生物对 POPs 的生物吸附是其生物富集的第一步。生物吸附是被动过程,其机制包括静电相互作用、表面络合、离子交换、疏水作用等多种化学、物理和代谢过程[22]。浮游生物群落中生物吸附的主要载体是微藻,这是因为微藻的细胞壁能够提供羟基(—OH)、氨基(—NH_2)、硫醇(—SH)、羧基(—COOH)、硫酸根(SO_4^{2-})和磷酸根(PO_4^{3-})等官能团。这些官能团分别用作结合位点和离子交换剂,用于形成金属离子络合和吸附有机污染物[23]。微藻对

POPs的吸附过程通常是高效且快速的,这个过程一直持续到吸附量和在液体中的剩余浓度之间达到平衡[24]。目前已发表的文献研究了微藻细胞对多种POPs的吸附作用,包括PBDEs[25-26]、PCBs[27-29]、五氯苯酚[30]、PAHs[31-32]、PFASs[33]等。微藻对POPs的生物吸附与其细胞大小、细胞壁结构等有关,例如Fan和Reinfelder[24]认为真核藻类对菲的吸附总量与细胞大小成反比。此外,有研究结果表明微藻分泌的胞外聚合物(extracellular polymer substances, EPS)也在POPs的吸附过程中发挥了重要作用。微藻EPS主要由多糖、蛋白质、核酸和脂质组成[34],其含量和组成均能影响微藻对POPs的生物吸附[35]。比如:Lv等[36]发现在光限制和氮饥饿条件下,小球藻的结合态EPS含量上升从而导致对BDE-47的胞外吸附量增加。但Po等[26]认为微藻细胞壁上的多糖会减少细胞对BDE-47的吸附量,因此,EPS对微藻吸附POPs的影响仍需进一步研究。

不同类型的化合物进入微藻细胞的途径存在差异。例如中性化合物和亲脂性化合物(尤其是小分子)一般通过被动扩散进入微藻细胞[23],而离子型化合物一般通过电压门控离子通道或通道蛋白穿过藻类细胞膜[37];大分子的化合物可能需要通过特定的载体蛋白或内吞作用被藻细胞吸收[23]。由于微藻细胞膜的疏水性,被吸附的非极性和脂溶性的低分子量POPs有可能通过细胞膜进入藻细胞内部,与脂质或其他部分相结合,而低溶解度的高分子量化合物则很难通过[38]。传统疏水性POPs主要依靠被动扩散的方式通过细胞膜,且疏水性越强,渗透性越强,这反映了其更倾向于扩散到细胞中[39]。Chan等[40]发现在不改变细胞完整性的前提下,微藻活细胞与死细胞对PAHs的吸收量不同。除此之外,微藻对全氟辛酸(perfluorooctanoic acid, PFOA)的吸附在活细胞和死细胞中都能检测到,但对PFOA的吸收仅发生在活细胞中[41]。这可能意味着POPs的跨膜途径同时包括主动运输,但是当前研究并未深入挖掘到相关转运蛋白。与其他传统的POPs不同,PFASs具有两亲性,因此它们的结合位点和分配特点与其他POPs存在差异[42]。比如,全氟辛烷磺酸(perfluorooctanesulfonic acid, PFOS)虽然水溶性较高且挥发性较低,但在远低于影响细胞活性的浓度下,能够增加微藻细胞膜的通透性,同样会导致被动扩散[41]。在进入微藻细胞后,疏水性POPs一般会分配到藻细胞中富含脂质的部分,例如脂滴[43]和膜结构上。因此,微藻细胞的脂质含量能够影响POPs的富集量,而脂质含量会受到营养状态的调控。Chai等[44]等发现不同氮磷比条件下,中肋骨条藻(*Skeletonema costatum*)细胞的脂质含量会发生改变,进而影响对BDE-47的富集量;Lynn等[45]分别检测了低氮、低磷培养条件下极小冠盘藻(*Stephanodiscus minutulus*)对PCBs的吸收量,结果表明2种培养条件都增加了藻细胞中的脂质含量和PCBs富集量。浮游动物对水环境中POPs的富集方式一般是通过接触被污染的水[46]以及摄食吸附了POPs的悬浮态有机物[47]实现,亲脂性的POPs会倾向于进入并长期积累在浮游动物的脂质部分[48]。

