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Review 综 述

红树林湿地多环芳烃的微生物降解

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摘　要：红树林(mangrove)是海陆交汇带重要的湿地生态系统，也是环境污染物蓄积与转化的热区。多环芳烃(polycyclic aromatic hydrocarbons，PAHs)因其环境蓄积特点在红树林生境中广泛分布，威胁生态系统健康，其降解转化是近年的研究重点。本文聚焦红树林湿地多环芳烃的微生物降解研究现状，从红树林生境的 PAHs 生物降解规律、降解功能微生物、降解影响因素等角度综述了国内外最新的研究进展。总结发现，红树林中的 PAHs 含量高于林外光滩，集中于垂向 10−20 cm 深的沉积物中。PAHs 厌氧降解相应的电子受体中，以 SO_4^{2-}浓度最高，且渗入泥层更深，是红树林沉积物的主要电子受体；其次是 NO_3^-、CO_2、Fe(Ⅲ)和 Mn(Ⅳ)。PAHs 降解菌多样性高，其中以 *Sphingomonas*、*Bacillus*、*Novosphingobium* 和 *Sphingobium* 报道最多。红树林生境中好氧-厌氧交替的独特环境、湿地植物根际泌氧和分泌物以及外源生物刺激因子是影响 PAHs 生物降解的主要因素。目前多数结果都是基于室内实验，而红树林生境复杂，建议未来面向 PAHs 污染修复的

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实际需求，针对红树林的环境特点挖掘相应的 PAHs 降解功能微生物种质资源，并从应用工艺等方面开展深入的研究。

关键词：红树林；沉积物；多环芳烃降解；电子受体；微生物

Advances in microbial degradation of polycyclic aromatic hydrocarbons in mangrove wetlands

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Abstract: Mangrove forest is an important ecosystem in the sea-land interface zone and a hot zone for pollutant accumulation and transformation. Polycyclic aromatic hydrocarbons (PAHs) are persistent organic pollutants widely distributed in mangrove wetlands, threatening ecosystem health. The degradation and transformation of PAHs have attracted increasing attention of researchers in recent years. This paper reviews the available studies about microbial degradation of PAHs in mangrove wetlands from the perspectives of biodegradation rules, functional microorganisms, and influencing factors of PAH degradation in mangrove habitats. We found that the PAHs in mangrove forests had higher content than those in the beach outside the forests, and they accumulated in the sediments at a depth of 10–20 cm. Sulfates were the main electron acceptors (EAs) for anaerobic degradation of PAHs, as they had the highest concentration and infiltrated deeper into the sediments. EAs nitrate, bicarbonate, Fe(III), and Mn(IV) were also distributed in mangrove sediments and played roles on PAH-degradation. PAH-degrading bacteria had high diversity, among which *Sphingomonas*, *Bacillus*, *Novosphingobium*, and *Sphingobium* were reported frequently. The aerobic-anaerobic alternation condition, radial oxygen loss, root exudates, and exogenous biostimulators were the main factors affecting the biodegradation of PAHs in mangrove habitats. We suggest that researchers can focus on the application technologies of PAH-degrading microorganisms to meet the actual needs of wetland remediation.

Keywords: mangroves; sediments; PAH degradation; electron acceptors; microorganism

红树林是在海洋和陆地交界处的森林，生长于热带及亚热带海岸的潮间带，由于长期受到周期性潮汐浸淹，形成了不同于陆地生态和海洋生态的结构与功能，但又兼具两者的性质，拥有独特的强酸性、强还原性和高盐的生境。红树林是防止陆地污染向海洋生态系统扩散的一道防线，也因此蓄积了大量营养盐、重金属、有机污染物，是污染的热区。

多环芳烃是由线性、角状或簇状排列的稠合芳香环组成的毒害性有机污染物，具有较强的疏

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水性，在水体中常吸附于颗粒物而随流迁移，在水流平缓的红树林湿地中容易蓄积，并对湿地生态系统和人体健康造成潜在的危害[1]。沉积物中 PAHs 的污染水平可划分为 4 个等级：轻度污染(0−100 ng/g)、中度污染(100−1 000 ng/g)、高度污染(1 000−5 000 ng/g)和重度污染(>5 000 ng/g)[2]。此前大量研究表明，PAHs 在红树林中广泛存在，且达到轻到中度污染水平。例如 Raza 等[3]在马来西亚半岛的红树林沼泽沉积物中检出 PAHs 总浓度为 20−112 ng/g；Shilla 等[4]发现坦桑尼亚鲁菲吉河口红树林的表层沉积物中 PAHs 浓度达 127−376 ng/g；在印度胡格利河口红树林、孙德尔本斯红树林和马哈拉施特拉邦红树林沉积物中都能检测出总浓度在 3.3−1 643.0 ng/g 之间的 PAHs[5−7]；我国也相继在香港、广东、广西、福建及海南的红树林地区检出了不同浓度的 PAHs[8−11]。随着城市化进程，沉积物中的 PAHs 浓度呈逐渐上升趋势，对生态造成了不利的影响[12]，因此，PAHs 的降解和污染沉积物的修复引起了研究者与环境管理者的广泛关注。

