Linking Chemical Speciation, Desorption Kinetics, and Bioavailability of U and Ni in Aged-Contaminated Sediments: A Scientific Basis for Natural Attenuation and Risk Assessment

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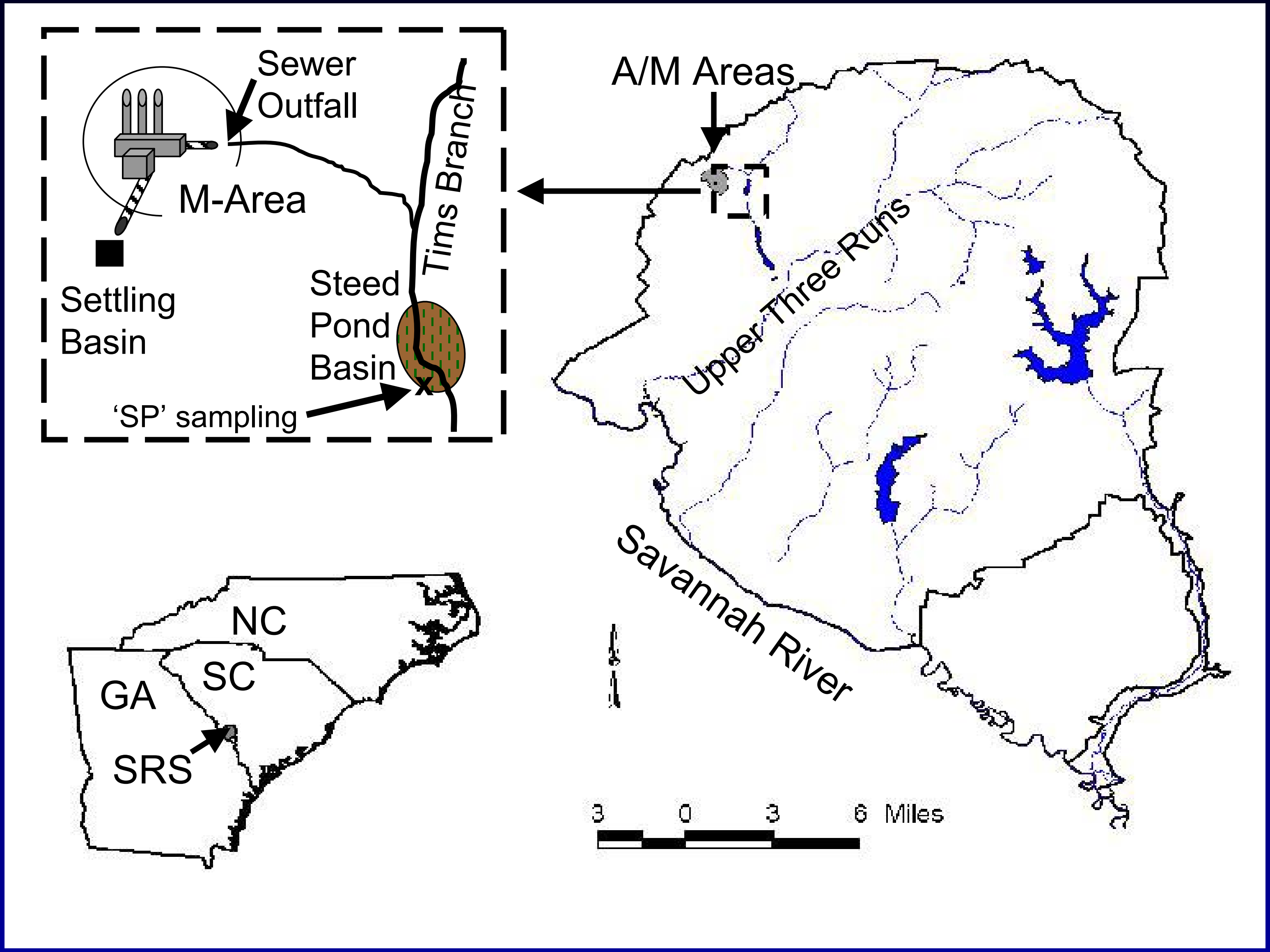
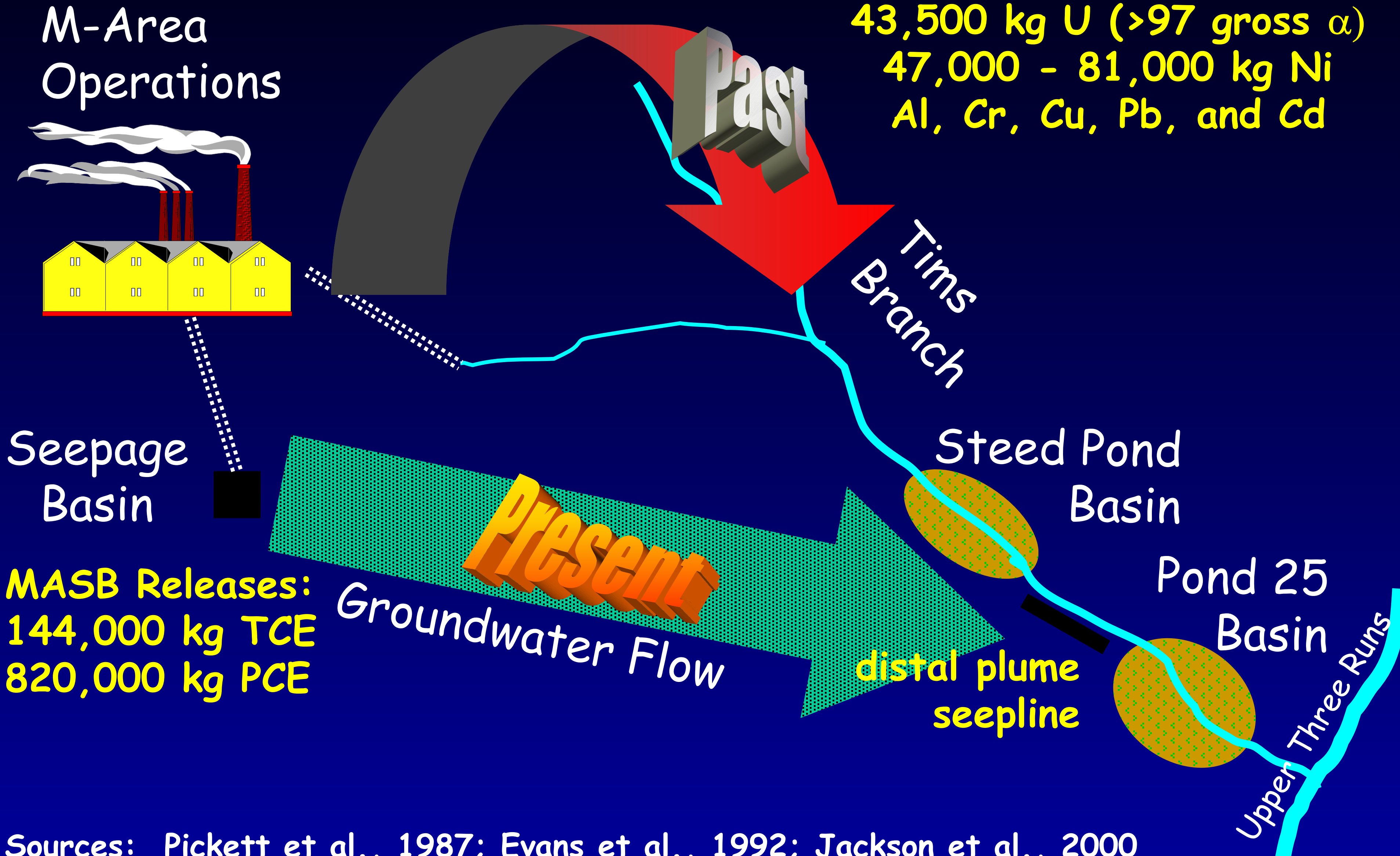
The University of Georgia

EMSP Annual PI Meeting
Richland, WA
May 2003

U.S. DOE's Savannah River Site



Tims Branch Contamination



Tims Branch Releases:
43,500 kg U (>97 gross α)
47,000 - 81,000 kg Ni
Al, Cr, Cu, Pb, and Cd

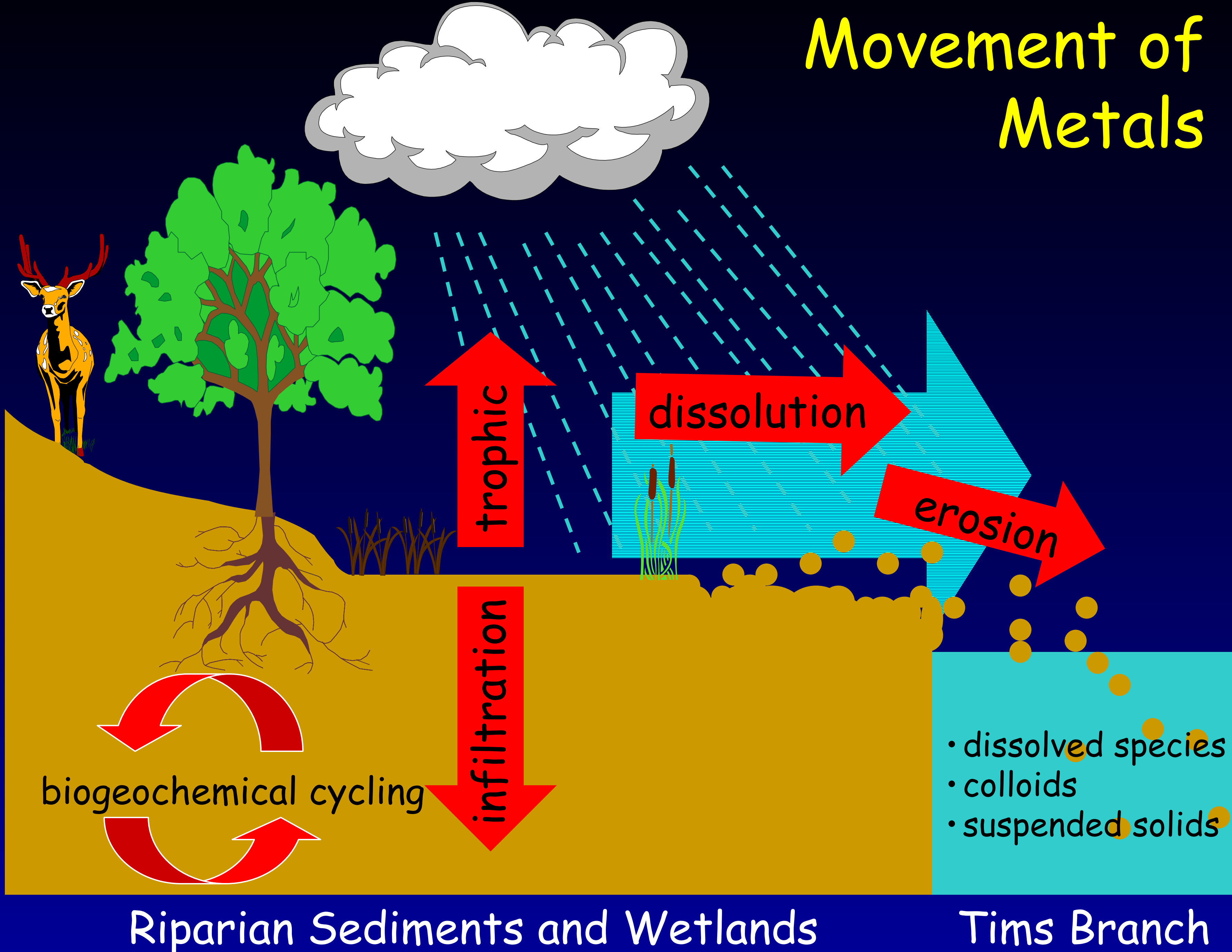
MASB Releases:
144,000 kg TCE
820,000 kg PCE

