

# Long-term Stability of Biogeochemically Reduced U and Cr in Contaminated Sediments

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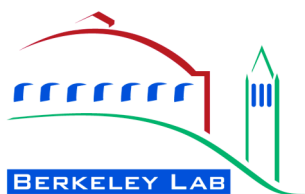
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# Long-term Stability of Biogeochemically Reduced U and Cr in Contaminated Sediments

## General Goal

Diminish concentrations of metals/radionuclide in groundwaters of contaminated sites to below MCL values through reduction to lower solubility species.

## Challenges

- Establishing metal/radionuclide reduction in the subsurface
- Maintaining metal/radionuclide reduction in the subsurface

## Specific examples from our laboratory studies:

Uranium (VI)  $\rightarrow$  (IV): 2 year study, 4 year study,  
1.3 year study (continuing)

Chromium(VI)  $\rightarrow$  (III): 5 year study

## Some Challenges in Establishing Effective Metal/Radionuclide Reduction in the Subsurface

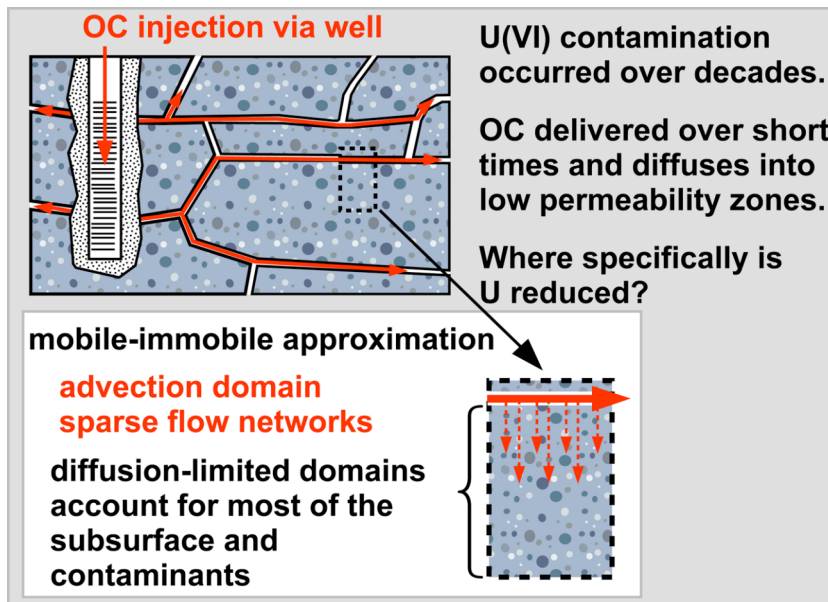
- Preferential flow
  - treatment of groundwater and sediment
  - monitoring of groundwater
  
- Unfavorable, competing reactions
  - bicarbonate production
  - U(VI) aqueous complexes with carbonate
  
- Persistence of terminal electron acceptors
  - Mn(III,IV)
  - Fe(III)

# Preferential flow

**Preferential flow during treatment:** Organic carbon (OC) dispersal and establishment of reduction in much of the subsurface is diffusion-limited.

- Diffusion-limited transport of electron donor - superficial reduction

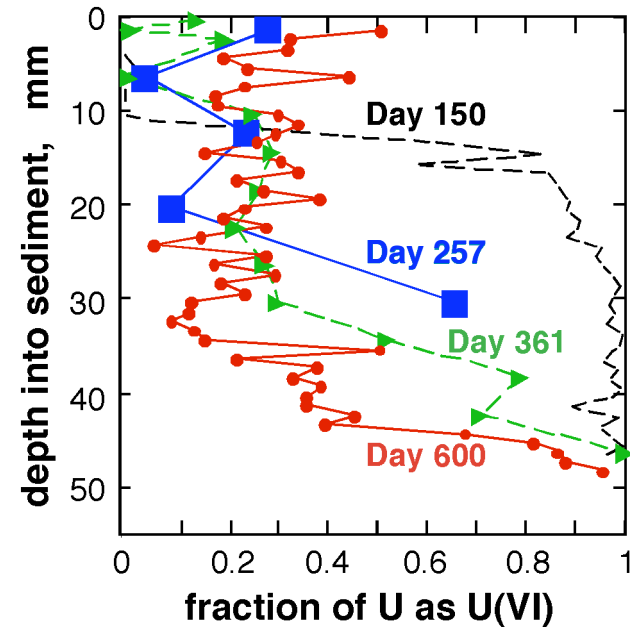
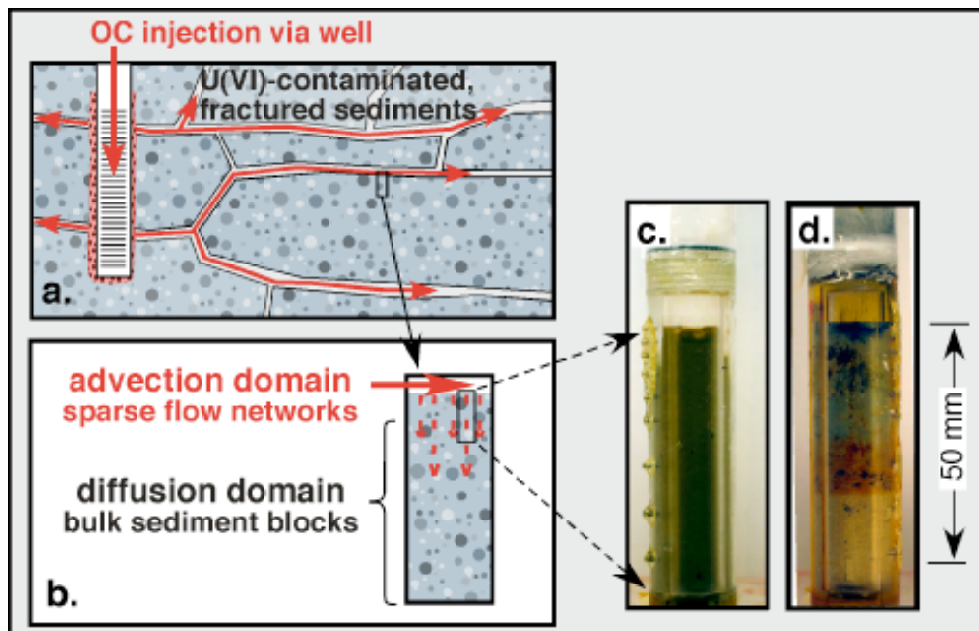
**Preferential flow during monitoring:** Monitoring wells provide groundwater samples that are flux-weighted, and often not volume averages of local pore waters.