PAHs 在环境中的降解途径包括物理、化学和生物过程 3 种。物理降解主要指热、强射线的裂解作用，在自然界发生的条件相对苛刻；化学降解包括化学氧和光电催化，主要发生在表层界面[13]；生物降解指微生物以 PAHs 为碳源和电子供体，将 PAHs 降解转化为小分子有机物或二氧化碳的过程。目前的研究普遍认为生物降解是对环境影响最小的修复途径，也是维持生态平衡最适合的途径[14]。红树林沉积物由河流或海浪带来的泥沙等外源矿物颗粒和腐烂的红树凋落物等组成，因此，富含大量营养物质，孕育着丰富的微生物资源[15]。由于微生物种类多样、代谢速率高，利用微生物降解功能消除红树林生境中 PAHs 污染对污染场地的修复、碳循环利用和生态系统的可持续发展具有重要的意义。研究发现许多细菌、真菌和藻类都具有降解或转化 PAHs 的能力[16−18]。本文通过总结 PAHs 及其生化反应相关电子受体[O_2、NO_3^-、SO_4^{2-}、CO_2、Fe(Ⅲ)和 Mn(Ⅳ)]的空间分布规律和红树林湿地中 PAHs 降解微生物类群，综述 PAHs 在红树林沉积物的生物降解潜力，为红树林湿地中 PAHs 降解微生物种质资源挖掘和 PAHs 污染修复提供科学依据。

1 红树林湿地中 PAHs 的生物降解规律

PAHs 的低溶解度和疏水特性使其容易吸附于悬浮颗粒物上，并随流沙运动分布于林下、光滩和潮沟等小生境[19]。小生境中的有机质含量、电子受体种类、还原氧化电位等要素具有显著差异，从而影响着 PAHs 降解途径与效率[9,20−21]。

1.1 PAHs 在红树林湿地中的分布

依据红树林的地貌特征，从陆地到海洋可大致将红树林湿地划分为潮上带、潮间带和潮下带。红树植物通常生长在潮间带平均海平面至平均高潮线的区域内，此处淤泥较厚，红树生长茂盛。光滩则位于平均海平面到平均低潮线范围内，靠近潮下带，与红树林生境有较大差异[22]。图 1A 总结了近年报道的数据，比较了 PAHs 在光滩和林下的分布[10,23−25]，可见林下沉积物蓄积的 PAHs 略高于光滩。其原因在于林下沉积物的总有机碳和黏土含量显著高于无植被的沉积物[10]，有机质和黏土的含量对 PAHs 的浓度和分布都有不同程度的影响[26]，Zhang 等[27]的研究表明，PAHs 的含量与总有机碳呈显著正相关，Liang 等[28]也发现腐殖质等有机质可以作为 PAHs 的吸附剂从而阻隔 PAHs 的降解，即老化现象(aging effects)。同时，PAHs 的空间分布还与潮流有关，潮汐会促进 PAHs 的迁移和扩散[29]，光滩沉积物由于缺少红树的拦截作

用，PAHs 的含量比林下沉积物低。

图 1B 归纳了 PAHs 在红树林沉积物的垂向分布[30–33]。由图可见，高浓度的 PAHs 主要集中在 10–20 cm 深的沉积物中，且以 3–4 环 PAHs 为主，并随沉积物深度呈下降趋势。PAHs 的垂向分布取决于污染沉积与降解转化的平衡。表层沉积物经历好氧-厌氧交替过程，PAHs 以好氧降解为主，降解效率较高。深层沉积物往往处于厌氧状态，PAHs 的降解速率取决于厌氧电子受体的供给，一般来说低于好氧降解速率，因此，PAHs 一旦蓄积在深层沉积物中就比较难消除。

1.2 PAHs 生物降解的电子受体

PAHs 的生物降解本质是微生物以 PAHs 为碳源(电子供体)发生的氧化反应，在此过程中需要氧化剂(电子受体)参与。自然界中常见的电子受体包括 O_2、NO_3^-、SO_4^{2-}、CO_2、Mn(Ⅳ)和 Fe(Ⅲ)(以氧化还原电位高低排序)，其中以 O_2 作为电子受体的降解反应称为好氧降解，不利用 O_2 的降解反应称为厌氧降解。电子受体的种类和浓度决定着 PAHs 的生物降解速率。从热力学角度，O_2 的氧化还原势能最高，因此，好氧降解使微生物获得更高的能量，是生物利用有机碳最为有效的形式。然而，在湿地沉积物环境中 O_2 因其低溶解度而较难进入深层沉积物，在动力学上效率较低，因此，其他电子受体在 PAHs 厌氧降解环境中发挥着更为重要的作用。作者前期研究发现，NO_3^-和 SO_4^{2-}的增加可改变沉积物微生物群落的结构和演替方向[34]，其中 NO_3^-显著地提高了 PAHs 降解功能基因的丰度，从而提高 PAHs 特别是高分子量 PAHs 的降解[35]；SO_4^{2-}可刺激沉积物中广泛存在的硫酸盐还原菌，通过共代谢降解 PAHs[36]。因此，了解电子受体分布是认识红树林沉积物中 PAHs 生物降解规律的关键。

