张泽晗,尚长健,贾永锋,等.有机污染物微生物降解机制及生物指示效应研究进展 [J]. 中国环境科学, 2026,46(2):1000-1014.
Zhang Z H, Shang C J, Jia Y F, et al. Research progress on the microbial degradation mechanism of organic pollutants and their biological indicator effects [J]. China Environmental Science, 2026,46(2):1000-1014.

有机污染物微生物降解机制及生物指示效应研究进展

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摘要：针对当前研究存在的微生物降解有机污染物机制认识不足、环境因子影响复杂且其对自然衰减进程的指示作用不明确等问题,梳理了微生物降解代谢机制、关键环境因子的调控作用及自然衰减评估中微生物指标的应用.研究表明,有机污染物的生物降解具有多途径协同的特征,微生物在功能基因调控下合成特定生物酶通过多种途径实现高效降解.污染物浓度、电子供/受体等关键环境因子通过调控微生物活性与群落结构,直接影响自然衰减效能,生物代谢产物、微生物群落结构和功能基因等微生物指标能够有效指示自然衰减的进程与潜力.基于上述,本文深入了微生物代谢机制、环境因子作用及其指示功能的系统性理解,不仅构成了优化自然衰减管理的核心理论基础,也为建立基于微生物响应的监测与调控策略提供了科学依据.

关键词：自然衰减；有机污染；生物降解；环境影响因子；微生物指标
中图分类号：X703.5 **文献标识码**：A **文章编号**：1000-6923(2026)02-1000-15

Research progress on the microbial degradation mechanism of organic pollutants and their biological indicator effects.

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Abstract：In response to existing research gaps—such as insufficient understanding of the mechanisms of microbial degradation of organic pollutants, the complex influence of environmental factors, and the unclear indicative role of these factors in natural attenuation processes—this study systematically reviews the metabolic mechanisms of microbial degradation, the regulatory effects of key environmental factors, and the application of microbial indicators in natural attenuation assessment.The research reveals that the biodegradation of organic pollutants exhibits synergistic multi-pathway characteristics, where microorganisms synthesize specific enzymes under the regulation of functional genes to achieve efficient degradation through diverse pathways. Key environmental factors, including pollutant concentration and electron donors/acceptors, directly affect the efficacy of natural attenuation by regulating microbial activity and community structure. Microbial indicators such as metabolic products, community structure, and functional genes can effectively reflect the progress and potential of natural attenuation.Based on these findings, this paper deepens the systematic understanding of microbial metabolic mechanisms, the role of environmental factors, and their indicative functions. This not only forms the core theoretical foundation for optimizing natural attenuation management but also provides a scientific basis for developing monitoring and regulation strategies based on microbial responses.

Key words：natural attenuation；organic pollution；biodegradation；environmental impact factors；microbiological index

监控自然衰减(MNA)属于原位修复的一种.该技术主要利用自然环境对污染物天然存在的降解作用,通过减弱环境中污染物毒性、浓度、质量并改变污染物存在形态,降低其迁移能力来降解水和土壤介质中污染物质的方法[1],因其环境友好,成本效益低等优点被广泛应用.自然衰减过程包括生物和非生物降解,其中生物降解是自然衰减的核心降解过程[2],有研究表明有机污染自然衰减时生物降解占比超过 50%,其中苯系物更是 90%以上的降解由生物降解主导[3].因此污染物的生物降解成为评价自然衰减修复能否进行的重要因素[4].

污染场地的微生物特征与场地内污染降解效率存在显著联系性,这种污染物-菌群的适配性源于场地微生物的代谢功能:在基因层面,其降解过程受

收稿日期：2025-07-18
基金项目：京津冀环境综合治理国家重大科技专项资助;京津冀区域地下水复合污染高分辨指纹识别及多维源解析技术研究(2025ZD1205703)
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到功能基因的转录调控网络精确控制[5-6];在细胞代谢层面,微生物利用不同的生物酶及代谢途径实现污染物的转化[7-8];在群落生态层面,微生物群落间还可以通过种间互作形成协同降解网络[9].同时场地内环境因子的差异对微生物降解能力存在巨大影响,例如污染浓度影响微生物细胞功能、电子供/受体影响氧化还原反应速率、土壤及岩性条件影响污染物的迁移转化进而影响生物代谢功能[10].基于生物代谢原理,一些学术观点认为通过微生物的指示性功能可以完成对自然衰减能力的指示性功能,进而提升自然衰减技术的应用可行性,微生物指标由表及里分别为通过生物代谢产物表征微生物降解状态,进一步通过分析微生物群落结构及互作关系解析群落降解潜力,最后通过功能基因丰度探讨降解能力基础[11-12].但是,环境因子、微生物互作等的多种影响因素导致单一微生物指示功能的不确定性,而且现有研究多聚焦于单一或少数几类微生物指示指标,缺乏对各类微生物指标的系统性梳理与整合.因此深入理解微生物降解有机污染物的生物代谢原理,综合考虑环境因子对生物代谢的影响并系统探讨微生物对有机污染物降解的指示性功能及其内在机制对于高效应用自然衰减技术极为重要.

本文以期通过研究酶和功能基因、代谢途径及微生物间的互作关系,提供对污染物生物代谢原理及污染场地中影响微生物降解能力的环境因子的深入揭示,并进一步探讨微生物在污染降解过程中的指示作用.

1　微生物降解有机污染物的生物代谢原理

微生物降解污染物是在热力学条件下利用一定的营养条件,使微生物作为反应的催化剂,通过产生各种具有高度专一性的酶,利用氧化物质和还原物质之间电子转移进行氧化还原反应来获取能量进行生理代谢反应的过程(图 1)[7,13-14].此外微生物还可以通过种间互作、趋化性等方式合作降解污染物(图 2、图 3)[15].