Laboratory experiment on OC diffusion into U-contaminated sediment

- Oak Ridge sediment (60 mm columns)
- 323 mg U(VI) kg<sup>-1</sup> (uranyl nitrate)
- 330 mmol OC kg<sup>-1</sup> y<sup>-1</sup> (lactate)
- $\mu$ -XAS for U oxidation states

- Dispersal of OC in the subsurface is diffusion-limited domains and establishment of reducing conditions is very slow.
- OC sorption/desorption significantly retards propagation of the reduction front ( $K_d \approx 5$  to  $10 \text{ mL g}^{-1}$ ).



Tokunaga et al., Environ. Sci. Technol., 2005

Large inventories of U(VI) can remain unreduced and undetected in the subsurface, especially where fractures, macropores, and textural boundaries are prominent.

## U(VI) bioreduction with advective OC supply

OC infusion into U(VI)-contaminated sediment

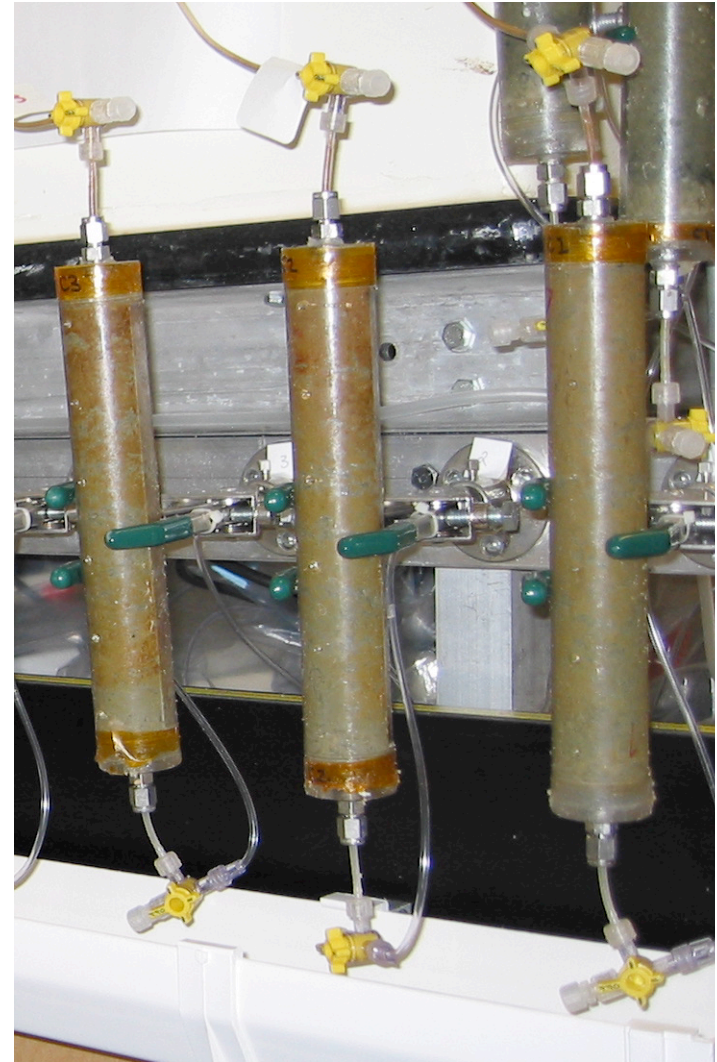
- FRC Area 2 sediment (208 mg U kg<sup>-1</sup>)
- OC conc. (32 mM, 10.6 mM lactate)
- Flow rate = 10 mm day<sup>-1</sup> (pore velocity)
- OC supply rate = 0.6 mmol kg<sup>-1</sup> day<sup>-1</sup>  
= 200 mmol kg<sup>-1</sup> y<sup>-1</sup>

Characterization

- Effluent chemistry
- Sediment U oxidation state
- Sediment microbial community

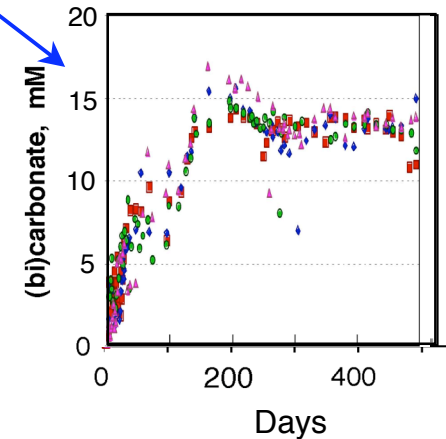
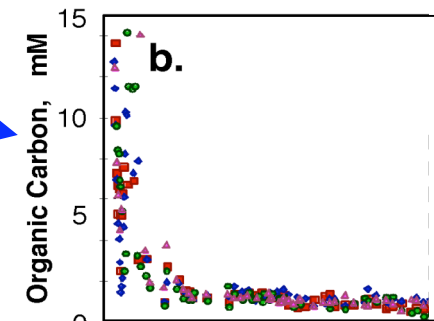
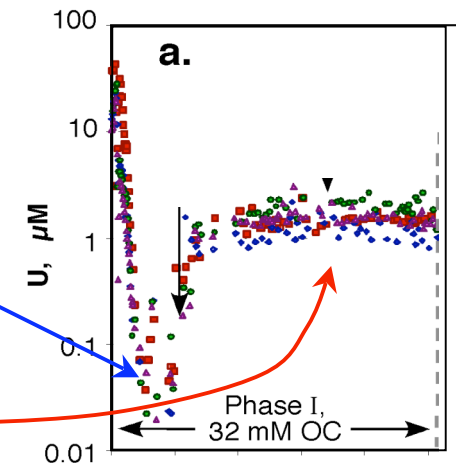
Wan et al., Environ. Sci. Technol., 2005.

Brodie et al., Appl. Environ. Micro., 2006.

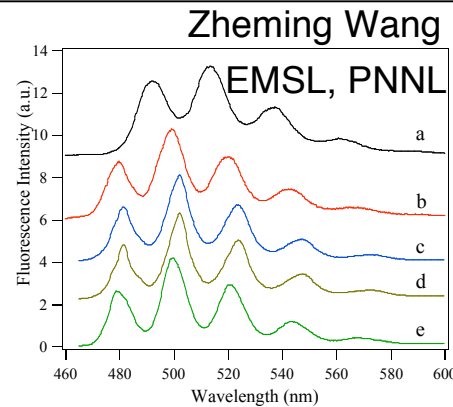


## U(VI) bioreduction with advective OC supply

- Effluent U concentrations were reduced below MCL within the 1<sup>st</sup> 100 days, and bioreduction appeared successful.
- However, effluent U concentrations then increased to  $\approx 1 \mu\text{M}$ , under sustained reducing conditions.
- Most of the OC supplied was depleted.
- Bicarbonate and methane concentrations became elevated in effluents. Was U(VI) solubility enhanced by formation of carbonato complexes?



- Yes. Laser fluorescence spectroscopy confirmed that effluent U(VI) occurred primarily as  $\text{UO}_2(\text{CO}_3)_3^{4-}$  and as  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ .



Wan et al., Environ. Sci. Technol., 2005.



