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Integrated geomicrobiological controls on arsenic and per- and polyfluoroalkyl in Gangetic aquifer: Legacy and emerging threats to drinking water

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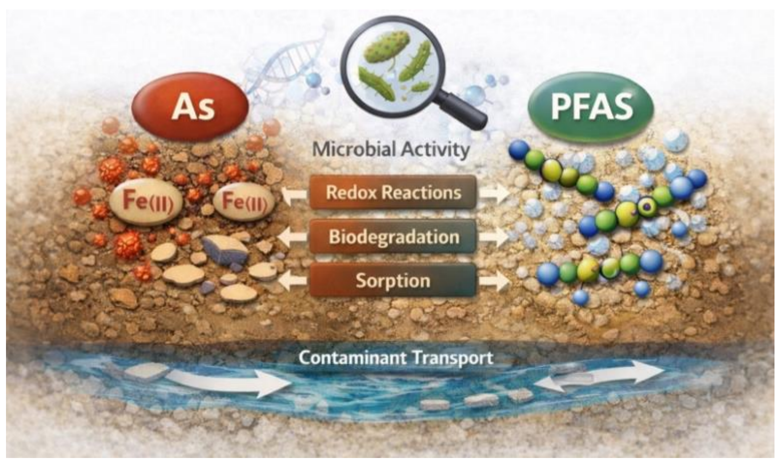
Graphical abstract



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Highlights

- *Geomicrobiological control on arsenic mobilization in groundwater.*
- *Microbial processes can transform certain PFAS precursors.*
- *Integrated geomicrobiological processes to advance understanding on PFAS behavior.*
- *Next generation remediation technologies and OMICS data integrations are important.*

Abstract

Groundwater contamination by arsenic (As) and per- and polyfluoroalkyl substances (PFAS) represents one of the most pressing environmental and public health challenges globally. While As contamination is predominantly geogenic and widespread in alluvial aquifers, PFAS contamination is largely anthropogenic, arising from industrial activities, landfill leachates, and aqueous film-forming foams (AFFF). Traditionally, scientific research has emphasized hydrogeological transport and contaminant chemistry; however, emerging evidence suggests that geomicrobiological processes play a critical role in regulating the mobility, transformation, and persistence of both contaminant classes. This emerging situation necessitates an integrated framework that explicitly links microbiology, geochemistry, and hydrology, particularly in vulnerable regions such as South Asia, including India and Bangladesh, where groundwater is the primary source of drinking water for millions of inhabitants.

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1 Introduction

Groundwater contamination by arsenic (As) and per- and polyfluoroalkyl substances (PFAS) is an emerging global concern with complex environmental, social, and health implications (Maruzzo et al., 2025). Their co-occurrence highlights the need to understand coupled geochemical and microbiological controls together with integrated management strategies (Wu et al., 2025a; Zhang et al., 2024a). Geomicrobiological processes critically influence As speciation and PFAS transport, yet their interactions remain poorly understood. Addressing these integrated mechanisms is crucial to enhancing risk assessment and informing future remediation strategies.

2 Geomicrobiological controls on arsenic mobilization

Arsenic contamination in groundwater is primarily associated with Holocene alluvial aquifers, where it is released from iron (Fe) oxyhydroxides under reducing conditions. Microbially mediated reductive dissolution of Fe(III) minerals is widely recognized as the dominant mechanism controlling As mobilization. Iron-reducing bacteria utilize Fe(III) as an electron acceptor, leading to mineral dissolution and the release of sorbed As into groundwater (Jiang et al., 2019; Zhang et al., 2023).

At the molecular level, microbial functional genes play a central role in As transformation (Zhu et al., 2017; Schlesinger et al., 2022). The *arsC* gene facilitates the reduction of arsenate [As(V)] to arsenite [As(III)], which is more mobile and toxic, while the *arsM* gene mediates methylation, producing volatile organic As species. These transformations significantly influence As speciation, toxicity, and transport behavior.

Arsenic mobilization is strongly coupled with subsurface biogeochemical cycles. Organic carbon availability drives microbial respiration, creating reducing conditions that favor As release. Nitrogen cycling pathways, including denitrification and dissimilatory nitrate reduction to ammonium, interact with Fe cycling and indirectly influence As dynamics. Emerging evidence also highlights the potential role of Fe(III)-dependent anaerobic ammonium oxidation in modulating redox conditions (Zhang et al., 2024b), although its quantitative contribution remains uncertain.

Sulfur cycling introduces additional complexity. Sulfate-reducing bacteria can generate sulfide, promoting As immobilization through sulfide precipitation; however, this process is often limited by preferential sulfide binding with Fe minerals, thereby reducing its effectiveness as a long-term attenuation mechanism.