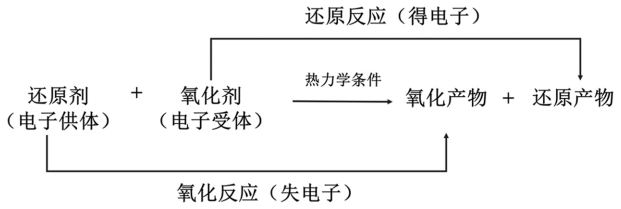


图 1　有机污染物的微生物地球化学反应方程[7]

Fig.1　Equation of microbial geochemical reaction of organic pollutants

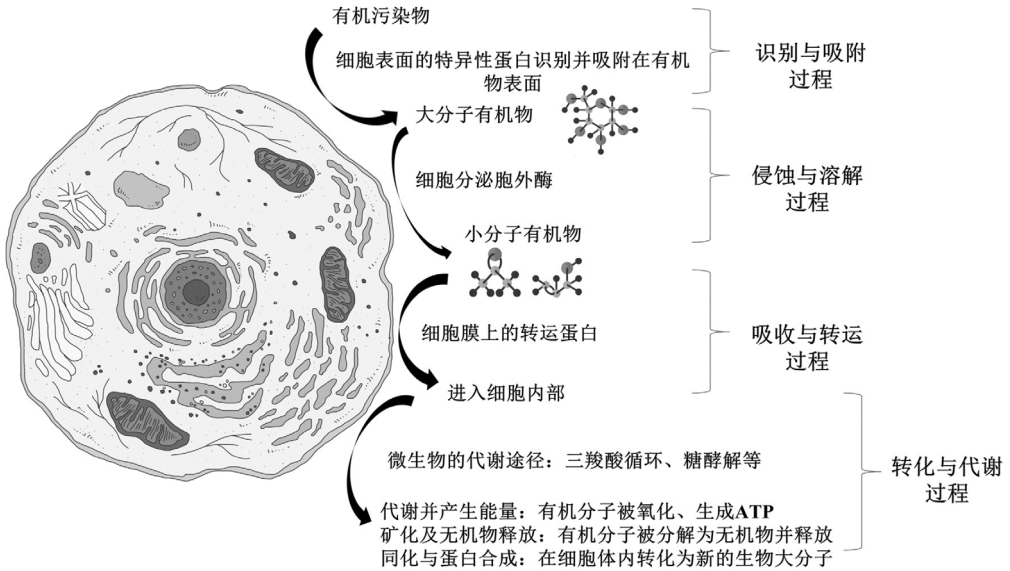


图 2　微生物细胞识别、吸收及代谢污染物过程

Fig.2　The process by which microbial cells recognize, absorb and metabolize pollutants

1.1　微生物降解有机污染物的功能基因和酶

在微生物降解过程中功能基因和酶的调控是重要的一环,功能基因通过转录-翻译指导酶蛋白的合成,酶是由微生物细胞合成的生物催化剂(多为蛋白质),通过降低反应活化能加速有机污染物分解的生化反应速率.

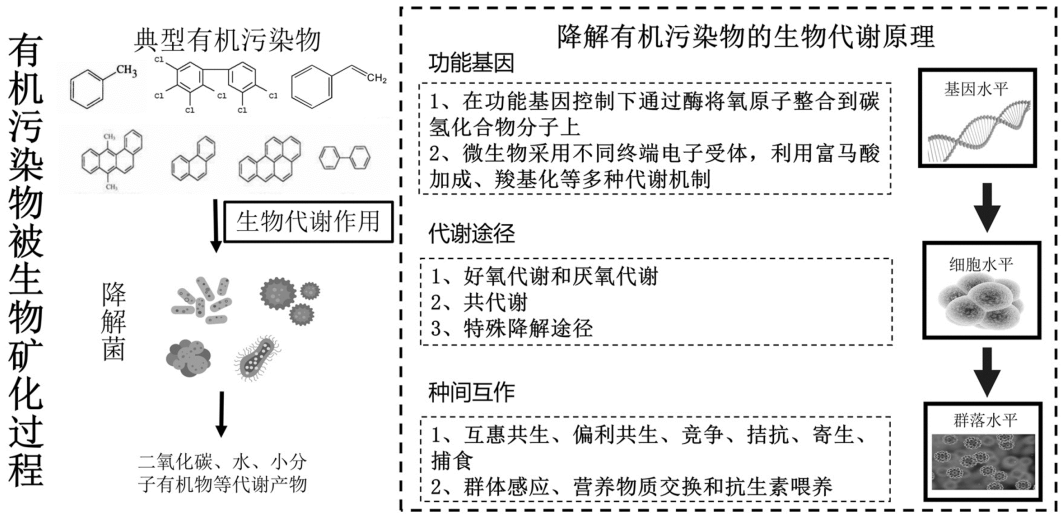


图 3 微生物降解有机污染物生物代谢过程

Fig.3 The biological metabolic process of microbial degradation of organic pollutants