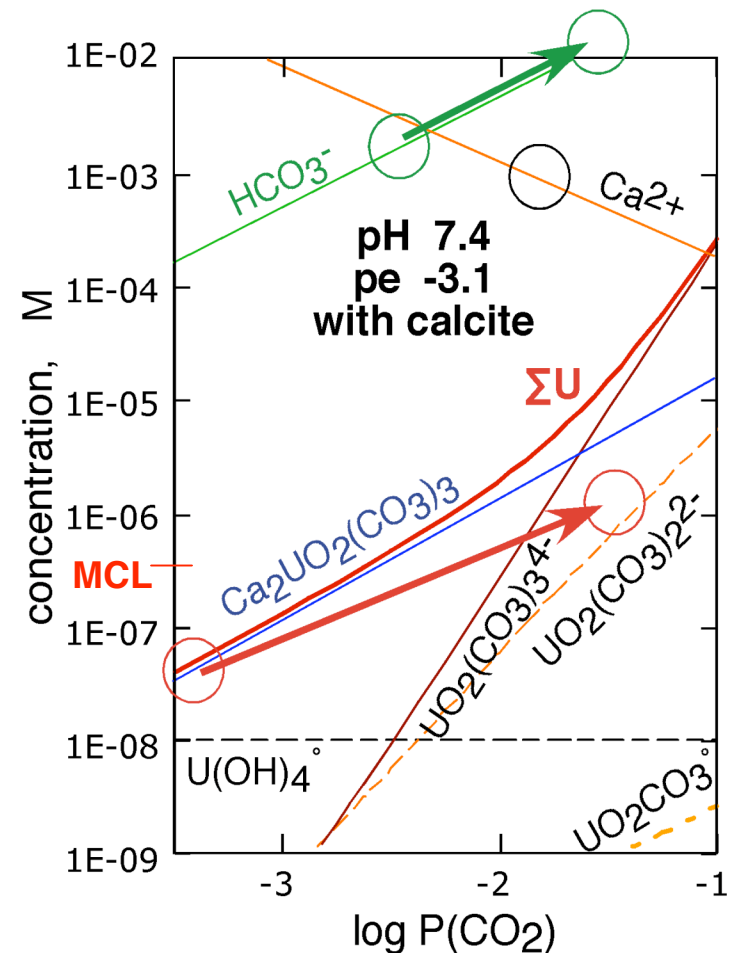
## Microbial respiration increases bicarbonate concentrations in groundwater, thereby promoting higher U(VI)<sub>aq</sub> concentrations

Very strong complexes  $\text{UO}_2(\text{CO}_3)_3^{4-}$  and  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$  (Bernhard et al. 1996, 2001) support higher U(VI) levels at circum-neutral pH.

Thus, OC-stimulated U bioreduction is a more difficult immobilization strategy in calcareous sediments.

Other impacts of  $\text{Ca}_2\text{UO}_2(\text{CO}_3)_3$ :

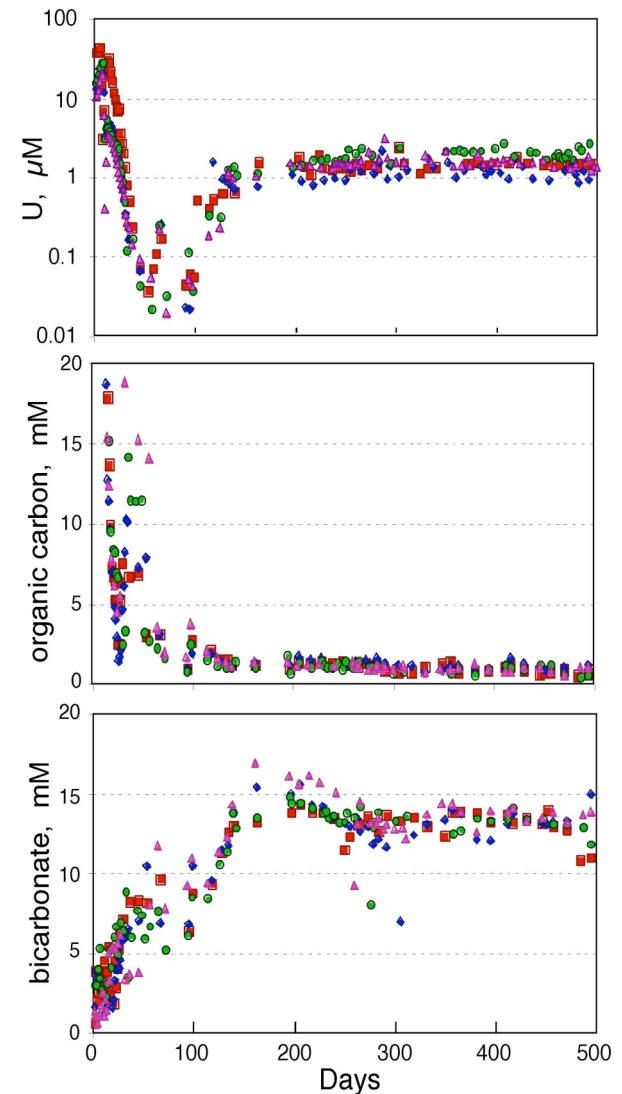
1. can slow U(VI) bioreduction (Brooks et al., 2003).
2. diminishes U(VI) sorption (Zheng et al., 2003).
3. enhances U(VI) diffusion (Tokunaga et al., 2004).



Based on the stability of U(VI)-carbonato complexes, we predicted a counter-intuitive effect that increasing OC supply rates would release more U(VI) into groundwater.

