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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 (e.g., Johannesson et al., 1999; 2011). 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 to evaluate 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 evaluation of pH, oxidation-reduction potential, specific contaminants, and other parameters depending on the specific application. The REEs are another potential tool that offer some advantages.

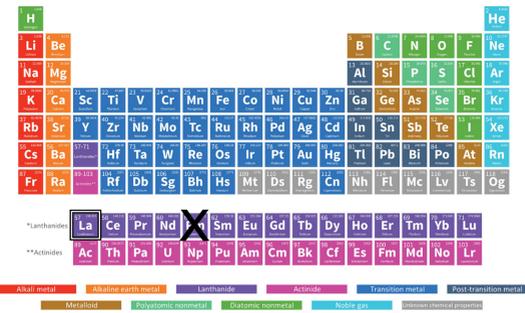


Figure 1. The Lanthanides share similar characteristics including the following:

- REE are mainly in the +3 oxidation state;
- the +2 oxidation state is important for Eu and the +4 oxidation state is important for Ce;
- REEs show decreasing coordination number across the series (lanthanide contraction);
- REEs have preference for more electronegative elements (such as O or F); and,
- REE ionic complexes undergo rapid ligand-exchange.

Note the half-life for Pm is 17.7 years so this element is not naturally present in the environment.

Methods

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. Groundwater 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.

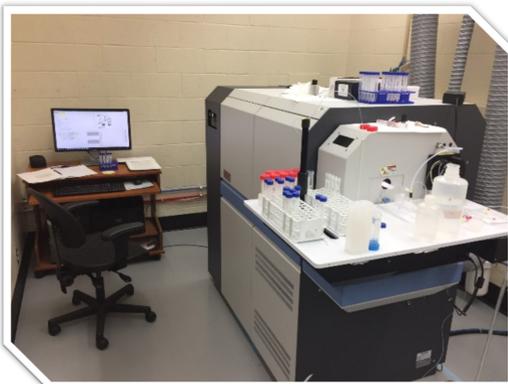
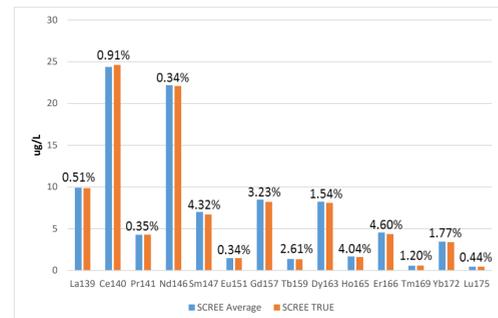


Figure 2. REEs were analyzed using HR-ICP-MS. The elements: Nd, Sm, Eu, Dy, Ho, and Yb were analyzed in medium resolution mode; and, the elements: La, Ce, Pr, Gd, Tb, Er, Tm, and Lu were analyzed in high resolution mode to avoid isobaric interferences with Ba and the notorious light REE (LREE) oxide interferences on heavy REEs (HREE). Rhodium was used as an internal standard in both resolution modes (1 µg/L). A series of interference check solutions were prepared to meet the analytical challenges of the REEs. Results of USGS REE reference waters (µg/L, SCREE) are shown at 50x dilution. Blue bars show values determined using HR-ICP-MS (n=2) and orange bars are the most probable values provided by Verplanck et al. (1999); % error shown.



Results & Discussion

Shale-normalized REE patterns of contaminated groundwater (up-gradient from the in-situ treatment zones) from the Elizabeth City (ZVI PRB) and Delatte Metals (manure-limestone PRB) show flat REE trends (Figure 3). Higher REE concentrations were observed at the Delatte Metals site due to low pH (<3.5). Groundwater pH at the Elizabeth City site was near 6.5 (influent to the ZVI PRB). Groundwater pH is a key variable for controlling REE concentrations (Noack et al., 2014).

