

## **Broad-scale evidence for pH as a control on interactions between iron- and sulfate-reducing microbes in aquifer systems**

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Critical to sustaining future human growth, groundwater resources are threatened by environmental changes such as leakage of waste materials from subsurface storage reservoirs, agricultural contamination, hydraulic fracturing, and climate change. The impact that these changes have on subsurface water resources in part depends on the response of aquifer microbial communities to perturbed conditions. As such, understanding fundamental controls on aquifer microbiology is essential to predicting impacts of future environmental change and managing water resources.

This study examines whether broad-scale geochemical evidence exists for pH as a control on interactions between iron- and sulfate-reducing microorganisms in aquifers. We extracted geochemical data from the U.S. Geological Survey National Water Information System for 19 principal aquifer systems. We then removed samples with chemical compositions inconsistent with iron- and sulfate-reducing environments and evaluated the relationships between pH and other parameters using Spearman's rho rank correlation tests.

Overall, iron concentration and the iron-sulfide concentration ratio of groundwater share a statistically significant negative correlation with pH ( $P < 0.0001$ ). These relationships indicate that the significance of iron reduction relative to sulfate reduction tends to increase with decreasing pH. Thermodynamic calculations show that, as the pH of groundwater decreases, iron reducers gain an increasing energetic advantage over sulfate reducers. Hence, the balance between each group may vary in response to thermodynamic controls on microbial activity.

Our findings indicate that pH is an important control on interactions between iron- and sulfate-reducing microbes across different regional aquifer systems. Environmental changes that perturb groundwater pH can affect water quality by altering interactions between these groups.