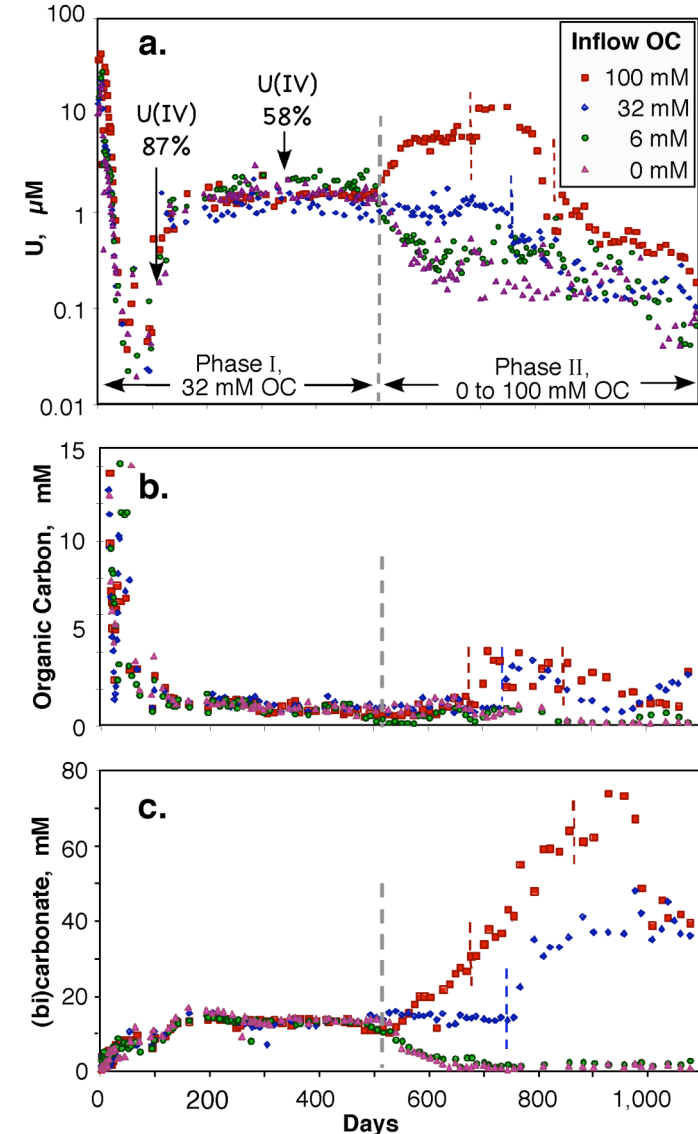
Our earlier U bioreduction study on flow-through columns of FRC Area 2 sediments was conducted with 32 mM OC (lactate), supplied at 200 mmol OC kg<sup>-1</sup> y<sup>-1</sup>. What results from changing the OC supply rate?

After 510 days, these columns were switched to solutions containing 0, 6, (32), and 100 mM OC (0, 40, 200, and 700 mmol OC kg<sup>-1</sup> y<sup>-1</sup>).



*Under already established reducing conditions,*

- Increasing the OC supply (from 200 to 700 mmol OC kg<sup>-1</sup> y<sup>-1</sup> ) yielded increases in effluent bicarbonate and U(VI) concentrations.
- Decreasing the OC supply (from 200 to 40 or 0 mmol OC kg<sup>-1</sup> y<sup>-1</sup> ) yielded decreases in effluent bicarbonate and U(VI) concentrations.
- These responses clearly demonstrate the negative impact of excessive OC supply.
- At much later times (> 800 days), effluent U concentrations decreased in all systems, indicating depletion of the TEA(s) for U reoxidation.

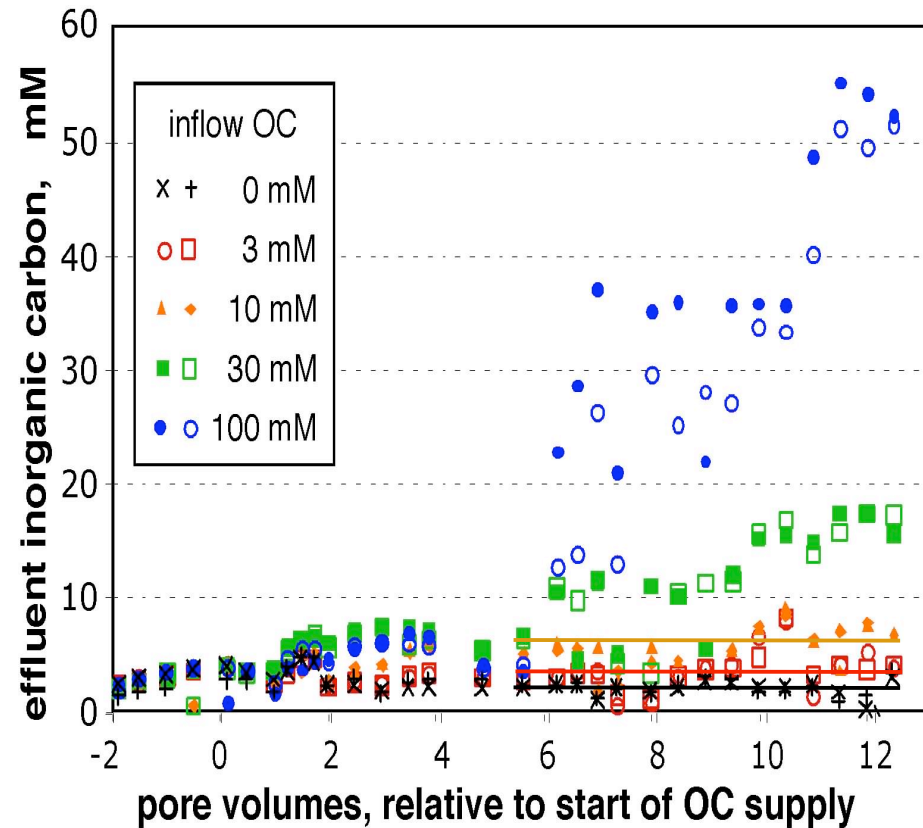


## What is the impact of supplying OC at lower rates, throughout treatment?



OC conc. mM	OC supply rate $\text{mmol kg}^{-1} \text{ year}^{-1}$
0	0
3	16
10	55
30	160
100	550

pore water velocity =  $3.0 \text{ m y}^{-1}$

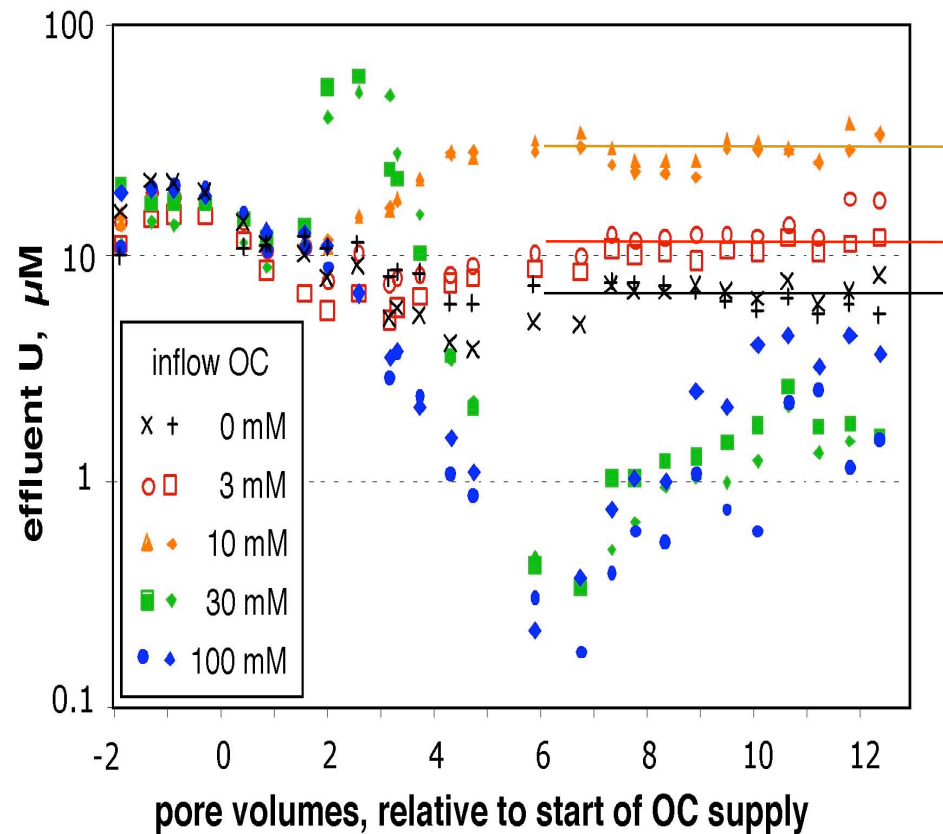


Microbial respiration results in concentrations of bicarbonate in effluents remaining proportional to influent OC supply (acetate or lactate).