Sources: Pickett et al., 1987; Evans et al., 1992; Jackson et al., 2000

Tim Branch Contamination

- 1954 - 1985 direct process discharges to Tims Branch
  - U^{nat}/DU, Ni, Cr, Cu, Zn, Pb
  - 1966 - 69 peak (61% of U)
  - 43,500 kg (70%) U^{nat}/DU in Steed Pond; ??? kg Ni
- Shallow but extensive contamination of 5-km riparian/wetland corridor
- Complex, organic- and mineral-rich environment
- Physical transport and trophic transfer of metal inventories out of sediments = human and ecological risk

Movement of Metals



Hypotheses

I. Contaminant (U and Ni) aging leads to less labile, bioavailable forms
   a. Chemical speciation and biogeochemical cycling of U and Ni are primarily controlled by different sequestration mechanisms
   b. Spiked (un-aged) will exhibit very different speciation and biogeochemical cycling

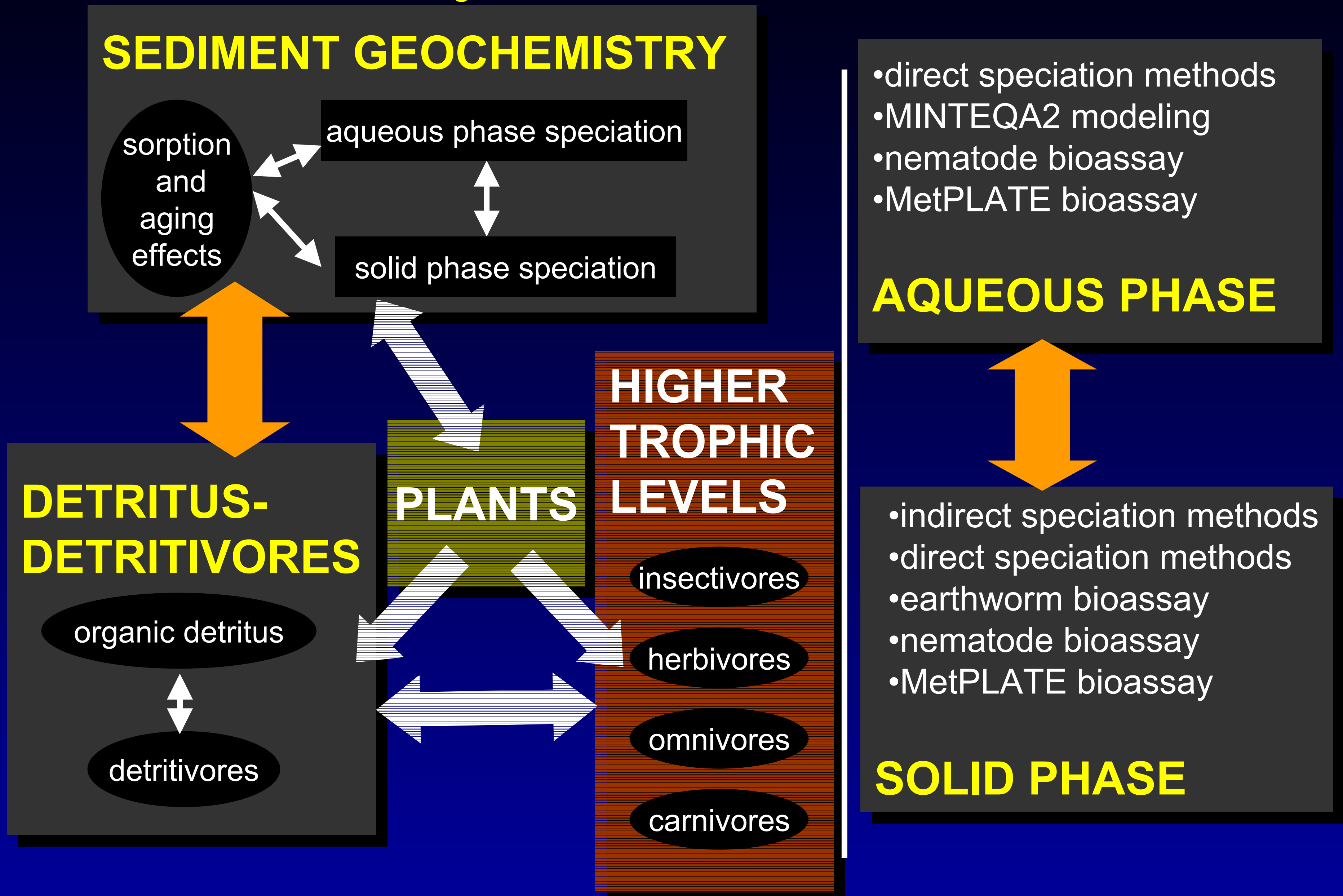
II. A clear relationship exists between chemical speciation, sediment properties, and sorption/desorption processes for U and Ni

III. A clear relationship exists between chemical speciation and simple biological metrics (uptake indices and toxicity assays)

Research Plan

- Phase I: Investigation of contaminant aging mechanisms
- Phase II: Linking aging and speciation to solubility and desorption kinetics
- Phase III: Incorporation of biological endpoints

Project Overview

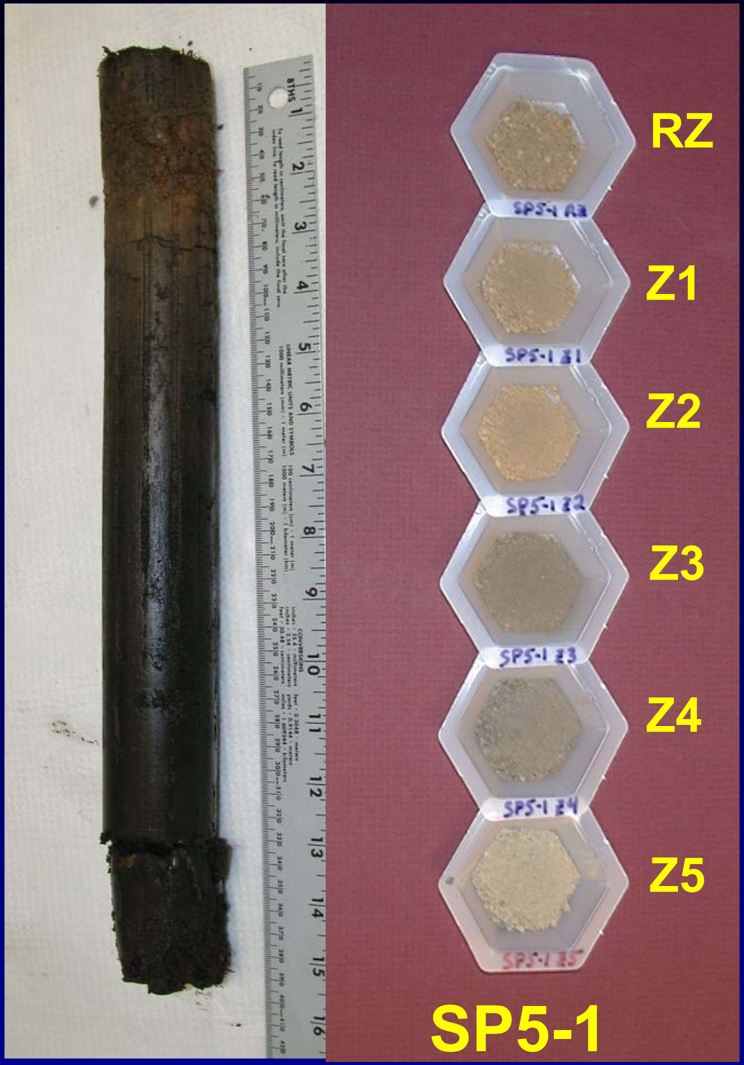


Phase I: Solid phase characterization

- Indirect speciation and characterization
  - bulk elemental analysis
  - sequential and non-sequential extractions
  - electron microscopy
- Direct speciation techniques
  - spatially-resolved elemental analysis
    - electron microprobe
    - synchrotron XRF 2D mapping
    - laser ablation ICP-MS
  - spatially-resolved spectroscopy
    - XANES and EXAFS
    - FT-IR, -Raman
    - laser fluorescence/luminescence

Sediment Characteristics

- Acidic, highly weathered sediments
- Clay to silty clay loam
- 1 - 14% sediment organic carbon
- Seasonal and aperiodic flooding and drying cycles: -100 to +600 mV Eh
- Fe-, clay-, and silt- rich strata overlying sandy bottom sediments
- ≤4900 mg kg^{-1} U and ≤3200 mg kg^{-1} Ni



