

Original Paper

Mechanisms of Microbially Mediated Mercury Methylation and Demethylation in the Environment

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Abstract

*The environmental behavior and toxicity of mercury are largely determined by its chemical speciation, and microbially mediated mercury transformations play a crucial role in controlling its mobility, bioavailability, and bioaccumulation. This review systematically examines two key microbial transformation processes: the methylation of inorganic mercury (Hg^{2+}) and the demethylation of methylmercury (MeHg), with an emphasis on the major microorganisms involved and the underlying molecular mechanisms. Specifically, this review focuses on the *hgcAB*-mediated mechanisms of mercury methylation and the methylation potential of different functional microbial groups, as well as the *mer* system-mediated demethylation of MeHg and the associated microorganisms. It further examines the effects of environmental factors, including the coupling of organic matter, iron, and sulfur cycling, salinity and ionic composition, and climate warming, on microbially mediated mercury methylation and demethylation. This review aims to advance our understanding of microbial regulation of mercury biogeochemical cycling and provide a theoretical basis for mercury pollution risk assessment and the development of bioremediation strategies.*

Keywords

mercury, methylmercury, microbial methylation, demethylation, environmental factors

1. Introduction

Mercury is a highly toxic and volatile global heavy metal pollutant, and its elemental form (Hg^0) can undergo long-range atmospheric transport and participate in the global biogeochemical cycle[1]. The major sources of mercury emissions include natural sources, such as volcanic eruptions, forest fires, and emissions from vegetation, as well as anthropogenic sources, such as fossil fuel combustion, metal mining, and smelting. Based on chemical form, mercury can be classified as: elemental mercury (Hg^0),

inorganic divalent mercury (Hg^{2+}), and organic mercury[2]. Mercury toxicity is closely related to its chemical speciation, with MeHg being a highly toxic mercury compound that can cross the blood–brain barrier and cause irreversible damage to the central nervous system[3]. Under suitable environmental conditions, inorganic mercury can be converted into the more toxic MeHg by microorganisms; MeHg can enter aquatic food chains and undergo bioaccumulation and biomagnification, particularly in fish, thereby posing a potential threat to human health^[1]. In addition, rice is a MeHg hyperaccumulator, and the consumption of MeHg-contaminated rice represents another important pathway of human exposure to MeHg[4].

Mercury in natural environments can undergo biogeochemical transformations, including methylation and demethylation, which collectively control its mobility, toxicity, and bioavailability in environmental media. Therefore, mercury speciation and transformation are critical to the global mercury cycle and mercury exposure risks. Mercury transformation processes can be divided into biotic and abiotic processes, with biotic processes playing a dominant role. As key drivers of environmental mercury cycling, microorganisms participate in the transformation of various mercury species through specific metabolic pathways and functional genes. In anaerobic environments, anaerobic microorganisms, including sulfate-reducing bacteria (SRB), iron-reducing bacteria (FeRB), and methanogens, can convert inorganic mercury into the more toxic MeHg and also demethylate MeHg; these two processes jointly determine the net production of MeHg[5]. In recent years, advances in metagenomics, transcriptomics, and stable isotope tracing techniques have enabled researchers to gradually elucidate the key roles of the mercury methylation genes *hgcAB* and the mercury resistance gene cluster (*mer* system) in microbial mercury transformations. Microbial communities across different ecosystems collectively influence the environmental fate of mercury by regulating its methylation and demethylation.

This paper takes microbially mediated mercury methylation and demethylation processes as the main thread, reviews their molecular mechanisms, functional microbial groups and research progress, discusses the limitations of current understanding, and prospects future research directions.

2. Mechanisms of Mercury Methylation by Microorganisms

The key to microbial mercury methylation lies in the transfer of a methyl group to Hg^{2+} , a process that is closely related to the production and metabolism of intracellular methyl donors. Different mercury-methylating microorganisms may obtain methyl donors through different metabolic pathways. Currently, the acetyl-CoA pathway is the most thoroughly studied metabolic pathway related to mercury methylation; furthermore, S-adenosyl-L-methionine (SAM) has been shown to act as a direct methyl donor for HgcAB in vitro, while the relationship between dimethylsulfoniopropionate (DMSP) metabolism and mercury methylation requires further experimental validation[6].

