

Biogeochemical Redox Transformations in Hanford 300 Area Subsurface Sediments

Project Participants: Jim K. Fredrickson¹, Ji-Hoon Lee¹, David W. Kennedy¹, Andrew E. Plymale¹, Allan E. Konopka¹, Ken Kemner², and Eric Roden³
 Poster represents post-doctoral research by Ji-Hoon Lee in collaboration with Dave Kennedy & Andy Plymale
¹Pacific Northwest National Laboratory, Richland, WA 99354; ²Argonne National Laboratory, Argonne, IL 60439; ³University of Wisconsin, Madison, WI 53706



Introduction

As part of PNNL's Scientific Focus Area "Role of Microenvironments and Transition Zones in Reactive Contaminant Transport" this project is characterizing biogeochemical processes in Hanford 300 Area subsurface sediments with an emphasis on defining redox reactions at the pore scale projected to influence the subsurface fate and transport of U and Tc. In coordination with the Hanford Integrated Field Research Challenge (IFRC), a series of subsurface core samples were collected during July 2008 from the 300A IFRC site as part of site characterization efforts and a series of sediment microcosm experiments initiated to explore biogeochemical processes that may impact contaminant fate and transport in the Hanford subsurface.

Motivation & Fundamental Science Issues

Cross section illustrating physical heterogeneity of Hanford sediments

Reactive mineral particles in Ringold Formation sediment

Redox proteins localized to the bacterial cell envelope

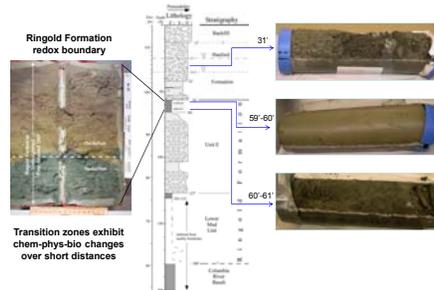
- Tc & U are major risk-driving contaminants at Hanford (and other DOE sites) due to their relatively high mobility in oxic groundwaters and the difficulty in predicting their subsurface behavior.
- Both contaminants are subject to microbial and geochemical redox and complexation reactions that can alter their solubility and hence transport in the subsurface.
- Microenvironments and transition zones can exert significant control over contaminant behavior, often disproportionate to their mass, and are common features of the Hanford subsurface.
- Nature and distribution of biogeochemical processes in the poorly-understood Hanford subsurface.
- Potential for native microbes to utilize various terminal electron acceptors (EAs: oxygen; nitrate; ferric iron; sulfate etc.) common to the Hanford unconfined aquifer. (Belaiev SFA project)
- Nature of EA reduction end-products; their form, distribution, and reactivity with contaminants at the pore scale (Liu & Zachara projects).
- In situ reactions and rates in relation to aquifer physical, chemical, and biological properties (Konopka SFA & IFRC projects).

Sediment Microcosms

- Hanford subsurface sediments were incubated in the synthetic groundwater media (SGW1) with and without exogenous electron acceptors or donors.
- One gram sediment in 10 mL of SGW1 formulated based on 300A groundwater geochemistry.
- Incubation conditions: pH 7.8; 22°C; electron donor mix - 0.9 mM acetate, 0.6 mM lactate, and 0.3 mM glucose or H₂ (10 mL to headspace of pressure tubes).
- Sterile (heat-treated) = 100°C exposure for 15 min or autoclaved (nitrate and Tc experiments) on three consecutive days.

Hanford Synthetic Groundwater	SGW1 medium		
	SGW1 (1x)	w/o nitrate	w/o nitrate or sulfate
Sodium bicarbonate	1.44 mM	1.44 mM	1.44 mM
Potassium bicarbonate	0.16 mM	0.16 mM	0.16 mM
Magnesium sulfate	0.51 mM	0.51 mM	-
Magnesium chloride	-	-	0.51 mM
Calcium sulfate	0.12 mM	0.12 mM	-
Calcium nitrate	0.23 mM	-	-
Calcium chloride	0.65 mM	0.88 mM	1.0 mM

Hanford 300A IFRC Site Subsurface Sediments



- Hanford formation, 30-31 ft. <4.75 mm
- Ringold Formation 59-60 ft. (oxidized), unsieved
- Ringold Formation 60-61 ft. (reduced), unsieved

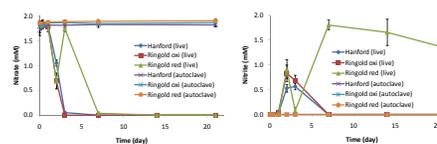
Sediment Properties

Sample	Sieved	Inorganic C (%)	Organic C (%)	Total Fe (%)	Total Fe (mmol/g)
Hanford	< 0.5 mm	0.03	0.09	7.16	1.279
Ringold oxidized	< 0.5 mm	0.06	0.08	3.61	0.645
Ringold reduced	< 0.5 mm	<0.02	0.09	3.79	0.677