0 - 25 mm
14% OC

25 - 65 mm
14% OC

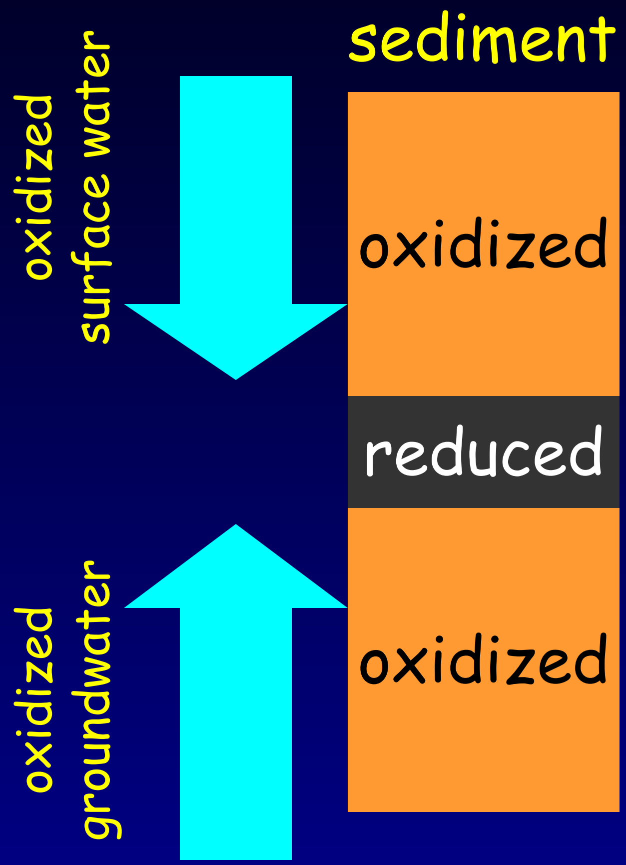
65 - 130 mm
4.4% OC

130 - 175 mm
3.7% OC

175 - 275 mm
1.5% OC

275 - 360 mm
0.4% OC

Sediment Redox Profile

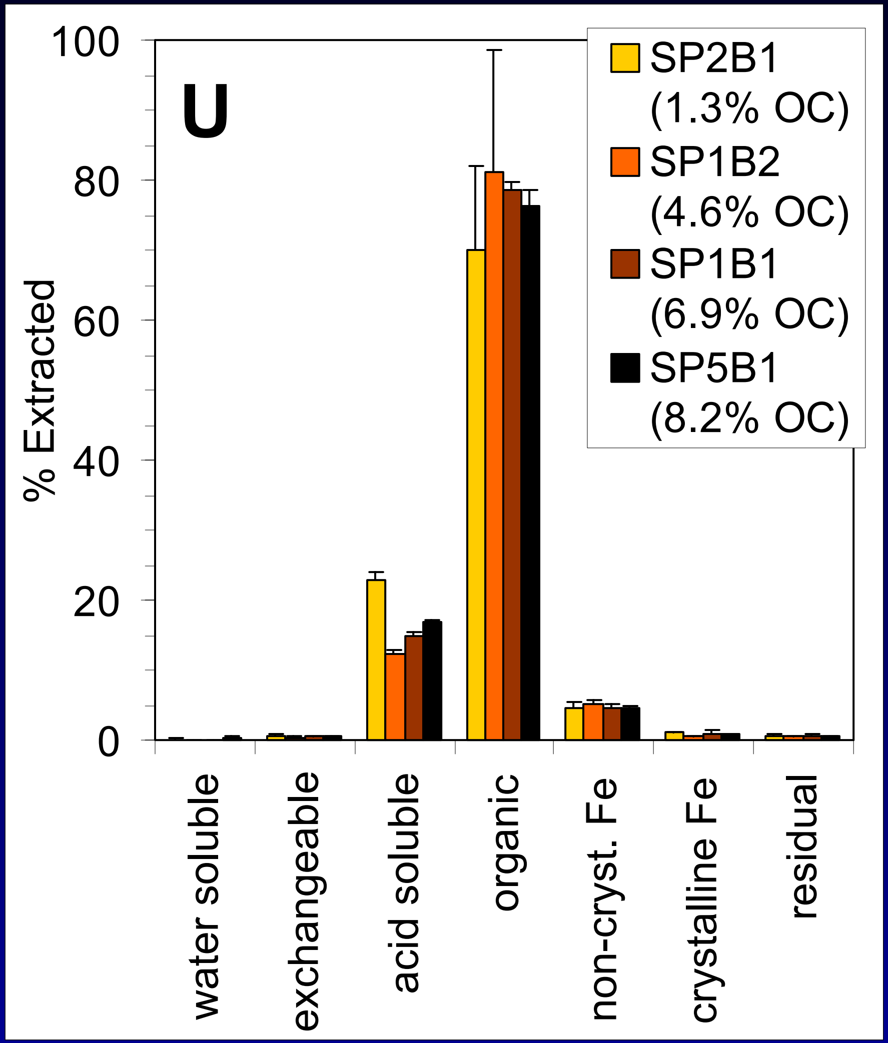


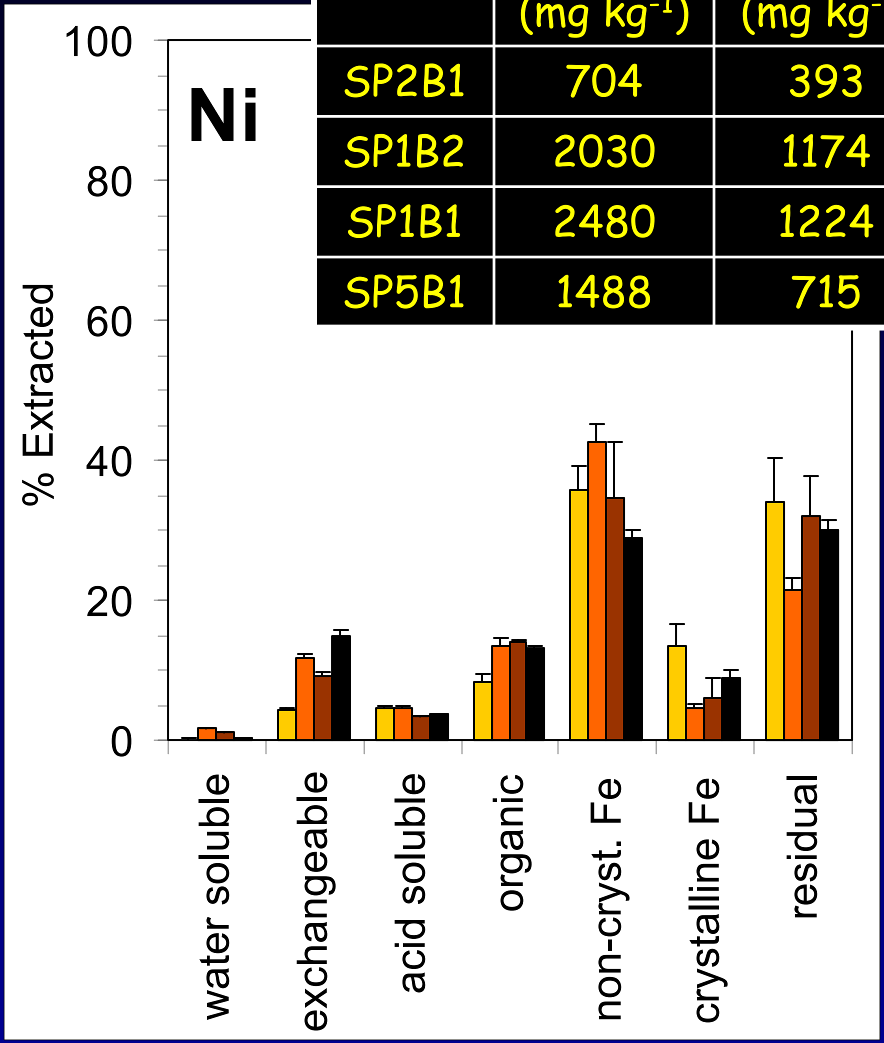
Depth (cm)	Eh (mV)
surface	~400 to 600
10 - 20	50
30	75
60	190 to 250
120	250 to 350
180	330 to 375

Source: Bertsch and Dosskey, unpublished data

Previous Sequential Extraction Results*

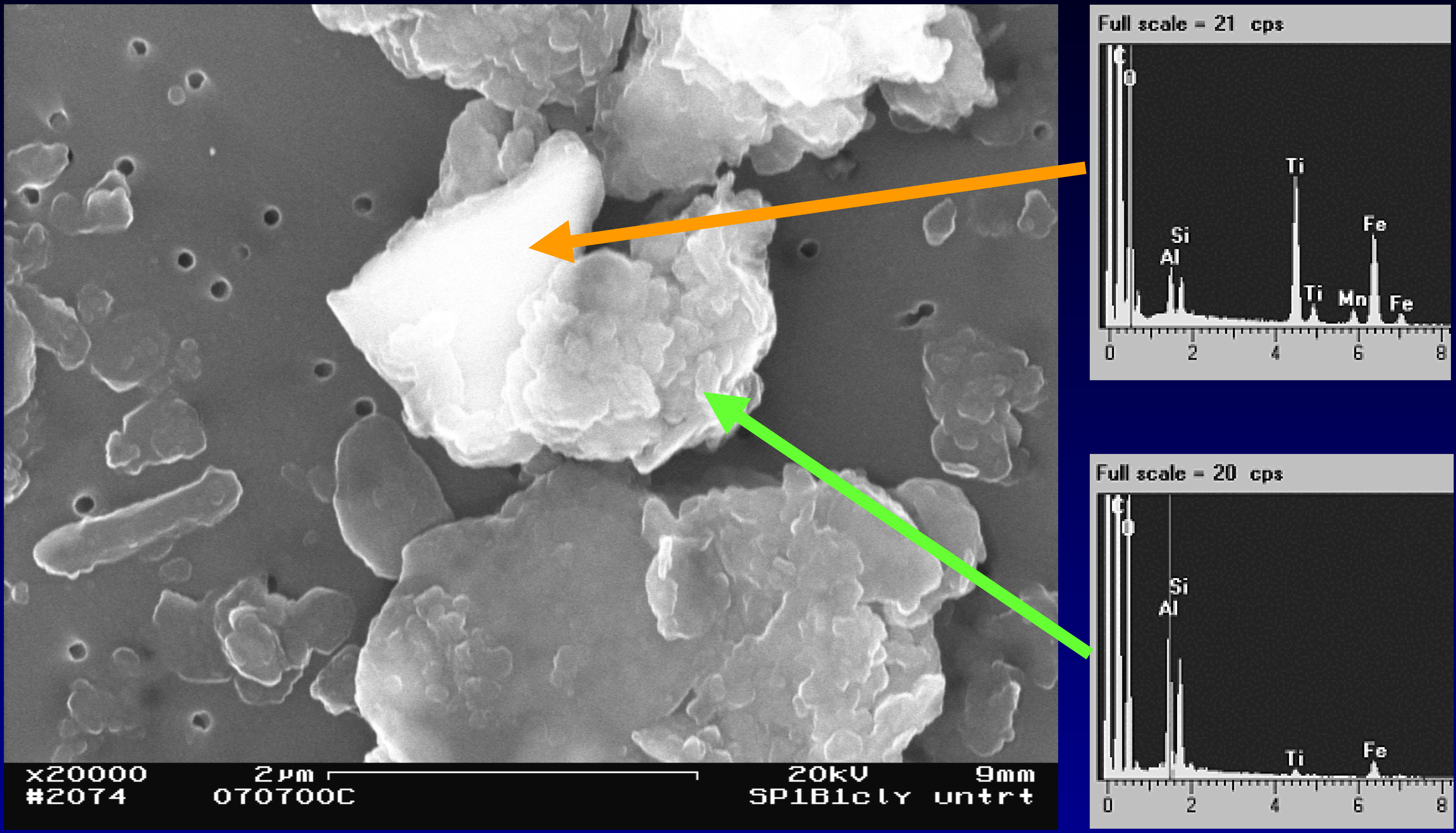
	U (mg kg^{-1})	Ni (mg kg^{-1})
SP2B1	704	393
SP1B2	2030	1174
SP1B1	2480	1224
SP5B1	1488	715