2.1 The Acetyl-CoA Pathway

Mercury methylation is an enzyme-catalyzed process, and the acetyl-CoA pathway has long been

considered a major pathway involved in microbial mercury methylation[7]. Prior to this, Wood et al.[8] first reported that methylcobalamin could transfer a methyl group from Co(III) to Hg^{2+} through an enzymatic reaction in extracts of methanogens. Subsequent studies further demonstrated that, although other methyl donors exist in living organisms, methylcobalamin was considered at that time to be the only methyl donor capable of transferring a methyl group as a carbanion (CH_3^-)[9]. After SRB were identified as major mercury-methylating microorganisms, researchers proposed an acetyl-CoA pathway-mediated mechanism of mercury methylation based on studies of the SRB *Desulfovibrio desulfuricans* LS, in which methyl groups derived from the C-3 position of serine or from formate are transferred to tetrahydrofolate (THF) to form methyltetrahydrofolate (CH_3 -THF), and subsequently transferred to a cobalamin-containing protein via the acetyl-CoA pathway to form methylcobalamin, which participates in mercury methylation[10-12].

However, Ekstrom et al.[13] investigated the relationship between the acetyl-CoA pathway and the mercury methylation capacity of SRB by inhibiting acetyl-CoA pathway activity with chloroform. The results showed that mercury methylation was inhibited in complete oxidizers, whereas the methylation capacity of incomplete oxidizers remained unaffected. It was not until 2013 that researchers identified the mercury methylation genes *hgcAB* through comparative genomics and structural biology approaches, marking a major breakthrough in understanding the molecular mechanisms of microbial mercury methylation[14]. The study showed that *hgcA* encodes a putative corrinoid protein that acts as a methyl carrier and catalyzes the conversion of Hg^{2+} to MeHg, whereas *hgcB* encodes a ferredoxin containing two $[4\text{Fe}-4\text{S}]$ clusters that serves as an electron donor for the reduction of HgcA. The *hgcAB* genes are closely associated with C_1 metabolism. Qian et al.[15] used comparative proteomics to investigate the effects of deleting the *hgcAB* and *omcBESTZ* genes on key metabolic processes in the iron-reducing bacterium *Geobacter sulfurreducens* PCA, and found that *hgcAB* function was associated with C_1 metabolism in the folate branch of the acetyl-CoA pathway, which provides the methyl groups required for mercury methylation. Similarly, studies have shown that deletion of the *hgcAB* genes in the SRB *Desulfovibrio desulfuricans* ND132 significantly increased the abundance of proteins associated with the methyl branch of C_1 metabolism (i.e., the folate branch) in the reductive acetyl-CoA pathway[16]. These findings suggest that microbial mercury methylation may not be merely a detoxification response but may also be closely linked to cellular C_1 metabolism and methyl donor production.

2.2 L-Methionine Biosynthesis

Studies have shown that complete-oxidizing SRB can methylate Hg^{2+} via the acetyl-CoA pathway, whereas incomplete oxidizers lack this ability[17]. However, some incomplete-oxidizing SRB can still methylate Hg^{2+} in the absence of acetyl-CoA pathway activity or when this pathway is inhibited[13, 17], indicating that mercury methylation by these bacteria is independent of the acetyl-CoA pathway and may not require vitamin B₁₂. These findings suggest that SRB and other mercury-methylating microorganisms may possess alternative mercury methylation pathways beyond the acetyl-CoA

pathway, potentially involving methyl group transfer and enzymatic catalysis. Early studies proposed that the methionine biosynthetic pathway was involved in MeHg biosynthesis in the fungus *Neurospora crassa*, as the addition of L-cysteine and DL-homocysteine to the culture medium increased MeHg levels, whereas methionine supplementation inhibited MeHg production, suggesting a close association between mercury methylation and the methionine biosynthetic pathway[18].