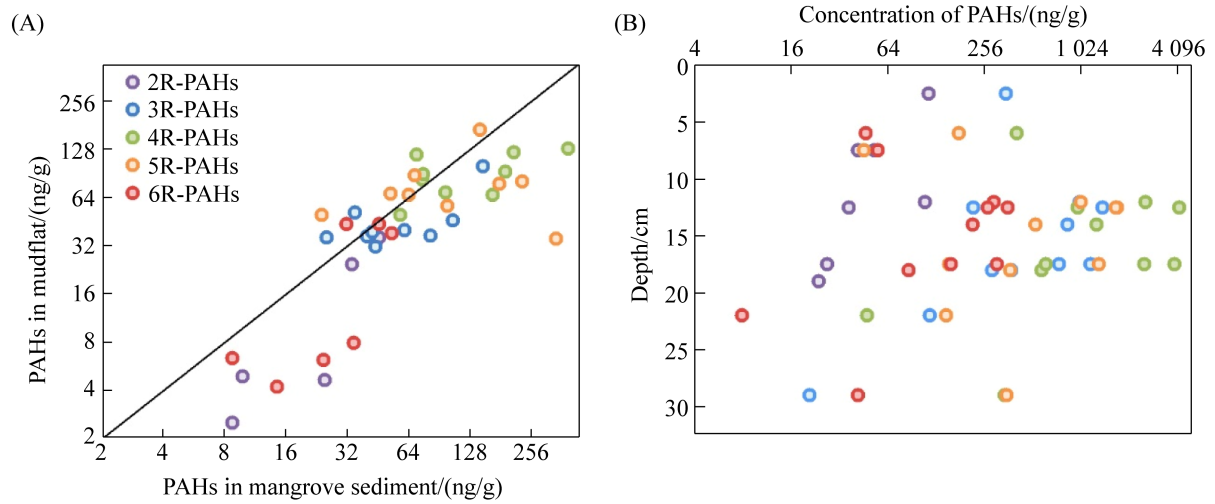

图 1 PAHs 在红树林湿地的横向(A)和垂向(B)分布

Figure 1 Lateral (A) and vertical (B) distribution of PAHs in mangrove wetlands. R presents the number of PAH-rings; PAHs counted included naphthalene (2R), acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene (3R), fluoranthene, pyrene, benzo[a]anthracene and chrysene (4R), benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene and dibenzo [a, h] anthracene (5R), indeno[1,2,3-cd]pyrene and benzo[g, h, i]perylene (6R). The data of figure A was collected from references [10, 23–25], and figure B was collected from references [30–33].

目前关于电子受体在红树林湿地中横向分布的研究不多，主要是 SO_4^{2-}、NO_3^-和 Fe(Ⅲ)的报道。曹超等[37]观测了广东淇澳岛红树林湿地中沉积物孔隙水的 SO_4^{2-}浓度和分布，发现在林下表层沉积物孔隙水中的 SO_4^{2-}浓度显著高于林外光滩；Pan 等[38]研究了福建九龙江河口潮间带沉积物的 SO_4^{2-}浓度，发现红树林湿地中央的 SO_4^{2-}浓度总体略高于红树林边缘及光滩的 SO_4^{2-}浓度。Konnerup 等[39]取哥伦比亚北部的圣玛尔塔大沼泽红树林湿地表层 5 cm 沉积物测定 NO_3^-的浓度，结果显示，在 Rinconada 的美洲红树(*Rhizophora mangle*)和白骨壤(*Avicennia germinans*)林下沉积物中的 NO_3^-的浓度比位于卡尼奥德拉加多(Caño Dragado)的无植被光滩中的低。Kristensen 等[40]测定了澳大利亚昆士兰霍顿河口红树林沉积物中 Fe(Ⅲ)的浓度，发现在沉积物 0−7 cm 处，光滩中的 Fe(Ⅲ)浓度比红树林中的高，而 7−15 cm 处相反，红树林中的 Fe(Ⅲ)浓度高于光滩，归因于白骨壤根系分泌的氧气导致了沉积物中的 Fe(Ⅱ)被氧化，故而 Fe(Ⅲ)的浓度升高。

图 2 总结了红树林湿地中的电子受体垂向分布情况[33,37,41−43]，可见电子受体主要集中在沉积物 0−20 cm 处，其浓度按从高到低依次为 SO_4^{2-}>Fe(Ⅲ)>NO_3^->Mn(Ⅳ)。红树林沉积物的 SO_4^{2-}来源于海洋，其浓度水平低于海洋沉积物[44]，因此不同于海洋沉积物中以硫酸盐还原占据绝对优势的微生物过程，Fe(Ⅲ)、NO_3^-、Mn(Ⅳ)的还原反应同样占有比较重要的地位。铁是地壳中丰度最高的金属元素，受潮汐复氧和红树根际泌氧的影响，呈 Fe(Ⅲ)-Fe(Ⅱ)周转[45]。硝酸盐来源于上游径流和氨氧化[46]，在红树林沉积物中的浓度比在河流沉积物中的低[47]。Mn(Ⅳ)来源于沉积物中的锰氧化物[48]，目前对其研究较少。总体而言，电子受体的浓度随深度逐渐降低，归因于沉积物从表层氧化条件向深层还原条件的变化。值得注意的是，在所有电子受体中 SO_4^{2-}不但浓度更高，且渗入泥层更深，可能是红树林沉积物中 PAHs 降解的主要电子受体[49]。

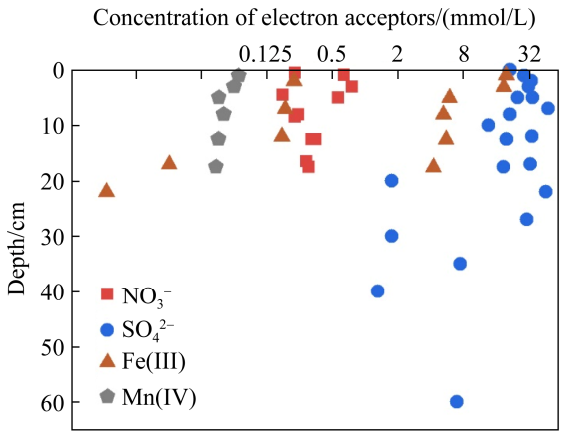

图 2 电子受体在红树林湿地的垂向分布[33,37,41–43]
Figure 2 Vertical distribution of electron acceptors in mangrove wetlands[33,37,41–43].