At lower OC supply rates, less (bi)carbonate is generated.

However, reducing conditions do not develop under lower OC supply rates.

U remains unreduced, and more U(VI) partitions into the aqueous phase in strong U(VI)-carbonato complexes.



**If OC supply rate is not high enough to generate reducing conditions, it will mobilize more U(VI) than OC-free groundwaters.**

## The Organic Carbon Supply Tradeoff

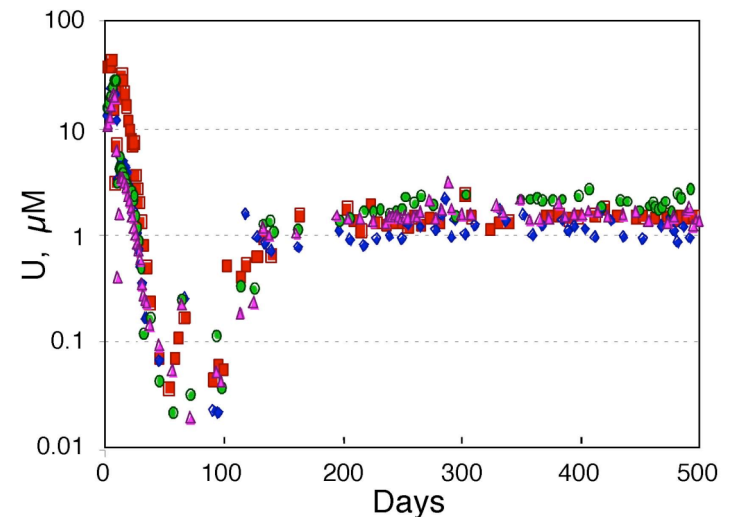
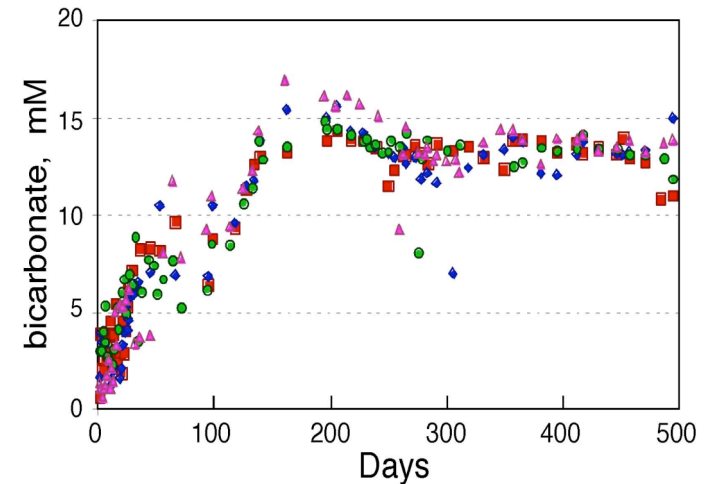
OC needs to be provided to stimulate U(VI) bioreduction to lower solubility U(IV).

However, microbial mineralization of OC increases U(VI)<sub>aq</sub> concentrations through carbonate-complexation.

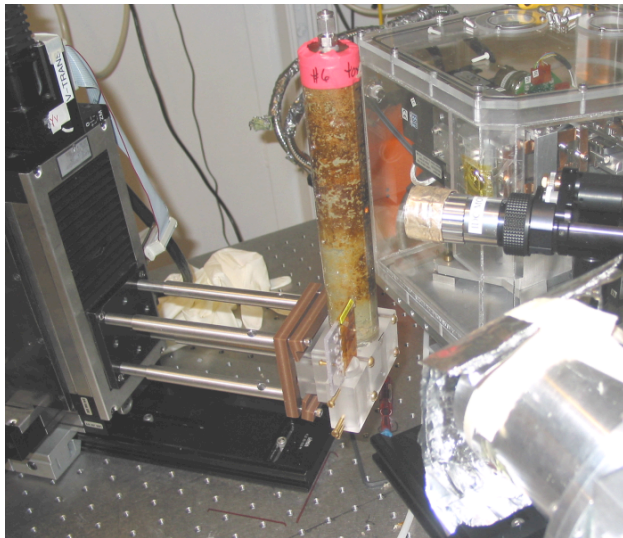
### More questions:

Is there an optimal OC supply rate?  
Perhaps it is in the range of 100 to 200 mmol kg<sup>-1</sup> year<sup>-1</sup> in this sediment (for establishing reduced conditions), but more work is needed.

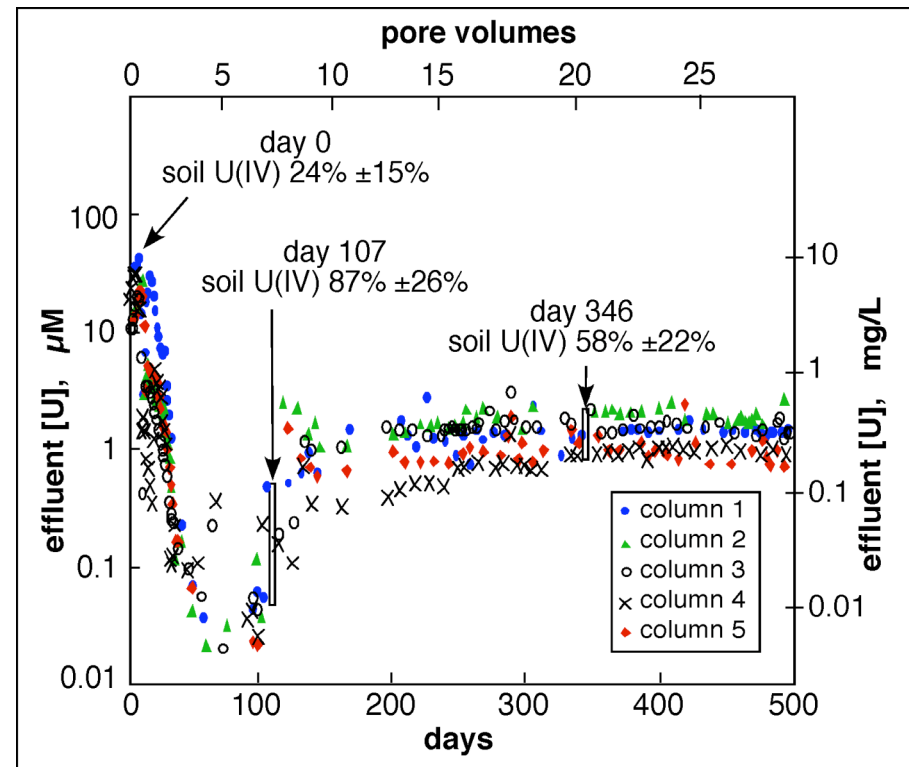
Was U(VI) reduction achieved within the sediments?