In the metabolism of L-methionine, L-methionine can be converted into SAM under the catalytic action of methionine adenytransferase (MAT), and SAM serves as a source of methyl groups in many enzymatic reactions [17, 19]. By heterologously expressing and purifying the HgcAB complex, Zheng et al. [20] found that SAM can transfer a methyl group to Co(I)-HgcA, producing S-adenosyl-L-homocysteine (SAH) and a methyl-Co(III)-cobalamin intermediate, with the latter subsequently methylating Hg^{2+} . Therefore, while existing in vitro experiments have confirmed that SAM can act as a direct methyl donor for HgcAB, the actual contribution of L-methionine to MeHg formation in microorganisms via the SAM pathway still requires further verification.

2.3 Biological Degradation or Metabolism of Dimethylsulfoniopropionate (DMSP)

DMSP is an organic sulfur compound primarily synthesized by marine phytoplankton and algae [19, 21, 22], and its biodegradation represents another potential pathway for mercury methylation. Larose et al. [23] first reported a close association between DMSP metabolism and mercury methylation in Arctic snow: a clear negative correlation was observed between biogenic mercury and MeHg in the snowpack, whereas MeHg was significantly positively correlated with methanesulfonate concentrations. Based on these observations, the researchers proposed that microorganisms involved in DMSP cycling under aerobic conditions may drive mercury methylation through methyl group transfer, with mercury serving as a methyl acceptor. However, few studies have examined how the role of DMSP as a methyl donor for mercury ions varies across different environments, and given the complexity of DMSP metabolic pathways, the reaction mechanisms and regulatory processes underlying mercury methylation remain unclear.

3. Mercury-methylating Microorganisms

The ability to methylate mercury is not a trait exclusive to any single group. Based on culture experiments and *hgcAB* gene surveys, SRB, FeRB, and methanogens are the three groups of anaerobic mercury-methylating microorganisms that have been studied most systematically to date[24]. It is worth noting that there is no clear correlation between methylation capacity and the phylogeny of the 16S rRNA gene[24]; therefore, this chapter organizes the discussion by functional groups rather than taxonomic units.

3.1 Sulfate-reducing Bacteria(SRB)

SRB are a group of obligate anaerobic bacteria that use sulfate as the terminal electron acceptor and organic compounds such as acetate, lactate, and pyruvate as electron donors. In 1985, Compeau et al.[25] demonstrated the mercury methylation capacity of SRB in aquatic sediments: the addition of

sodium molybdate, a specific inhibitor of sulfate reduction, reduced Hg^{2+} methylation by more than 95%, whereas the addition of 2-bromoethanesulfonate, a specific inhibitor of methanogenesis, significantly increased MeHg production. They also isolated the first mercury-methylating SRB strain, *Desulfovibrio desulfuricans* LS, from sediments. Since then, SRB have been recognized as major mercury-methylating microorganisms in aquatic ecosystems [26-28]. In early studies, *D. desulfuricans* LS [7] and *Desulfovibrio desulfuricans* ND132[29] were commonly used as model strains to investigate the mechanisms of microbial mercury methylation.

However, not all SRB are capable of mercury methylation[13], and MeHg production rates vary considerably among mercury-methylating microorganisms[28]. Phylogenetic analyses based on 16S rRNA gene sequences have shown that mercury methylation capability is not phylogenetically conserved among SRB[24, 30]. Early studies suggested that SRB primarily belonged to the class *Deltaproteobacteria* [29]. A study published in 2013 further demonstrated that SRB belonging to the class *Clostridia* within the phylum *Firmicutes* were also capable of mercury methylation[24]. Overall, 36 mercury-methylating SRB strains have been reported, including 31 belonging to the phylum *Proteobacteria* and 5 to the phylum *Firmicutes* [24, 31].