一般使用生物浓缩系数(bioconcentration factors, BCFs)来描述浮游生物仅从水中富集POPs这一过程(非摄食),该指标被认为与POPs的辛醇-水分配系数(K_{OW})有关[39]。例如,低K_{OW}的POPs会以较快的速度进入和离开浮游动物体,而K_{OW}较高的往往生物富集较慢,但也以较低的速度消除[49]。以PCBs为例,浮游植物富集的PCBs在一定K_{OW}范围内,其对数与BCFs成正比[50],但较大K_{OW}的PCBs由于溶解度较低和大分子的立体效应,BCFs趋向于饱和,这一点同样适用于PBDEs、多氯二苯并对二噁英(polychlorinated dibenzo-*p*-dioxins, PCDDs)和多氯二苯并呋喃(polychlorinated dibenzofurans, PCDFs)等其他疏水性有机污染物[39]。然而,基于K_{OW}的标准并不适合预测PFASs在生物体内的富集情况[51],阴离子官能团和碳-氟键的双极性为这些化合物提供了疏水、疏脂的性质[52],这导致它们对有机物的吸附效果较差,例如在5 mg·L^{-1}到20 mg·L^{-1}的低浓度下,8 d内淡水微藻莱茵衣藻(*Chlamydomonas reinhardtii*)和斜生栅藻(*Scenedesmus obliquus*)对PFOA的吸附仅为5.5%到7.5%[33]。相对于浮游植物的生长速度,高疏水性POPs的吸收较慢,因此不能完全以K_{OW}来预测浮游植物的富集能力[53]。

1.2 浮游生物对POPs的累积和传递作用

浮游植物是水生环境中的初级生产者[23],而浮游动物既是它们的主要捕食者,也是浮游生物食性鱼类和仔鱼的主要猎物[54]。因此,浮游生物构成了水生态系统的能量基础,同时也为POPs进入更高的营养级中积累提供了重要途径[55]。生物积累系数(bioaccumulation factors, BAFs)被用于描述浮游生物从所有途径(即摄食、水、通过体表和摄入接触沉积物)接触POPs的过程,常用于比较浮游生物对环境

中 POPs 的综合富集能力[56]。当浮游植物富集的 POPs 被浮游动物摄取时,它们可以保留在生物体内,以粪便颗粒的形式排出,或排泄到溶解相中[57]。在低营养级食物网中,POPs 的 BAF 往往也与 K_{OW} 相关。Berrojalbiz 等[58]测量了桡足类 *Paracartia grani* 捕食浮游植物后的 PAHs 含量,发现 BAF 与 K_{OW} 存在显著的线性相关性,类似的结论也在关于中国莱州湾和华南珠江三角洲的研究中被发现[59-60],当 PAH 的 log K_{OW} 小于 7 时,log BAF 随 log K_{OW} 的增加而增加。Zhang 等[11]调查了大西洋西北沿岸地区浮游生物中的 PFASs,发现七碳到十一碳的直链全氟羧酸(perfluorocarboxylic acid, PFCAs)的 BAFs 随碳链长度线性增加。Frouin 等[61]检测了加拿大海洋浮游生物中的 PCBs 和 PBDEs 浓度,数据描述了 log BAFs 与 log K_{OW} 的抛物线关系,且在 log K_{OW} 为 5 ~ 7 时生物累积系数达到峰值。