1.1.1 好氧微生物 好氧代谢是好氧微生物以氧气为最终电子受体的生物氧化过程.该过程的初始关键步骤是,在相应功能基因的控制下,通过生物酶将分子氧中的一个或两个氧原子引入污染物分子,使其发生羟基化或环裂解等反应,实现对污染物的初始活化,为后续的彻底氧化降解奠定基础.表 1 列举了部分好氧微生物降解有机污染物涉及的功能基因[16-17],烷烃类污染物一般由单加氧酶完成,芳香族污染物由双加氧酶、环裂解酶,酚类污染物由酚羟化酶、脱氢酶等完成降解[18-20],例如在降解烷烃时,微生物首先产生烷烃羧化酶或烷烃单加氧酶,根据不同的电子传递系统和分子结构又分成了红霉素依赖酶和细胞色素,然后对烷烃分子进行降解[15].红霉素依赖酶是由烷烃羟化酶(*AlkB*)、红霉素还毒素(*AlkG*)和红霉素还毒素还原酶(*AlkT*)形成的复合物[18,21],因此 *AlkB* 基因被认为是石油烃降解中的功能性生物标志物基因,在分枝杆菌属(*Mycobacterium*),戈登氏菌属(*Gordonia*),红球菌属(*Rhodococcus*)等多种石油烃降解菌中都存在,通过 *AlkB* 基因的丰度可间接表示微生物群落降解石油烃能力强弱.

此外真核生物和原核生物的血红蛋白中大量存在细胞色素 P450 单加氧酶[18-19].细胞色素 P450 在很多碳氢化合物降解中都有重要的作用.例如中链烷烃降解菌中广泛存在 CYP153 一类的细胞色素 P450,通过电子传递氧化多种化合物[15,22];在芳香化合物降解中 P450 使分子羧基化并增加溶解度[23-24],因此细胞色素 P450 单加氧酶的丰度可以作为表示微生物降解碳氢化合物潜力的指示性指标.

表 1 在好氧条件下微生物降解有机污染物所涉及的功能基因

Table 1 Functional genes involved in microbial degradation of organic pollutants under aerobic conditions

样本来源	污染物	功能基因	资料来源
土壤	原油	*alkB 1*,*alkB 2*,*p450*,*almA 1*,*almA 2*	[25-26]
土壤	蒽、菲、苯并[a]芘	*PAH-RHDα*	[27]
海水	原油、四氢大麻酚、过氧酰基硝酸酯	*alkB*,*nagG*,*pchCF*,*catA*	[28-29]
实验室培养	儿茶酚、苯酚、苯甲酸	*catA*	[30]
河流沉积物	芴、菲、芘	*PAH-RHDα*	[31]
土壤	六氯苯、五氯硝基苯	*C-hcbA*,*C-pcpB*	[32]
土壤	萘	*nahAc*	[33]
实验室培养	多氯联苯	*bphA*	[34]
土壤	石油中的直链烷烃	*alkB*, *Cyp153A*	[35]

1.1.2 厌氧微生物 在厌氧条件下厌氧微生物采用不同终端电子受体,如硝酸盐、铁及硫酸盐还原等[36-37],其中涉及富马酸加成、羧基化等多种代谢机制[15],通过上述机制微生物将代谢物完全氧化代谢或

吸收同化为生物质[38].由 *assA*、*masD* 和 *bssA* 功能基因控制下的富马酸加成是脂肪族、芳香族等碳氢化合物降解的主要途径[39],因此一直以来 3 种功能基因的丰度被认为是检验厌氧条件下微生物降解碳氢化合物能力的指标(表 2)[15,40-41],图 4 列举了厌氧条件下微生物降解菲的功能基因和酶的变化[42].

表 2　在厌氧条件下微生物降解有机污染物所涉及的功能基因

Table 2　Functional genes involved in microbial degradation of organic pollutants under anaerobic conditions

样本来源	污染物	功能基因	资料来源
土壤	甲苯	*bssA*, *bamA*	[43]
土壤	苯	*bam* 样基因(*AbcA*, *AbcD*), (*BzlA*)	[44]
含水层沉积物	萘和 2-甲基萘	八个基因簇(*bnsABCDEFGH*)	[45]
河口沉积物	碳氢化合物	*assA*	[46]
炼油厂废污泥	脂肪族和芳烃	*mcrA*, *dsrB*	[47]
实验室培养	多环芳烃	*ben ABCD*, *cat ABC*, *pca DL*	[48]
实验室培养	苯甲酸	*ben ABC*, *ben D*	[48]
土壤	烷烃类	*assA*, *masD*	[41]
实验室培养	多氯联苯和五氯酚	*cprA*, *bzd*	[49]