3.2 Iron-reducing Bacteria (FeRB)

In addition to SRB, FeRB in sediments can also methylate Hg^{2+} [32-34]. Early studies showed that microbial mercury methylation activity persisted when Fe(III) was added to sediments as a terminal electron acceptor, although the rate of MeHg production was inhibited[35]. In 2006, Fleming et al.[33] found that the addition of molybdate, an inhibitor of sulfate reduction, to sediments inhibited mercury methylation by less than 50%. They further isolated the iron-reducing bacterium *Geobacter* sp. strain CLFeRB from sediments in Clear Lake, California, USA, and found that its mercury methylation rate was comparable to that of the SRB strain *Desulfobulbus propionicus* 1pr3. Kerin et al.[32] subsequently systematically evaluated the mercury methylation capacity of FeRB belonging to the genera *Geobacter*, *Desulfuromonas*, and *Shewanella*. They found that, when grown under comparable conditions with the same electron acceptors and donors, including Fe(III), nitrate, and organic substrates, strains of *Geobacter* and *Desulfuromonas* were capable of methylating Hg^{2+} , whereas *Shewanella* strains produced MeHg at levels below those observed in abiotic controls. All *Geobacteraceae* strains tested to date have exhibited mercury methylation capability, indicating that mercury-methylating strains are relatively prevalent within this family. Recent studies have identified *Geobacteraceae* as one of the major groups of mercury-methylating microorganisms in lake sediments[36, 37], boreal forest soils[38], attached biofilms[39], and paddy soils[40, 41], with the relative abundance of their *hgcA* gene exceeding that of SRB in some habitats[37, 38].

Previous studies have reported eight mercury-methylating FeRB strains, primarily belonging to the phyla *Proteobacteria* and *Firmicutes*, with *Proteobacteria* accounting for the largest number of reported strains. These include seven strains belonging to the family *Geobacteraceae* and one belonging to the family *Desulfuromonadaceae*[24, 32, 33, 40, 42, 43]. Although some FeRB exhibit mercury

methylation capabilities comparable to those of SRB, the number of reported mercury-methylating FeRB strains is considerably lower than that of SRB. Future research should focus on further screening and identifying mercury-methylating FeRB and elucidating the coupling between iron reduction metabolism and *hgcAB*-mediated mercury methylation.

3.3 *Methanogens*

In the mid-to-late 1960s, researchers discovered that cell extracts of *Methanobacterium bryantii* could methylate Hg^{2+} , with methylcobalamin serving as the sole methyl donor for methyl transfer to Hg^{2+} [8, 44]. Methanogens were therefore considered the major group of mercury-methylating microorganisms. However, as SRB[25] and FeRB[32] were subsequently identified as the major mercury-methylating groups in anaerobic sediments, the contribution of methanogens to mercury methylation was largely overlooked or dismissed. It was not until 2011 that metabolic inhibitor experiments and 16S rRNA gene sequencing provided renewed evidence of the mercury methylation capability of methanogens. The addition of BESA (2-bromoethanesulfonic acid), an inhibitor of methanogenesis, to lake-associated biofilms completely inhibited MeHg production, whereas molybdate addition increased MeHg production 45-fold, indicating that methanogens were the dominant mercury-methylating group in the studied lake environment[45]. Pure-culture experiments with *Methanospirillum hungatei* JF-1 showed that its mercury methylation rate in sulfide-free medium was comparable to that of certain SRB and FeRB, although its MeHg yield was higher[46]. In contrast, the methanogens *Methanomethylovorans hollandica* and *Methanobrevibacter tindarius* exhibited lower MeHg production rates under sulfide-containing culture conditions[47]. This may be because sulfide reduces the bioavailability of Hg^{2+} , and mercury methylation by methanogens occurs primarily in environments with low sulfide concentrations.

The discovery of the *hgcAB* gene cluster has greatly facilitated the identification of mercury methylation potential in methanogens. Mercury-methylating methanogens have been identified in various habitats, including Arctic permafrost[48], human feces[49, 50], rice paddies[40], northern lake sediments[36], peatlands[51], attached biofilms[45], and landfills[52]. A recent study examined nine methanogenic strains carrying *hgcAB* and found intrinsic differences in their mercury methylation rates, with some strains exhibiting MeHg production rates comparable to or even higher than those of known SRB and FeRB[47]. Previous studies have identified eight mercury-methylating methanogenic strains, primarily belonging to the classes Methanomicrobia (seven strains) and Thermoplasmata (one strain) [24, 47].