U oxidation states were determined directly on sediment columns using micro- X-ray absorption spectroscopy.



GSECARS beamline 13-IDC,  
APS, Argonne National Laboratory



U was being reduced shortly after OC supply was initiated, but then reoxidized, under continuously reducing conditions.

Wan et al., Environ. Sci. Technol., 2005.

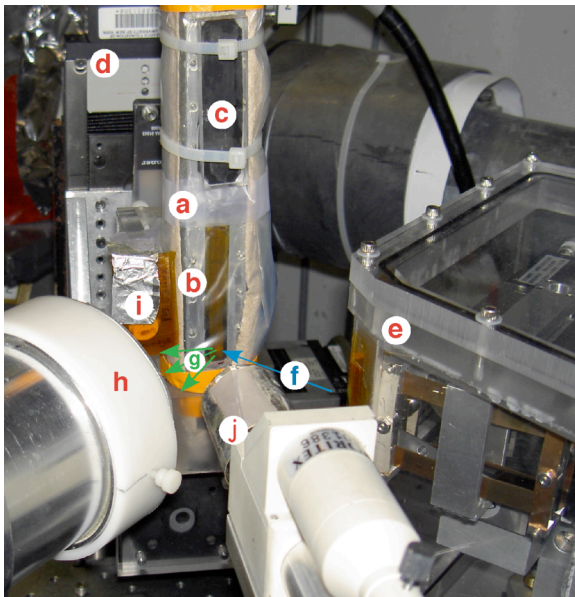
What oxidants (terminal electron acceptors) remained to reoxidize U(IV) while reducing conditions were maintained?

$O_2$ ,  $NO_3^-/NO_2^-$ , Mn(III,IV), and Fe(III) are all thermodynamically and kinetically effective oxidants of U(IV), but the effluent is depleted of  $O_2$  and  $NO_3^-/NO_2^-$ .

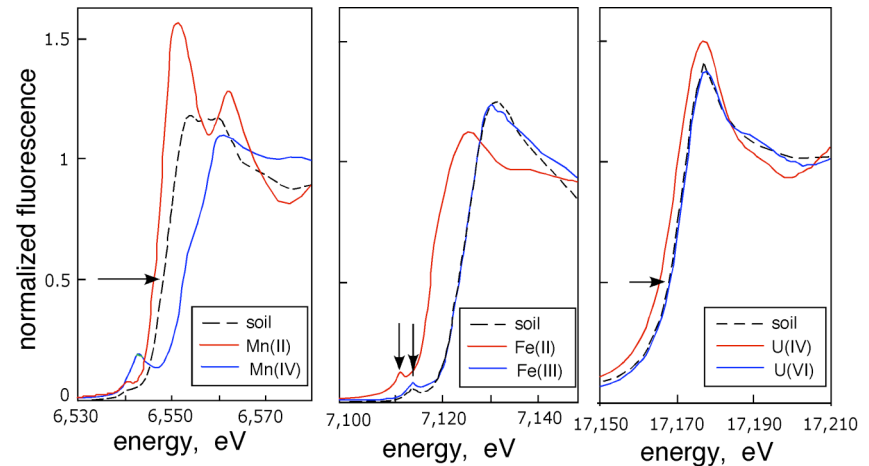
# Are Mn(III,IV) and/or Fe(III) the terminal electron acceptors for U(IV) reoxidation under reducing conditions?

Presence of Mn and Fe oxides, at much higher concentrations than U, could control U redox changes.

Mn(native sediment)	49.1 mmol kg <sup>-1</sup>
Fe(native sediment)	1,185 mmol kg <sup>-1</sup>
U(contaminant)	1.1 mmol kg <sup>-1</sup> (260 mg kg <sup>-1</sup> )



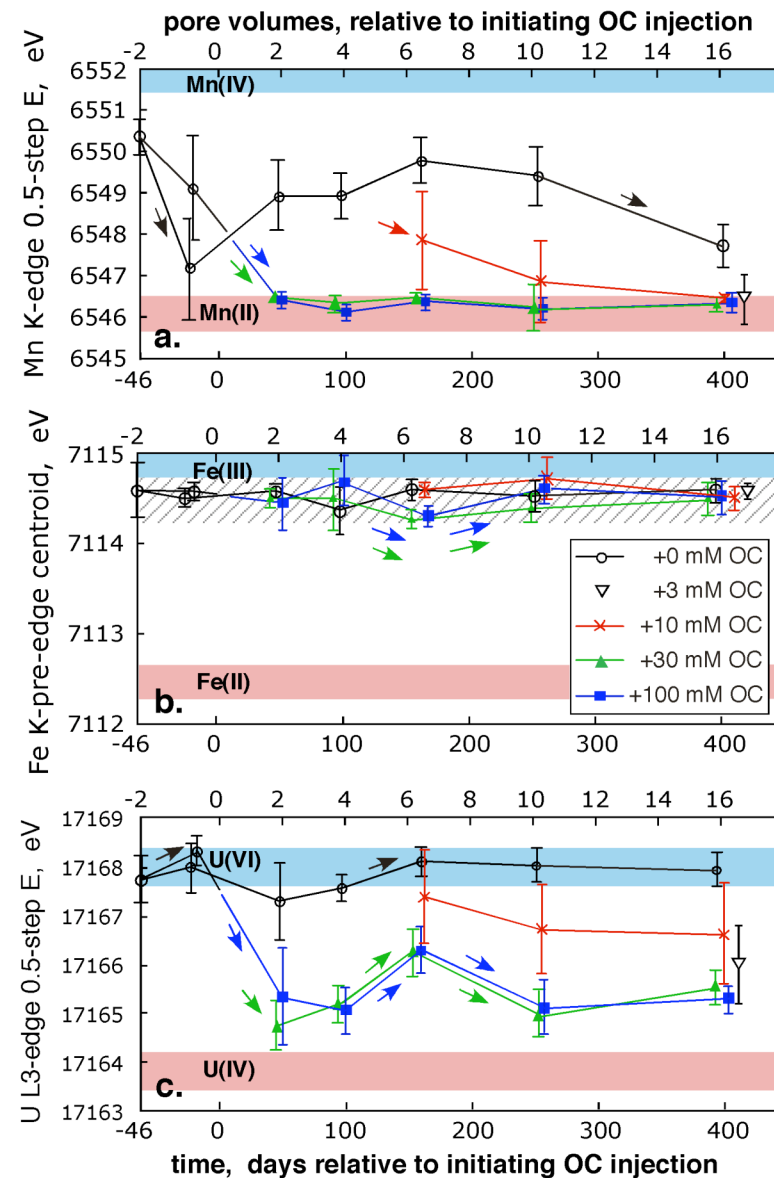
FRC Area 2 sediment being analyzed for Mn, Fe, U oxidation states by  $\mu$ -XAS. NSLS, Beamline X26A.