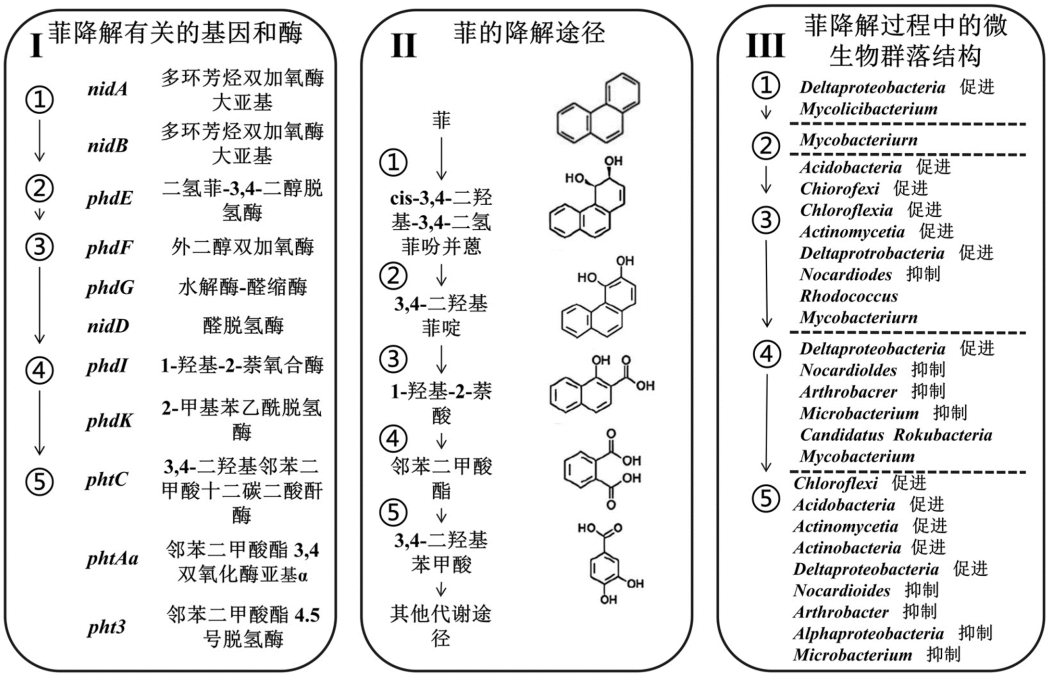


图 4　微生物降解菲示意[42]

Fig.4　Schematic diagram of microbial degradation of phenanthrene

1.2　微生物降解有机污染物的代谢途径

微生物降解有机污染物主要有好氧代谢、厌氧代谢、共代谢及趋化性等特殊降解途径.

1.2.1　好氧代谢　微生物代谢途径的选择依赖于环境氧化还原条件,在氧气充足条件下主要利用卡尔文循环、三羧酸循环(TCA 循环)等好氧代谢过程将有机污染物完全矿化为 CO_2 和 H_2O,例如假单胞菌属(*Pseudomonas*)在好氧条件下通过 TCA 循环将硝基苯分解为无害化物质[48,50],对于大分子有机污染物的降解,微生物利用双模式酶解策略,一方面通过胞外水解酶(如脂肪酶、蛋白酶)实现聚合物的初步解聚;另一方面利用氧化酶系(如单加氧酶、双加氧酶)催化特异性氧化反应.例如降解石油烃时 *Pseudomonas* 等降解菌利用单加氧酶(*alkB*)插入单个氧原子来催化 C−H 键[51],进而添加氧原子转化为乙醇[52],再利用乙醇脱氢酶(*ADH*)将乙醇转化为醛,

进一步转化为脂肪酸.

1.2.2 厌氧代谢 厌氧代谢是缺氧或无氧条件下微生物通过还原代谢实现对有机污染物的转化,核心机制包括电子受体调控下的还原脱基反应与协同代谢,例如氯化烃类(如四氯乙烯、三氯乙烯)在厌氧条件下可发生还原脱卤,此过程由微生物提供的电子直接攻击碳一卤键,逐步脱去氯原子生成低氯代产物乃至完全脱氯(如乙烯),是实现该类持久性污染物解毒与彻底降解的关键厌氧途径[7].此外,邻硝基对甲基苯酚还原是由固氮螺菌属(*Azospira*)和 *Pseudomonas* 完成[53],首先通过硝基还原酶(*Pnca*)催化生成邻亚硝基对甲基苯酚中间体,继而经羟胺还原酶(Hao)作用形成终产物邻氨基对甲基苯酚[54]:菲在厌氧条件下通过硝态氮还原酶逐步转化为邻苯二甲酸及 3,4-二羟基苯甲酸(图 4)[42].

此外部分难降解污染物(如 2,4-二硝基甲苯)的彻底代谢需依赖分阶段代谢策略,硝基的还原脱除需在低氧条件(DO<0.5mg/L)下启动,而后续矿化则依赖好氧氧化[55-56],这是因为芳香化合物的电子亲核机制和硝基排斥电子作用导致芳香族硝基苯不利于被氧攻击[57],因此还原降解途径主要是硝基被还原为亚硝基后再被还原成氨基或羟氨基[58-59].

1.2.3 共代谢 共代谢是指微生物将易降解有机污染物作为主要碳源来进行生长代谢的同时通过非特异性酶或活性中间体的作用,同时降解其他难降解污染物的代谢方式.例如脱卤拟球菌(*Dehalobacter*)和脱卤单胞菌(*Dehalogenimonas*)两种菌对氯苯类物质进行还原脱氯反应的过程是将氯苯类化合物作为碳源和电子受体[60],通过脱氯共呼吸将 1,2,4-三氯苯脱氯为二氯苯的同分异构体,最终脱氯形成苯[61].此外共代谢可以与好氧/厌氧代谢联合完成污染物的降解,共代谢过程中产生的加氧酶(如双加氧酶)与还原酶(如苯甲酰辅酶 A 还原酶)可直接整合至好氧或厌氧代谢途径中,形成跨氧化还原条件的降解方式.

1.2.4 特殊降解途径 除了生化反应外微生物还可以通过如趋化性、产生生物表面活性剂等机制增强对污染物的降解(表 3)[62].趋化性是微生物通过定向运动响应环境变化的重要生物学特性,表现为趋向有利化学物质或规避有害物质的空间迁移行为.此外细胞表面的蛋白质、鞭毛等通过增加微生物与碳氢化合物的接触,增大吸收率[63],对微生物降解污染物也有重要作用.例如因为茋分子在脂质中的高度可溶性,茋通过与短芽孢杆菌(*Brevibacillusbrevis*)细胞膜磷脂疏水结合,然后跨膜进入细胞质后被相关生物酶降解[64];生物表面活性剂则可以降低不同相之间的表面张力,利于非混合相的融合,从而提高吸收率[65],例如不动杆菌属(*Acinetobacter*)通过分泌生物表面活性剂提高生物利用度促进菲的降解[66].