浮游动物能够同时从水和食物中摄入并积累 POPs。一般通过生物放大系数(biomagnification factors, BMFs)评估某种污染物在食物网中的生物放大能力,BMF>1 代表该种污染物从被捕食者到捕食者逐级积累,BMF<1 则反之。例如,Liu 等[62]利用 C^{14} 放射性示踪技术研究了 BDE-47 在“蛋白核小球藻(*Chlorella pyrenoidosa*)—大型蚤(*Daphnia magna*)”食物链中的营养转移,发现存在生物放大作用。Pouch 等[63]检测了北极地区海洋浮游生物中多种 POPs 的含量,结果显示 PCBs 表现出很强的生物累积性。但对于 PAHs,这种作用并不显著,一些现场调查数据显示 PAHs 在水生食物网中会发生营养稀释效应,这可能是由于不同营养级的物种存在摄入效率和代谢途径差异[59,64-68]。在关于食物链传递的相关研究中,浮游动物经常被视为一个整体,通常忽略其复杂的群落结构[56,69]。海洋浮游动物包括甲壳类(Crustacea)、腔肠类(Coelenterata)、轮虫类(Rotifer)以及原生动物(Protozoa)等,它们对 POPs 的富集能力有很大差异[63,70]。同时,浮游动物的摄食习性和生长阶段也会影响 POPs 的积累量。PCBs 和 PAHs 在肉食性浮游动物种群体内积累量更高[63]。另外,Øverjordet 等[71]评估了北极桡足类 *Calanus hyperboreus* 不同发育阶段对原油组分的代谢动力学,研究表明富脂阶段的生物富集潜力明显大于贫脂阶段。因此,在评估环境中浮游动物对 POPs 的富集能力时,应综合考虑其不同的种群组成、生长阶段和摄食习性。

以浮游生物为基础的食物链研究可以评估 POPs 向更高营养级传递的潜在风险。已经有大量相关文献报道了传统和新型 POPs 沿浮游生物向更高营养级的传递特征,主要表现出 2 种传递趋势——生物放大和生物稀释。总体而言,POPs 在食物链中的传递作用主要取决于生物富集和降解的速度,同时也会受到污染来源及水文条件的影响。例如,溴代阻燃剂(brominated flame retardants, BFRs)由于其强疏水性和难降解性,在环境中整体具有生物放大作用,但 BDE-209 主要呈现生物稀释趋势,这可能是由于 BDE-209 在生物体内的吸收效率低,但清除效率高[72-75];水生食物网中 PCBs 的生物富集性在不同生态系统中差异很大[76],但整体而言,食物网中的 PCBs 浓度表现出随营养等级的提高而上升的趋势[77-80],且分子量较大、氯原子较多的 PCB 同系物往往具有更大的生物放大潜力[81];水生食物链中的 PAHs 在实地考察中普遍具有生物稀释作用[59,64-65,82];PFASs 的生物累积模式因盐度和营养状态而异[11,83],PFOA 和 8 ~ 12 个碳原子的 PFCAs 被认为具有较强的生物放大作用[84-86],而短链 PFCAs 在海洋浮游生物以外的样本中较少被检测到[42,87-88],它们一般被认为不具有生物放大作用[51]。

2　POPs 在浮游生物中的转化途径(Transformation pathways of POPs in plankton)

大量研究表明浮游生物具有降解转化 POPs 的潜力,降解途径包括对 POPs 的脱卤代谢、氧化代谢以及与共生微生物的联合代谢。

2.1　脱卤代谢

卤代 POPs 是含有卤族元素的有机化合物[89],在各种环境中被广泛检测到,它们的主要降解途径之一就是脱卤。生物体介导的脱卤途径和机制研究主要涵盖了哺乳动物、鱼类等物种,而针对浮游生物的相关研究仍然较少。