XANES spectroscopy was used to determine oxidation states of Mn, Fe, and U in Oak Ridge sediments during OC-stimulated bioreduction.



- Mn reduction to Mn(II) was rapid, complete, and not reversed while reducing conditions were maintained.
- Only a small portion of the initial Fe(III) was reduced to Fe(II), supporting our earlier hypothesis that a reactive Fe(III) fraction can remain to oxidize U(IV) under reducing conditions.
- U reduction was initially rapid in sediments receiving higher OC influxes.
- Reoxidation of U(IV) occurred in the more reducing sediments.
- Later stage net U reduction occurred, but about 20% of the U persisted as U(VI) up to at least 400 days.



**Nevertheless, these experiments have collectively shown that effectively complete U bioreduction is achievable with long-term OC infusion.**

**However, maintaining low U concentrations though sustaining reducing conditions is another 800 pound gorilla...**



At sites where regional groundwaters are oxidizing, how can reducing conditions be maintained over decades, centuries, millennia?

Maintaining a supply of OC for such very long times seems impractical.

## Long-term maintenance of low U concentrations

At sites where regional groundwaters are oxidizing, how can reducing conditions be maintained over decades, centuries, millennia?

Maintaining an OC supply level for such very long times appears impractical.

U bioreduction can be an important part of a broader remediation strategy that also employs other mechanisms for keep U concentrations low, including

- precipitation of low-solubility U(VI) phases
- permeability reduction or other hydraulic controls

## Biogeochemically Reduction of Chromium

Cr(VI) is an important metal contaminant at many sites. Some source areas are large, and very heavily contaminated, with soil Cr concentrations ranging from 100s to 1,000s of  $\text{mg kg}^{-1}$ .

Reduction of Cr(VI) to Cr(III) greatly lowers the solubility, mobility, and toxicity of Cr.

Cr(VI) reduction can occur enzymatically, and abiotically through reactions with OC, Fe(II), and sulfide.

The only kinetically favorable oxidants of Cr(III) in the subsurface are Mn(III,IV) oxides.

## How Stable is Biogeochemically Reduced Chromium in Heavily Cr-contaminated Soils?

Can organic carbon infusion reduce Cr(VI) to Cr(III) in heavily-contaminated soils?

Altamont soil (Livermore, CA)

pH 8.3 (calcareous)

1.0% native organic C (830 mmol kg<sup>-1</sup>)

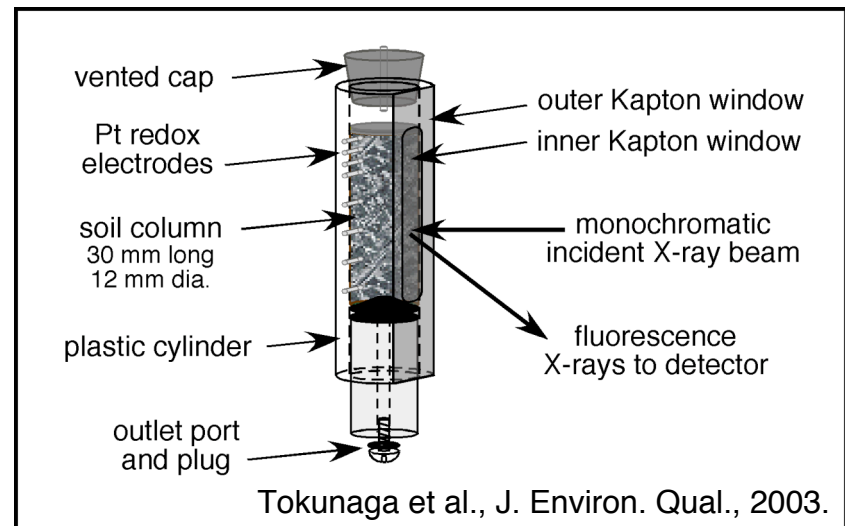
“Low” Cr(VI) contamination: 4.9 mmol kg<sup>-1</sup>  
(260 mg kg<sup>-1</sup>)

High Cr(VI) contamination: 49 mmol kg<sup>-1</sup>  
(2,600 mg kg<sup>-1</sup>)

Organic carbon (OC) treatments,  
advectively supplied:

0, 9.3, and 47 mmol kg<sup>-1</sup>

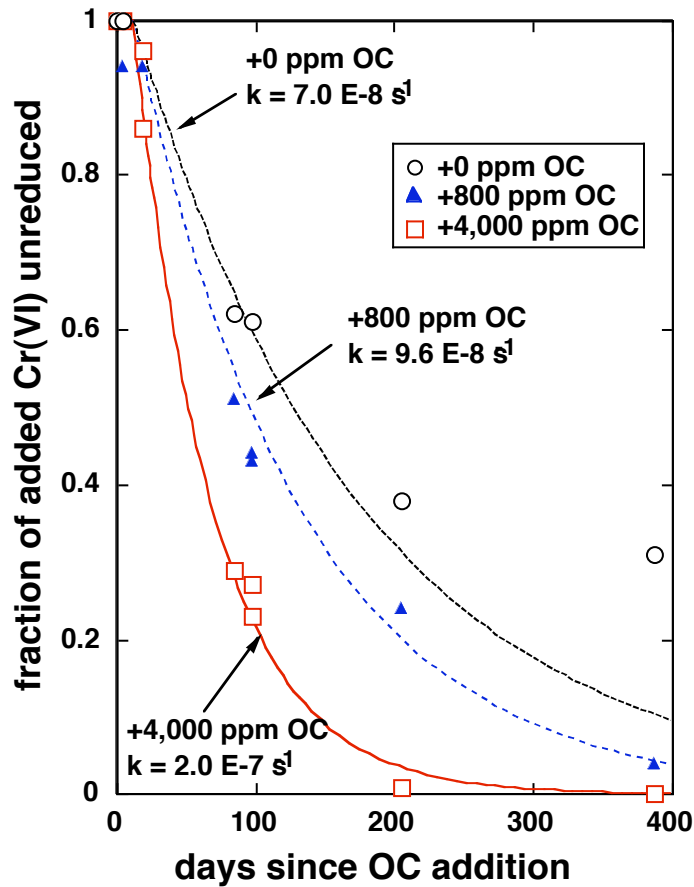
Periodic in-situ determination of oxidation states by  $\mu$ -XANES spectroscopy, and sampling for microbial community analyses.