*Sowder et al., J. Environ. Qual., 2003

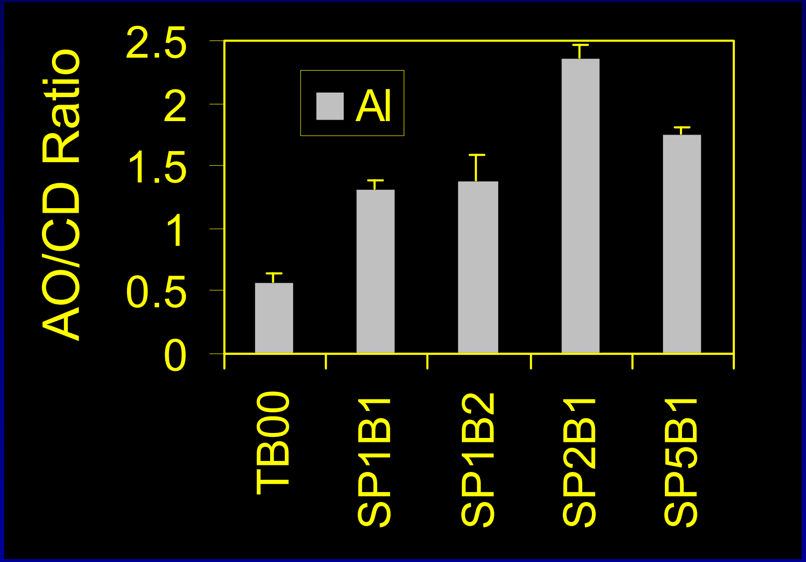
Iron Oxide Surface Coatings

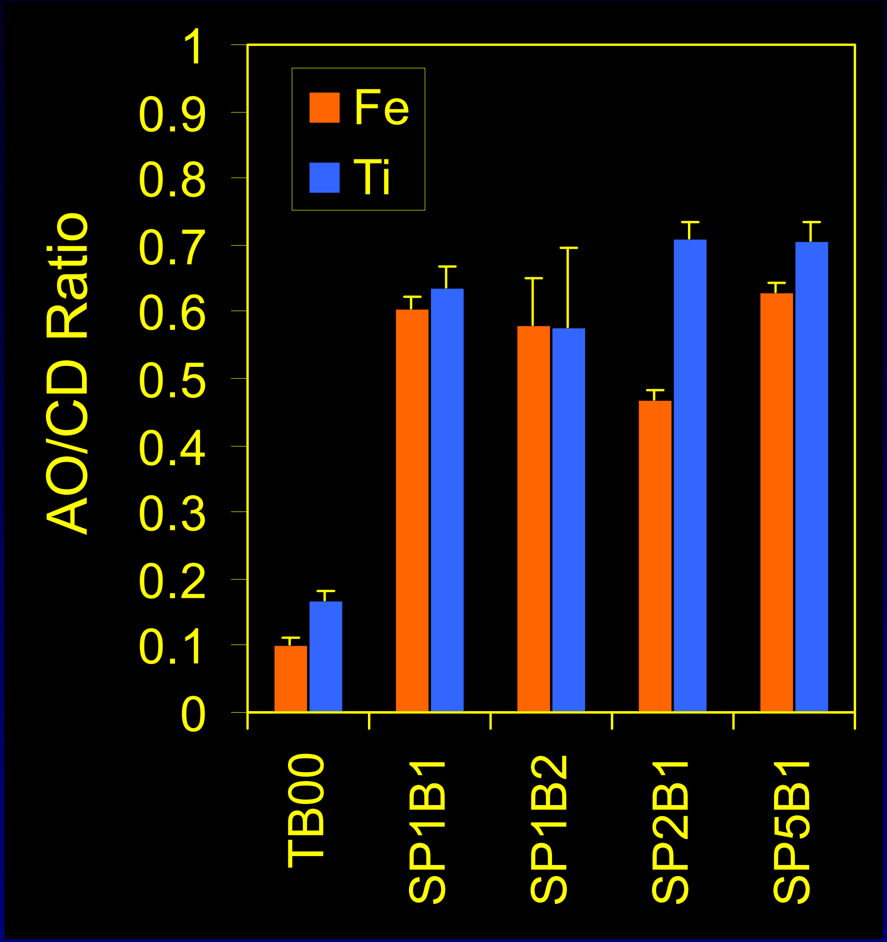


Sowder et al., J. Environ. Qual., 2003

Non-Crystalline Fe in Sediments

- non-sequential extractions with ammonium oxalate (dark reaction) and citrate dithionite reagents
- ~10% Fe in "non-crystalline" form in upland soil TB00
- 50 - 60% Fe as "non-crystalline" in SP sediments

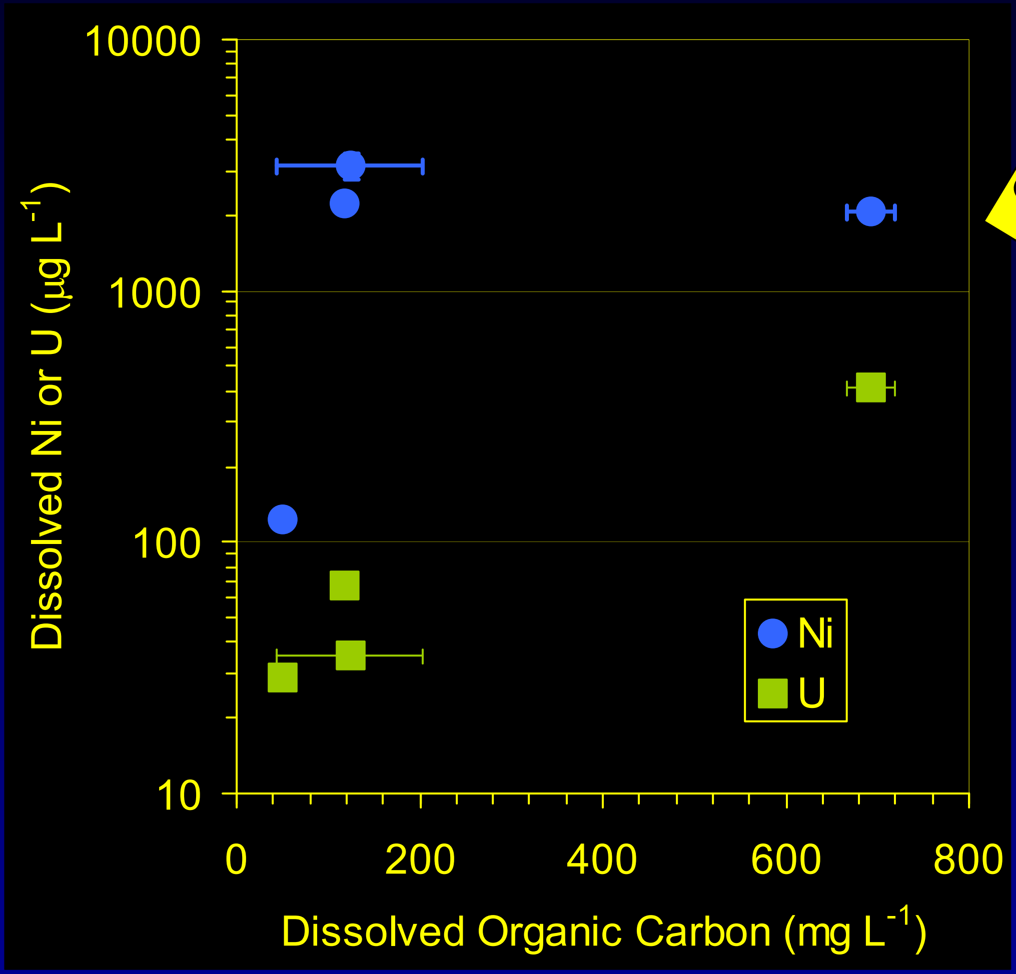




- Ti tracks Fe
- highly labile Al

Sowder et al., J. Environ. Qual., 2003

Previous 1:1 Sediment-Water Extraction Results*



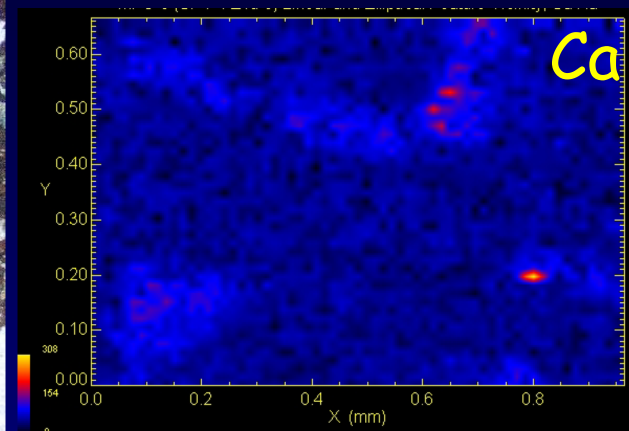
Correlation vs. DOC	R^2 (p-value)
$[U]_{aq}$	0.96 (<0.0001)
$[Ni]_{aq}$	0.04 (0.53)

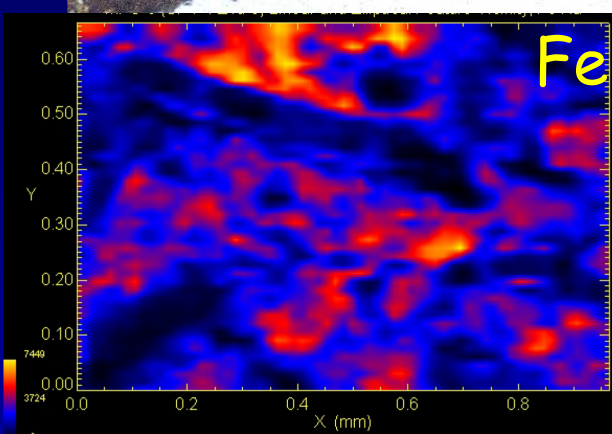
*Sowder et al., J. Environ. Qual., *In Press*

