Acceleration of Field-Scale Bioreduction of U(VI) in a Shallow Alluvial Aquifer: *Temporal and Spatial Evolution of Biogeochemistry*

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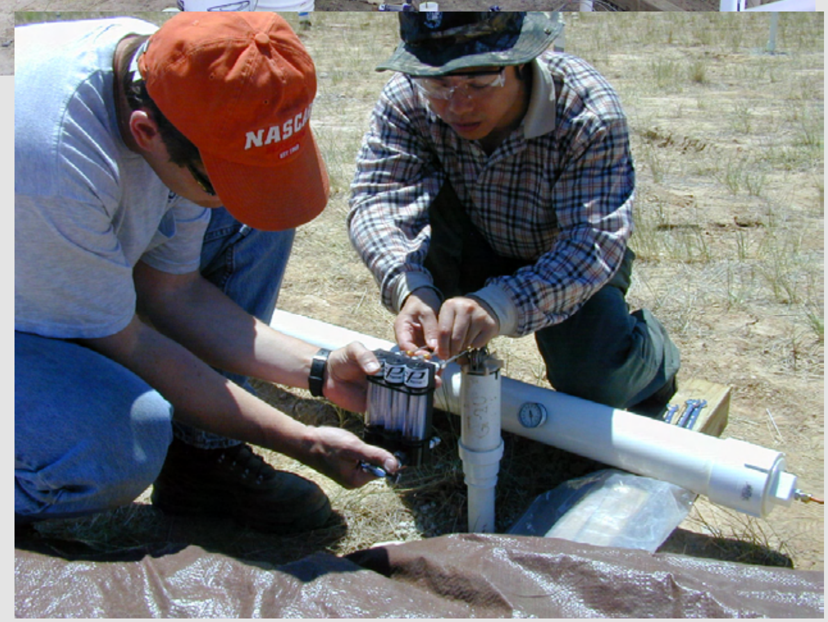
Outline of Presentation

- Background and overall objectives of field-scale experiments
- Overview of biostimulation experiments (2002, 2003, 2004)
- Predictions for U(IV) re-oxidation
- Observed U(VI) behavior
- Possible mechanisms for prolonged U(VI) loss
- Planned future experiments
- Summary



Old Rifle UMTRA Site Collaborators

Collaborators	Principal Activities
Derek Lovley, Kelly Nevin, Helen Vrionis, Regina O'Neil, Irene Ortiz-Bernad, Dawn Holmes (Umass)	Microbiology, genomics, 16s clone libraries, mRNA, geochemistry
David White, Aaron Peacock, Janet Chang (Univ. of Tennessee)	Phospholipid fatty acid profiles, Stable isotope probing (SIP), in-well coupons
Richard Dayvault and Stan Morrison (S.M. Stoller Corp.)	Drilling and sampling field activities, sorption measurements
Peter Jaffe (Princeton), John Zachara (PNNL)	Reoxidation column studies, solids characterization
Susan Hubbard, Ken Williams (LBNL)	Geophysics (complex resistivity)
C. Tom Resch, Phil Long, Jim McKinley (PNNL)	Field sampling, in-well incubator analysis, geochemistry, hydrology
Steve Yabusaki, Yilin Fang (PNNL)	Reactive transport modeling
Darrell Chandler (ANL), Ann Jarrell, (PNNL)	DNA Chip and Bead Arrays

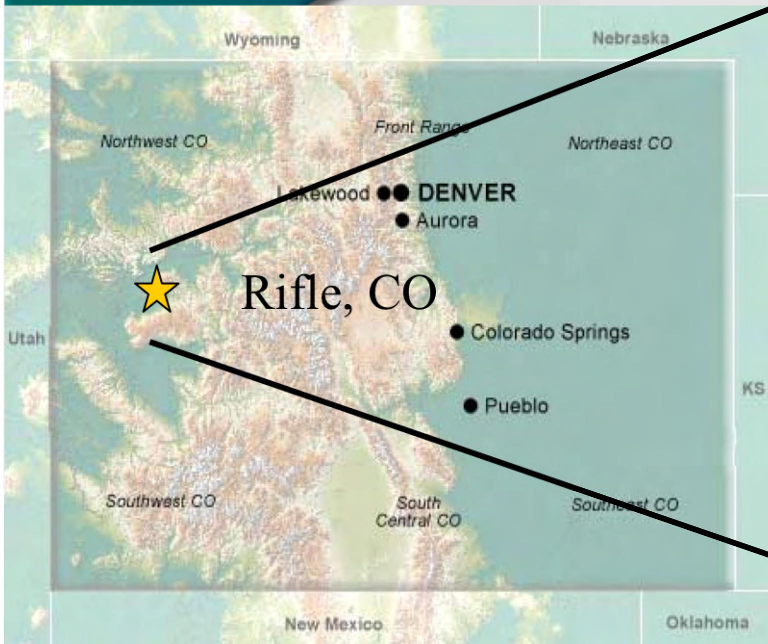
Background and Overall Objectives

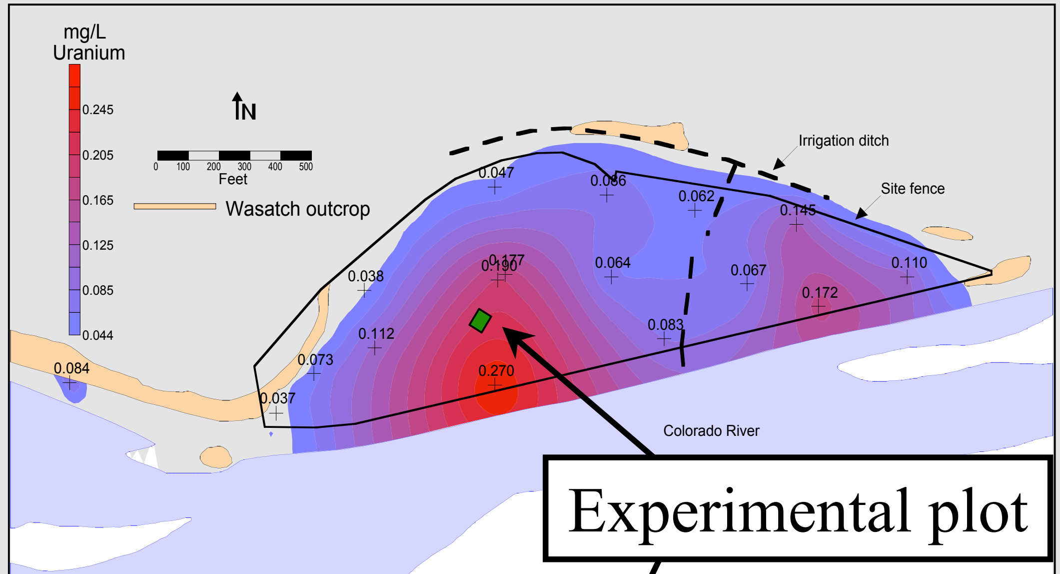
Uranium mill tailings sites provide access to uranium-contaminated groundwater at sites that are *shallow and low hazard*, making it possible to address the following scientific objectives:

- *Determine the dominant electron accepting processes at field sites with long-term metal/rad contamination*
- *Define the biogeochemical transformations that may be important to either natural or accelerated bioremediation under field conditions*
- *Examine the potential for using biostimulation (electon donor addition) to accelerate reduction of U(VI) to U(IV) at the field scale*

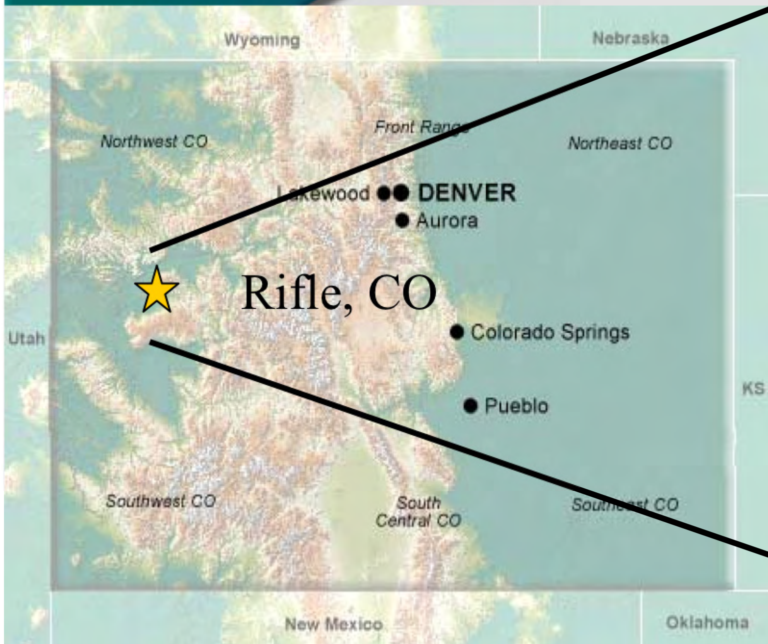
Summary of Field Experiments

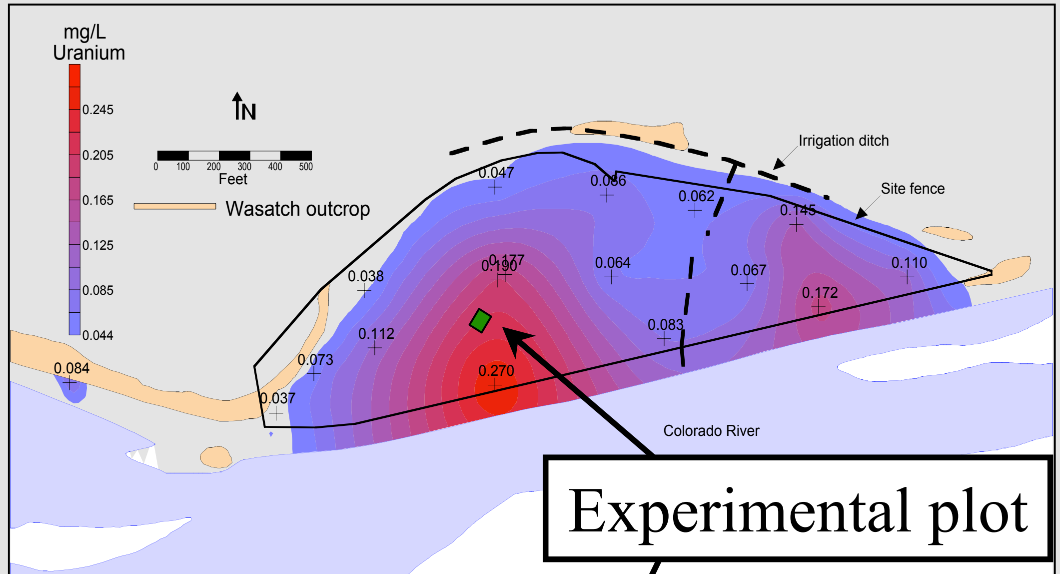
Field Experiment	*Objectives*	*Observations*	*Conclusions*
2002	Determine if biostimulation removes U(VI) from groundwater	U(VI) loss; loss rate decreases with sulfate reduction; Geobacter growth	Electron donor amendment works at the field scale, Geobacter responsible for U(VI) loss
2003	Extend Fe(III) reduction and U(VI) loss in time and space by increasing acetate concent.	Extensive sulfate reduction, Fe(III) reduction down gradient, U(VI) loss; prolonged U(VI) reduction post-acetate addition	Increasing electron donor works, but sulfate reduction may be problematic or may help limit reoxidation
2004	Replicate U(VI), obtain genomic and mRNA samples, stable isotope probing, test geophysics for detecting biostimul.	U(VI) similar to 2002 experiment. Geobacter dominance, ^{13}C observed in PLFA, complex resistivity response	U(VI) loss replicable at field scale, mRNA promising for site assessment and monitoring of remediation, others TBD

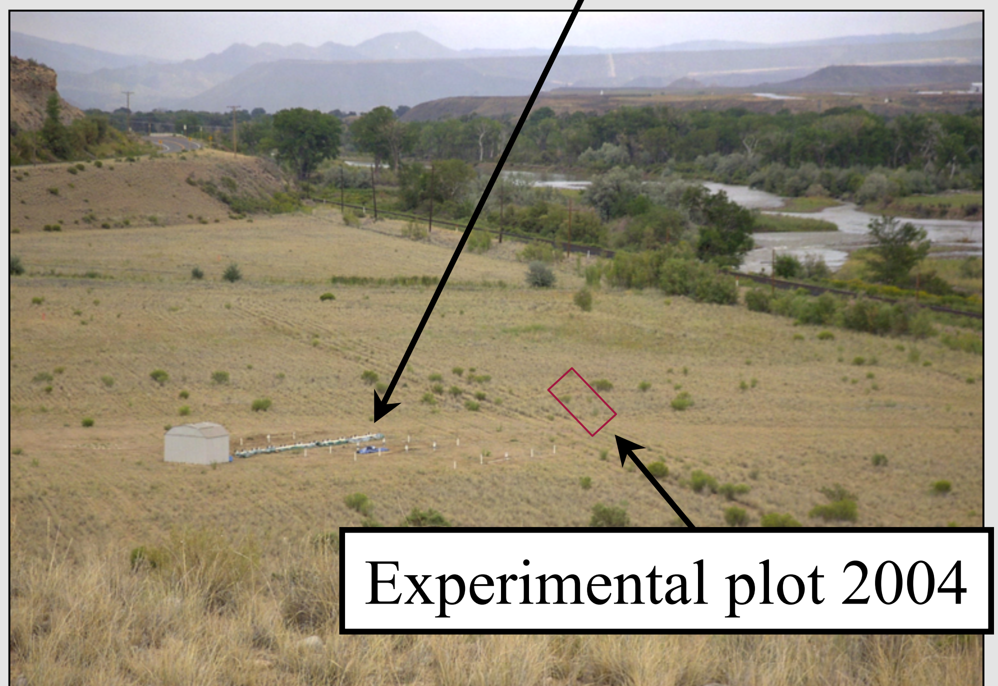




The experimental plot is located in a part of a uranium plume with ~ 0.6 to 1.2 uM U(VI), residual from when the site was used as a uranium ore processing facility. The Colorado River flow has a major impact on groundwater flow at the site.







