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Proxy-Enabled Redox Classification Expands TEAP Assignments in Nationwide Groundwater Datasets

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Reduction–oxidation (redox) conditions control contaminant mobility by influencing solubility, speciation, and biodegradation pathways. A widely used approach, developed by McMahon and Chapelle (2008), uses threshold-based criteria to identify Terminal Electron Accepting Processes (TEAPs) from routine groundwater-quality measurements. However, incomplete analyte coverage in large monitoring datasets (e.g., missing dissolved oxygen, iron, or sulfide) limits TEAP assignment to a subset of samples and can systematically bias quantification of redox zonation at regional and national scales.

Here we develop and test an amended redox-classification scheme for groundwater data that (1) identifies the dominant TEAP, and (2) leverages data-driven redox proxies to extend classification to samples missing key constituents. Using a compilation of continental-scale groundwater dataset (n = 241,309), we apply statistical learning and threshold optimization to evaluate whether proxy combinations (e.g., Fe–DO patterns, sulfide presence, methane occurrence, and related redox-sensitive ions) reproduce TEAP assignments derived from complete records. Model performance is assessed by cross-validated agreement with the 2008 framework on complete samples and by quantifying the increase in classifiable records under realistic missing-data patterns.

Our results indicate that proxy-enabled rules increase the number of classifiable samples from 34.5% to 47.2% while retaining high concordance with baseline TEAP assignments. Specifically, we find that iron and manganese are suitable indicators to delineate anoxic conditions and provide support for thresholds set by McMahon and Chapelle. We evaluate arsenic as a redox-sensitive contaminant to determine whether proxy-enabled TEAP assignments reproduce systematic redox-dependent enrichment patterns. Arsenic concentrations vary across TEAP regimes, with the highest enrichment in Mn-reducing zones, intermediate levels in sulfate-reducing zones, and comparatively low concentrations in Fe-reducing environments, highlighting the utility of proxy-enabled redox mapping for contaminant assessment.

The amended framework provides an interpretable, scalable approach for redox mapping and for strengthening constituent thresholds in large observational datasets under incomplete data conditions. By extending TEAP classification coverage, this approach improves national-scale assessments of groundwater vulnerability and contaminant behavior.

[1] McMahon & Chapelle (2008), *Ground Water* 46, https://doi.org/10.1111/j.1745-6584.2007.00385.x.