A) REE characteristics at ZVI sites: The Elizabeth City and East Helena ZVI PRBs were installed in 1996 and 2005, respectively (Wilkin et al., 2009; 2014). The PRBs were installed to treat groundwater contaminated with TCE plus hexavalent chromium (Elizabeth City) and arsenic (East Helena). At both sites we observed that REE concentrations, within and down-gradient of the PRBs, were essentially removed from groundwater. Coherent REE patterns were not detected after groundwater interaction with the treatment material; only sporadic detections of individual elements were observed (Figure 4; data from Elizabeth City are shown). Total REE concentration (ΣREE) versus pH profiles show that REE levels are in the range between 0.001 and 0.1 µg/L within and down-gradient of the Elizabeth City PRB (Figure 4); whereas, groundwater up-gradient of the PRB has REE levels >1 µg/L. **Importantly, there was no rebound effect observed down-gradient of the PRB.** This suggests that REE patterns can be used as a probe to determine if groundwater has in fact interacted with treatment materials employed in the subsurface.

B) REE characteristics at an organic carbon PRB: The Delatte Metals PRB was installed in 2003 to treat groundwater acidity and elevated concentrations of lead, cadmium, and nickel. Influent groundwater to the PRB has high ΣREE values (~1000 µg/L) due to low groundwater pH (2.8 to 3.5). Groundwater is neutralized by reactions between groundwater and limestone. Alkalinity is also produced by microbial sulfate reduction. As groundwater pH increases, ΣREE levels decrease (~0.5 to 10 µg/L; Figure 5). Also note that after interaction with organic carbon, groundwater typically shows a negative Eu anomaly (Figure 5). The Eu anomaly [Eu*] was calculated from shale-normalized concentrations using

$$Eu^* = 2 \times [Eu]_n / ([Sm]_n + [Gd]_n)$$

This degree of fractionation is used to describe the overall "unevenness" of the PAAS-normalized profile (Noack et al., 2014). The negative anomaly in this context indicates that Eu is reduced in the PRB to Eu²⁺ and is preferentially removed relative to the adjacent trivalent REEs. Eu* values ranged from 1 to about 0.2 for samples with the most apparent negative anomalies.

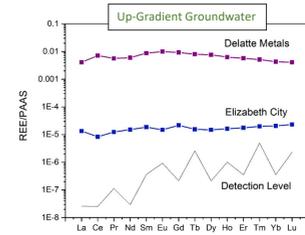


Figure 3. Shale-normalized REE patterns in groundwater influent to a ZVI PRB (Elizabeth City, NC) and to a manure-limestone PRB (Delatte Metals, LA); element-specific detection levels are shown for comparison.

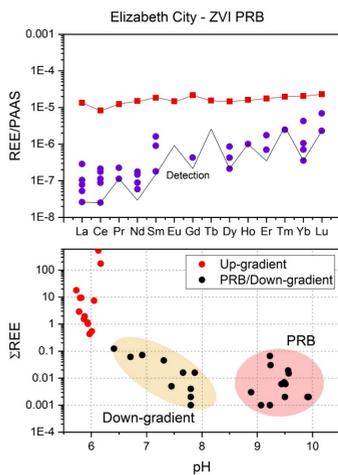


Figure 4. REE patterns in groundwater from up-gradient (red squares) and in-wall/down-gradient (blue circles) locations relative to the PRB. Coherent REE profiles are eliminated by the PRB. REE concentrations do not show a rebound-effect in down-gradient locations.

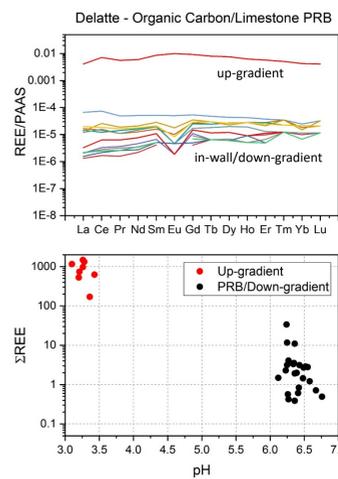


Figure 5. REE patterns in groundwater from up-gradient (red line) and in-wall/down-gradient (multiple colored lines) locations relative to the PRB at the Delatte Metals site. Coherent REE profiles are still present and negative Eu anomalies are observed. The lower ΣREE profile and negative Eu anomaly can be used as indicators of groundwater interaction with reducing treatment materials employed in the subsurface.