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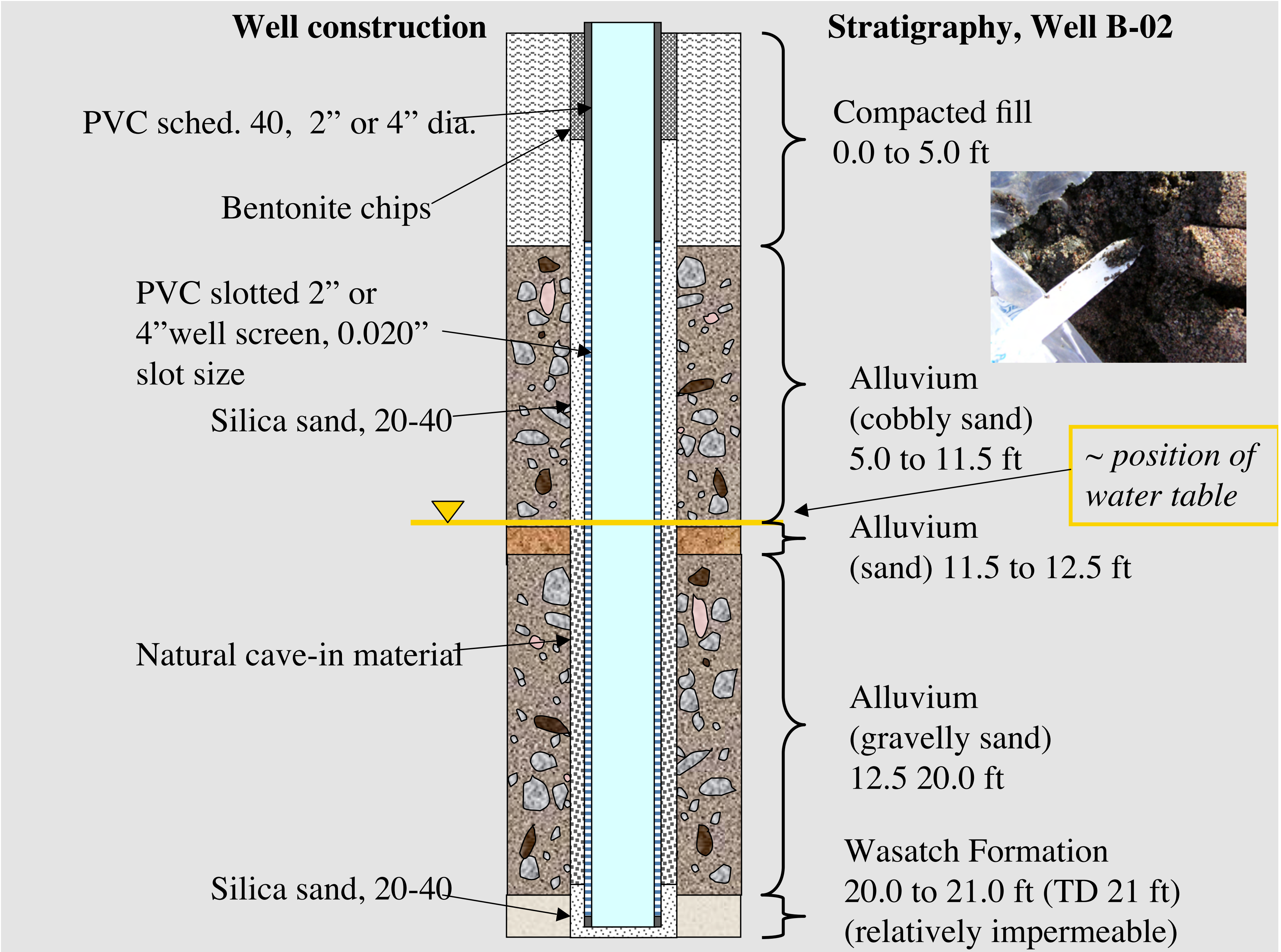
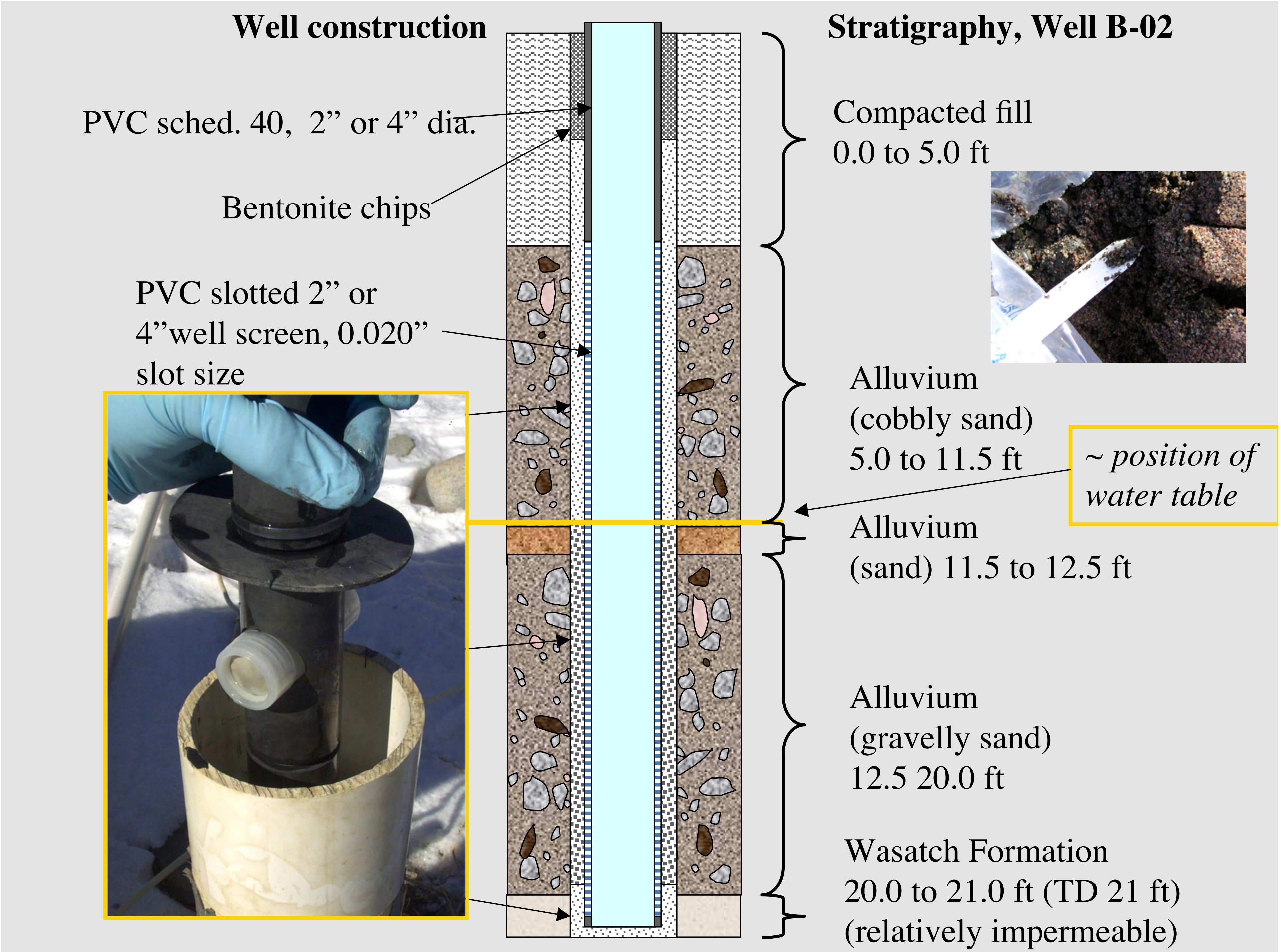