对于高度卤化的芳香族化合物而言,碳-卤键的键能高,稳定性强,打开碳-卤键需要有较高的能量[90]。一些藻类物种被证明能够转化或降解环境中的卤代 POPs。Peng 等[91]首次报道了包括四尾栅藻(*Scenedesmus quadricauda*)、尖状栅藻(*Scenedesmus acuminatus*)和蛋白核小球藻在内的 6 种淡水微藻都能够将四溴双酚 A(tetrabromobisphenol A, TBBPA)脱溴转化为三溴双酚 A,同时检测出多种代谢途径的产物如硫酸四溴双酚醚、硫酸四溴双酚葡糖苷、硫酸化四溴双酚葡糖苷和四溴双酚单甲醚。Lv 等[25]

在接触过 BDE-209 的小球藻细胞中检测出脱溴产物 BDE-153、BDE-99 和 BDE-47，Deng 等[92]报告称小球藻分离物暴露于 BDE-47 后检测出脱溴产物 BDE-28 和 BDE-15。某些种类的蓝藻能够完全去除高度氯化林丹中的 6 个氯原子，产生非卤代芳香烃代谢物[93-94]；Matamoros 和 Rodríguez[95]将农业径流水中生长的小球藻和栅藻联合培养后修复受污染水体，检测到林丹脱氯产物 γ-五氯环已烷。滴滴涕(dichlorodiphenyltrichloroethane, DDT)会被淡水微藻脱氯降解为滴滴滴(dichlorodiphenyldichloroethane, DDD)和滴滴伊(dichlorodiphenyldichloroethylene, DDE)并释放到培养基中[96]。一般而言，卤化程度越高的芳香族化合物的生物脱卤速度越慢，这可能与溶解度低和生物利用率低有关[97-98]。

2.2 氧化代谢

近年来，人们对浮游生物体内专门用于代谢外源性化学物质的解毒系统的认识不断加深，该系统一般分为 3 个阶段。第 1 阶段是细胞中的氧化酶以 O_2 或 H_2O_2 为供体，将带有氧原子的活性官能团加到外源性化合物上，转化为水溶性更强的酚类化合物，生物体内主要依靠细胞色素 P450 酶(cytochrome P450, CYP)驱动代谢；第 2 阶段是将谷胱甘肽(glutathione, GSH)等极性化合物通过共轭作用连接到外源性化合物的初步代谢物上，从而打开苯环，为细胞提供抗氧化保护，这一阶段主要发挥作用的酶包括谷胱甘肽巯基转移酶(glutathione S-transferase, GST)和 UDP-葡萄糖酰转移酶(UDP-glucuronosyltransferases, UDPGT)等[99-102]；第 3 阶段为排泄，浮游植物能够将外源性物质的代谢物排出细胞壁外或分隔在液泡中，有研究发现微藻 *Pseudokirchneriella subcapitata* 能够将甲基菲转化为极性化合物后排出，因此代谢物在培养基中的含量远高于细胞内[103]。相对于高等哺乳动物进化完善的免疫系统，这种非特异性的分子反应机制更加保守，某些种类的浮游生物在进化过程中发展出独特的氧化代谢机制，因此需要对浮游生物的相关基因组做更进一步的探究和了解。