表 3 各种有机污染物的降解机制[13]

Table 3 Degradation mechanism of various organic pollutant

化合物	降解机制
PCE	还原脱氯
TCE	还原脱氯,共代谢
DCE	还原脱氯,直接生物氧化
氯乙烯	还原脱氯,直接生物氧化
TCA	还原脱氯,水解,脱氢卤化
1.2-DCA	还原脱氯,直接生物氧化
四氯化碳	还原脱氯,共代谢,非生物过程
三氯甲烷	还原脱氯,共代谢
二氯甲烷	直接生物氧化
氯苯类	直接生物氧化,还原脱氯,共代谢
苯	直接生物氧化
甲苯	直接生物氧化
乙苯	直接生物氧化
二甲苯	直接生物氧化
1,2-二溴乙烷	还原脱卤,水解,直接生物氧化

1.3 微生物降解有机污染物的种间互作关系

微生物种群间通过互相作用显著提升了复杂污染物的降解效率[67].不同微生物间相互作用可以极大程度地改变群落代谢和营养循环过程[68-69].微生物互作关系包括互惠共生、偏利共生、竞争、拮抗、寄生、捕食.例如发酵微生物与产甲烷古菌的互惠共生,发酵微生物将复杂有机污染物转化为 H_2、乙酸等,产甲烷古菌消耗 H_2 和乙酸,为发酵微生物营造良好的生存环境[70],也有一些菌属因为目标降解物质发生相互作用、氧化还原电位调整、发酵或者抢夺电子受体导致菌属之间呈现竞争、拮抗等关系(图 5)[71],例如在地下水微生物网络中由于降解菌属间具有合作降解芳香族化合物的能力[12,72],因此 *Acinetobacter* 与寒冷菌属(*Polaromonas*)、紫色杆菌属(*Janthinobacterium*)等呈显著正相关,但是短波单胞菌属(*Brevundimonas*)与降解菌争夺电子受体等物质,而且参与 Cr(Ⅵ)和 As(Ⅴ)等重金属的还原,对降

解菌产生毒害作用[12,73],因此该菌与降解菌丰度呈负相关[12],并影响有机污染物的降解效果.

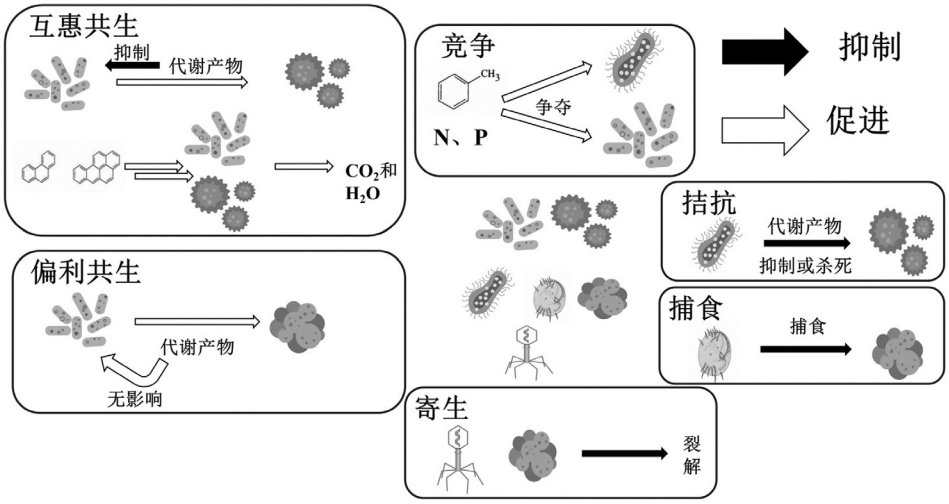


图 5　微生物之间的相互作用机制

Fig.5　Mechanisms of microbial interaction

除了互惠共生、偏利共生、竞争、拮抗、寄生、捕食以外,微生物间也会存在特定类型的相互作用,例如群体感应、营养物质交换和抗生素喂养等作用[74],有研究表明微生物可以利用信号分子通过抑制群体感应来影响其他物种的基因表达[75],此外微生物与邻近物质竞争时会使用分泌系统直接将有毒蛋白输送到邻近细胞中用来干扰正常生理功能[71],这种分泌介导的竞争会显著影响微生物的种内竞争来影响微生物的分布情况[76].

2　微生物降解有机污染物的影响因子

2.1　污染浓度对生物降解的影响

高浓度的污染物会影响微生物细胞膜内蛋白功能、膜的完整性及排泄功能等,进而导致场地中微生物代谢功能、群落结构发生较大变化,例如革兰氏阴性菌的外膜可以对溶剂休克迅速做出反应[77-80],因此在地下水环境中高浓度的苯(≥600mg/L)会导致革兰氏阴性微生物转变为革兰氏阳性微生物[81].

此外污染物浓度会显著影响微生物生物量[82],高浓度污染会导致微生物生长受限,随着暴露时间延长导致微生物死亡并改变群落结构[83-84].但较低的污染浓度会导致微生物所需碳源有限,进而降低了微生物的活性,抑制了微生物的生长[38],导致微生物多样性水平明显下降[82,85-86].因此在一定浓度范围内随着污染场地浓度的增加,微生物种群数量呈现先上升后下降的趋势.

2.2　电子供/受体对生物降解的影响

微生物降解过程中电子供/受体能显著影响微生物降解速率[12].例如丁酸盐是硫曲霉菌属(*Sulfuricurvum*)脱氯过程中的电子供体,所以丁酸盐浓度与该菌丰度呈正相关[87];*Azospira* 利用硝酸盐作为电子受体对亚铁进行氧化,因此与硝酸盐浓度呈正相关[88-90].表 4 总结了环境条件变化微生物降解芳香烃所需电子受体的变化.