Well construction
Stratigraphy, Well B-02
PVC sched. 40, 2” or 4” dia.
Bentonite chips
PVC slotted 2” or
4”well screen, 0.020”
slot size
Silica sand, 20-40
Natural cave-in material
Silica sand, 20-40
Compacted fill
0.0 to 5.0 ft
Alluvium
(cobbly sand)
5.0 to 11.5 ft
~ position of
water table
Alluvium
(sand) 11.5 to 12.5 ft
Alluvium
(gravelly sand)
12.5 20.0 ft
Wasatch Formation
20.0 to 21.0 ft (TD 21 ft)
(relatively impermeable)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PVC sched. 40, 2” or 4” dia.
Bentonite chips
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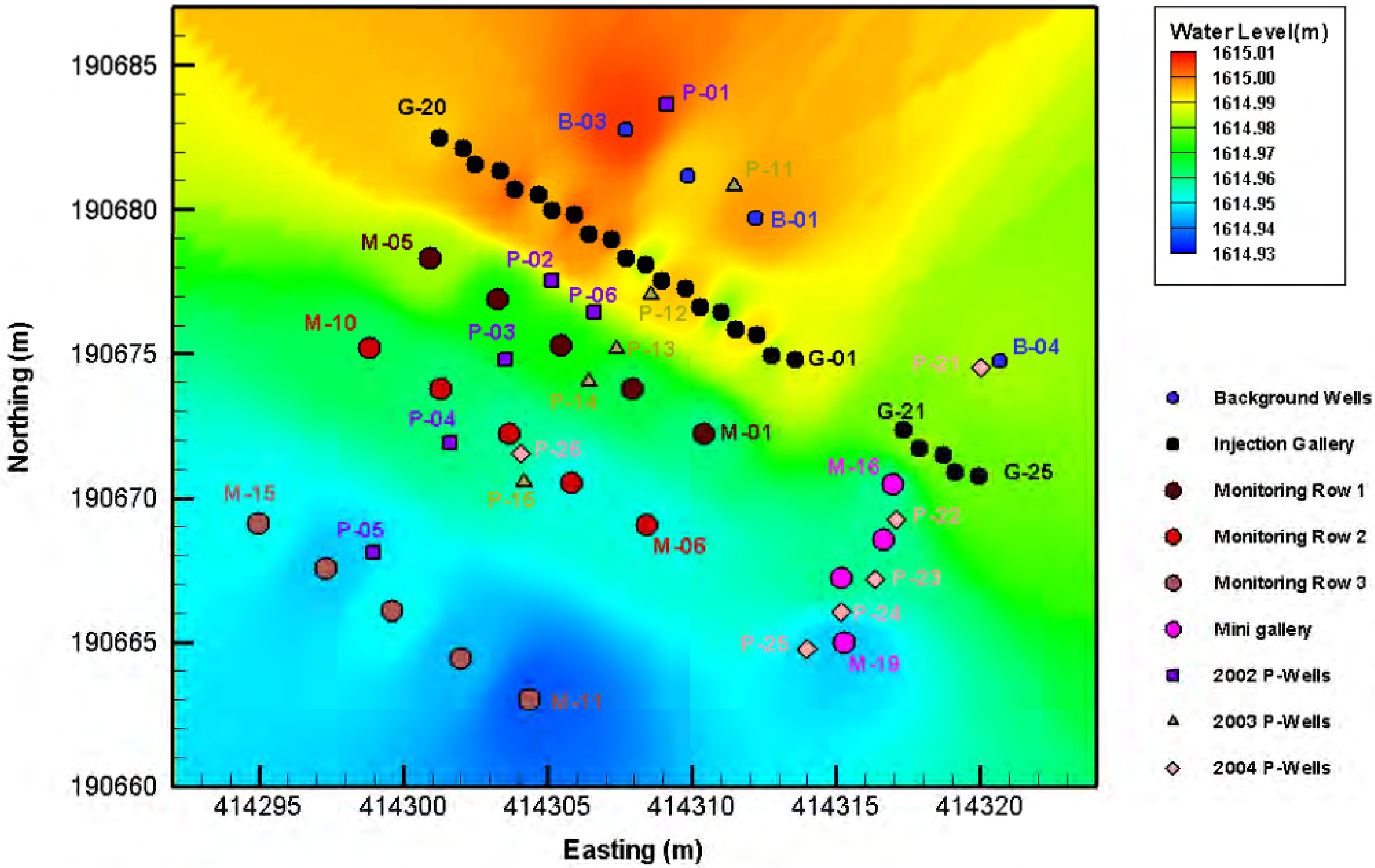
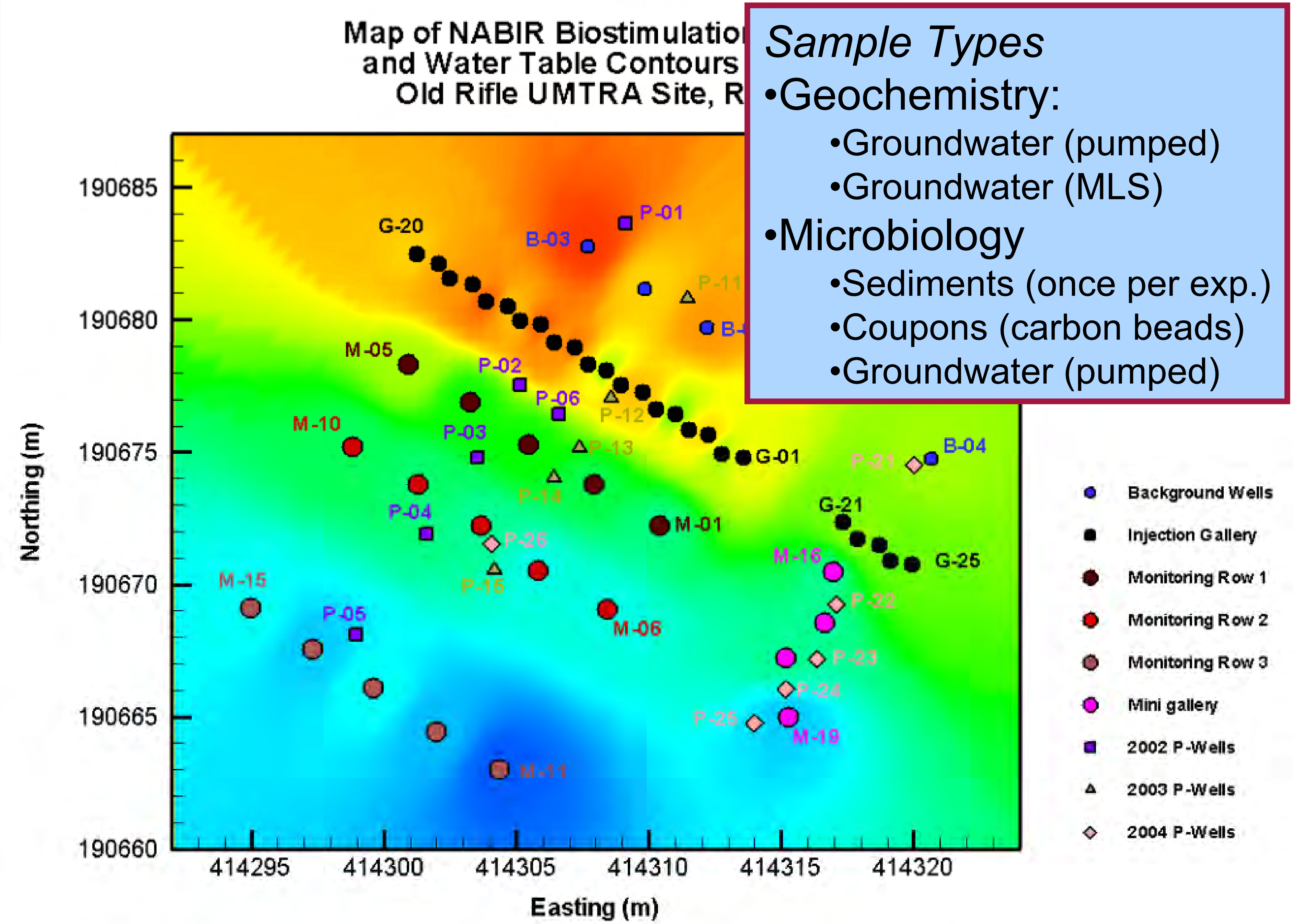
Compacted fill 0.0 to 5.0 ft
Alluvium (cobbly sand) 5.0 to 11.5 ft
~ position of water table
Alluvium (sand) 11.5 to 12.5 ft
Alluvium (gravelly sand) 12.5 20.0 ft
Wasatch Formation 20.0 to 21.0 ft (TD 21 ft) (relatively impermeable)

Map of NABIR Biostimulation Well Field
and Water Table Contours (04/07/05)
Old Rifle UMTRA Site, Rifle, CO

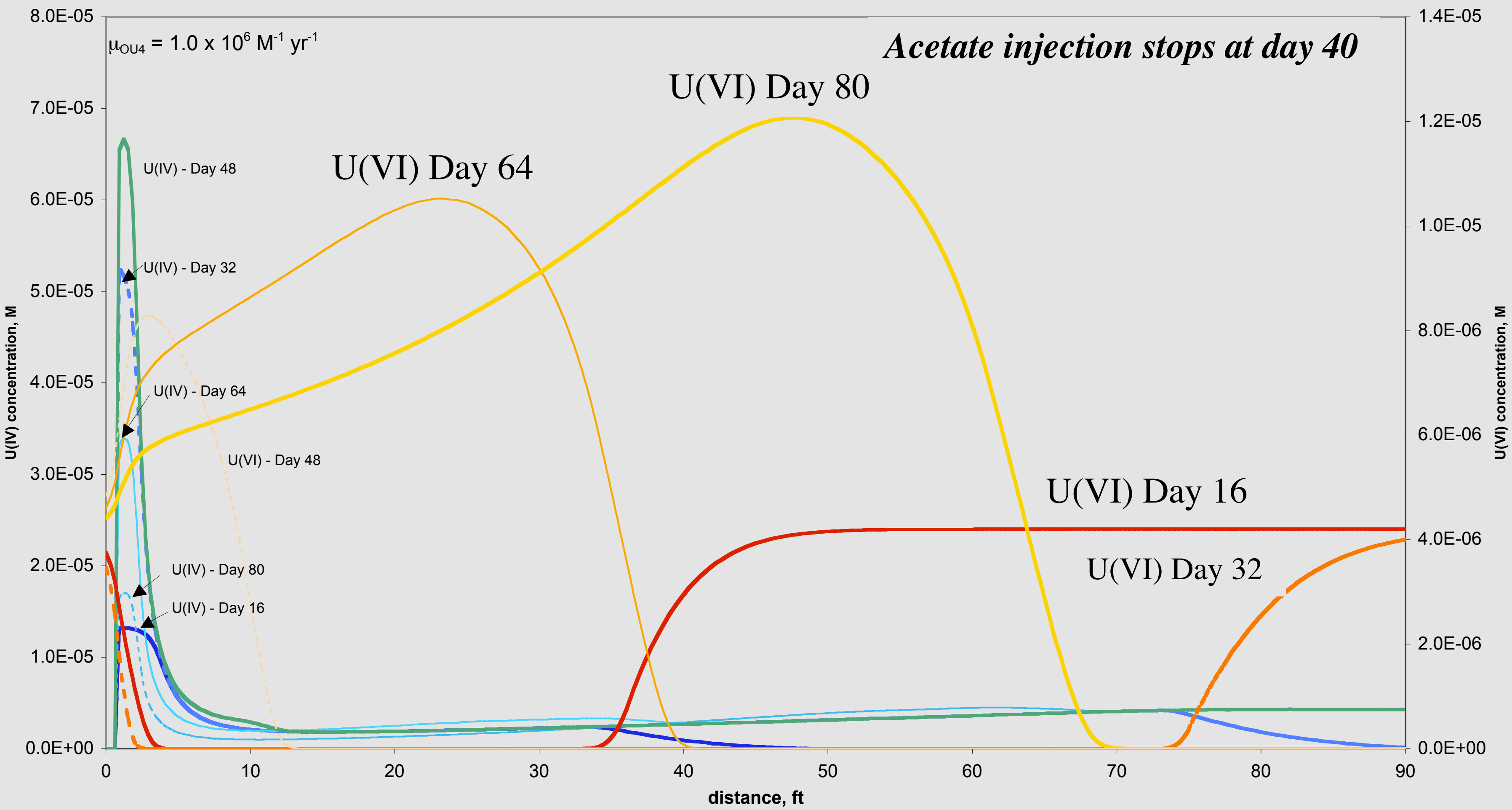




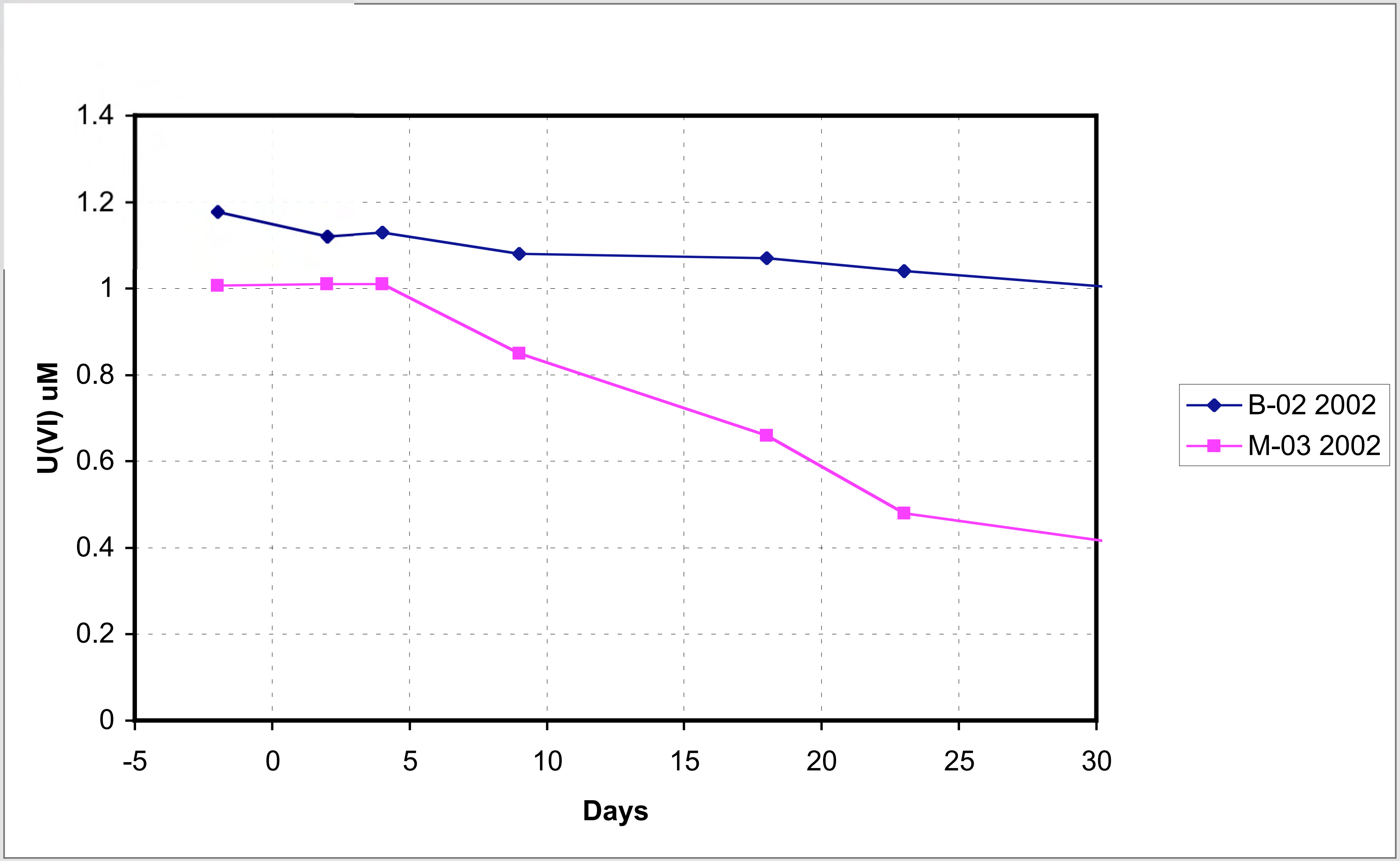
Sample Types

- Geochemistry:
  - Groundwater (pumped)
  - Groundwater (MLS)
- Microbiology
  - Sediments (once per exp.)
  - Coupons (carbon beads)
  - Groundwater (pumped)