1.3 PAHs 生物降解规律

微生物代谢电子受体的种类决定了 PAHs 的降解途径和降解速率，关于此类研究已有诸多报道。图 3 总结了红树林沉积物中的 PAHs 在不同电子受体条件下的降解速率常数(k)[50−56]。结果显示，对于较难降解的高环 PAHs (5−6 环)，仅见于好氧降解和反硝化降解的报道[53,56]；而对于 3−4 环 PAHs，PAHs 在 SO_4^{2-}还原条件下的降解速率明显高于其他电子受体。硫酸盐还原条件下获得较高的 PAHs 降解速率是因为红树林沉积物有较高浓度的 SO_4^{2-}，且长期富集了大量的硫酸盐还原菌。研究表明，硫酸盐还原菌能介导菲、萘、芴、芘等 PAHs 的降解[57−59]。Chang 等[52]以同样的红树林沉积物作为接种源，发现硫酸盐还原条件下 PAHs 降解速率是反硝化条件下的 2 倍。从前人研究结果可见，硫酸盐还原是红树林沉积物 PAHs 降解的主要途径。

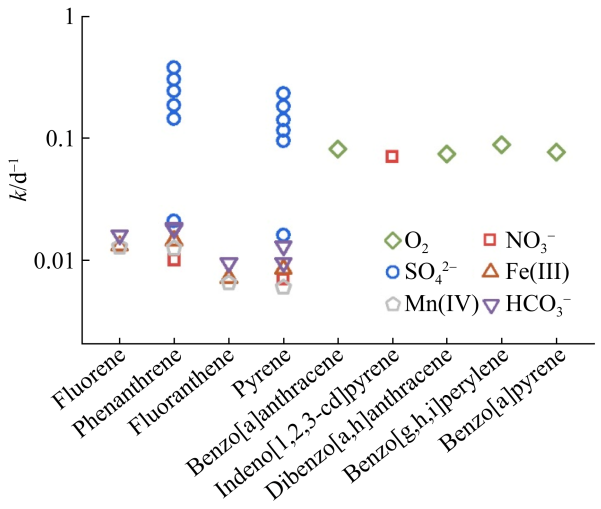

图 3　红树林湿地中电子受体降解 PAHs 的速率[50–56]
Figure 3　Degradation rates of PAHs by electron acceptors in mangrove wetlands[50–56].

2　红树林湿地 PAHs 降解功能微生物

具有 PAHs 降解功能的微生物多种多样，目前已报道了 100 多个属、200 多个种的藻类、真菌和细菌通过氧化还原、脱羧、脱氮、水解及脱水等代谢过程降解 PAHs[60]。其中，PAHs 降解细菌占绝大多数，而藻类和真菌的报道相对较少[61]。

2.1　红树林湿地的 PAHs 降解功能藻类和真菌

藻类可以在单加氧酶和双加氧酶的作用下降解 PAHs[62]。有研究发现，藻类的细胞色素 P450 单加氧酶在低分子量和高分子量的 PAHs 降解过程中都发挥了重要作用[63]，且藻类的光合作用能提高 PAHs 的降解率[64]；Olmos-Espejel 等[65]发现微藻 *Selenastrum capricornutum* 可以通过双加氧酶将苯并[a]芘降解为二氢二醇。目前对于红树林中藻类降解 PAHs 的研究不多，Hong 等[12]在九龙江河口红树林中富集得到的硅藻中，*Skeletonema costatum* 和 *Nitzschia* sp.能显著降解菲和荧蒽，且这 2 种藻类对 PAHs 混合物的去除效率比对单一 PAH 的去除效率更高。

真菌降解 PAHs 有两种途径，一是通过胞内细胞色素 P450 单加氧酶催化环氧化，再在环氧化物水解酶的作用下进一步降解 PAHs[66]，例如 Cerniglia[67]发现 *Cunninghamella elegans* 能利用单加氧酶将萘、芘、芴、菲等降解为酚和醌。二是通过胞外双加氧酶(包括木质素过氧化物酶、锰过氧化物酶和漆酶)氧化过程产生的羟基自由基将 PAHs 氧化成醌和酸[68]，例如 Wu 等[69]将从中国香港马湾红树林中分离得到的 *Fusarium solani* 与蒽和苯并[a]蒽分别培养 40 d 后，发现其对蒽和苯并[a]蒽的降解率分别达到 40%和 60%，其中漆酶在 PAHs 的降解过程中起主要的作用；Bankole 等[70]从尼日利亚三角洲红树林中分离出的 *Aspergillus sydowii* 能在 3 d 内降解 99.5%的蒽。值得注意的是，白腐真菌可以同时利用胞内单加氧酶和胞外双加氧酶联合降解 PAHs[71]。

2.2　红树林湿地中可分离培养的 PAHs 降解功能细菌

细菌降解 PAHs 的途径可分为好氧降解和厌氧降解。好氧降解是细菌利用加氧酶(包括单加氧酶和双加氧酶)将芳香环羟基化，形成顺式或反式二氢二醇，随后生成三羧酸循环中间物，最终转化为 CO_2 和 H_2O[72]。厌氧降解则基于还原反应，可分为硫酸盐、硝酸盐、产甲烷和金属还原体系。细菌可以利用 SO_4^{2-}、NO_3^-、CO_2、Fe(Ⅲ)和 Mn(Ⅳ)等作为末端电子受体进行呼吸作用，降解 PAHs 等有机物[73]。

本文收集了近年来报道的 50 株从红树林湿地中分离得到的 PAHs 降解细菌，它们来自 21 个属、16 个科、12 个目、6 个纲，归于厚壁菌门(*Firmicutes*)、放线菌门(*Actinobacteria*)和变形菌门(*Proteobacteria*) 3 个门，如图 4 所示[74–81]。其中报道菌株数目最多的菌属为鞘氨