但是生物降解能力与电子受体浓度并不呈现严格的线性关系,过量的电子受体会抑制生物降解能力.在具体环境中普遍存在多种电子受体,这些混合电子受体体系间存在显著的竞争抑制作用[91].这种竞争抑制作用来源于当某一种电子受体浓度显著升高时会降低其他电子受体的可利用性或者一些电子受体在代谢过程中会产生具有细胞毒性的代谢产物,进而破坏细胞膜完整性或干扰关键酶活性等途径[92-94].例如在石油污染地下水修复中,硝酸盐和硫酸盐作为两种主要电子受体常同时存在,并存在竞争抑制作用.然而硫酸盐的还原代谢会产生具有较高生物毒性的 S^{2-}离子,因此硫酸盐浓度增加会减弱生物降解作用.反观硝酸盐主导的代谢过程不仅可以通过反硝化过程实现污染物降解,而且其代谢产物 NO_2^-还可激活硫氧化菌(SOB)的硫代硫酸盐氧化酶系统,实现 S^{2-}向 SO_4^{2-}的定向转化,这种电

子受体的双重优势使添加硝酸盐成为一种广泛采用的优化策略[92,94].

表 4 微生物降解芳香烃时使用的终端电子受体[95-96]

Table 4 Terminal electron acceptor used by bacteria to degrade aromatic hydrocarbons

项目	好氧条件	厌氧条件		
	氧化	微氧/缺氧	缺氧	严格厌氧
终端电子受体	O_2	NO_3^-	Mn(Ⅳ),Fe(Ⅲ)	SO_4^{2-},CO_2
产物	H_2O	N_2,NH_4^+	Mn(Ⅱ),Fe(Ⅱ)	HS^-,CH_4
微生物代谢所需电位 E(mV)	+700~ +400	+300~ +200	+100~ -100	-200~-300

2.3 温度对生物降解的影响

温度对生物降解的影响通常呈现“钟形曲线”关系,即温度过高或过低均会抑制降解活性.其作用机制主要体现在三个方面:影响酶反应动力学、改变细胞膜流动性以及调节污染物的理化性质.低温会显著降低酶活性,延缓微生物生长与代谢速率,并使细胞膜流动性下降,阻碍物质跨膜运输;而高温则易导致酶蛋白变性失活和细胞膜结构损伤[96-98].

然而,某些微生物类群(如 *Proteobacteria*、*Bacteroidetes* 和 *Firmicutes* 中的部分物种)在高温条件下仍能维持甚至提高其降解效率.以有机氮降解为例,该过程依赖于胞外酶作用和跨膜转运蛋白,遵循 Q_{10} 温度法则,适度升温可显著提升酶促反应速率并增强膜流动性,从而促进底物摄取与代谢[96,99].此外,另有观点认为,温度变化会引发生物群落结构的适应性调整.上述类群多属于 r–对策菌,相较于生长缓慢的 k–对策菌,它们对环境波动具有更快的响应能力,能够迅速占据生态位[100-102].因此,观测到的降解效率提升可能源于这些菌群相对丰度的增加,而非单纯个体代谢速率的加快.

上述两种观点,前者关注细胞生化结构,后者侧重于生物群落演变,两种观点各有侧重但均有一定的局限性,将二者整合分析是温度调控生物降解的全面系统认知.

2.4 pH 值对生物降解的影响

与温度类似,pH 值对生物降解的影响也通常呈现“钟形曲线”关系,多数微生物的最适 pH 值范围在 6.5~8.5 之间.过高或过低的 pH 值主要通过影响微生物细胞生理状态及污染物的存在形态来抑制降解活性.在酸性条件下,高浓度的 H^+不仅会对细胞产生直接毒性,还可能促使土壤或沉积物中的重金属离子溶出,进而对微生物群落产生复合毒害效应[103].碱性条件则易导致酶蛋白变性失活,并破坏细胞膜的正常结构.然而,自然界中存在一些耐酸碱的微生物类群,能够在偏离中性的环境中保持降解功能[104-107].例如,环状芽胞杆菌(Bacillus circulans)在 pH 值为 8 的碱性条件下对甜菜碱具有极高的去除率,展示了其对特定 pH 值环境的适应性[104,108].

2.5 土壤及岩性条件对生物降解的影响

土壤及岩性条件对通过影响污染物的迁移转化、吸附等对生物代谢活动产生较强影响[109].

岩性差异通过调控多孔介质结构特征对污染物迁移转化过程产生显著影响.岩性颗粒粒径直接决定孔隙通量,进而影响传质过程及其驱动的物理化学和微生物相关过程(图 6)[110-111].渗透性低的岩土养分转移能力差,不利于微生物生存的同时也限制了降解过程中的氧有效性和水分含量[112-113],通过抑制营养物质等的转移进一步抑制微生物的生物膜活性及生物量[111,114-115].例如粘土的低水力传导率,高有机质含量,导致污染物迁移受阻,但存在较好的厌氧条件和大量可供微生物活动的孔隙,因此该岩性下卤代烃污染物的还原脱卤效果更好[116-117].相反,渗透性强的岩土会使得水分、氧气和营养物质在沉积物中的转移较快,例如砂质岩土的高孔隙度,高含氧量,可提供微生物较多的生长空间,较强程度的稀释减少了微生物间、电子供受体对电子的竞争,具有较好的生物代谢能力,因此该岩性条件下烃类污染物的生物降解性较高[118-120].