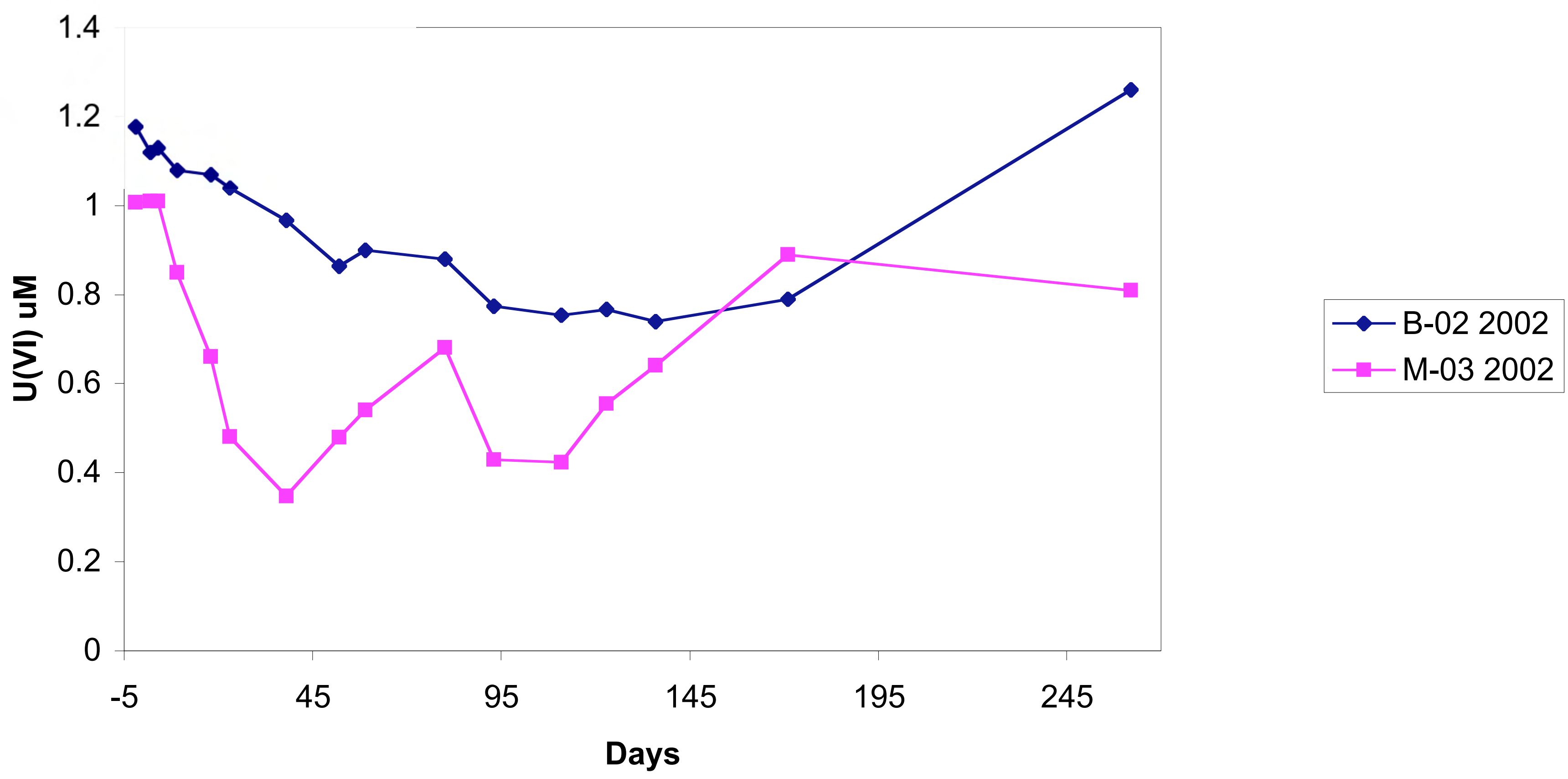
Simulated U Concentrations over 80 days



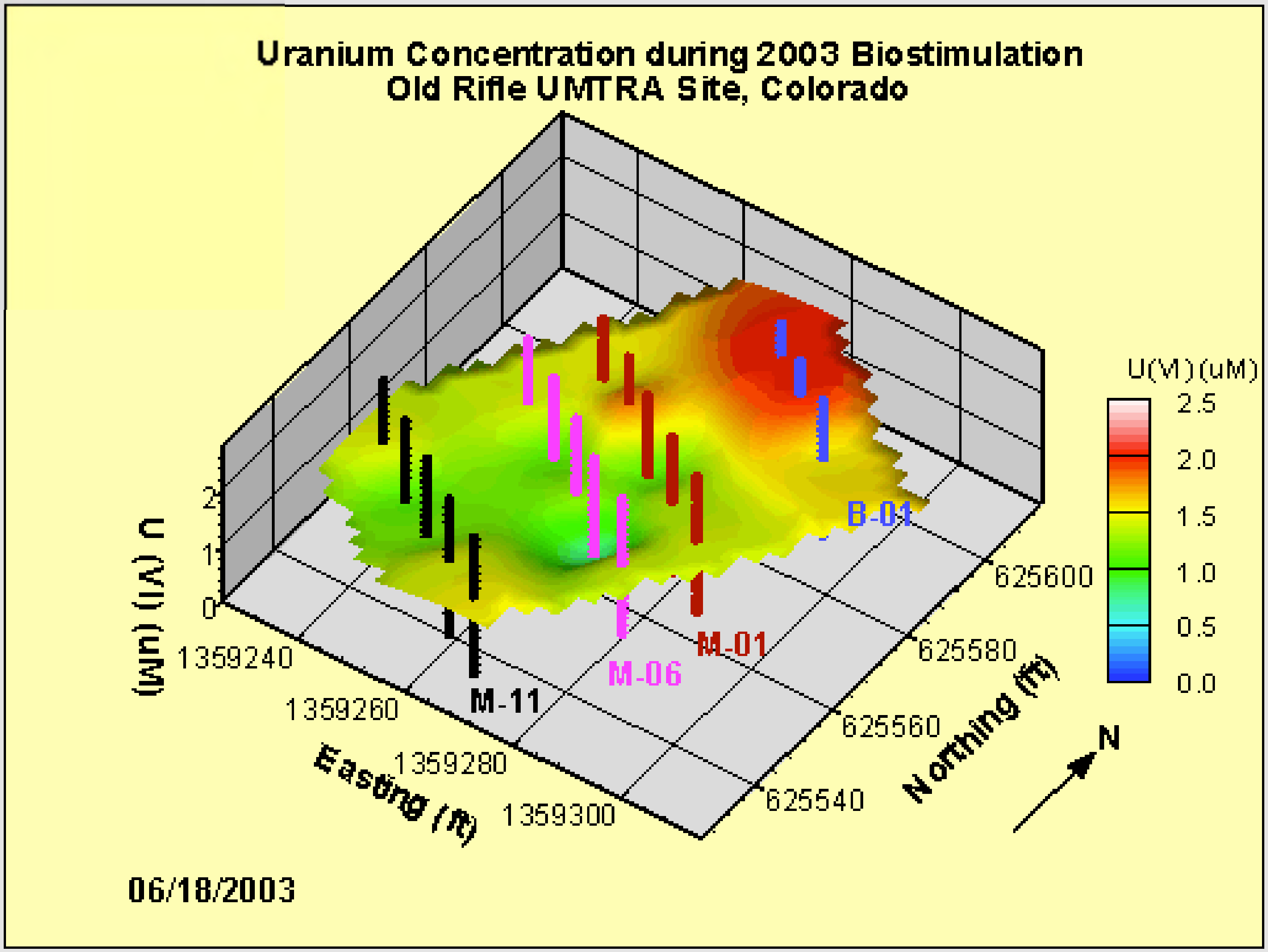
U(VI) Loss for the 2002 Field Experiment