原核与真核生物都具有氧化芳香族化合物的潜力[3]，一般认为原核生物降解 PAHs 第一阶段主要依靠双加氧酶产生顺式二氢二醇，再代谢为邻苯二酚等产物，而真核生物则是通过单加氧酶将 PAHs 代谢为芳烃化合物，再进一步转化为反式二氢二醇[104]。Cerniglia 等[105-106]检测了 18 种微藻在光照条件下对萘的降解产物，所有实验对象都产生了 1-萘酚，这项工作成为研究微藻降解 PAHs 产物的开端。在此后的报告中，许多微藻种类表现出对单种或混合 PAHs 的氧化降解能力[107]，降解产物包括醇类、醛类和羧酸[3]，但不同物种的微藻降解转化 PAHs 的机制和产物会有所差异。Lei 等[31]发现微藻去除混合 PAHs 的效率要高于单一污染物；颤藻(*Oscillatoria* sp.)JCM 株能够将萘代谢为顺式-1,2-二羟基-1,2-二氢萘和 4-羟基-1-四氢萘酮，而 O_2 被作为氧原子的供体[106]；Ke 等[108]检测了混合 PAHs 对淡水绿藻羊角月牙藻(*Selenastrum capricornutum*)的影响，其降解中间产物主要为单羟基化合物和少量双羟基化合物，推测它们可能源于二氢二醇类的进一步降解[40]，Becerril Mercado 等[109]采用色谱和电泳技术对暴露于苯并[a]芘的羊角月牙藻粗提取物进行了分析，结果证实了顺式二氢二醇类代谢物的存在，并且描述了能够降解苯并[a]芘的多组分酶蛋白特征；在小球藻对荧蒽的代谢中，邻苯二酚-2,3-二加氧酶发挥了重要作用[104]；SureshKumar 等[110]构建了凯氏拟小球藻(*Parachlorella kessleri*)的 CYP 酶三维结构，从分子水平上阐明了微藻中的 CYP 酶能够有效降解 PAHs 的结构优势。Luo 等认为[111]莱茵衣藻在苯并[a]蒽降解过程中的相关酶还包括尿黑酸 1,2-二氧化酶、羧甲烯丁烯羟酸内酯酶、1,5-二磷酸核酮糖羧化酶/加氧酶和泛醇氧化酶。

早期研究发现，浮游动物能够迅速从环境中富集 PAHs，但排泄物已并非原来的物质[112-114]，这被认为是浮游动物能够代谢 PAHs 的证据之一。此后的调查发现，暴露于 PAHs 中会引发浮游动物细胞 *CYP* 基因表达量的上调，且呈现剂量和时间效应，说明浮游动物有氧化代谢 PAHs 的潜力。*CYP* 超家族由多个基因亚族组成，可对不同的化学物质发挥代谢作用，在脊椎动物中，芳烃受体(aryl hydrocarbon receptor, AhR)介导的 CYP1A 酶信号途径能够有效抵御外源性有机物，然而，人们对浮游动物中的 *AhR* 和 *CYP* 基因家族了解很少[115]。已有文献描述了朝鲜臂尾轮虫(*Brachionus koreanus*)[99]、圆型臂尾轮虫(*Brachionus rotundiformis*)[116]、剑水蚤(*Paracyclopina nana*)[101]等浮游动物的 *CYP* 基因超家族。由于缺少脊椎动物的 *CYP1A* 基因，浮游动物抵御 PAHs 时高度表达的几个 *CYP* 基因可能在代谢过程中共同起到补偿作用，包括朝鲜臂尾轮虫的 *CYP2* 族的 2 个成员基因(*CYP3043A* 和 *CYP3048A1*)以及圆型臂尾轮虫的 *CYP3* 族的一个成员基因(*CYP-*

3027F2)。但是,目前仍未确定 PAHs-AhR-CYP 信号通路是否也出现在浮游动物中,仅有研究显示桡足类日本虎斑猛水蚤(*Tigriopus japonicus*)受苯并[a]芘影响而增加了 AhR 和芳烃受体核转运蛋白(aryl hydrocarbon receptor nuclear translocator, ARNT)的表达量[115]。