Extractable Metals (units: μmol/g)		0.5N HCl extraction (wet sediments)			
		OHamine-HCl extraction	DCB extraction	1 h, 24 h	
Hanford formation (<4.75 mm)	Fe(II)	41.8 ± 2.7	49.1 ± 5.1	9.7 ± 0.7	61.6 ± 5.7
	Fe	48.8 ± 3.7	51.3 ± 6.4	33.0 ± 1.0	149.9 ± 12.1
	Al	31.8 ± 0.9	9.7 ± 0.5	27.7 ± 0.3	79.1 ± 3.5
Ringold oxidized (unsieved)	Mn	1.5 ± 0.2	1.2 ± 0.2	1.2 ± 0.0	2.5 ± 0.2
	Fe(II)	28.5 ± 3.1	53.9 ± 3.7	3.2 ± 0.9	14.0 ± 2.2
	Fe	34.2 ± 2.8	55.8 ± 5.1	24.7 ± 5.5	114.1 ± 17.6
Ringold reduced (unsieved)	Al	55.1 ± 1.8	8.8 ± 0.8	45.2 ± 6.2	151.9 ± 28.1
	Mn	3.0 ± 1.0	1.9 ± 0.1	1.2 ± 0.3	3.5 ± 0.5
	Fe(II)	47.4 ± 2.9	30.7 ± 0.7	34.7 ± 3.0	124.8 ± 7.7
Ringold reduced (unsieved)	Fe	55.0 ± 2.1	29.9 ± 1.4	40.5 ± 2.5	154.4 ± 7.6
	Al	58.7 ± 1.1	7.8 ± 0.2	47.4 ± 3.1	159.7 ± 6.0
	Mn	0.9 ± 0.0	0.2 ± 0.0	0.3 ± 0.0	1.3 ± 0.0

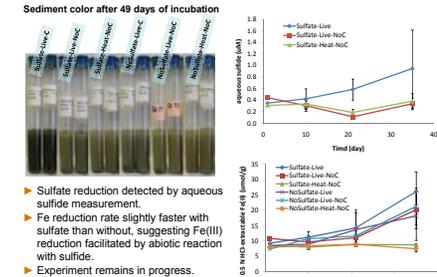
- All sediments are mineral, <0.1% organic carbon, and high in total iron.
- Weak acid-extractable Fe(II) amounts; Ringold red > Hanford fines > Ringold oxic.
- Fe(II) from phyllosilicates as implied by the weak acid-extractable Fe and Al at 1 h and 24 h extraction times.

Nitrate Reduction in Sediment Microcosms



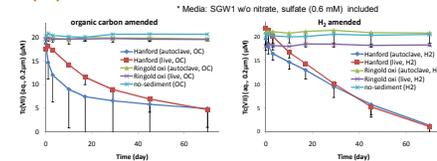
- Nitrate is rapidly consumed in all sediments with transient appearance of nitrite.
- Respiratory pathway appears to be denitrification - no ammonia detected.

Sulfate & Fe Reduction in Hanford Sediment Microcosms



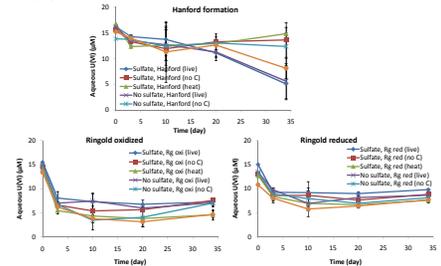
- Sulfate reduction detected by aqueous sulfide measurement.
- Fe reduction rate slightly faster with sulfate than without, suggesting Fe(III) reduction facilitated by abiotic reaction with sulfide.
- Experiment remains in progress.

Tc(VII) Behavior in Sediment Microcosms



- Tc(VII) is reduced in Hanford formation sediment regardless of treatment (i.e., live vs. autoclaved) indicating abiotic redox reaction, likely with native Fe(II).
- No biotic or abiotic reaction in Ringold oxidized sediment (note - pertechnetate is reduced in Ringold reduced sediment - see Zachara et al. SFA poster).

U(VI) Behavior in Sediment Microcosms



- Microbial U(VI) reduction in Hanford formation sediments amended with electron donor (OC mix) upon extended incubation, with or without sulfate.
- Initial rapid loss of U(VI) from solution in Ringold oxidized sediments suggests adsorption.
- Experiment remains in progress.

Preliminary Findings

- Hanford and Ringold sediments (oxidized and reduced) rapidly denitrify under anoxic condition when provided with electron donor.
- Upon extended (~3 weeks) incubation sulfate and Fe(II) are reduced in Hanford formation sediments with or without electron donor amendment; little evidence of Fe(III) or sulfate reduction in Ringold sediments (scoping experiment - not shown); indirect evidence of abiotic Fe(II) reduction by sulfide.
- Pertechnetate is reduced in anoxic live and autoclaved Hanford formation sediment suggesting abiotic reduction by native Fe(II); no Tc(VII) reduction observed in Ringold oxidized sediment.
- Uranium(VI) loss from solution observed upon extended incubation in Hanford sediment with organic amendment consistent with microbial reduction. Rapid but limited loss of U(VI) from solution in Ringold sediment indicative of adsorption.

Future Research

- Fe Mossbauer analysis of Hanford sediments before and after incubation to characterize Fe(III) phases and identify microbial reducible Fe(II) forms.
- Reactivity of biogenic Fe(II) and sulfide in Hanford sediment using pertechnetate as redox probe, subsequent reactivity of reduced Tc with O₂.
- Molecular speciation of Tc in Hanford sediment and dependence upon sediment incubation treatment.
- Molecular speciation of U in bio-reduced Hanford sediment and Ringold sediments.
- Explore in situ biogeochemical reactions in 300A subsurface (with Hanford IFRC) using defined Fe phases.

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