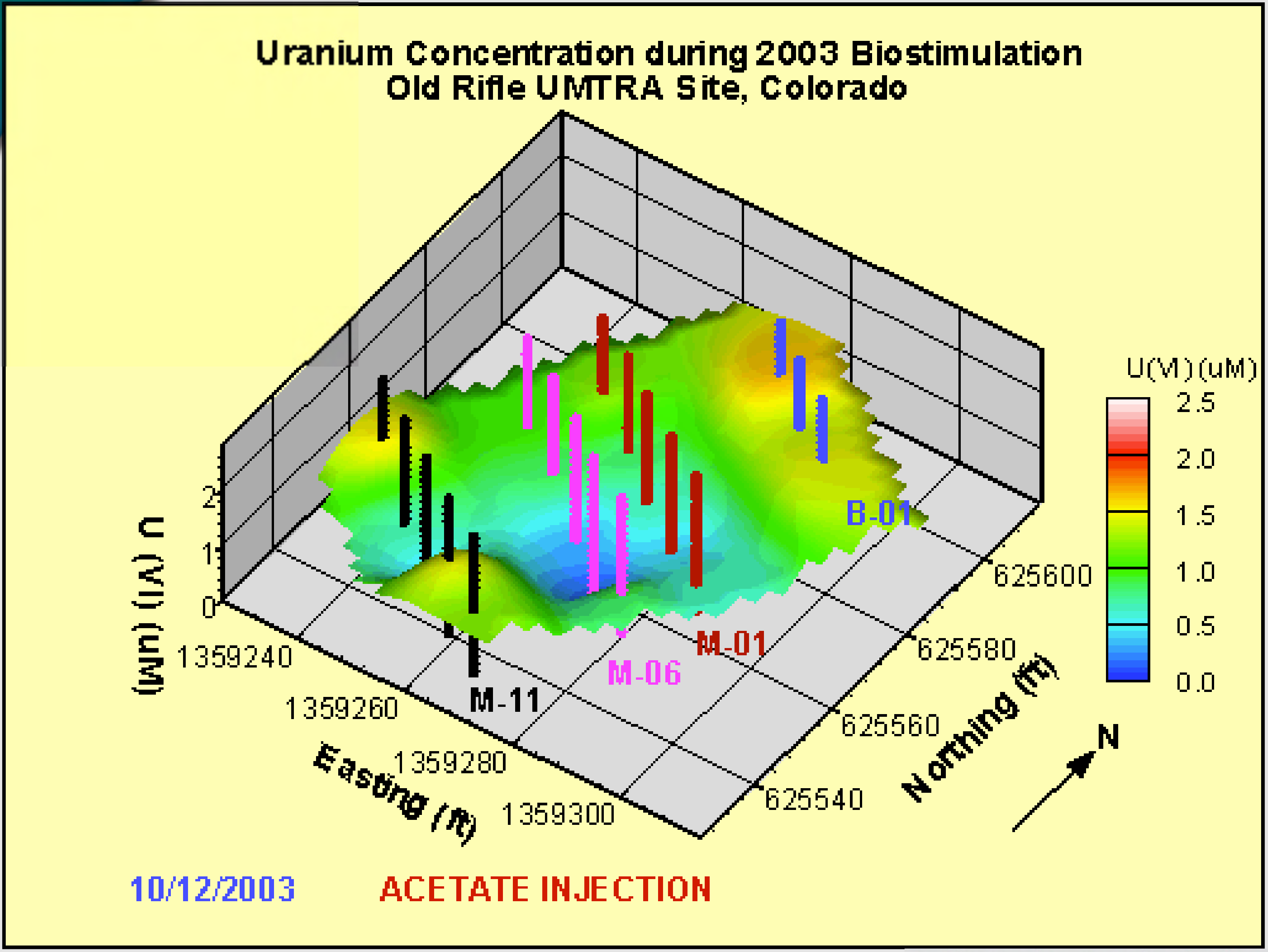


2002 U(VI) loss



U(VI) at start of 2003





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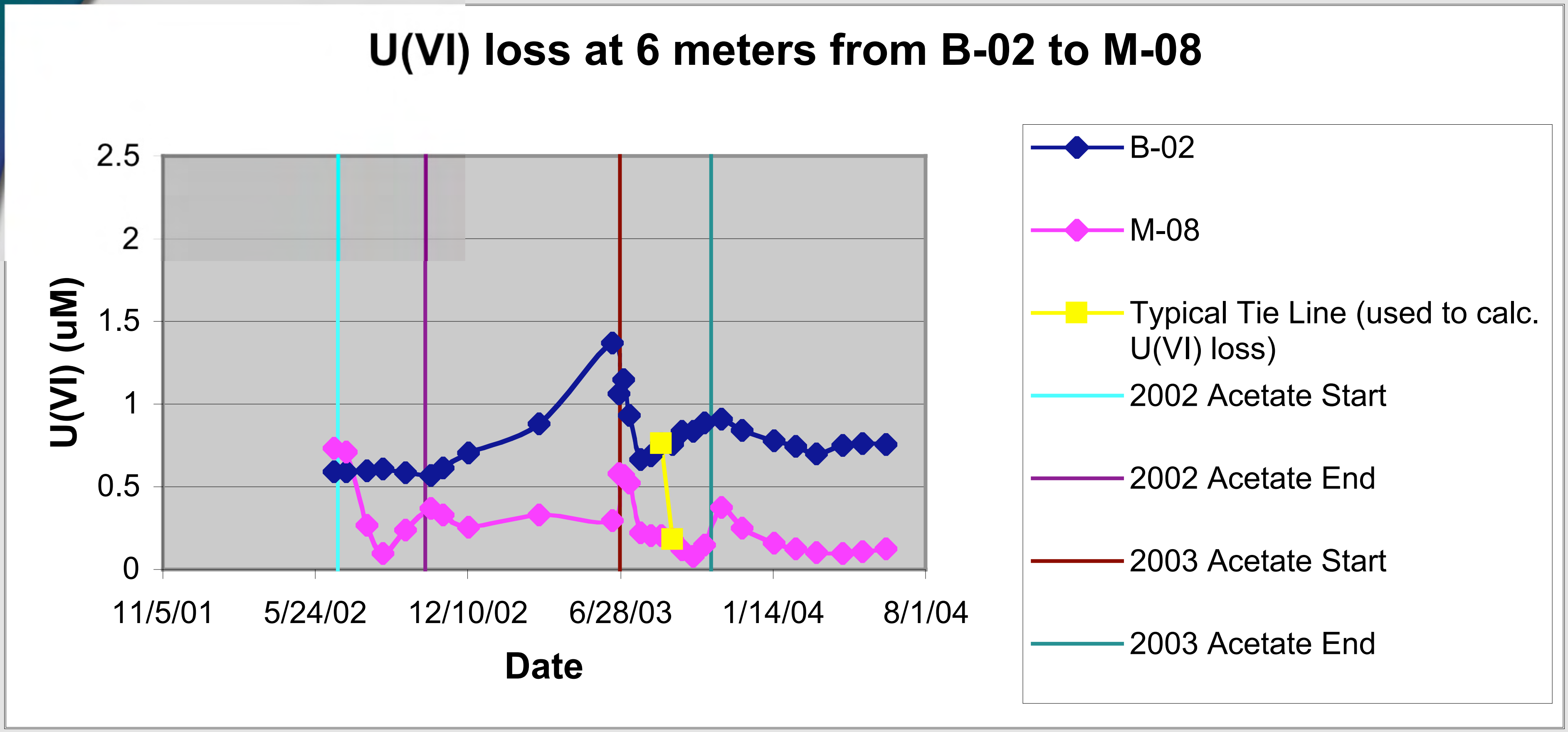
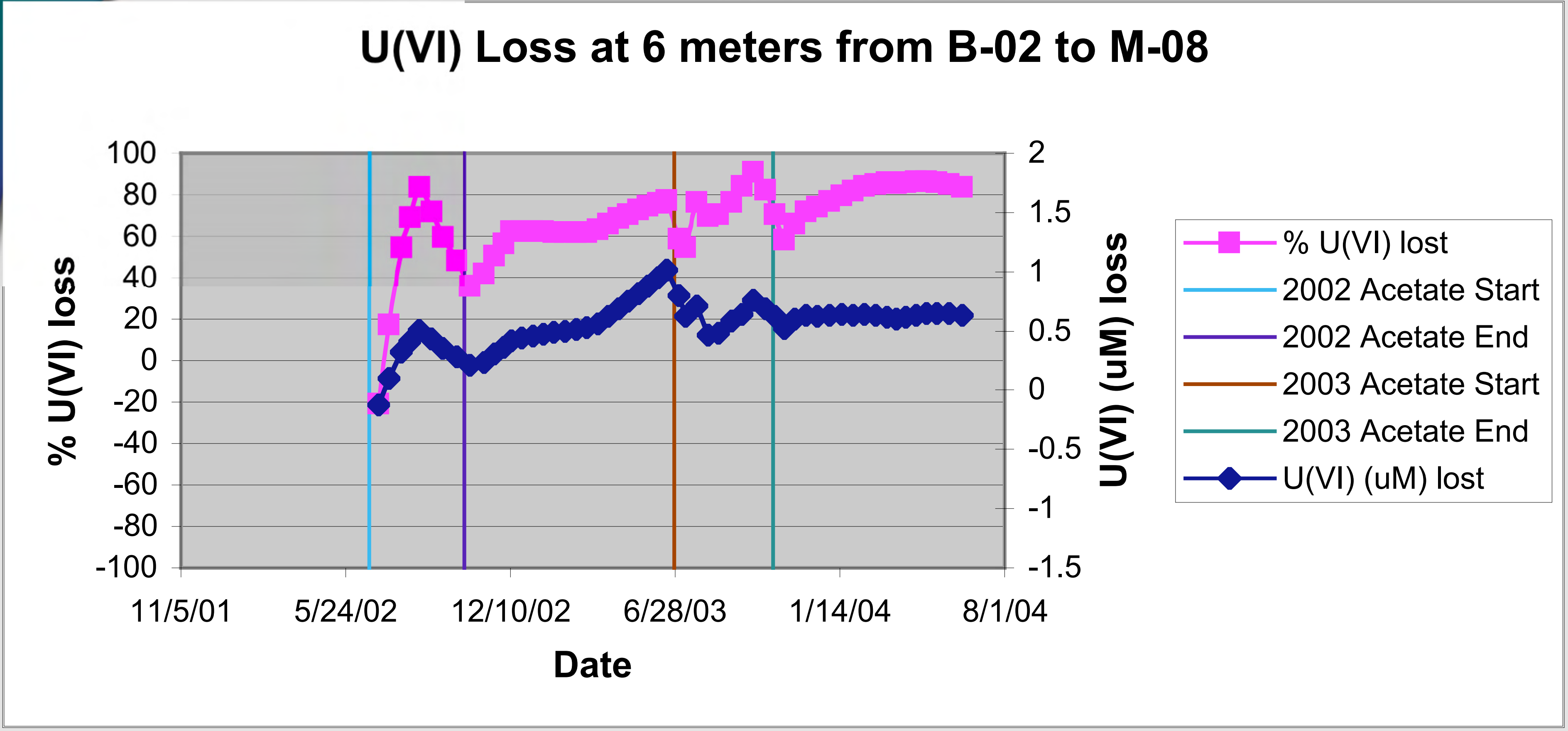
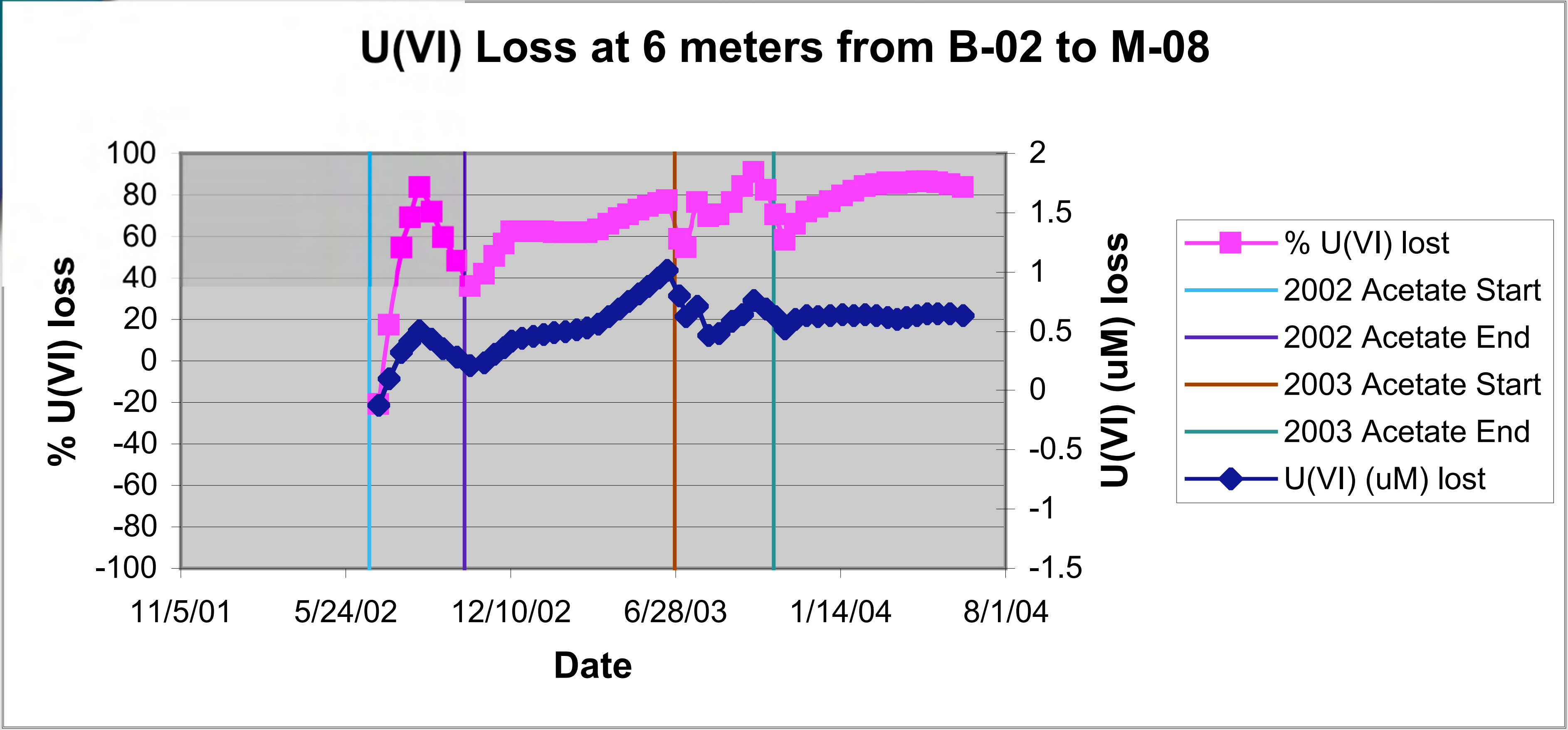

U(VI) loss at 6 meters from B-02 to M-08
2.5
2
1.5
1
0.5
0
U(VI) (uM)
11/5/01
5/24/02
12/10/02
6/28/03
1/14/04
8/1/04
Date
B-02
M-08
Typical Tie Line (used to calc. U(VI) loss)
2002 Acetate Start
2002 Acetate End
2003 Acetate Start
2003 Acetate End