PBDEs 和 PCBs 在生物氧化中的途径都包括芳环裂解、羟基化和甲氧基化[97]。它们的羟基化、甲氧基化衍生物在自然界中的存在已经不能被忽视[117-118]。这 2 类化合物都被报道能够影响生物体的内分泌平衡,包括抗雄性激素、抑制芳香酶活性、抑制甲状腺素水平[119-120]。关于它们在浮游生物体内的来源研究较少。羟基化多溴联苯醚(hydroxylated polybrominated diphenyl ethers, OH-PBDEs)和甲氧基化多溴联苯醚(methoxylated polybrominated diphenyl ethers, MeO-PBDEs)并非工业产物,也没有作为含溴化学品产品的杂质被报道过,它们很可能是作为天然产物和/或工业产物的代谢物出现[121]。一般被认为是自然产生的 MeO-PBDEs 和 OH-PBDEs 在二苯醚氧的邻位具有甲氧基/羟基,而经生物代谢后添加的羟基会连接在醚桥的邻位、间位或对位的任何位置[122]。在野外调查中发现浮游生物体内含有 MeO-PBDEs 和 OH-PBDEs,但仍无法确定是否源于 PBDEs 的代谢途径,目前被认为具有氧化降解 PBDEs 潜力的微藻种类有球等鞭金藻(*Isochrysis galbana*)[26]和小球藻[92]。同时,BDE-47 能够引起剑水蚤的 *CYP* 基因表达量显著上调,这可能表明桡足类中存在与 PBDEs 相关的需氧代谢途径[123]。PCB-126 能够引起桡足类 *AhR* 和 *ARNT* 基因的转录表达响应[115],但目前并没有关于 PCBs 在浮游生物中的降解产物研究。

2.3　细菌-微藻联合代谢

与实验室培育的单一物种不同,自然界中的微藻并非孤立存在于生存环境中,各种藻类与真菌、细菌的共生关系已广为人知。微藻的细胞表面可以为细菌提供稳定的栖息地[124],将污染物富集在微藻胞外也更有利于细菌降解。

微藻对 POPs 的初级氧化产物能够促进细菌的进一步降解[125]。Luo 等[126]构建了羊角月牙藻和分支杆菌(*Mycobacterium* sp.)的联合体来降解 PAHs 中的芘,研究发现细菌对芘的快速降解和代谢产物促进了藻类生长,联合培养后产生了更多的最终产物酚酸。Patel 等[127]利用集胞藻(*Synechocystis* sp.)与 2 类需氧异养菌构建菌-藻联合培养体,能够广泛降解 PAHs 类有机物。索罗金小球藻(*Chlorella sorokiniana*)和米氏假单胞菌(*Pseudomonas migulae*)的联合体在无需外部氧气供应的情况下降解硅油或十四烷中的菲[128]。栅藻和类芽胞杆菌(*Paenibacillus* sp.)能够共同将林丹降解为氯苯类、氯代直链烃类和羟基化的脂肪族/芳香族化合物[129]。

3　浮游生物与 POPs 的生物泵效应(Plankton and biological pump effect of POPs)

POPs 在全球范围内的分布受多种环境因素长期调控,包括气温[130]、水团[131]、大气[132]和生物泵等。其中生物泵是生物地球化学循环的重要组成部分,包括初级生产者的碳固定、有机碳向深海的垂直运输和沉积[133]。浮游植物承担有机物的生产,浮游动物则通过摄食、降解、排泄、产卵和垂直迁徙等行为调节有机物从表层水域的输出通量,大多数有机碳在表层海水即可被生物的呼吸作用消耗[21],而其余有机碳则以藻类细胞聚集体或浮游动物排泄物等形式下沉到深水层[134],微生物能够将这些有机物缓慢再矿化,只有约 1% 的表层产物能够进入海底沉积物中[135]。POPs 的生物泵效应主要是指浮游生物的生命活动促进了 POPs 从大气向水体中扩散和溶解,进而向深水输入的过程。

由于具有疏水性和难降解性等物理性质,POPs 在自然环境中的地球化学循环会受到生物泵的影响,主要体现在 POPs 的水-气交换平衡,相分配与垂直迁移等方面。浮游植物能够从表层水中积累 POPs,造成空气与水体中 POPs 的浓度差。以此作为驱动力,空气中的 POPs 会持续通过水-气接触界面进入水体中[14]。Dachs 等[21]首次评估了浮游植物生物量和生长速度对 POPs 在水气界面和水溶相分配的影响,研究显示生物量和种群增长率越高,水气交换达到平衡的时间将越晚。近几十年来,富营养化引起藻类大量繁殖,极大地影响了水生生态系统[136-137]。在藻华现象的中后期,POPs 从溶解相不断进入浮游生物体内,而后向沉积物中输出,这段时期测得的溶解相中 POPs 含量明显降低[4],而沉积物中的 POPs 含量上升[138]。由于频繁的人类活动,河流、湖泊和近海水域的 POPs 受到陆源输入影响更强,同时丰富的营养盐和颗粒有机物会促使浮游生物快速降解 POPs 或向下层水体沉降,同样会导致表层水中溶解态 POPs 浓度降低[139]。