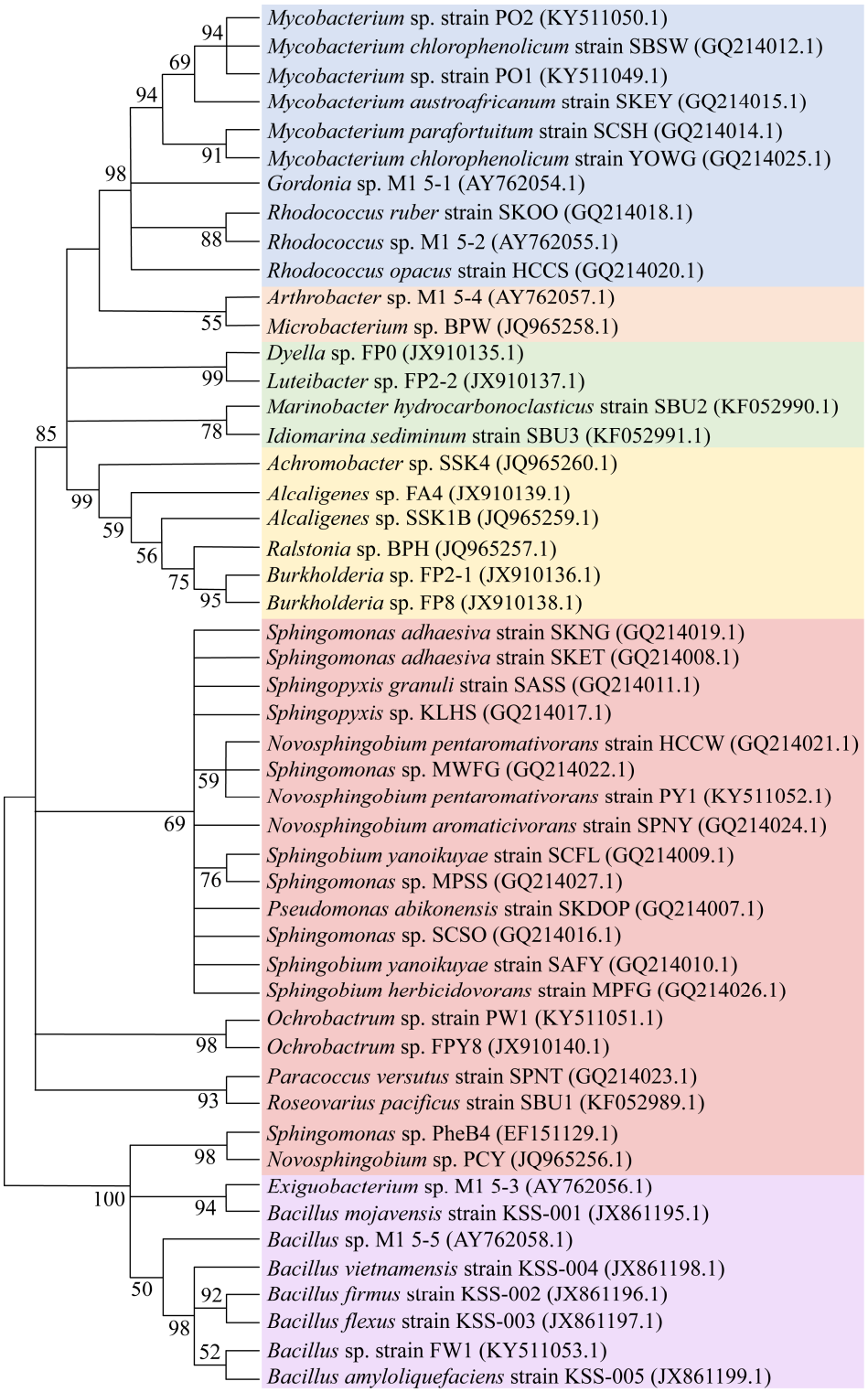

图 4　红树林湿地中分离的 PAHs 降解菌[74–81]

Figure 4　PAHs-degrading bacteria screened in mangrove wetlands[74–81]. The sequence number of the corresponding strain in NCBI database is in brackets; the number on the branch point indicates the reliability of the branch; the branch length indicates the evolutionary distance.

醇单胞菌属(*Sphingomonas*)，占菌株总数的12%，其次为芽孢杆菌属(*Bacillus*)、鞘鞍醇杆菌属(*Novosphingobium*)和鞘脂菌属(*Sphingobium*)，都占菌株总数的8%。

2.3 红树林湿地源 PAHs 降解功能菌群

红树林中存在着大量 PAHs 降解菌，这些降解菌在红树林生境中形成降解菌群共同发挥作用。表 1 整理了 PAHs 降解细菌混合培养体系中菌株的组成、菌群能降解的 PAHs 类型、PAHs 降解时间和降解率。

分析发现降解菌群对 PAHs 具有良好的降解能力，多数菌群能高效降解中低环 PAHs，例如龚莹等[82]从海南红树林中富集得到的由贪噬菌和剑菌组成的菌群 Q15 对菲的降解率达到95.3%，由伯克氏菌和鞘脂单胞菌组成的菌群Q12 对芘降解率达 94%；Yu 等[83]从香港蚝涌红树林富集得到的降解菌群在培养 4 周后能完全降解菲、芴和芘；Muangchinda 等[75]从泰国红树林中富集得到的 PAHs 降解菌群能在 56 d 内完全降解苊和菲；Liu 等[84]在福建省红树林表层沉积物中富集得到的降解菌群也能在 20 d 内完全降解菲。