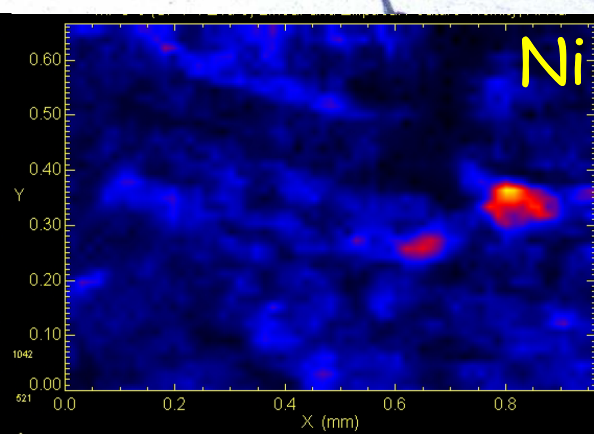
2D SXRF Mapping

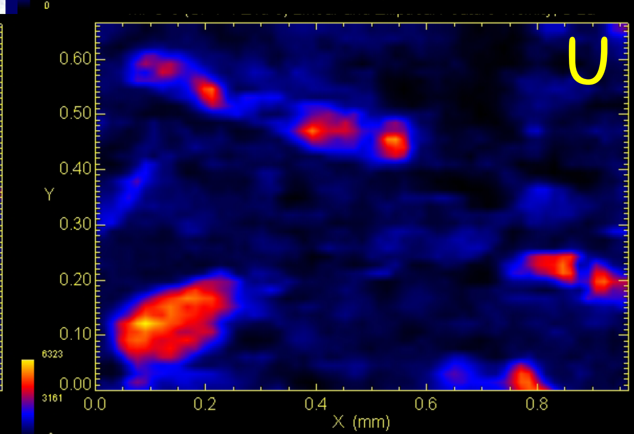
0.95 x 0.65 mm field
15 µm step size
10 x 15 µm spot size
20 sec. dwell time

- U with Ca-rich features (organic)
- Ni with Fe-rich regions (mineral)

