

## **Rare Earth Elements: Potential Natural Tracers for In Situ Remediation of Groundwater**

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**Background/Objectives.** The Rare Earth Elements (REEs; lanthanum to lutetium, excluding promethium) have increasingly been used as natural tracers in studies of groundwater flow and groundwater-surface water interactions. The application of REEs as natural tracers takes advantage of their uniform trivalent charge and within-group fractionation behavior that is controlled by aqueous complexation and redox-driven processes. To date, REEs have not been used extensively in the evaluation of groundwater remediation technologies. A common question to answer as part of performance monitoring activities associated with in situ remediation is whether groundwater has, in fact, passed through and interacted with the emplaced/injected reactive materials used for contaminant removal. This issue becomes especially important in situations where down-gradient contaminant concentrations fail to decrease within predicted timeframes. In addition to tracking contaminant concentration trends, other geochemical tools for examining down-gradient impacts typically include the evaluation of pH, oxidation-reduction potential, and other parameters depending on the specific application. The REEs are another potential tool that offer some advantages.

**Approach/Activities.** We measured concentrations of REEs dissolved in groundwater at two zero-valent iron (ZVI) permeable reactive barriers (PRBs) installed to treat groundwater contaminated with arsenic and a mixed contaminant plume containing volatile organic compounds and hexavalent chromium, and one organic-carbon/limestone PRB designed to treat groundwater acidity and heavy metal contamination. REE concentrations were determined in up-gradient, in-PRB, and down-gradient regions. REE concentrations were measured using high-resolution inductively coupled plasma-mass spectrometry (HR-ICP-MS). Using this method, detection limits for the REEs were in the range from 1 to 4 ng/L. Samples were filtered and preserved with nitric acid in the field.

**Results/Lessons Learned.** Some of the key observations from this work include: 1) the abundance of REEs in groundwater was largely controlled by pH; thus, the pH of up-gradient/contaminant-bearing groundwater is an important control on whether this natural tracer will be informative; 2) ZVI, in both field examples, was effective in decreasing REE concentrations to below levels of detection; 3) recovery of REEs on the down-gradient side of the ZVI PRBs was not observed; thus, REEs are a very sensitive probe for tracking the interaction of groundwater with ZVI; and, 4) REE concentrations were also significantly reduced compared to up-gradient concentrations in the organic carbon/limestone PRB and negative europium anomalies were observed, providing information about redox conditions within the treatment zone. Removal mechanisms of the REEs in the reactive media have not been examined, but likely include precipitation or co-precipitation at alkaline pH and/or surface adsorption. This is an abstract of a proposed presentation and does not necessarily reflect EPA policy.