岩性差异也会导致吸附能力会有所差别,吸附能力强的岩土界面张力强,有机污染物不易解吸扩散.总体上沉积物的颗粒越细,天然胶体及有机质等吸附剂类含量越高,则其对有机污染物的吸附能力就越强[121-122],然而,对于污染物疏水性起主导作用的情况,土壤粒径粗细对吸附能力的影响则不明显[123].

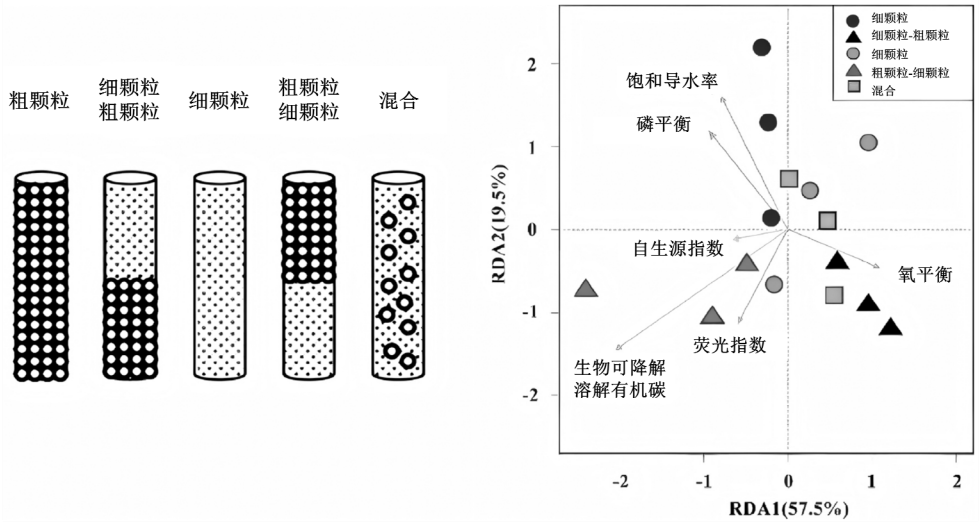


图 6　岩性颗粒大小影响污染物自然衰减的物理化学和微生物过程[110]

Fig.6　The physicochemical and microbial processes in which the lithologic particle size affects the natural attenuation of pollutants

微生物降解有机污染物时,最为理想的状态是需要沉积物的吸附解吸能力能够使污染物羽流处于稳定可控的状态,且有合适程度的解吸以提高生物降解过程中的生物有效性,因此不同岩性条件下的渗透性和吸附能力直接影响了生物降解效率[124].

3　微生物降解有机污染物的指示性功能

自然衰减过程是缓慢且整体性的现象.所以在实际应用中判断自然衰减过程的进展程度显得尤为关键.在自然衰减过程中微生物指标具备指示污染物降解过程的能力.通过监测相关微生物指标,能够有效识别场地自然衰减进程并据此评估场地污染物的降解状况.

3.1　生物代谢产物对污染的指示性功能

在受污染的土壤及地下水环境中,最简单的方式就是通过检测微生物还原过程中代谢产物及电子受体等,可以间接证实微生物降解过程的进度,并据此判定地下水中污染物的种类、浓度及其空间分布特征.例如在石油烃污染下,监测 O_2、NO_3^-、Mn^{4+} 等指标[125],能够有效地指示污染阶段及生物代谢的变化,这些指标敏感地反映了微生物活性和污染物降解状况;此外石油烃的地球化学足迹(电子受体(主要是 O_2,NO_3^-,Fe(Ⅲ)和 SO_4^{2-})、生成的受体还原产物(如 Fe(Ⅱ)和 CH_4)、有机酸(石油烃的中间代谢产物)、溶解的无机碳浓度增加、碱度特征性的增加[126])都表明了石油碳氢化合物在某地发生自然衰减的过程[127].

虽然上述方法具有方便快捷、指示效率高等优点,但是由于代谢路径的多样性,会产生多种中间产物,而有些中间产物具有较高毒性(例如多环芳烃氧化为醌类物质),因此现有代谢检测技术难以全面识别量化风险性,导致污染效果修复的高估[128].

3.2　微生物群落结构及互作关系对污染的指示性功能

由于污染场地中的微生物群落结构呈现出显著的种群特异性,因此通过识别关键降解功能菌属分析微生物群落结构,可以有效地评价判断场地生物降解潜力.特定菌属尤其是那些参与特定污染物降解的菌属相对丰度增加,通常被视为自然衰减过程的重要指示性信号[129-130].例如在石油污染环境中,微生物主要的代谢功能是甲醇氧化、甲基化、尿解和还原性丙酮生成.这些微生物主要为 *Proteobacteria*、厚壁菌门(Firmicutes)、拟杆菌门(Bacteroidota)、浮霉菌门(Planctomycetes)、疣微菌门(Verrucomicrobia),因此这几种微生物丰度是判断石油污染程度的关键物种[12,131].同样在硫酸盐还原中硫酸盐还原菌(SRB)主要以 H_2 或有机污染物为电子供体,硫酸盐和硫单质为电子受体进行生长代谢(图 7),因此 SRB 的丰度与污染场地中硫酸盐污染自然衰减潜力密切相关[132-134].

但是在适度的环境压力下微生物群落会产生功能冗余(不同菌群同享一种代谢功能)维持降解能力,因此导致微生物群落结构指标无法准确预测实际降解指标.