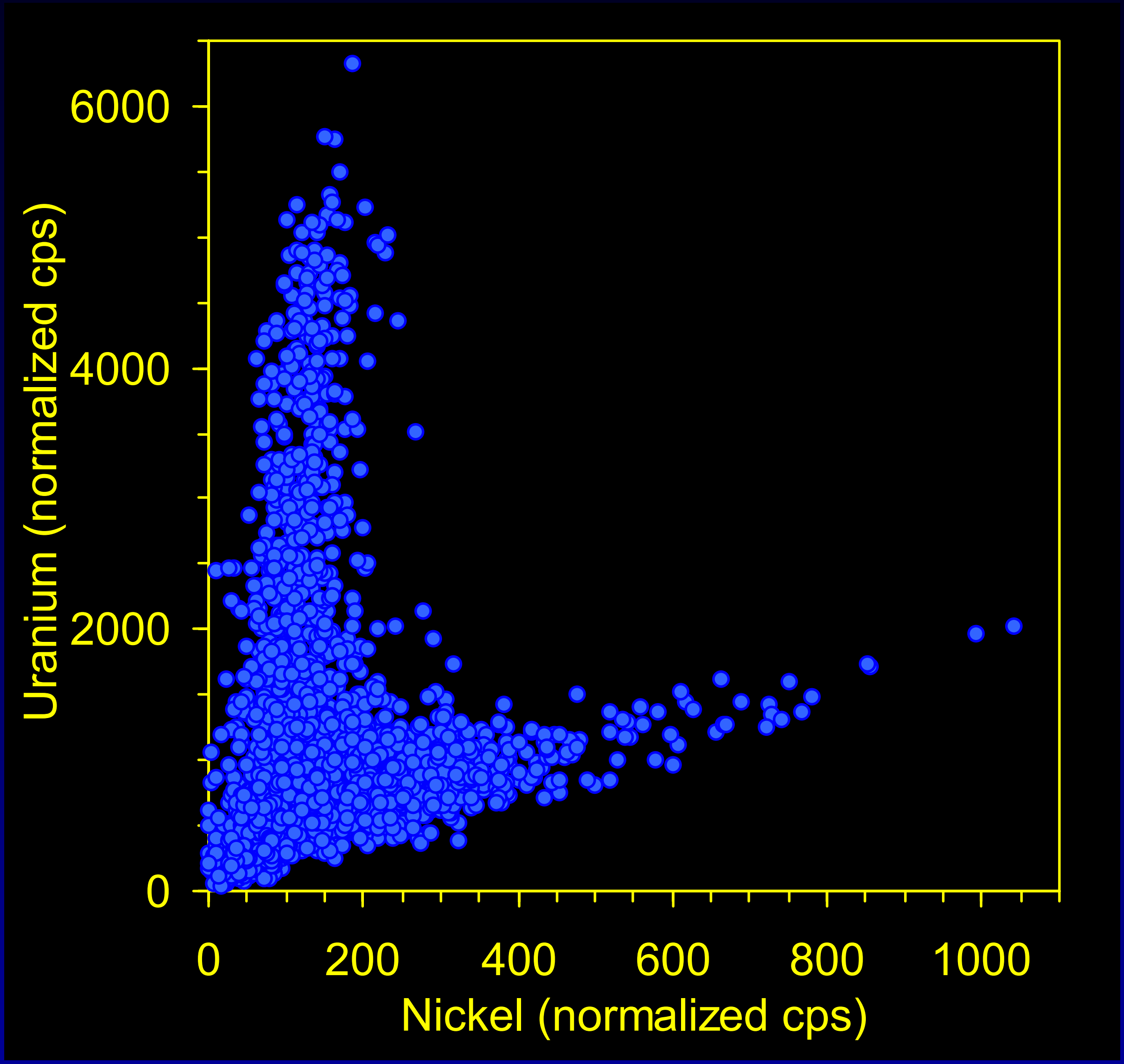






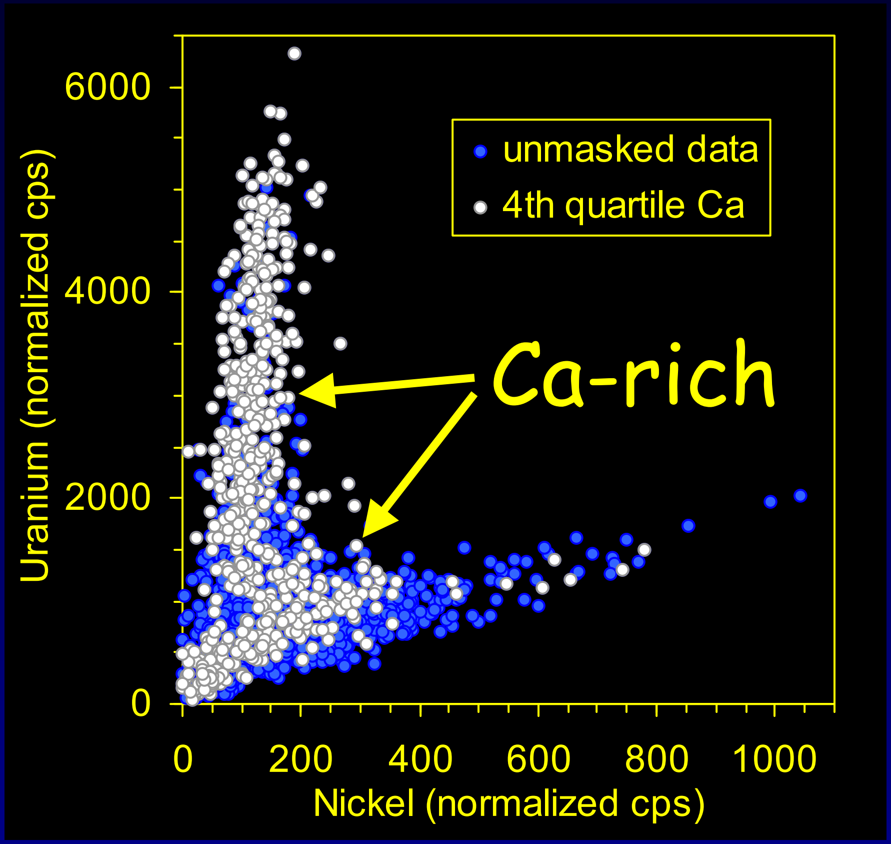


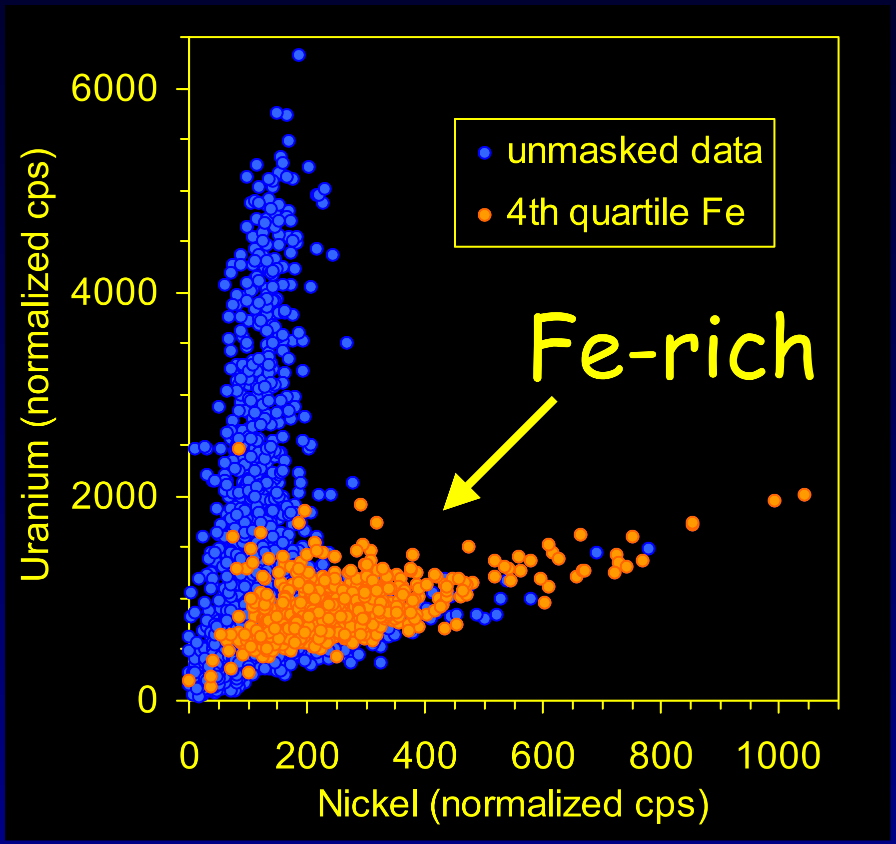
U and Ni Correlations



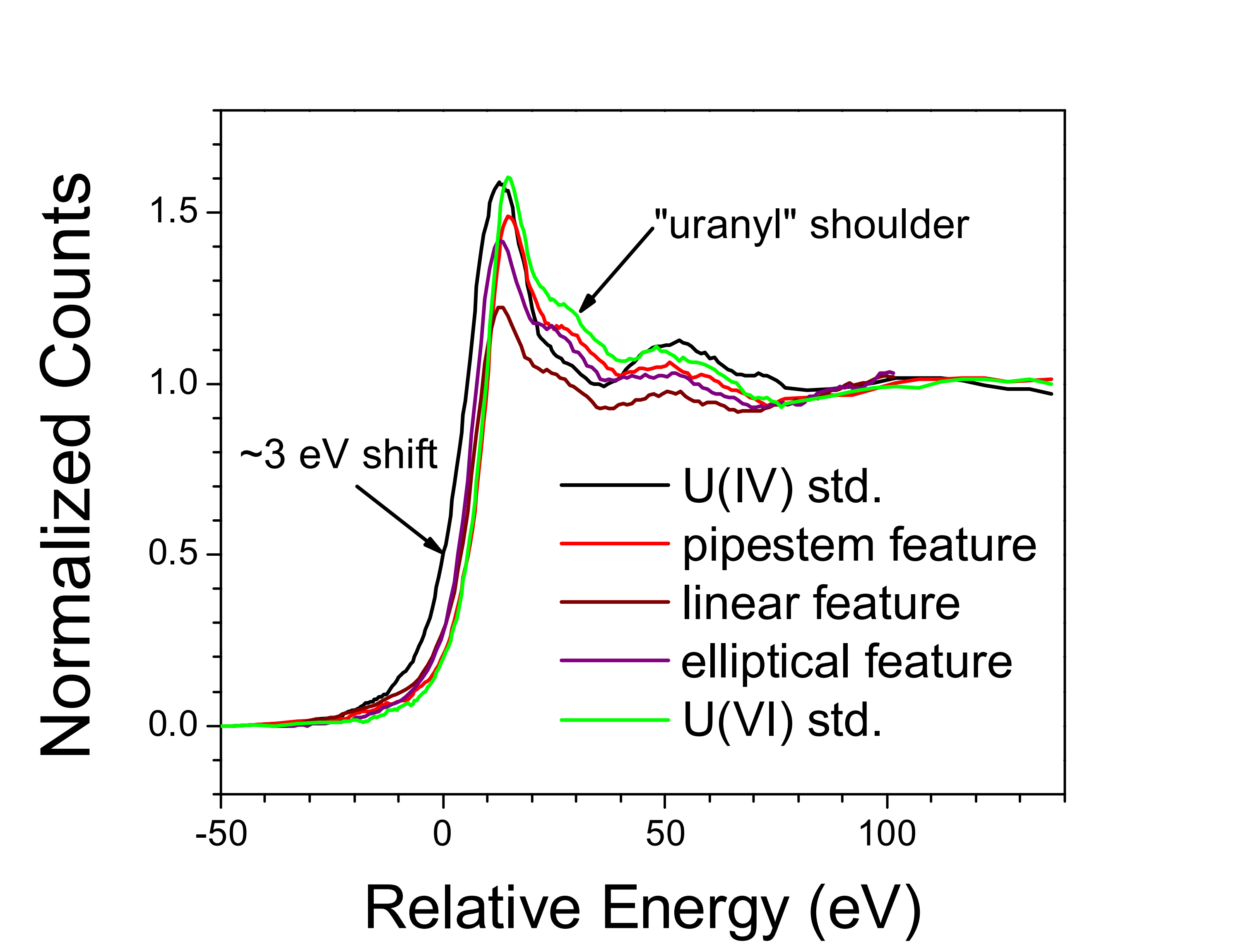
Correlations of U and Ni

with 4th Quartile Ca & Fe Masking

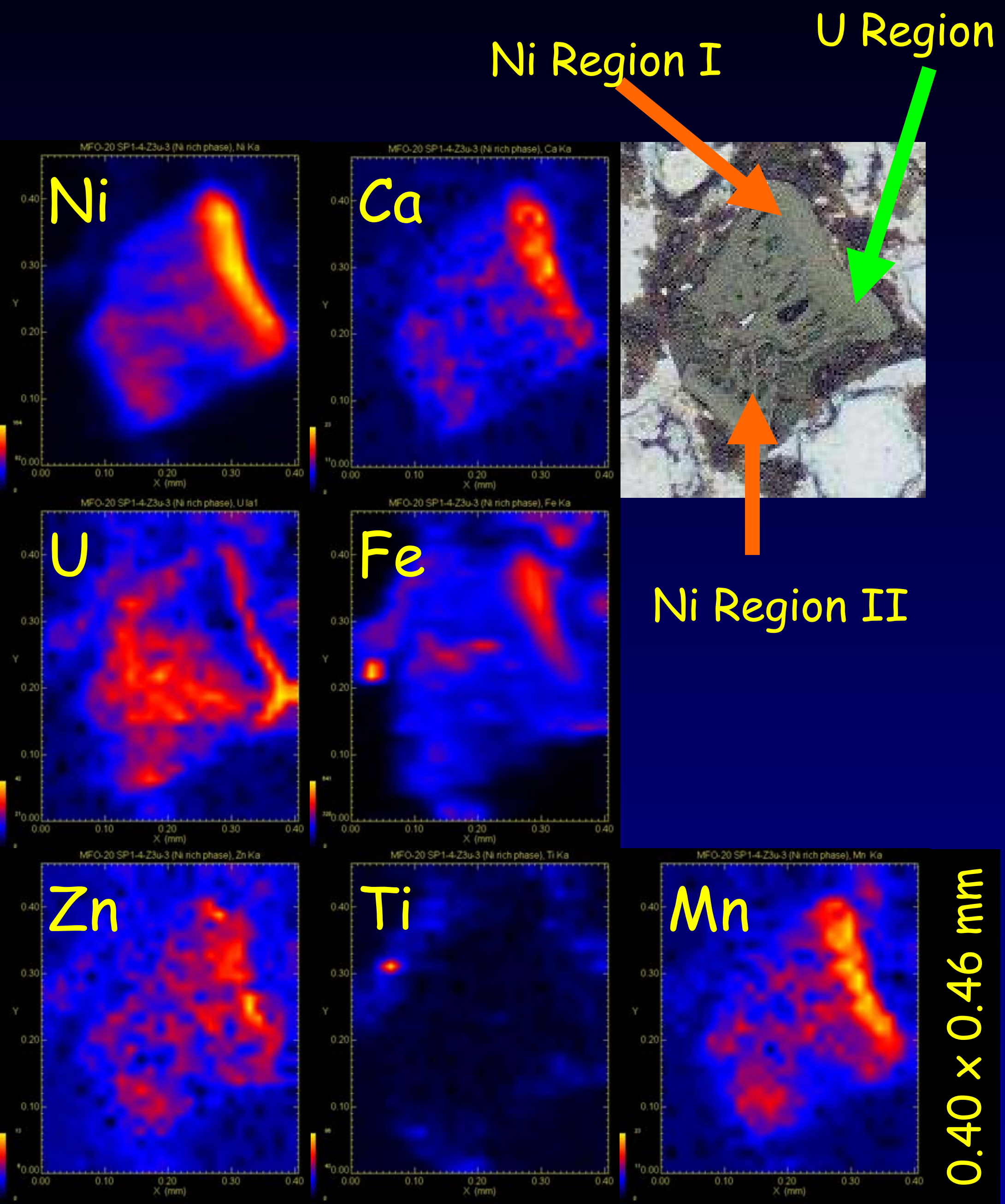


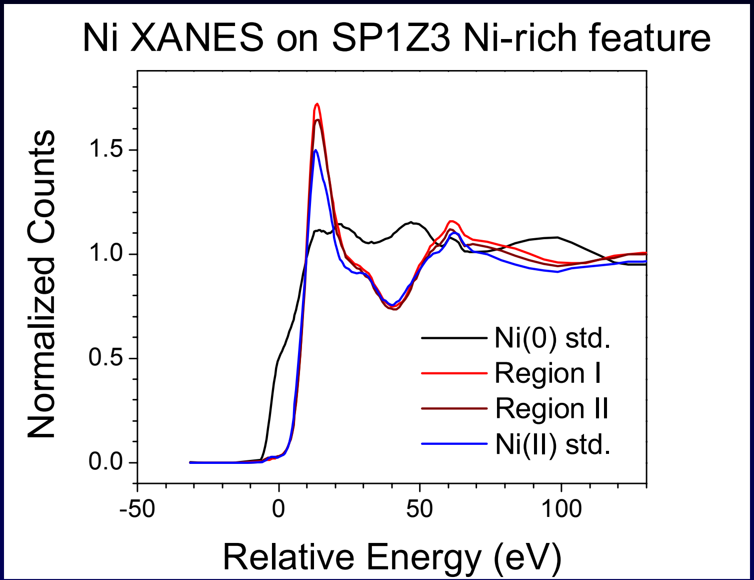


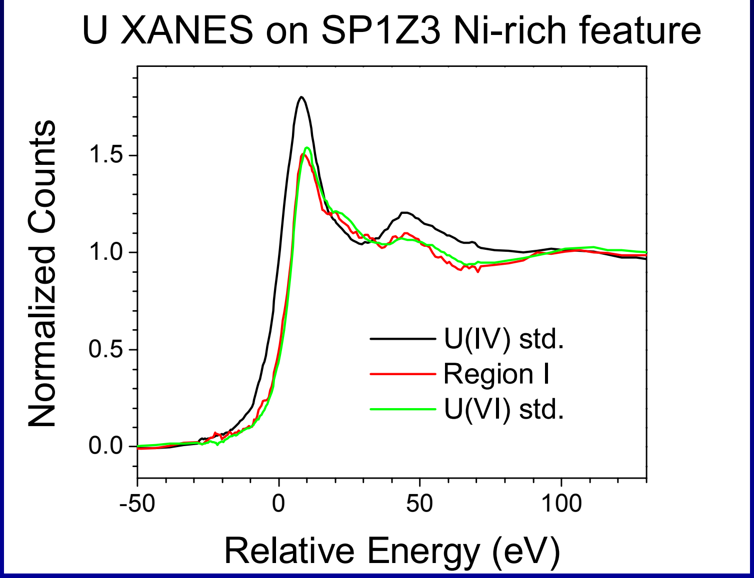
U-XANES on Organic Features



SXRF and XANES characterization of Ni-rich feature, SP1Z3



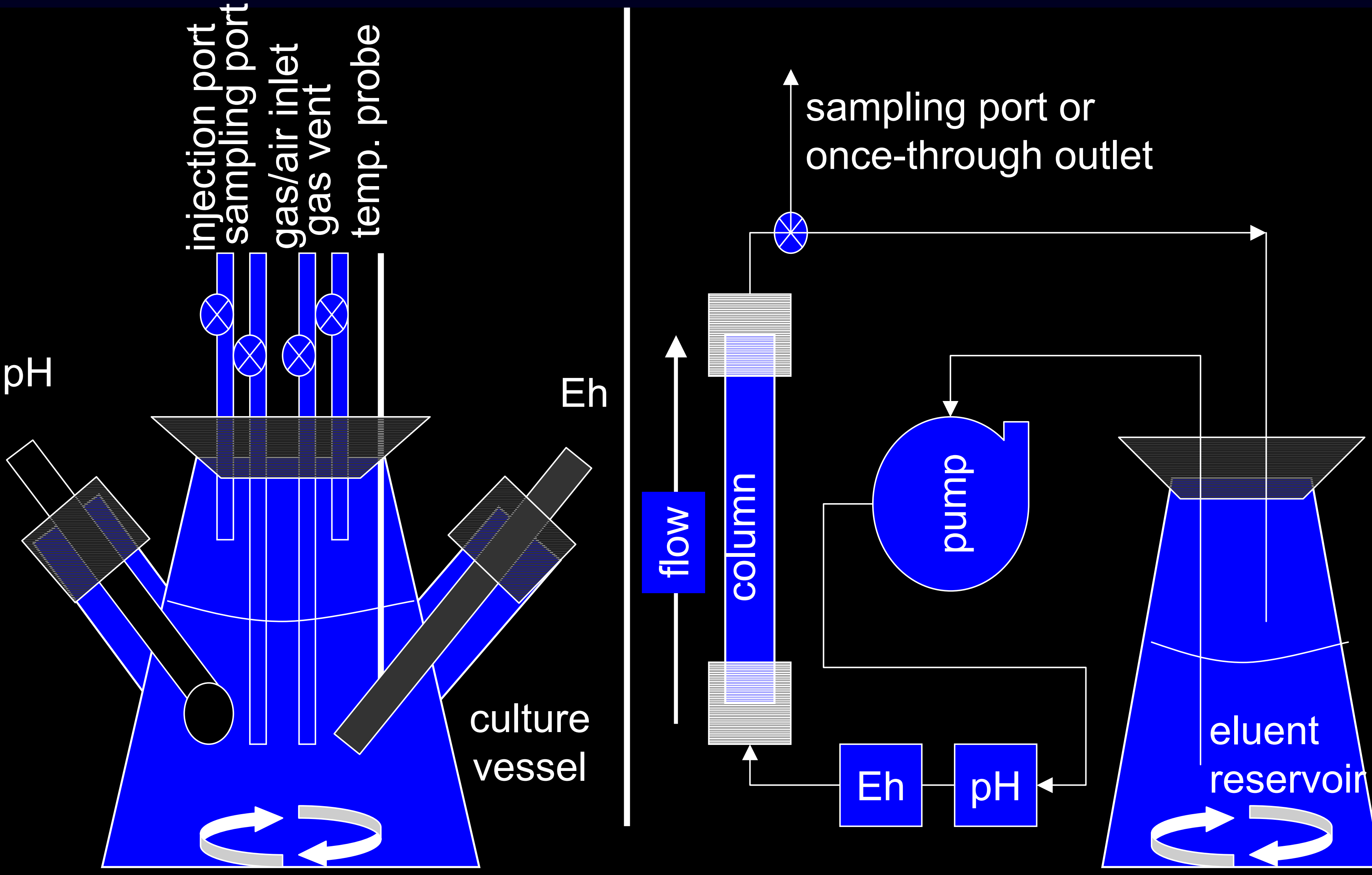




Phase II: Solubility, desorption kinetics, and aqueous speciation

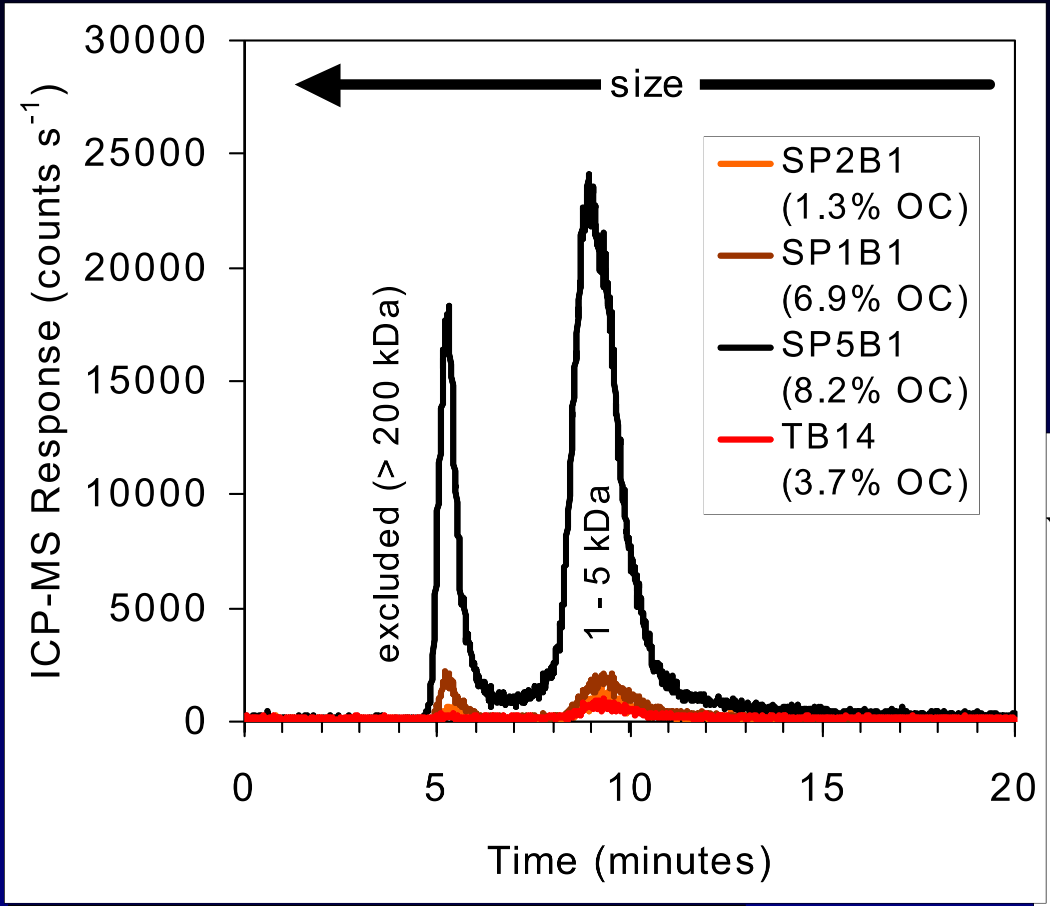