3.4 *Other Methylating Microorganisms*

In addition to the three major groups of mercury-methylating microorganisms described above, other microorganisms are also capable of methylating Hg^{2+} . Studies have shown that fermentative, acetogenic, and cellulolytic bacteria within the phylum Firmicutes can also methylate mercury. These bacteria have mainly been isolated from rice paddies, wastewater, and animal intestines. Among them, the fermentative bacterium *Ethanoligenens harbinense* YUAN-3 and the acetogenic bacterium *Acetone*

longum APO-1 possess *hgcAB* homologs and produce significantly higher MeHg levels than the controls[24]. In addition, potential mercury-methylating microorganisms carrying *hgcAB* have been identified in other phyla, including Bacteroidota, Chloroflexota, and Nitrospina[47]. For example, a study first detected *hgcA*-like sequences in the marine microaerophilic bacterium *Nitrospina* in Antarctic sea ice, suggesting that it may represent a potential source of MeHg in sea ice [53]. Subsequent research has further suggested that *Nitrospina* may be a major mercury-methylating microorganism in the global ocean, carrying and actively expressing the *hgcA* gene[54]. Furthermore, some facultative anaerobic and aerobic microorganisms are also capable of mercury methylation[55, 56], although the underlying mechanisms remain to be elucidated.

4. Mechanisms of Demethylation in Microorganisms

4.1 Reductive Demethylation

Researchers isolated a mercury-resistant bacterium, *Pseudomonas* sp. K-62, from soil contaminated with organic mercury and found that it could adsorb Hg^{2+} and reduce it to Hg^0 , which subsequently volatilized into the atmosphere[57]. Subsequently, an enzyme (S-1) capable of cleaving carbon–mercury bonds in organic mercury compounds was identified in cell-free extracts of strain K-62. A metallic mercury-releasing enzyme (MMR enzyme) was also found to be involved in the NADPH-dependent reduction of Hg^{2+} to Hg^0 [58]. Meanwhile, Spangler et al.[59] isolated several bacterial strains from lake sediments that could rapidly degrade MeHg into methane and Hg^0 under pure-culture conditions.

MeHg demethylation is associated with the mercury resistance *mer* operon in mercury-resistant prokaryotes[60, 61]. The microbial mercury resistance system degrades MeHg through the coordinated action of organomercurial lyase (MerB) and mercuric reductase (MerA)[62, 63]: MerB catalyzes the cleavage of the C–Hg bond in MeHg, producing Hg^{2+} and CH_4 , while MerA subsequently reduces Hg^{2+} to Hg^0 in an NADPH-dependent reaction. Among microbial MeHg degradation mechanisms, the organomercury resistance system encoded by the bacterial *mer* operon has been the most extensively studied. Broad-spectrum mercury-resistant strains possess a *mer* system encoding both MerB and MerA, enabling the cleavage of MeHg to release Hg^{2+} , followed by its reduction to Hg^0 and subsequent release into the environment. In contrast, narrow-spectrum mercury-resistant strains possess only the mercuric reduction machinery and can detoxify Hg^{2+} but not organomercury compounds[64].

4.2 Oxidative Demethylation

Korthals et al. [65] used a radiolabeled tracer ($^{14}\text{CH}_3\text{HgI}$) to investigate MeHg demethylation activity in a lake system and detected not only CH_4 but also CO_2 among the products, indicating the presence of a demethylation process distinct from that mediated by the *mer* system. This process, in which CO_2 is the major product, is referred to as oxidative demethylation (OD)[66, 67]. Oremland et al.[68] found that both SRB and methanogens in river sediments were capable of oxidatively demethylating MeHg, producing large amounts of CO_2 and small amounts of CH_4 , although their demethylation efficiency

was relatively low. Pak et al.[69] subsequently observed efficient MeHg degradation in cocultures of SRB and methanogens, with CO₂ as the predominant product. Although OD has been less extensively studied than reductive demethylation (RD), it predominates in certain environments, including some peat soils, freshwater sediments, and estuarine sediments[70, 71]. The mechanism of OD is thought to resemble the degradation of monomethylamine or methanol by methanogens and the oxidation of acetate by SRB, although the specific pathways and key enzymes involved remain unidentified[68, 70].