REE Removal Processes: Processes that possibly control REE uptake in ZVI systems include hydroxide precipitation and/or sorption to iron corrosion products and other neo-formed precipitates such as calcium carbonate, iron hydroxy carbonate, and mackinawite. In organic carbon substrates, removal could be the result of adsorption and/or precipitation (e.g., Edahbi et al., 2018). Lab studies are underway to investigate some of these possibilities. Preliminary geochemical modeling reveals surprising results.

Taking lanthanum as an example in a ZVI system, Figure 6 shows that groundwater up-gradient (red circles) and within the PRB (black squares) are undersaturated with respect to La(OH)₃, indicating that lanthanum hydroxide precipitation may not be the controlling uptake mechanism – although the in-wall pH-La trend is suggestive of a pH-controlled removal process. Formation of a mixed precipitate would be expected to form a more insoluble solid compared to pure La(OH)₃.

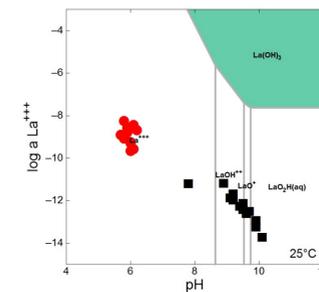


Figure 6. pH versus log activity La – Elizabeth City ZVI PRB. Up-gradient (red circles) and in-wall (black squares) groundwater is undersaturated with respect to La(OH)₃. Diagram constructed using the Geochemist's Workbench software (v. 11) and the thermo.com.V8.R6+ database.

Taking europium as an example for an organic carbon-based PRB, Figure 7 shows an Eh-pH diagram for Eu (10⁻⁸ molal; 25°C). Up-gradient groundwater (red circles) is low in pH, undersaturated with respect to Eu(OH)₃, and within the Eu³⁺ stability field. In-wall and down-gradient groundwater (black squares) remains within the undersaturated region and within the Eu³⁺ field. The negative Eu anomaly observed suggests that reducing surfaces may allow conversion from Eu³⁺ to Eu²⁺, which is not predicted to occur in free solution based on the measured pH/Eh.

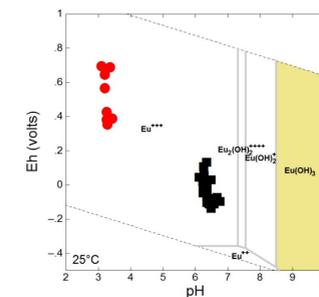


Figure 7. pH versus Eh diagram – Delatte Metals manure-limestone PRB. Up-gradient (red circles) and in-wall (black squares) groundwater is undersaturated with respect to Eu(OH)₃ and within the Eu³⁺ stability field. Diagram constructed using the Geochemist's Workbench software (v. 11) and the thermo.com.V8.R6+ database.

Conclusions

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 factor determining whether these natural tracers will be informative;
- 2) ZVI, in both field examples, was effective in decreasing REE concentrations to levels at and below detection;
- 3) recovery of REEs on the down-gradient side of the ZVI PRBs was not observed; thus, REEs are a 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.

- REE concentrations are a potential probe of groundwater interaction with emplaced reactive materials
- Natural tracer
- Sensitive to pH

Removal mechanisms of the REEs in the reactive media have not been examined, but likely include precipitation and/or co-precipitation at alkaline pH and/or surface adsorption. Surface removal processes are currently being explored in lab-based studies.

Acknowledgments: This work was funded by the US EPA. This poster does not necessarily reflect EPA policy. We thank Kim Schuenger for help with lab studies and Kathy Tynsky for preparing the poster.

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