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Acetoclastic Methanogenesis Drives Arsenic Methylation in Reducing Aquifers: Pathway-Specific Mechanisms and Global Risk Implications

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The puzzling global distribution of methylated arsenic (MeAs) in reducing groundwater systems arises from an unresolved question regarding how specific methanogenic pathways regulate arsenic biomethylation, a critical issue in arsenic biogeochemistry and risk assessment. To address this, we integrated hydrogeochemical characterization, carbon isotopic tracing, metagenomic analysis, and functional microbiota enrichment experiments, taking MeAs-rich alluvial-lacustrine aquifers in the central Yangtze River Basin as an model for global reducing arsenic-contaminated groundwater. Our results confirm methanogenesis is the primary driver of arsenic biomethylation, supported by strong field correlations between MeAs and CH_4 , as well as between the key genes arsM and mcrA. Crucially, pathway-specific analysis revealed that acetoclastic methanogenesis, mediated by Methanosarcina, is uniquely responsible for efficient and stable MeAs production. This capability stems from the co-occurrence of both the arsM methyltransferase and glutathione S-transferase genes essential for complete methylation. In contrast, methylotrophic methanogenesis only yields transient monomethylarsenate, while hydrogenotrophic methanogenesis shows negligible arsenic methylation activity. Our findings systematically reveal that methanogen-mediated arsenic methylation is pathway-dependent, highlighting the biogeochemical link between methanogenesis and arsenic cycling in aquifer systems. These findings establish a pathway-specific framework that explains disparate global MeAs patterns and provides a targeted strategy for assessing and mitigating arsenic risks in contaminated aquifers worldwide.

Practically, our findings offer actionable strategies for mitigating MeAs risks, particularly in vulnerable rice-agroecosystems reliant on groundwater irrigation such as Southeast Asia and the Jianghan Plain in China. First, monitoring methanogenic pathways, using accessible proxies such as $\delta^{13}C$-CH_4 and *mcrA* gene-based community profiling, can serve as an early-warning tool for MeAs risk. This is critical because dimethylarsenate (DMA), a major MeAs species, is highly phytotoxic and readily accumulates in rice grains. Second, in identified high-risk areas, the quality and quantity of organic inputs should be carefully managed. Specifically, avoiding excessive application of labile organic amendments (e.g., certain types of straw) that preferentially stimulate acetoclastic methanogenesis can help mitigate MeAs production at its source and reducing DMA accumulation in rice grains. These measures address the dual challenge of groundwater protection and food security, with direct implications for public health in arsenic-affected regions.