4.3 Demethylating Microorganisms

Research on MeHg demethylation began earlier than that on mercury-methylating microorganisms. However, early studies primarily focused on screening mercury-resistant strains and investigating mercury resistance mechanisms, with the *mer* gene system-mediated mercury resistance mechanism being the most extensively studied[72]. Mercury resistance genes associated with the *mer* system are often located on plasmids, transposons, or bacterial chromosomes and can be horizontally transferred between different bacterial species. These *mer* genes have been identified in numerous Gram-negative and Gram-positive bacteria and detected in both aerobic and anaerobic environments[73], indicating that potential MeHg-demethylating microorganisms are phylogenetically diverse.

RD occurs primarily in certain mercury-resistant aerobic and facultatively anaerobic bacteria, whereas OD occurs in both aerobic and anaerobic microorganisms, including SRB and methanogens[66, 69, 73]. In recent years, numerous studies have shown that mercury-methylating and MeHg-demethylating microorganisms coexist within the same microbial communities, and that some mercury-methylating microorganisms are also capable of MeHg demethylation. Bridou et al.[74] used stable isotope tracing to simultaneously assess mercury transformation in pure cultures of multiple SRB strains and found that all strains capable of mercury methylation were also able to demethylate MeHg. Lu et al.[43] were the first to demonstrate that the FeRB *Geobacter bemidjiensis* Bem could not only efficiently methylate Hg²⁺ but also degrade MeHg via a reductive pathway.

Previously reported MeHg-demethylating microorganisms exhibit considerable phylogenetic diversity, spanning several bacterial phyla, including Proteobacteria, Firmicutes, Actinobacteria, and Bacteroidota[73], but unlike methylating microorganisms they have not been organized into a coherent phylogenetic framework. The main reasons are that *mer* genes are subject to extensive horizontal transfer and that no universally applicable marker for OD has been identified, so functional microorganisms cannot yet be identified in situ; most studies therefore remain limited to assessments of functional potential or to correlations with community composition.

5. Environmental Factors Affecting Microbially Mediated Mercury Methylation and Demethylation Processes

5.1 Coupling of Organic Matter, Iron, and Sulfur Cycles

Microbial mercury methylation is influenced not only by the environmental concentration of Hg²⁺ but, more importantly, by its bioavailability[75]. In natural environments, the cycling of iron, sulfur, and

organic matter is highly interconnected, exerting both promoting and inhibitory effects on MeHg accumulation under different environmental conditions. Dissolved organic matter (DOM) plays a central role in regulating mercury mobility and bioavailability in the environment. On the one hand, readily degradable organic matter can serve as a carbon source and electron donor for microorganisms, thereby promoting MeHg production. On the other hand, the reducing conditions generated by organic matter decomposition can facilitate the reductive dissolution of iron oxides and the release of adsorbed mercury, while also promoting sulfate reduction and the transformation of HgS into soluble polysulfide complexes, thereby increasing mercury bioavailability[76]. Subsequently, the released Fe^{2+} can react with sulfide to form FeS, which can immobilize Hg^{2+} through coprecipitation, ion exchange, and surface complexation, thereby inhibiting mercury methylation[77].

The effects of coupled organic matter, iron, and sulfur cycling on MeHg are environment-dependent, with the underlying mechanisms and outcomes varying across ecosystems. Wang et al.[78] found that organic matter, S^{2-} , and Fe^{2+} in black and odorous lake sediments acted synergistically to induce sediment blackening and odor formation while simultaneously enhancing mercury methylation potential. They also found that MeHg accumulation in sediments could be reduced by adjusting organic matter amendment levels and the sediment Fe/S ratio. Gao et al.[77] proposed an innovative conceptual model termed the “Fe–S wheel” and identified an S/Fe molar ratio of 0.25 as an important threshold influencing MeHg production in peatlands. This process is regulated by soil organic matter, dissolved oxygen, and redox potential. However, many aspects of the mechanisms underlying the coupling of organic matter, iron, and sulfur cycles remain unclear. Future research should further investigate these coupled cycles across different ecological environments to elucidate the patterns of mercury cycling in diverse ecosystems.