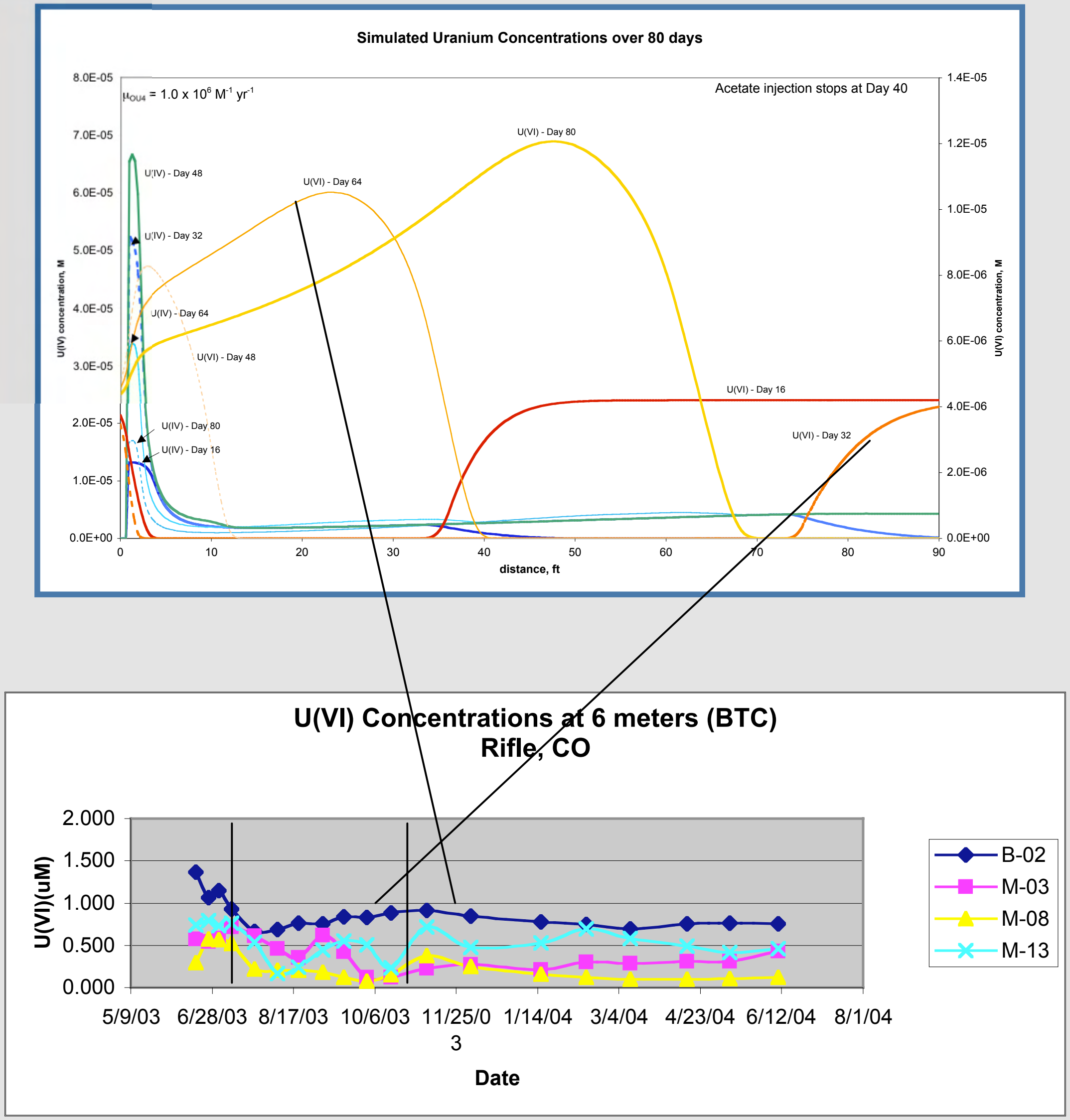
U(VI) loss for both 2002 and 2003 experiments



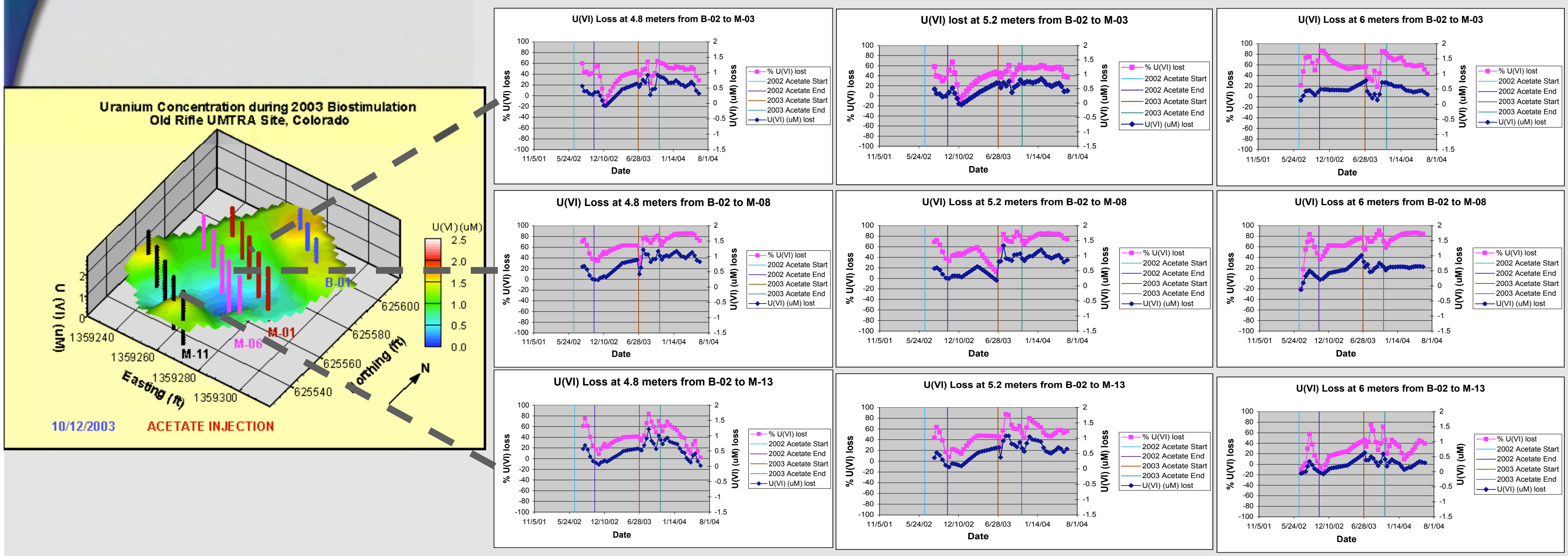
U(VI) loss for both 2002 and 2003 experiments



Current status as of April 7, 2005:
~50% loss 1.5 years post-acetate amendment


Simulated Uranium Concentrations over 80 days
Acetate injection stops at Day 40
U(VI) - Day 80
U(VI) - Day 64
U(VI) - Day 48
U(VI) - Day 32
U(VI) - Day 16
U(IV) - Day 48
U(IV) - Day 32
U(IV) - Day 64
U(IV) - Day 80
U(IV) - Day 16
U(VI) concentration, M
distance, ft
U(VI) Concentrations at 6 meters (BTC)
Rifle, CO
U(VI)(uM)
Date
B-02
M-03
M-08
M-13

U(VI) loss in 1st, 2nd, & 3rd rows at 4.8, 5.2, & 6.0 m



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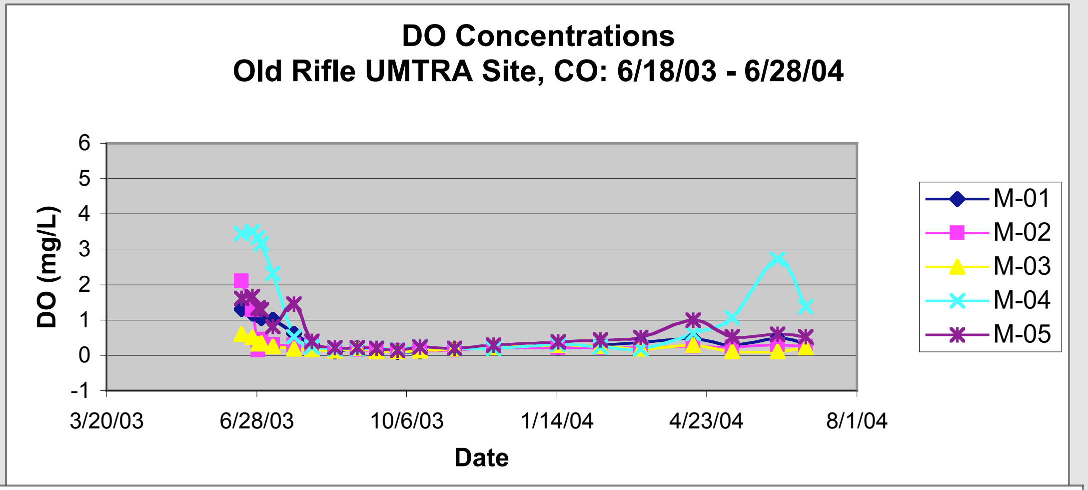
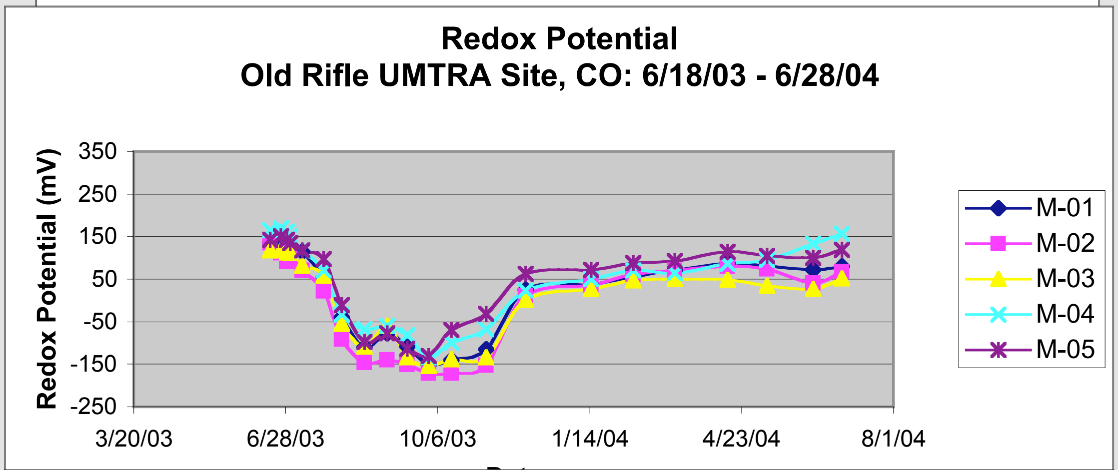
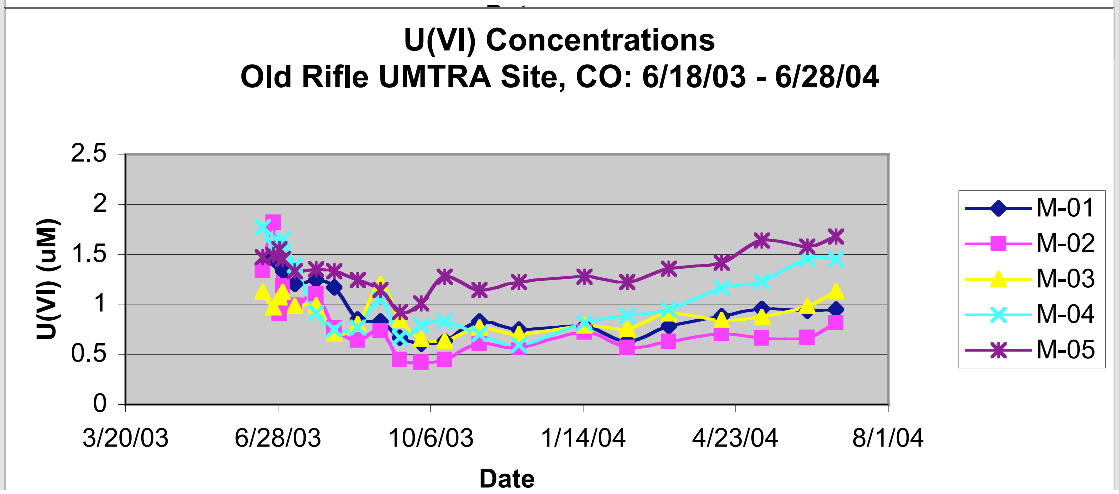
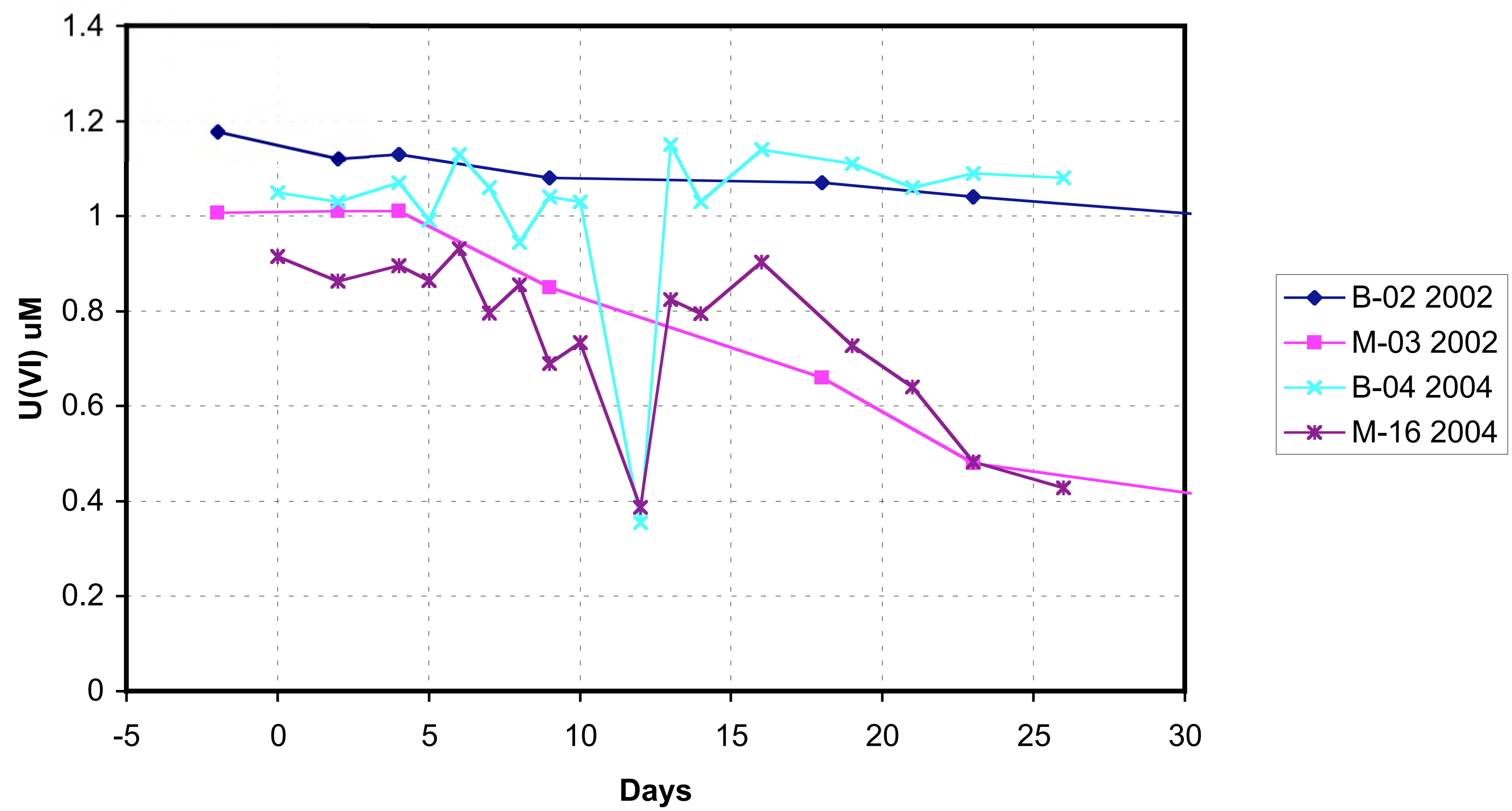