- Flow through column studies (once through)
  - aged and spiked sediments
  - kinetic desorption data
  - range of leaching conditions (eluant selection)
- Sediment incubations
  - batch and recirculating column systems
  - effects of key parameters: pH, Eh, IS
- Aqueous speciation data
  - size-exclusion chromatography (SEC)
  - field flow fractionation (FFF)
  - ion exchange chromatography
  - voltammetry (e.g., complexometric titrations with Cu ISE)

Incubation Setups

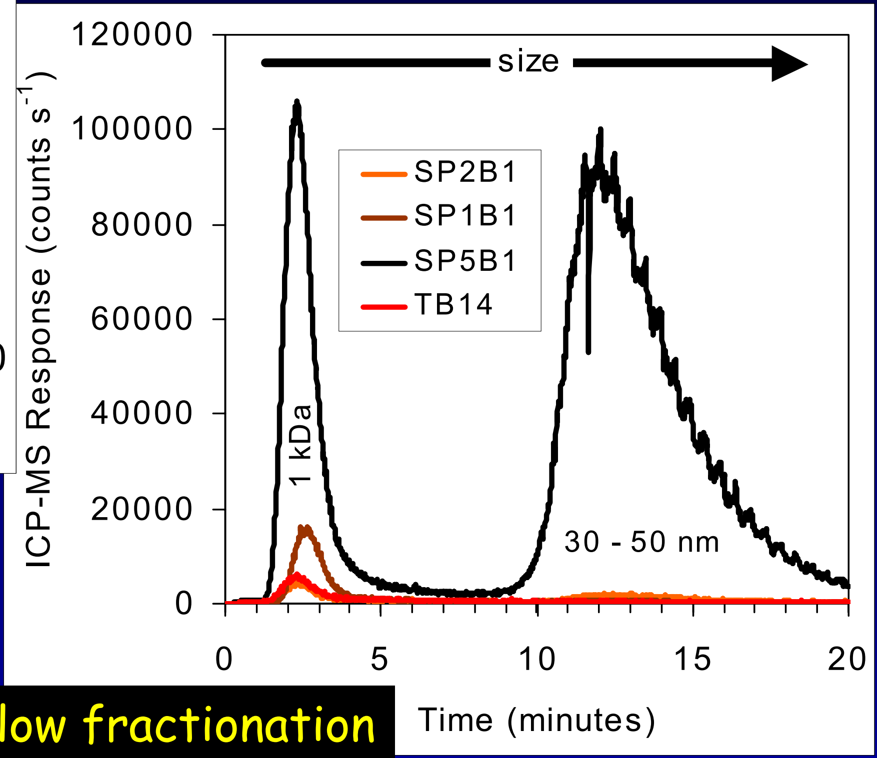


Aqueous U Speciation

- fulvic acid complexes
- organic and/or mineral colloids
- strong correlation with SOC and DOC
- unremarkable TB14