5.2 Salinity

Salinity is an important environmental factor influencing mercury transport and transformation in aquatic ecosystems, including estuaries, coastal wetlands, salt lakes, and oceans. In high-salinity environments, Hg^{2+} predominantly occurs as charged chloride complexes, such as HgCl_3^- and HgCl_4^{2-} , while the abundance of competing ligands can further inhibit mercury transport across cell membranes. In contrast, under low-salinity conditions, mercury primarily occurs as electrically neutral species, such as HgCl_2 and mercury hydroxide [$\text{Hg}(\text{OH})_2$]. These neutral species can cross cell membranes more readily than negatively charged mercury–chloride complexes, facilitating intracellular mercury methylation[79]. Boyd et al.[80] investigated the effects of salinity gradients on microbial mercury methylation in the Great Salt Lake and found a significant negative correlation between Hg^{2+} methylation rates and salinity. High salinity inhibited the activity of mercury-methylating SRB, thereby suppressing both mercury methylation and MeHg demethylation. Similarly, Zheng et al.[81] found that soil MeHg concentrations initially increased and then decreased with increasing floodwater salinity, with higher concentrations observed at salinities of 0.5%–1.0%. Soil MeHg concentrations were also significantly positively correlated with viable SRB counts. However, salinity is not the only factor

influencing mercury speciation and transformation. Numerous studies have focused on the combined effects of environmental factors, including salinity, DOM, temperature, and sulfide, which influence mercury methylation efficiency by altering mercury speciation, bioavailability, and microbial community structure.

5.3 Climate Warming

High-latitude Arctic and subarctic regions are highly sensitive to temperature changes and contain substantial stores of organic matter and historically deposited mercury. Consequently, studies investigating the effects of warming on mercury biogeochemical cycling have largely focused on high-latitude ecosystems, including Arctic permafrost, northern peatlands, marine environments, wetlands, and thermokarst lakes[82-85].

Permafrost thaw can release long-sequestered organic matter and inorganic mercury and create anoxic thermokarst wetland environments, providing abundant carbon sources and bioavailable mercury for mercury-methylating microorganisms, thereby stimulating microbial activity and MeHg production [86]. Warming can also affect MeHg demethylation, although methylation and demethylation processes exhibit different responses to temperature. One study found that warming had a significantly greater effect on mercury methylation rates than on demethylation rates, with no significant change in the demethylation rate constant as temperature increased. This difference was primarily attributed to the greater temperature sensitivity of mercury-methylating microorganisms compared with demethylating microorganisms[84]. Another study identified a seasonal shift in which mercury methylation predominated in winter, whereas demethylation dominated in summer, with this pattern also influenced by the abundances of mercury-methylating and demethylating microorganisms[82]. In contrast, warming was found to reduce the net MeHg production potential in paddy soils, an effect associated with the relative abundance of mercury-methylating microorganisms. This suggests that warming can regulate mercury methylation and demethylation by altering microbial community structure and diversity[87]. Overall, the effects of warming on net MeHg production are strongly environment-dependent, reflecting not only differences in the temperature responses of methylating and demethylating microorganisms but also the combined influences of organic matter, hydrological conditions, electron acceptors, and mercury bioavailability[82, 84, 87, 88].

6. Outlook for the Future

This review highlights the substantial progress made in understanding microbially mediated mercury speciation and transformation, particularly following the discovery of functional genes such as *hgcAB*, *merA*, and *merB*. However, current knowledge remains largely focused on specific functional genes, model microorganisms, and transformation processes under individual environmental conditions. A systematic understanding of the coupling among different mercury transformation pathways in complex natural environments and their relative contributions to net MeHg production is still lacking. Furthermore, currently identified functional genes may not encompass all mercury transformation

pathways in natural environments, particularly because the molecular basis of noncanonical demethylation pathways remains poorly understood. Natural environments also harbor numerous potential mercury-transforming microorganisms that remain uncultivated or lack conventional functional marker genes.

Future research should focus on the following directions: (i) integrating metagenomics, metatranscriptomics, metaproteomics, single-cell techniques, and mercury isotope tracing to elucidate the functional diversity and molecular mechanisms of microbial mercury transformation under conditions more closely resembling those in situ, while establishing quantitative relationships between functional gene expression and transformation rates; (ii) developing molecular markers and in situ identification methods for OD to identify the predominant microbial groups involved and the factors regulating this process; and (iii) elucidating the differential responses of microbial mercury methylation and demethylation to interactions among multiple environmental factors and their effects on net MeHg production.

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