表 5 污染物中的特殊降解菌[13]

Table 5 Special degrading bacteria in pollutants

污染物	微生物菌群	生物降解性
苯	*Pseudomonas putida, Prhodochrous, Paeruginosa, Acinetobacter., Methylosinus trichosporium* OB3b	中等偏高
甲苯	*Methylosinus trichosporium* OB3b, *Bacillus* sp., *Pseudomonas* sp., *P. putida*, *Cunninghamella elegans*, *P. aeruginosa*, *P. mildenberger*	高
乙苯	*Pseudomonas putida*	高
二甲苯	*Pseudomonas putida*	高
氯苯	*Alcaligenes*, *Pseudomonas*, *Staphylococcus epidermis*	中等偏高
氯代乙烷	*Alcaligenes*, *Pseudomonas*, *Staphylococcus epidermis*	中等

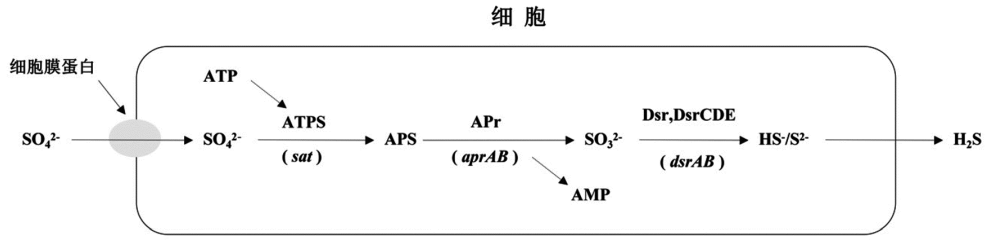


图 7 SRB 异养微生物还原硫酸盐的过程[133-134]

Fig.7 SRB heterotrophic bacterial sulfate reduction process

APR 是 APS 还原酶、APR 是 αβ 形式的低聚铁硫黄蛋白、AMP 是磷酸腺苷

3.3 功能基因对污染的指示性功能

在微生物降解过程中功能基因的调控是重要的步骤,功能基因的丰度可以代表污染场地微生物群落的降解潜力,相关降解的功能基因丰度越高则说明环境中存在更多携带该基因的微生物,降解能力越大.例如 *AlkB* 基因的丰度可表示微生物群落降解石油烃能力强弱、细胞色素 P450 单加氧酶的丰度可表示微生物降解碳氢化合物潜力、*assA*、*masD* 和 *bssA* 3 种功能基因的丰度被认为是检验厌氧条件下微生物降解碳氢化合物能力的指标(见 2.1 节).在已有研究中(表 6)充分展示出降解功能基因丰度与污染物浓度或降解速率间呈显著正相关关系,因此对生物降解作用有较好的指示性功能.

表 6 关键酶编码功能基因丰度与污染物间响应关系研究

Table 6 Study on the relationship between abundance of functional genes encoding key enzymes and response among pollutants

样品来源	功能基因	污染物	相关性	文献来源
克拉玛依油田土壤	*alkB*,萘降解基因 *nah*	脂肪烃,芳香烃,沥青质含量	显著正相关	[135]
大庆油田土壤	*alkB*,萘降解基因 *nah*	脂肪烃,芳香烃,沥青质含量	不显著	[135]
煤焦油污染沉积物	萘双加氧酶基因 *nagAc* 类基因	萘,菲含量	显著正相关	[136]
杂酚油污染土壤	PAHs 降解基因 *nah,phnA,pdo1* 之和	PAHs 含量	显著正相关	[137]
油田土壤	*alkB*	总石油烃,C33-C40 长链烷烃含量	显著正相关	[138]
	nah	总芳烃含量,16 种 多环芳烃含量之和	显著负相关	[138]
萘异位降解实验土壤	*nahAc*	好氧层萘矿化速率	显著正相关	[139]
	alkB	二十八烷矿化速率	不显著	[139]
异位降解实验土壤	甲苯降解基因 *xylE nahAc*	甲苯矿化速率	显著正相关	[140]
		好氧层萘矿化速率	显著正相关	[140]
芘异位降解实验土壤	芘降解基因 *nidA,nagAc*	芘矿化率	显著正相关	[141]
	nahAc	芘矿化率	不显著	[141]
土柱实验土壤	*alkB*	C8-C12 ,C13-C30 降解程度	显著正相关	[142]
	nah	萘,三环芳烃降解程度	显著正相关	[142]

但是在实际环境中基因表达受到环境条件影响,而现有的宏基因组技术无法区分基因是否表达活跃,因此导致在一些条件下观测的基因丰度与污染物去除效率不匹配,导致指示功能失效.因此单一

微生物指标(功能基因、代谢产物、关键代谢途径还有微生物群落互作网络)在一定条件下都会存在表征偏差,因此未来研究可基于多种微生物指示指标,联合多组学技术、结合机器学习算法,构建复合型微生物指示系统以实现对生物降解效率的高效准确观测[143].

4　结论及展望

4.1　污染场地的微生物特征与场地内污染降解效率存在显著关联性,微生物在基因层面,生化反应层面及群落生态层面联合调控场地内生物降解效率.

4.2　场地内环境因子的差异(如污染浓度、电子供/受体、土壤及岩性条件等)显著影响了微生物的代谢过程,进而影响自然衰减效率.

4.3　微生物指标对自然衰减能力具有指示性功能,在实际应用中分为三步,从最表面的生物代谢产物表征微生物降解潜力,到进一步通过分析微生物群落结构及互作关系解析群落降解潜力,到最后探讨功能基因丰度证明生物降解潜力的大小.

4.4　虽然微生物指标在一定程度上可以表征场地自然衰减能力大小,但由于环境因子,微生物互作等影响,导致单一微生物指标可能存在表征偏差,因此未来构建复合型微生物指示系统成为研究热点.

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