同时，降解菌群对一些高环的 PAHs 也有良好的降解效果。例如 Ahmad 等[85]在海南三亚的红树林中富集得到 2 个降解菌群 SH-PPHE 以及 BL-PPHE 对苯并[a]芘和苯并[a]荧蒽的降解率达到 56%−76%；Tian 等[8]从厦门红树林富集得到的 M1 菌群可以将苯并[a]芘作为唯一碳源，63 d 内对苯并[a]芘的降解率达 32.8%。

此外，一些研究将降解菌群和分离出的单菌对 PAHs 的降解效果分别进行对比，发现菌群混合培养降解相比较于单菌具有显著的优势，许多细菌之间存在协同关系，能共同作用提高降解率。例如 Aziz 等[53]在马来西亚红树林分离到的细菌 *Ochrobactrum anthropic*、*Stenotrophomonas acidaminiphila* 和 *Aeromonas salmonicida ss salmonicida* 在混合培养 8 d 后对苯并[a]芘的降解率达到 41%，比单菌的降解效率高了 50%；Shahriari 等[76]从伊朗 Nayband 湾分离得到 6 株菌株，将其分别进行单株及混合培养降解，结果表明，混合菌群对芴和菲的降解率显著高于单菌株，且对条件的适应性更好；Wanapaisan 等[79]将从泰国菲查布里省红树林中分离出的 PAHs 降解菌进行降解菌群人工构建，发现菌群对芘的降解率比单个菌株高 3 倍。Guo 等[86]将从中国香港红树林分离得到的分枝杆菌和鞘氨醇单胞菌进行混合培养，发现混合培养体系能在 4 d 内完全降解菲，而单菌则需要 7 d 才能完全降解；Li 等[55]从中国香港红树林中富集的菌群降解 PAHs 的实验证明，相比原生环境，接种富集的 PAHs 降解菌可显著提高 4 种 PAHs 的降解率，其中芴和菲的降解率提高 14%−15%，荧蒽和芘的降解率提高了 21%−34%。

然而，也有少数研究发现，降解菌群对某些 PAHs 的降解效果反而不如单菌。例如作者将红树林沉积物中分离得到的分枝杆菌 A1-PYR 和鞘氨醇单胞菌 PheB4 进行混合培养后，发现菲在 3 d 内的降解率达到 100%，荧蒽和芘在 7 d 内的降解率分别为 71.2%和 50%，与各自的纯培养降解相比，芘的降解率显著增加，菲和荧蒽的降解率反而降低了[87]，可能是混合降解后代谢产物增加，导致某些产物影响了菲和荧蒽的降解。为解决这一问题，作者研究了独立固定化策略的可行性，将不同的苯并芘降解菌分别固定化在载体上再混合为菌剂，解决了菌间抑制效应，保证了降解效率[88]。

综上所述，混合多种 PAHs 降解菌构建的微生物降解菌群可以缓解部分 PAHs 降解[89]，相比单菌降解 PAHs 有较大的优势。但是许多研究往往忽略了混合培养降解 PAHs 造成的

表 1 PAHs 降解细菌混合培养体系

Table 1 The mixed culture system of PAHs degradation bacteria

Main strains composition	Name of bacterial consortia	Name of PAHs	Concentration of PAHs/(mg/L)	Degradation time/d	Degradation rate/%	Literature sources
Variovorax sp., *Ensifer* sp.	Q15	Phenanthrene	20	14	95.30	[82]
Sphingopyxis sp., *Alicycliphilus* sp.	Q12	Pyrene	20	14	94.00	
Rhodococcus sp., *Acinetobacter* sp., *Pseudomonas* sp.	–	Fluorene	10	28	100.00	[83]
		Phenanthrene	10	28	100.00	
		Pyrene	10	28	100.00	
Marinobacter sp., *Enterobacter* sp., *Dethiosulfatibacter* sp.	–	Acenaphthene	30	56	100.00	[75]
		Phenanthrene	30	56	100.00	
Novosphingobium pentaromativorans, *Limnobacter* sp., *Thalassospira* sp., *Shewanella* sp.	–	Phenanthrene	50	20	100.00	[84]
Mycobacterium sp., *Novosphingobium* sp., *Pseudomonas* sp., *Sphingopyxis* sp., *Lactococcus* sp., *Algoriphagus* sp., *Flavobacterium* sp.	SH-PPHE	Phenanthrene	200	15	100.00	[85]
		Pyrene	100	30	100.00	
		Benzo (a) pyrene	40	30	76.00	
		Benzo (a) fluoranthene	40	30	68.00	
Novosphingobium sp., *Sunxiuqinia* sp., *Pseudomonas* sp., *Flavobacterium* sp., *Breoghania* sp., *Oceanicola* sp., *Modicisalibacter* sp.	BL-PPHE	Phenanthrene	200	15	91.00	
		Pyrene	100	30	100.00	
		Benzo (a) pyrene	40	30	65.00	
		Benzo (a) fluoranthene	40	30	56.00	
Gordona bronchialis, *Rhodococcus rubber*, *Rhodococcus* sp., *Arthrobacter protophormiae*, *Bacillus aquimaris*	M1	Benzo (a) pyrene	20	63	32.84	[8]
Ochrobactrum anthropi, *Stenotrophomonas acidaminiphila, Aeromonas salmonicida ss salmonicida*	–	Benzo (a) pyrene	50	8	41.00	[53]
Marinobacter hydrocarbonoclasticus, *Roseovarius pacificus*, *Pseudidiomarina sediminum*	–	Fluorene	500	7	64.00	[76]
		Phenanthrene	500	7	58.00	
Mycobacterium spp., *Novosphingobium pentaromativorans*, *Ochrobactrum* sp., *Bacillus* sp.	–	Pyrene	100	9	100.00	[79]
Sphingomonas yanoikuyae, *Mycobacterium parafortuitum*	–	Phenanthrene	50	4	94.30	[86]
		Fluoranthene	50	28	60.00	
		Pyrene	50	28	60.00	
Microbacterium sp., *Rhodococcus* sp., *Sphingomonas* sp.	EB	Fluorene	10	100	87.20	[55]
		Phenanthrene	10	100	87.00	
		Fluoranthene	10	100	63.70	
		Pyrene	10	100	64.60	
Mycobacterium sp., *Sphingomonas* sp.	–	Phenanthrene,	10	3	100.00	[87]
		Fluoranthene	10	7	71.20	
		Pyrene	10	7	50.00	