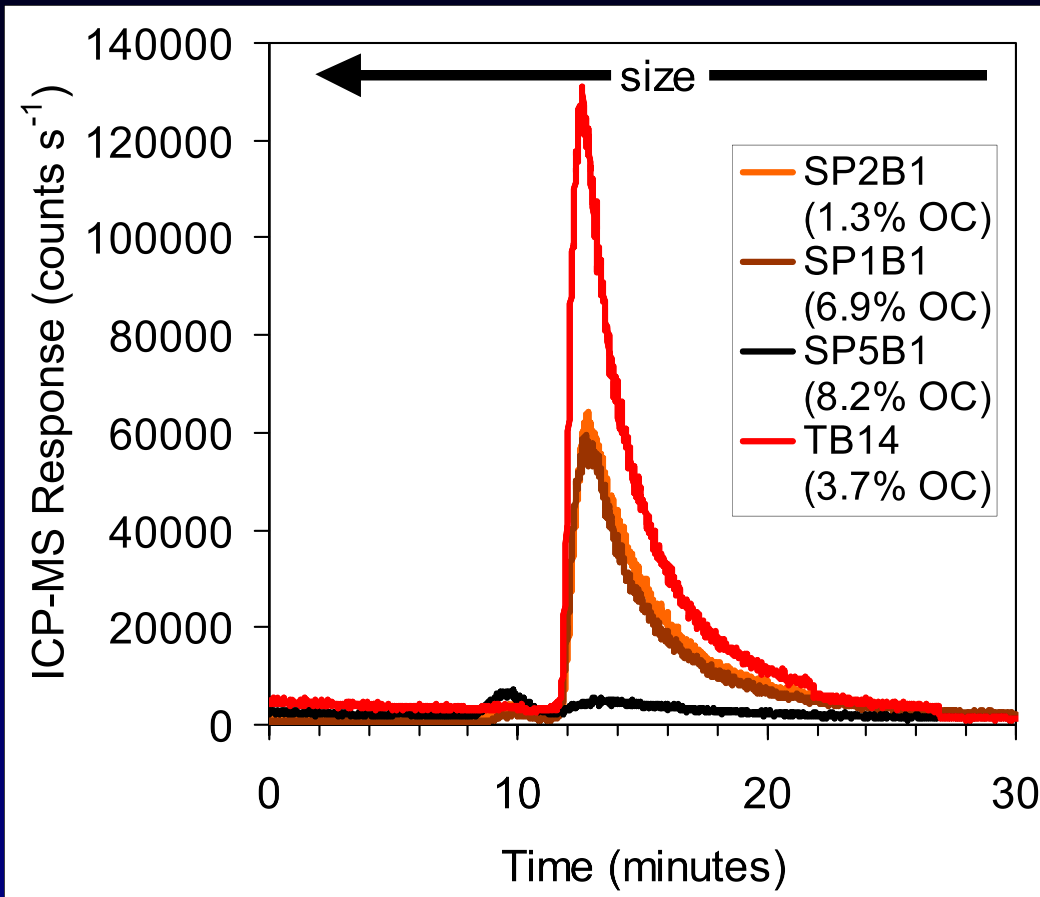
Size-exclusion chromatography



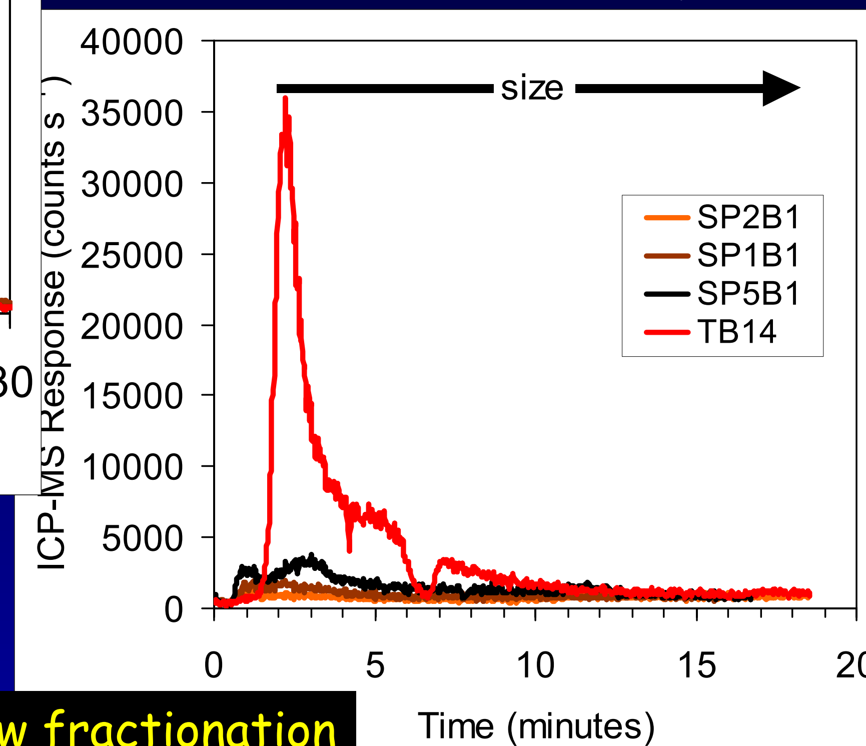
Field flow fractionation

Aqueous Ni speciation

- low MW complexes
- minimal colloidal Ni
- TB14 distribution
  - departure from SP
  - consistent with MetPLATE™ assays



Size-exclusion chromatography

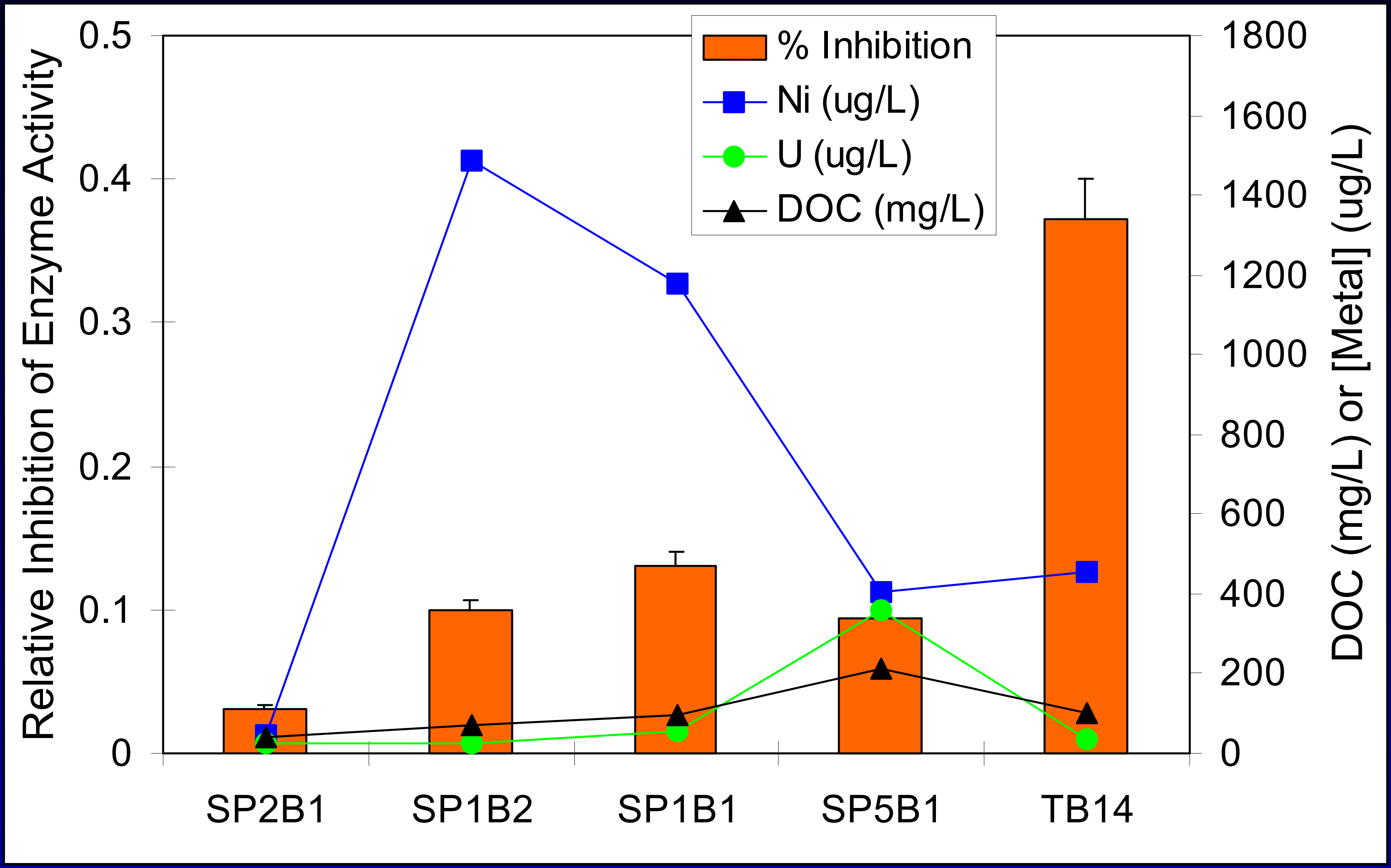


Field flow fractionation

Phase III: Biological endpoints

- Toxicity assays
  - MetPLATE™
- Uptake and toxicity assays
  - Earthworms
  - Nematodes

MetPLATE™ Toxicity Assay



Summary

- Ni more labile than U in sediments
- organic carbon
  - primary control for U
    - stationary phase
    - mobile colloids and aqueous complexes
  - secondary for Ni
- iron oxides
  - primary control for Ni
  - secondary for U
- heterogeneity at μm scale
- evidence for dynamic cycling in sediment-detritus system, especially Fe and organics

Acknowledgements

- Jim Ranville (Co. School of Mines)
- Tony Lanzirotti (Univ. of Chicago) and Bill Rao (Univ. of Georgia) at NSLS beamline X26A
- EPA/DOE/NSF/ONR Joint Program on Bioremediation for support of previous characterization and preliminary studies
- DOE-EMSP program for support of fundamental work on geochemistry of sediment-detritus cycling
- Paul Bayer (DOE-BER)

The End.

SXRF and XANES Methods

- Thin-sections
  - intact sediment cores embedded with resin
  - sectioned and polished to 30 μm
- SXRF and XANES performed at NSLS beamline X26A
  - Typical fluorescence setup
    - Kirkpatrick-Baez mirrors for focusing
    - Si(111) monochromator
    - Si(Li) detector at 90° and sample at 45° to beam
  - ~10 x 15 to 15 x 20 μm beam spot size
- 2D SXRF mapping
  - 15 to 20 μm step size
  - 17.2 keV monochromatic beam
- XANES
  - 0.5 eV monochromator step size
  - 17.166 keV U L_{III}-edge

Aqueous Speciation of Ni and U via Size Separation

- 2.5 : 1 (ml : g) DDI water of bulk sediments for 24 hours
- Size-exclusion chromatography (SEC)
  - 200 kDa exclusion gel-filtration column
  - 50 mM NH_4NO_3 carrier
  - pH 5.6
  - 1 ml min^{-1}
- Field flow fractionation (FFF)
  - 10 mM NH_4NO_3 eluant
  - pH 5.6
  - 1 ml min^{-1} channel flow
  - 3 ml min^{-1} cross flow for 2 min, linear decay to 0.1 ml min^{-1} at 10 min, 0.1 ml min^{-1} to 20 min
- Directly coupled to ICP-MS