在远离陆地和人类活动的深海,生物泵同样发

挥了重要作用。研究调查了 POPs 在深海中的发生和分布情况，包括印度洋[140-141]、北冰洋[137,142]、太平洋[143]等海域，甚至在最深的马里亚纳海沟[144]中也发现了 PCBs 和 PBDEs。生物泵是 POPs 自表层进入深海的重要途径[14]，能够与 POPs 结合并沉降的生物颗粒包括浮游生物的粪便、碎屑和卵等[58]。Kuzyk 等[145]检测了加拿大哈得逊湾沉积岩中 PCBs 的含量，研究发现浮游生物富集的区域，沉积物中 PCBs 的含量更高；在北极地区，生物泵驱动下的有机碳沉降封存了大气向水中扩散的 PCBs[146]。河流输入是海水中检测到的所有 PFASs 的主要来源，而长链 PFASs 在水体中的垂直迁移更受生物泵影响[11]。González-Gaya 等[147]在大西洋、太平洋和印度洋等海域采样，计算出与生物泵相关的 PAHs 平均沉降通量为 82.5 $ng \cdot m^{-2} \cdot d^{-1}$。

4 结论与展望(Conclusion and prospect)

综上所述，浮游生物对 POPs 在水环境中迁移和转化的影响总结如图 1：浮游植物和浮游动物能够迅速富集水环境中的 POPs，其富集过程分为吸附和吸收 2 个阶段，并受 POPs 特性、生物物种多样性、培养条件和胞外/体外化学基团等调控。进入浮游生物体内的 POPs 可以通过脱卤代谢，氧化代谢和微生物联合代谢转化为其他形式，引起更大的环境和生物风险。同时，浮游生物作为生物泵的主要成分，能够显著影响 POPs 的迁移和分布。目前，有关浮游生物对 POPs 迁移和转化影响的研究已得到广泛开展，但仍存在许多科学问题亟待解决，未来的研究应关注以下几个方面。

(1)深化浮游植物对 POPs 跨膜吸收的研究机制。目前的研究多集中于 POPs 的被动跨膜扩散过程，而浮游植物对 POPs 的主动运输研究十分匮乏，包括主动运输占总运输量的比例，运输载体蛋白的发现与功能探究，主动运输的种间差异性等，均亟待研究。

(2)进一步加强浮游生物对 POPs 生物代谢机制的研究，目前对 POPs 生物代谢主要集中于 PCBs、PAHs 等常见的传统 POPs，对于一些新兴的，存在形式复杂的 POPs，如 PBDEs、PFAS 等，对其代谢产物、代谢过程和机制的研究仍存在较多空白，需要结合分析化学和分子生物学手段，进行深入解析。