–: none.

代谢物累积可能对微生物造成负面影响，因此在不同降解菌进行混合培养的时候应做进一步的研究，深入比较纯培养与混合培养时微生物的降解能力，确定不同条件下最优的混合培养菌群类型。

3 红树林湿地中PAHs降解影响因素

红树林湿地的一些环境因子会直接或间接地影响红树林中微生物对 PAHs 的降解。常规的环境因子，如温度、pH、上覆水含氧量、金属离子等[90–95]，已在前人的综述中有较充分的论述，本文针对红树林湿地的特点，从好氧-厌氧交替环境、湿地植物根际泌氧和分泌物、外源生物刺激因子等角度，阐述 PAHs 生物降解的影响因素。

3.1 好氧/厌氧交替环境

红树林湿地处于海陆之间的动态界面，长期受到周期性海水浸淹，形成了有氧和无氧环境交替存在的生境[96]。当红树林未被咸潮淹没时处于好氧环境，氧气在有氧条件下会优先获得电子，故 PAHs 此时主要依靠微生物的好氧降解。由于氧气的强氧化性及在还原反应中释放的高能量，使得 PAHs 的生物好氧降解速率较高[97]。

随着海水的浸淹，红树林土壤处于厌氧环境，此时主要是微生物利用电子受体厌氧降解PAHs。反应体系主要以 NO_3^-为电子受体的反硝化还原反应体系、SO_4^{2-}为电子受体的硫酸盐还原反应体系、Mn(Ⅳ)或 Fe(Ⅲ)等为电子受体的金属还原反应体系以及 HCO_3^-或 CO_2 为电子受体的产甲烷还原反应体系为主[98]。相较于好氧降解将不完全降解产物遗留在环境中，PAHs 的厌氧降解更加彻底，大多生成小分子低毒易降解的中间产物并最终转变为二氧化碳[99]。

3.2 红树林根系泌氧

潮汐淹没时 O_2 进入沉积物受阻[100]，而红树植物进化出了强大的通气组织可持续向根系输送 O_2，使部分 O_2 用于根系自身的有氧代谢，另一部分过量的 O_2 扩散到根际土壤中，这个过程称为根系泌氧[101]。根系泌氧会导致根际氧化，促进需氧型微生物的生长，还可以氧化电子受体，潜在地影响微生物的降解过程，导致环境污染物形态的改变[102]。

在红树林生态系统中，以招潮蟹、跳跳鱼为主的底栖动物是主要的生物扰动者[103–104]。底栖动物的掘穴、爬行等活动改善了沉积物的通气条件，使得更多的氧气向沉积物的底层渗透，扩大了用于扩散交换氧气的界面面积，沉积物的氧化还原电位发生了较大的变化[105]，加速了沉积物中 PAHs 等有机物的降解去除过程。此外，蟹类的掘穴过程会将下层沉积物中的难降解有机物沉积在表面，也可以加快有机物的降解[105–106]。

3.3 红树林根系分泌物

PAHs 的高亲脂性使其很容易从环境中迁移到植物根部[107]。除了以 PAHs 为唯一碳源的微生物降解，微生物的共代谢作用在 PAHs 的降解和矿化中也扮演着重要角色，常用于高分子量的 PAHs 降解。共代谢是指微生物在利用某种易降解的物质作为碳源的同时，降解另一种不使其获得能量和营养的非生长物质[108]。植物根际的分泌物中，低分子量有机酸具有化学活性，可以作为微生物代谢的底物与 PAHs 进行共代谢[109]，还可以通过创造特定的根际微环境来促进微生物的降解[110–111]。柠檬酸、琥珀酸、苯甲酸、乳酸、苹果酸、马来酸等是红树植物根系分泌物中常见且研究较多的低分子量有机酸[109,112–113]。有研究表明，添加低分子量有机酸能显著地提高芘在沉积物中

PAHs 的生物可利用性和迁移率[114]，Sivaram 等[115]也发现柠檬酸和琥珀酸的浓度与 PAHs 的高降解率有显著的相关性，且与非根际沉积物相比，菲和芘在白骨壤根际的扩散能力明显更强[115–116]。

3.4 外源生物刺激因子

添加外源电子受体是提高 PAHs 厌氧生物降解速率的方式之一，SO_4^{2-}、NO_3^-、Fe(Ⅲ)、HCO_3^-等电子受体能明显促进厌氧条件下微生物对萘、菲、蒽、芘等 2−4 环 PAHs 的降解[117–121]。然而也有研究指出，在红树林沉积物中加入电子受体 Mn(Ⅳ)后，由于沉积物的强还原性使 Mn(Ⅳ)很快转化为具有毒性的 Mn(Ⅱ)，反而不利于微生物对 PAHs 的降解[55]。