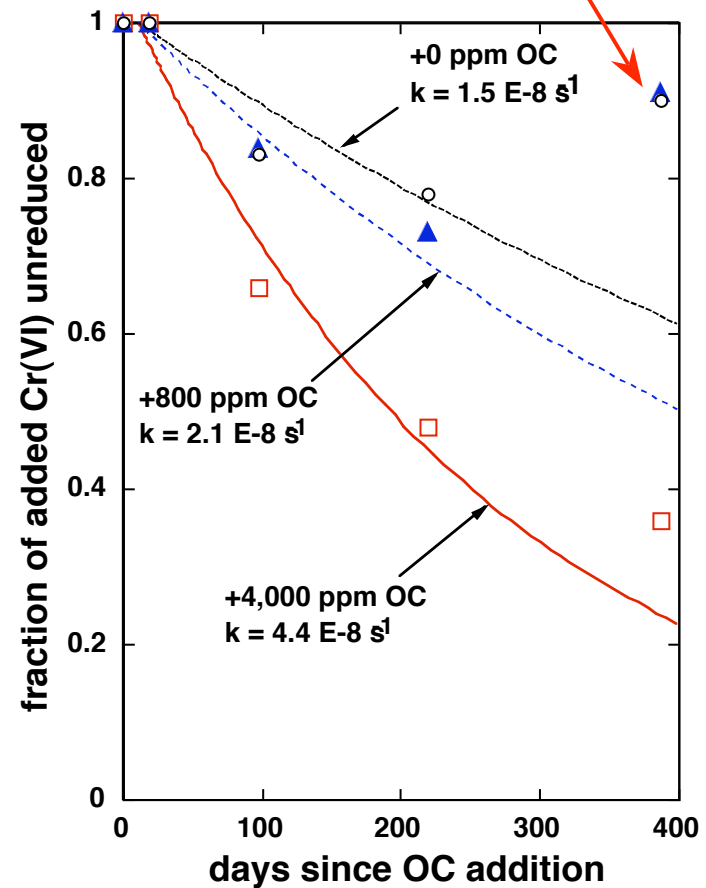
Soil microcosm for studies of metal redox reactions and microbial communities.

Results up to 210 days exhibited approximate 1<sup>st</sup>-order Cr(VI) reduction, but soils with higher contamination later have Cr(III) reoxidizing to Cr(VI).

Cr(VI)<sub>0</sub> = 260 mg kg<sup>-1</sup>  
initially 1,000 ppm Cr(VI) in pore waters

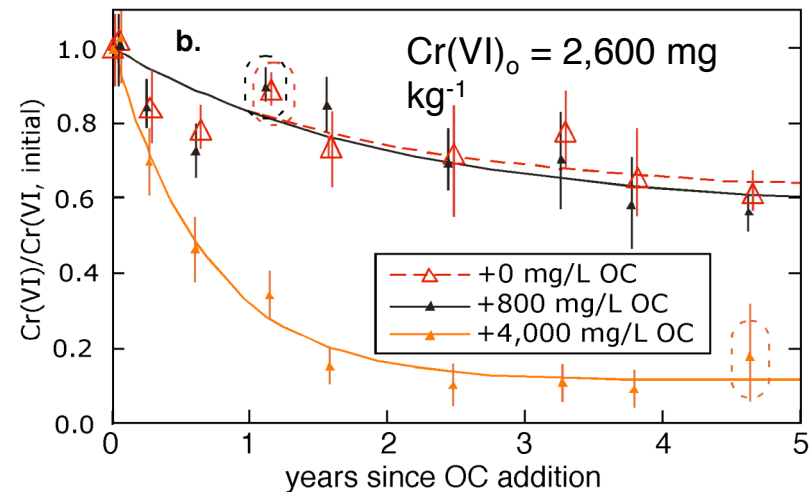
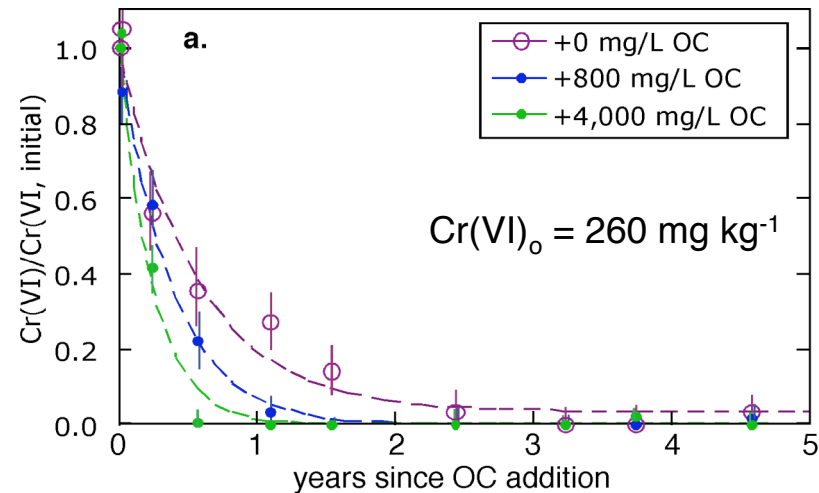


Cr(VI)<sub>0</sub> = 2,600 mg kg<sup>-1</sup>  
initially 10,000 ppm Cr(VI) in pore waters



## Even longer term measurements showed further Cr reduction.

- At lower Cr(VI) exposure, complete reduction to Cr(III) occurred in all soils.
- Completion of Cr(VI) reduction without treatment with OC showed the effectiveness of soil organic carbon in driving natural attenuation.
- The only kinetically favorable oxidants of Cr(III) in the subsurface are Mn(III,IV) oxides.
- Mn oxidation to Mn(IV) was significant in the higher Cr soils.



Tokunaga et al., Environ. Sci. Technol., 2007, accepted.

## Summary

Slow, natural attenuation of Cr(VI) to Cr(III) can occur in sediments with sufficiently high native organic carbon:Mn ratio.

Efficient distribution of reducing agents (OC) can be challenging.

For OC-stimulated U bioreduction, carbonate complexation of U(VI) presents a problem at low OC supply rates.

For OC-stimulated U bioreduction, carbonate complexation of U(VI) also occurs at intermediate times at higher OC supply rates.

Under sustained reducing conditions, reactive Fe(III) remains available at intermediate times to drive U(IV) reoxidation.



## **Opinions**

Preserving reducing conditions within regionally oxidizing environments is a high-maintenance task.

Therefore other solubility and transport controls used in conjunction with bioreduction may improve remediation efficiency.

Long-term experiments are needed to test long-term stability of proposed remediation strategies.