3 Hydro-biogeochemical heterogeneity and arsenic distribution

A defining characteristic of As-contaminated aquifers is their pronounced spatial and vertical heterogeneity. Variability in redox conditions, sediment composition (gray vs. brown sands), aquifer geometry, groundwater flow patterns, and recharge dynamics results in highly uneven As distribution (Nath et al., 2008). Factors such as monsoonal recharge, sea-level fluctuations, aquifer flushing, and land-use changes further modulate As mobilization (LeMonte et al., 2017; Kulkarni et al., 2018). Fine-grained sediments and low hydraulic gradients enhance reducing conditions and promote As release, while competing vertical and lateral groundwater flows influence contaminant transport pathways. These complexities highlight the need for coupled three-dimensional hydro-biogeochemical models capable of resolving spatial heterogeneity and process interactions.

4 PFAS in groundwater: Persistence and microbial interactions

In contrast to As, PFAS contamination is anthropogenic in nature and characterized by extreme persistence due to the strength of the carbon–fluorine bond. Their amphiphilic structure leads to complex partitioning behavior, facilitating long-range transport and widespread occurrence in groundwater systems (Rasmusson and Fagerlund, 2024; ITRC, 2025).

Although PFAS are often considered recalcitrant, recent studies indicate that microbial processes can transform PFAS precursors into more stable perfluoroalkyl acids (PFAAs). For example, fluorotelomer alcohols (FTOHs) can be biodegraded by bacterial genera such as *Pseudomonas*, forming intermediate compounds that ultimately yield persistent end-products such as perfluorooctanoic acid (PFOA) (Kim et al., 2012; Chiriac et al., 2023). Similarly, compounds such as EtFOSE can be microbially oxidized to perfluorooctane sulfonate (PFOS).

Importantly, these transformations do not result in complete mineralization but instead generate more recalcitrant compounds, thereby exacerbating long-term environmental persistence. Microbial activity thus plays a dual role – facilitating transformation while potentially increasing persistence.

5 Health implications and remediation challenges

Chronic exposure to As-contaminated groundwater leads to arsenicosis, skin lesions, and increased risks of cancers (skin, lung, and bladder), along with cardiovascular and neurological disorders (Chen et al., 2011; Wu et al., 2025b). On the other hand, PFAS exposure has been linked to endocrine disruption, immune dysfunction, metabolic disorders, and cancers (Gaillard et al., 2025; ITRC, 2025). Existing remediation approaches remain limited. Arsenic removal technologies, including Fe-based adsorption and membrane filtration, are often difficult to implement at scale in resource-limited settings. PFAS treatment technologies – such as granular activated carbon (GAC), ion exchange, and membrane systems – are effective for removal but do not destroy contaminants and generate secondary waste streams.

6 Knowledge gaps and emerging research needs

Significant knowledge gaps exist in both systems.

For As, unresolved questions include:

- The role of uncultured microbial communities in arsenic cycling
- Coupling between the Fe, nitrogen, and sulfur cycles
- Impacts of emerging co-contaminants such as antibiotics and microplastics
- Effects of climate change on redox dynamics and recharge patterns

For PFAS, key uncertainties include:

- Enzymatic and metabolic pathways of microbial transformation
- Mechanisms of partial defluorination
- Behavior of short-chain PFAS and novel substitutes

7 Future directions: Toward integrated solutions

Future research should prioritize interdisciplinary and technology-integrated approaches:

- ***Omics and data integration***
  Metagenomics, transcriptomics, and metabolomics can reveal microbial functional potential and activity. Integration with machine learning can enhance predictive modeling of contaminant behavior.
- ***Isotope tracers and process quantification***
  Stable isotopes (e.g., $\delta^{15}N$, and Fe isotopes) offer powerful tools for quantifying reaction pathways and coupling between biogeochemical cycles.
- ***Microbial process engineering***
  Advances in synthetic biology and CRISPR-based tools may enable the design of engineered microbial systems for As immobilization or PFAS transformation. However, biosafety and ecological risks must be carefully addressed.
- ***Next-generation remediation technologies***
  Hybrid systems combining adsorption and degradation, along with emerging technologies such as electrochemical oxidation, plasma treatment, and catalytic hydrothermal systems, show promise for complete defluorination (Verma et al., 2021; Dronjak et al., 2025).
- **Nature-based and decentralized solutions**
  Low-cost, community-scale approaches – particularly relevant for South Asia should complement high-tech solutions.

8 Conclusion

An integrated geomicrobiological perspective is essential for advancing our understanding of As and PFAS behavior in groundwater systems. By explicitly linking microbial processes with hydrogeochemical dynamics, it is possible to move beyond descriptive models toward predictive and solution-oriented frameworks. Such interdisciplinary approaches are critical for developing scalable, sustainable remediation strategies and for safeguarding groundwater resources in vulnerable regions worldwide.

9 Data availability statement

Not applicable.

10 Ethical statements

Not applicable.

11 Conflict of interest

The authors declare that there is no conflict of interest.

12 Author contributions

D. Chatterjee: Conceptualization, and writing – review & editing. J. Kewalramani: Writing – review & editing. J.

Adhikary: Writing – original draft. All the authors approved the final version of the manuscript

13 Copyright statement

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