Biogeochemical Controls on Technetium Mobility in FRC Sediments

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Introduction

Technetium-99 is a priority pollutant at numerous DOE sites, due to its long half-life (2.1 x 10^5 years), high mobility as Tc(VII) in oxic waters, and bioavailability as a sulfate analog. ^{99}Tc is far less mobile under anaerobic conditions, forming insoluble Tc(IV) precipitates. As anaerobic microorganisms can reduce soluble Tc(VII) to insoluble Tc(IV), microbial metabolism may have the potential to treat sediments and waters contaminated with Tc.

Baseline studies of fundamental mechanisms of Tc(VII) bioreduction and precipitation (reviewed by Lloyd et al, 2002) have generally used pure cultures of metal-reducing bacteria, in order to develop conceptual models for the biogeochemical cycling of Tc. There is, however, comparatively little known about interactions of metal-reducing bacteria with environmentally relevant trace concentrations of Tc, against a more complex biogeochemical background provided by mixed microbial communities in the subsurface.

Aims and Objectives

The objective of this new NABIR project is to probe the site specific biogeochemical conditions that control the mobility of Tc at the FRC (Oak Ridge, TN). This information is required for the rational design of *in situ* bioremediation strategies for technetium-contaminated subsurface environments.

We will use a combination of geochemical, mineralogical, microbiological and spectroscopic techniques to determine the solubility and phase associations of Tc in FRC sediments, and characterize the underpinning biogeochemical controls.

A key strength of this project is that many of the techniques we are using have already been optimized by our research team, who are also studying the biogeochemical controls on Tc mobility in marine and freshwater sediments in the UK in a NERC funded companion study.

Hypotheses

1. Tc(VII) will be reduced and precipitated in FRC sediments under anaerobic conditions in batch experiments (progressive microcosms).
2. Tc(VII) reduction and precipitation can be visualized in discrete biogeochemical zones in sediment columns using ^{99m}Tc and a gamma-camera.
3. Sediment-bound reduced ^{99m}Tc can be solublized by perturbations including oxidation by nitrate, and mobilization visualized in real-time using a gamma-camera.
4. The mobility of ^{99m}Tc in the sediment columns can be modelled using a coupled speciation and transport code.

Experimental Approaches

Batch studies (progressive microcosms)

Discrete microbial communities present in FRC sediments have effects on Tc mobility that are separated in time in progressive microcosms (Fig. 1)

- Sediment and groundwater from FRC background area, with and without added electron donor (acetate) were set up. Future work will examine sediments from Area 2 (pH 6.5, low nitrate, low ^{99}Tc) and Area 3 (pH 3.5, high nitrate, relatively high ^{99}Tc).
- A spike of ^{99}Tc was added for an initial concentration of 50 nM to 500 nM (2-20 Bq ml^{-1}).
- Parameters monitored: ^{99}Tc solubility, nitrate, nitrite, Fe(II), sulfate, acetate, pH, Eh, mineral phases, solid phase Tc associations.
- Also conducting molecular ecology and culture dependent analysis of microbial communities associated with Tc(VII) reducing sediments.

Column studies

Biogeochemical processes will be spatially separated along sediment columns

- Artificial groundwaters with and without added electron donor (acetate) will be used with flow rates representative of those at the FRC.
- Experiments will be conducted with and without competing anions at high concentration (e.g. nitrate, with columns containing Area 3 sediments).
- Spike of the short-lived gamma emitter ^{99m}Tc (50-200 MBq; half-life 6 hours) will be added, Tc mobility monitored in real time using a gamma-camera (Fig. 2). We will characterize the geochemistry, microbiology, and mineralogy of zones where Tc is immobilized.
- Reoxidation of immobilized, reduced Tc will be assessed using oxidants including nitrate and aerated water.
- Experimental results will be modeled using an established coupled speciation and transport code, to develop a predictive tool for the mobility of Tc in FRC sediments.

Figure 1. Progressive microcosms

Figure 2. Gamma-camera

Initial Results

Figure 3a. Experiments with 0.5 µM Tc and no additional electron donor

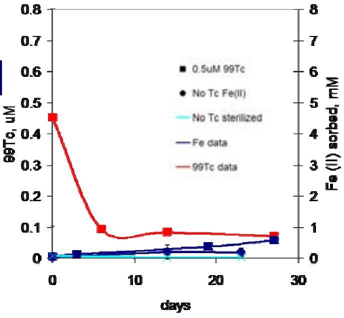

Figure 3b. Experiments with 0.5µM Tc, containing 10 mM acetate

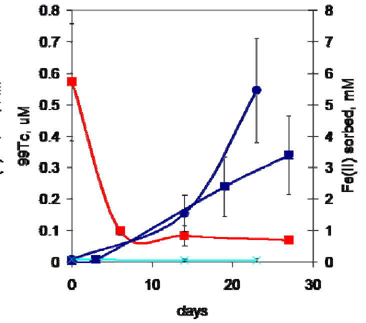

Fig 3: Batch studies of FRC sediments conducted at 20°C using ^{99}Tc at a starting concentration of 0.5 µM (20 Bq ml^{-1}) have confirmed that Tc(VII) is reduced to concentrations on the order of 0.05 µM within a few days, regardless of the presence or absence of additional electron donor. In contrast, the rate and extent of Fe(III) reduction was stimulated dramatically by acetate. Heat sterilized controls spiked with 0.5 µM ^{99}Tc did not show the same biologically mediated decrease in Tc concentration with time.

References

Lloyd, J.R., Chesnes, J., Glasauer, S., Bunker, D.J., Livens, F.R., and Lovley, D.R. (2002). Reduction of actinides and fission products by Fe(III)-reducing bacteria. Geomicrobiology Journal. 19, 103-120.

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