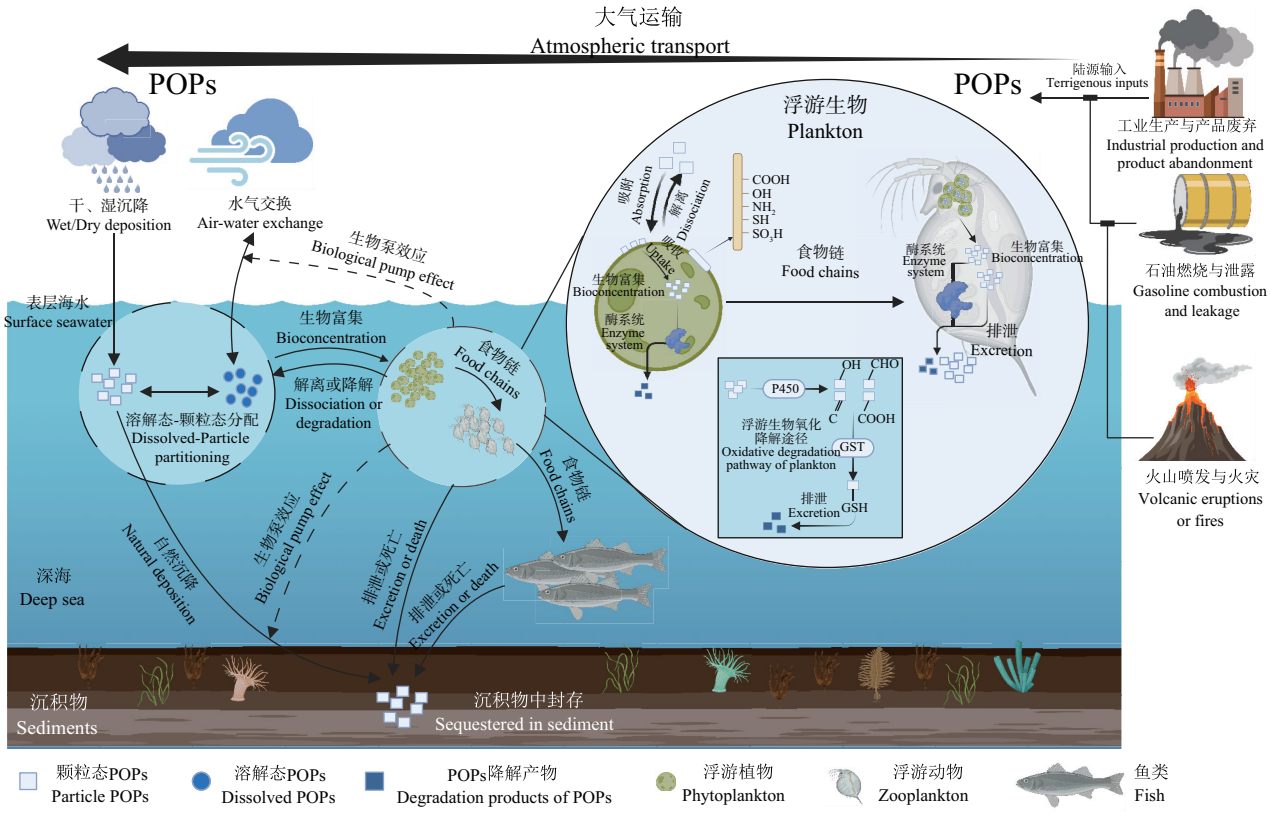

图 1 浮游生物对持久性有机污染物(POPs)在环境中的迁移和转化影响

Fig. 1 Effects of plankton on the transport and transformation of persistent organic pollutants (POPs) in the environment

(3)进一步量化浮游生物对 POPs 垂直迁移的生物泵效应,应加强不同属性 POPs(比如疏水性的差异、分子量的大小等)生物泵效应的差异认识,量化生物泵效应与海水垂直混合对 POPs 垂直迁移的贡献,建立浮游生物特性(种类、粒径、生物量等)与 POPs 生物泵效应的相关关系。

(4)气候变化(如全球变暖、水体酸化等)会对浮游生物的种群组成、生命周期以及水生食物网/链的营养结构产生一定影响,进而影响 POPs 沿海洋食物链的迁移和转化。因此,研究全球气候变化大背景下,浮游植物群落结构变化和生化过程改变对 POPs 吸附和富集的变化,浮游生物群落结构变化对 POPs 富集和转化的变化,以及浮游生物次级代谢产物(如胞外分泌物等)释放的改变对 POPs 环境迁移的影响,都值得深入研究。

通信作者简介:赵妍(1987—),女,博士,副教授,主要研究方向为海洋生态学。

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