养分是影响 PAHs 生物降解的重要因素，土壤中氮、磷、钾等的浓度会影响 PAHs 降解菌的数量从而影响 PAHs 的降解效率[122]。Yu 等[123]发现用人工海水接种沉积物时只有 30% 的芘被微生物降解，而在使用矿物盐(MSM)培养基接种的沉积物中芘的降解率提高至 97%，Sun 等[124]的研究表明，添加氯化铵和磷酸二氢钾进行生物刺激能增强 PAHs 的降解，并且通过将生物刺激和生物强化(菌株共培养)相结合能显著提高 PAHs 的去除效果。

表面活性剂有化学表面活性剂和生物表面活性剂，可以解吸沉积物中的 PAHs，增加 PAHs 在沉积物中的溶解度，提高 PAHs 的生物可利用性[125–126]。但化学表面活性剂可能会残留在环境中造成污染，并且本身的毒性容易毒害菌株不利于 PAHs 的生物降解[127]，所以生物表面活性剂更适合应用于环境。常见的生物表面活性剂有鼠李糖脂和槐糖脂等，可以使萘、菲、芘、苯并[a]芘等多种 PAHs 在沉积物中缓慢解吸并被微生物降解[128–130]。

生物炭是一种用于修复土壤烃类污染的新型修复材料，能有效促进 PAHs 的降解。大量的研究表明，生物炭可以增强土壤的持水能力，改善土壤的养分条件[131]，能使在 PAHs 降解和转化中起重要作用的微生物的脱氢酶活性显著提高[132]，其独特的多孔结构还为微生物的生长活动创造了良好的环境[133]，能吸引多种 PAHs 降解菌附着于生物炭表面，增加 PAHs 与 PAHs 降解菌之间的接触，从而提高细菌丰度，加快 PAHs 的降解[134]。

4 总结与展望

本文通过介绍红树林湿地沉积物中 PAHs 和电子受体的分布情况，揭示了其空间分布规律；并叙述了具有 PAHs 降解功能的微生物，以供研究人员了解和挖掘 PAHs 降解的菌种资源；最后阐述了红树林中降解 PAHs 的影响因素。图 5 对本综述的主要内容进行了归纳总结：PAHs 主要分布在林下沉积物 10−20 cm，鞘氨醇单胞菌、芽孢杆菌、鞘鞍醇杆菌等 PAHs 降解菌能利用 O_2、NO_3^-、SO_4^{2-}、HCO_3^-、Fe(Ⅲ)等电子受体对 PAHs 进行降解，降解速率受好氧-厌氧交替的生境、红树根系泌氧特性、根系分泌物和外源生物刺激因子的影响。尽管红树林湿地微生物降解 PAHs 的研究已开展多年，但在以下方面仍需要深入探索：

(1) 不同电子受体下微生物降解单一 PAHs 的具体途径尚不完全明确，不同电子受体对不同种 PAHs 的降解效率及影响因素的研究较少，特别是厌氧条件下 PAHs 的降解机制的研究有待新的突破。

(2) 对于高环 PAHs 的微生物降解研究仍有许多不足，从红树林筛选出的能降解高分子量 PAHs 的功能微生物较少，因此，高效降解种质资源的挖掘仍是未来努力的方向。

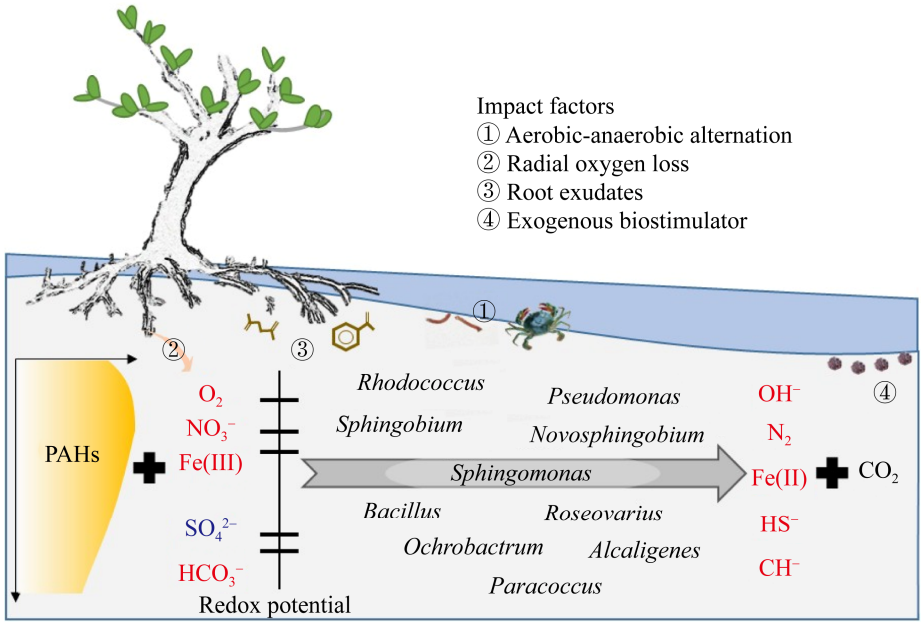

图 5　红树林湿地 PAHs 生物降解的关键要素

Figure 5　Key elements of PAHs biodegradation in mangrove wetland.

(3) 目前关于红树林湿地 PAHs 降解的研究仍处于实验室阶段，未来应更多地面向 PAHs 污染的场地修复开展应用技术研究，为海岸带生态环境健康的提升提供保障。

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