DO Concentrations
Old Rifle UMTRA Site, CO: 6/18/03 - 6/28/04
DO (mg/L)
6
5
4
3
2
1
0
-1
3/20/03
6/28/03
10/6/03
1/14/04
4/23/04
8/1/04
Date
M-01
M-02
M-03
M-04
M-05

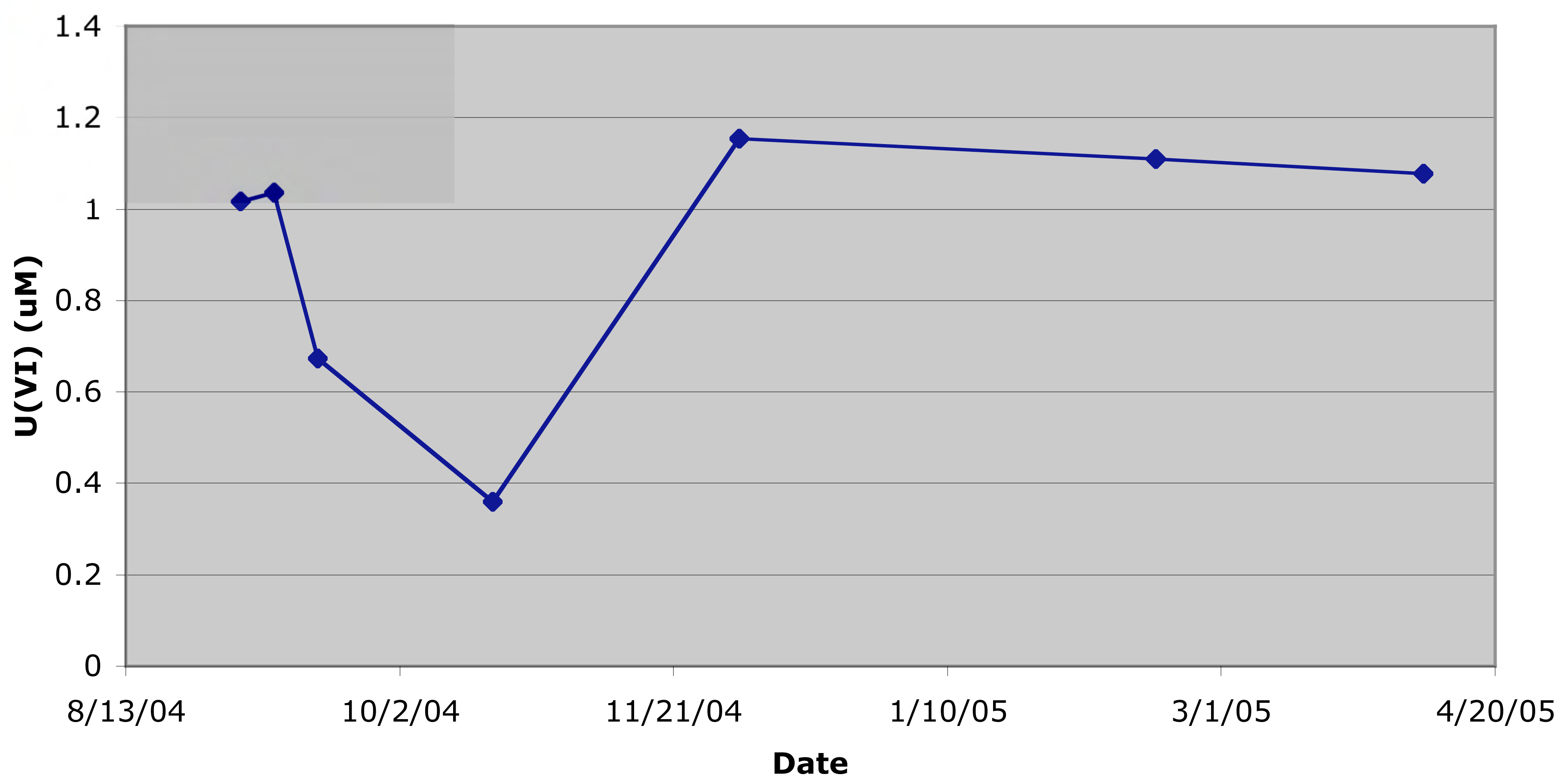

Redox Potential
Old Rifle UMTRA Site, CO: 6/18/03 - 6/28/04
Redox Potential (mV)
350
250
150
50
-50
-150
-250
3/20/03
6/28/03
10/6/03
1/14/04
4/23/04
8/1/04
M-01
M-02
M-03
M-04
M-05


U(VI) Concentrations
Old Rifle UMTRA Site, CO: 6/18/03 - 6/28/04
U(VI) (uM)
2.5
2
1.5
1
0.5
0
3/20/03
6/28/03
10/6/03
1/14/04
4/23/04
8/1/04
Date
M-01
M-02
M-03
M-04
M-05

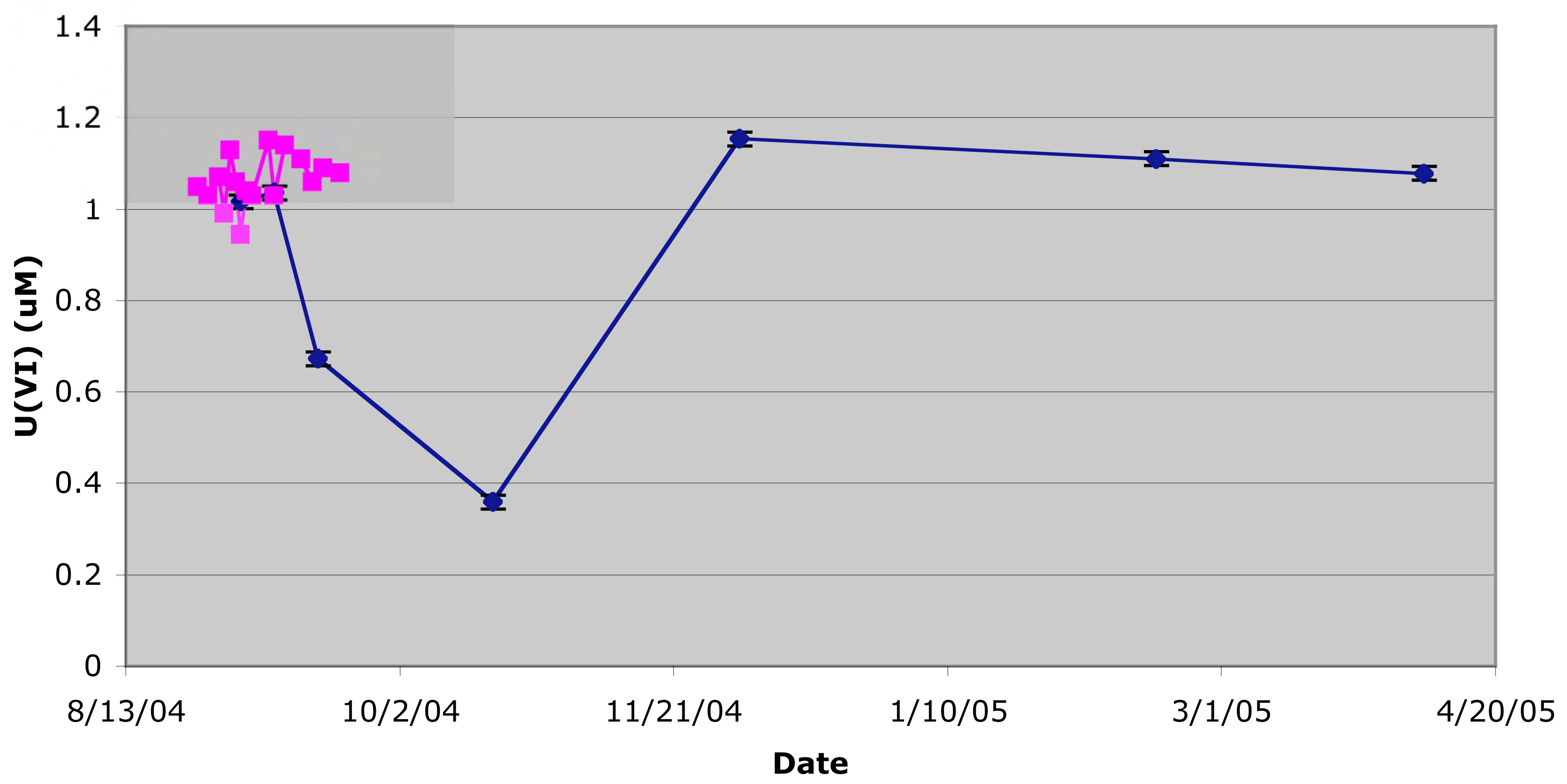
Comparison of U(VI) loss in 2002 and 2004 Field Experiments



U(VI) vs time for 5.1m depth in M-18



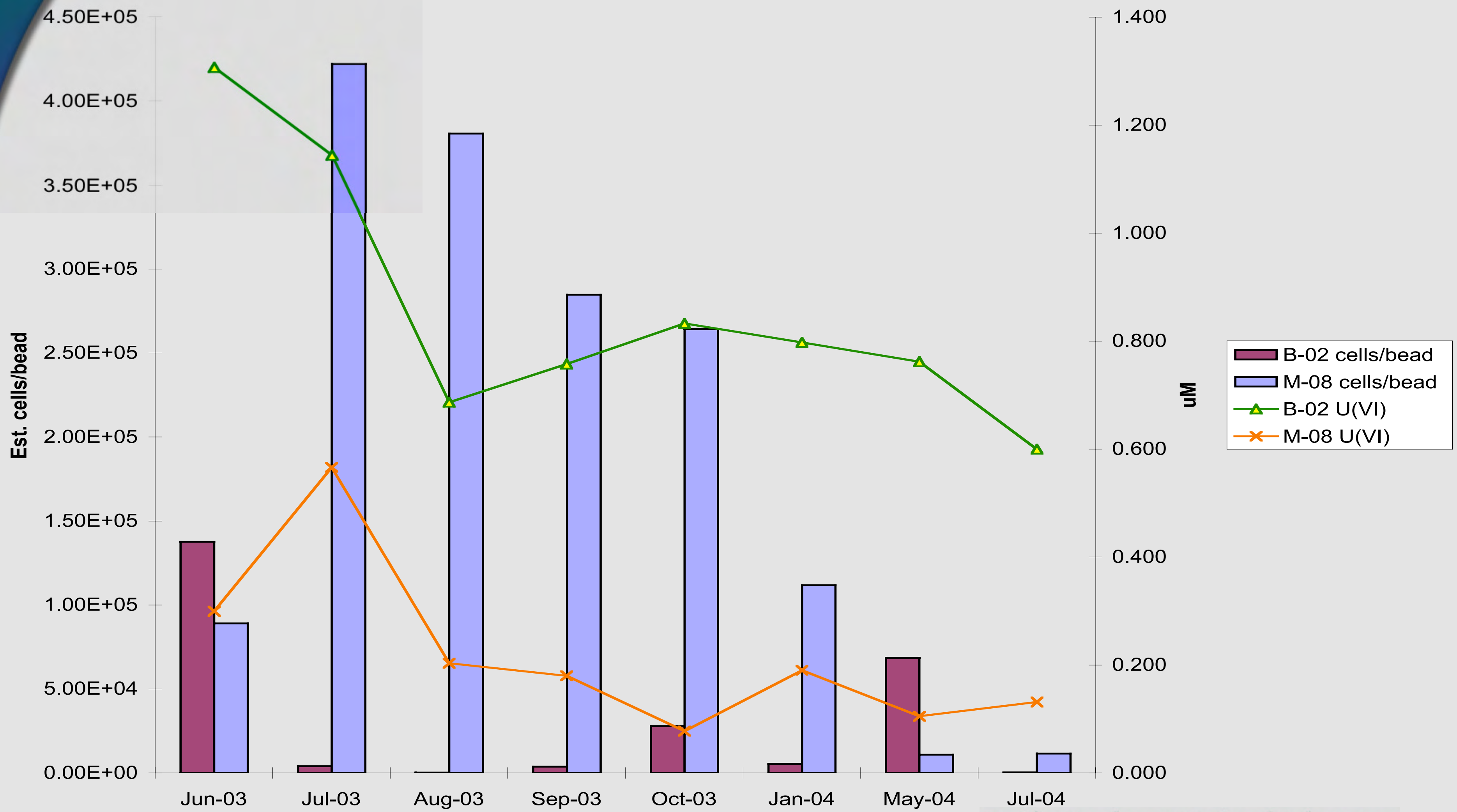
U(VI) vs time for 5.1m depth in M-18 with B-04 background data



What are possible mechanisms for prolonged U(VI) loss?

- Biotic
  - Residual Fe-reducer population
  - "Maintenance" population
- Abiotic
  - $FeS_{0.9}$ oxygen buffering and/or U(VI) sorption
  - Formation of new Fe(III) oxides sorbing U(VI)
  - Redox impact on U(VI) sorption

Change in PLFA biomass 2003/2004 (matched depth data set)



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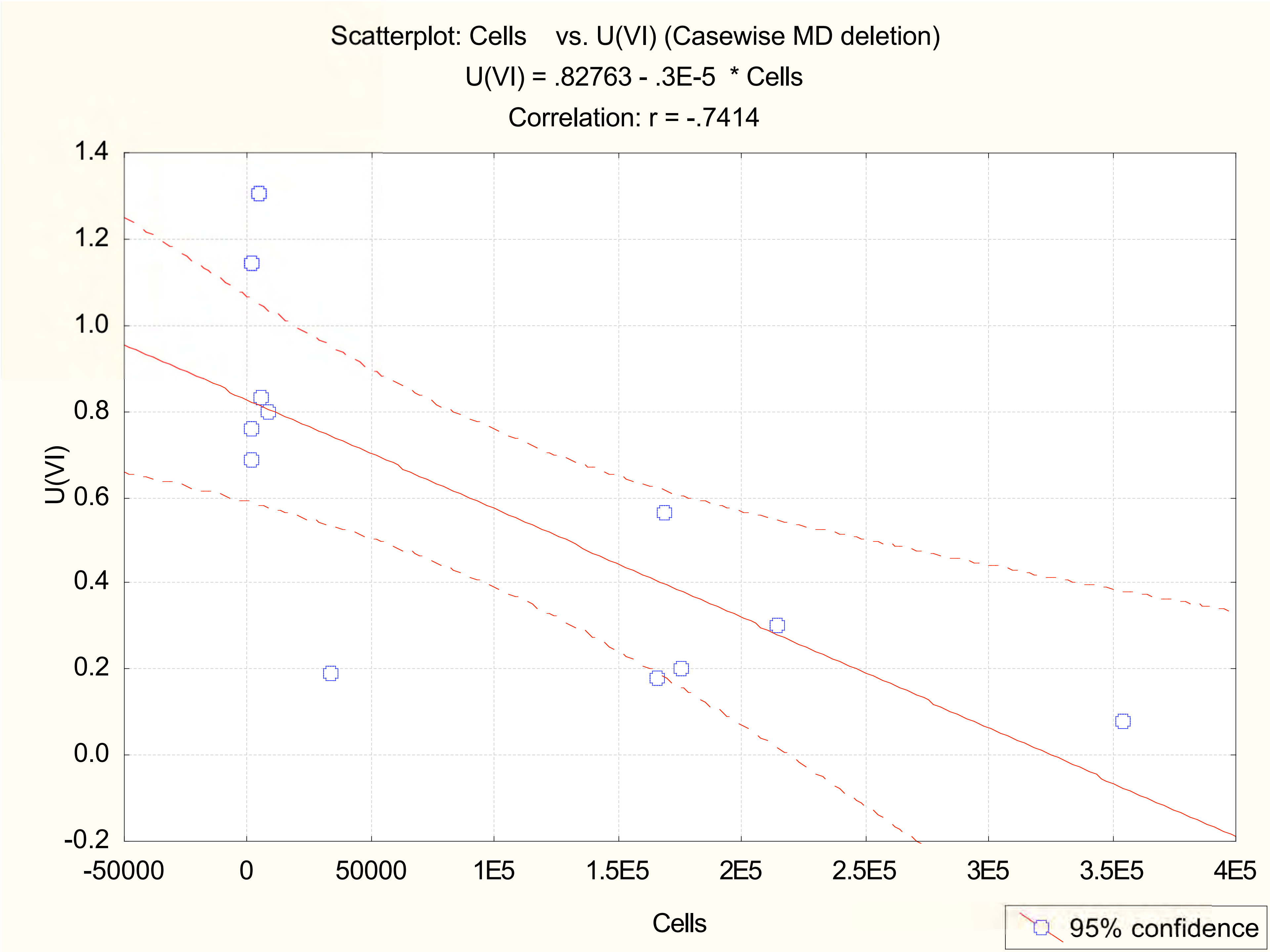

Scatterplot: Cells vs. U(VI) (Casewise MD deletion)
U(VI) = .82763 - .3E-5 * Cells
Correlation: r = -.7414
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
-0.2
U(VI)
-50000
0
50000
1E5
1.5E5
2E5
2.5E5
3E5
3.5E5
4E5
Cells
95% confidence

What are possible mechanisms for prolonged U(VI) loss?

- Biotic
  - Residual Fe-reducer population
  - “Maintenance” population
- Abiotic
  - $FeS_{0.9}$ oxygen buffering and/or U(VI) sorption
  - Formation of new Fe(III) oxides sorbing U(VI)
  - Redox impact on U(VI) sorption

Future Experiment at Old Rifle

Hypothesis: Prolonged U(VI) loss is controlled by TEAP reached during acetate amendment

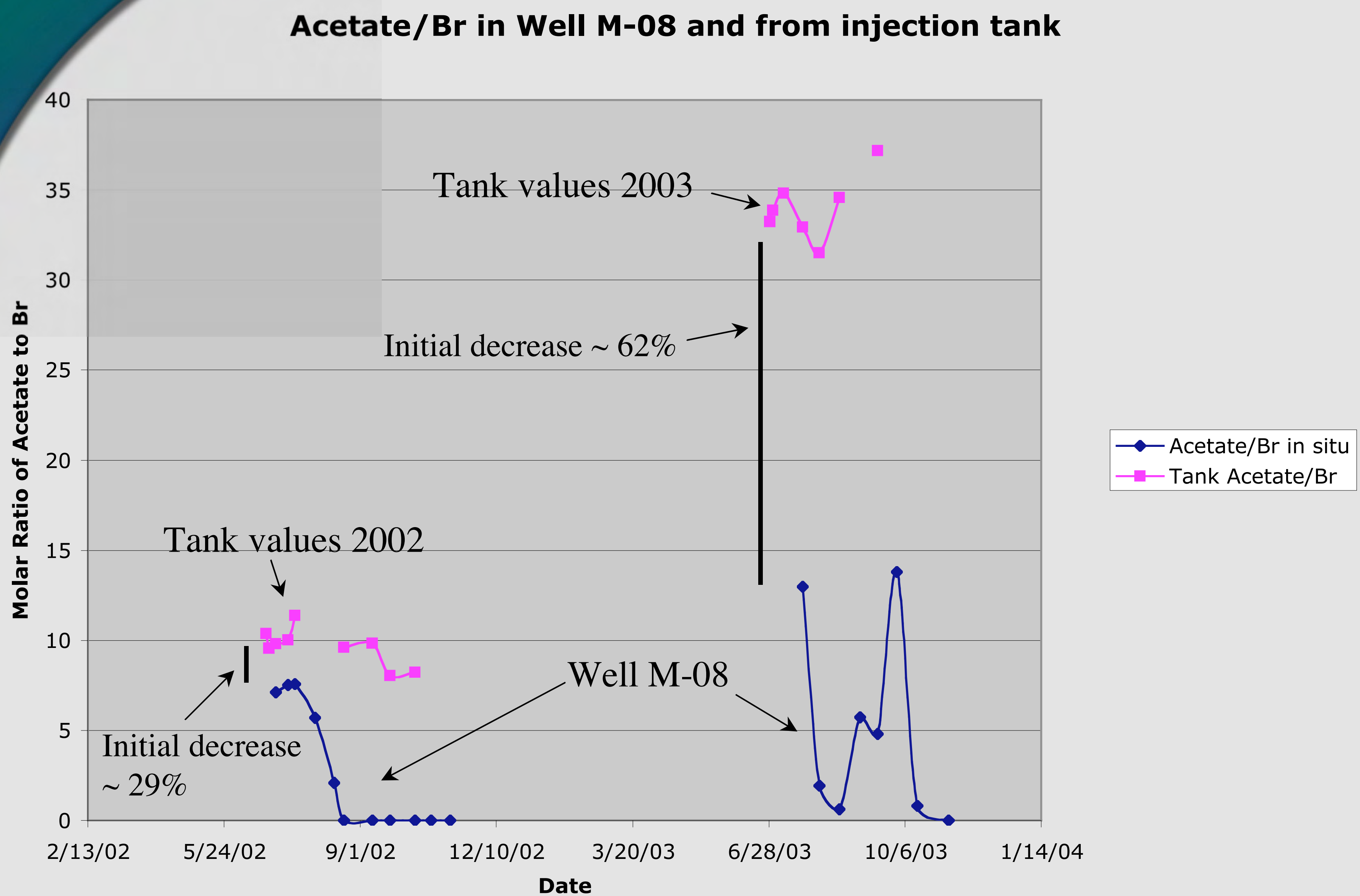
- Construct a new minigallery
- Run two experiments in parallel
  - Drive the existing minigallery to sulfate reduction
  - Stop acetate amendment in new minigallery during Fe-reduction
- High-frequency monitoring of post-amendment response, including geophysics. Compare genomics, ^{13}C PLFA/DNA, and mRNA of the two systems, during and post-amendment
- Additional laboratory studies are underway or proposed
- Reactive transport modeling (Yabusaki and Fang) will be used to explore match of mechanistic processes to field and lab data

Summary

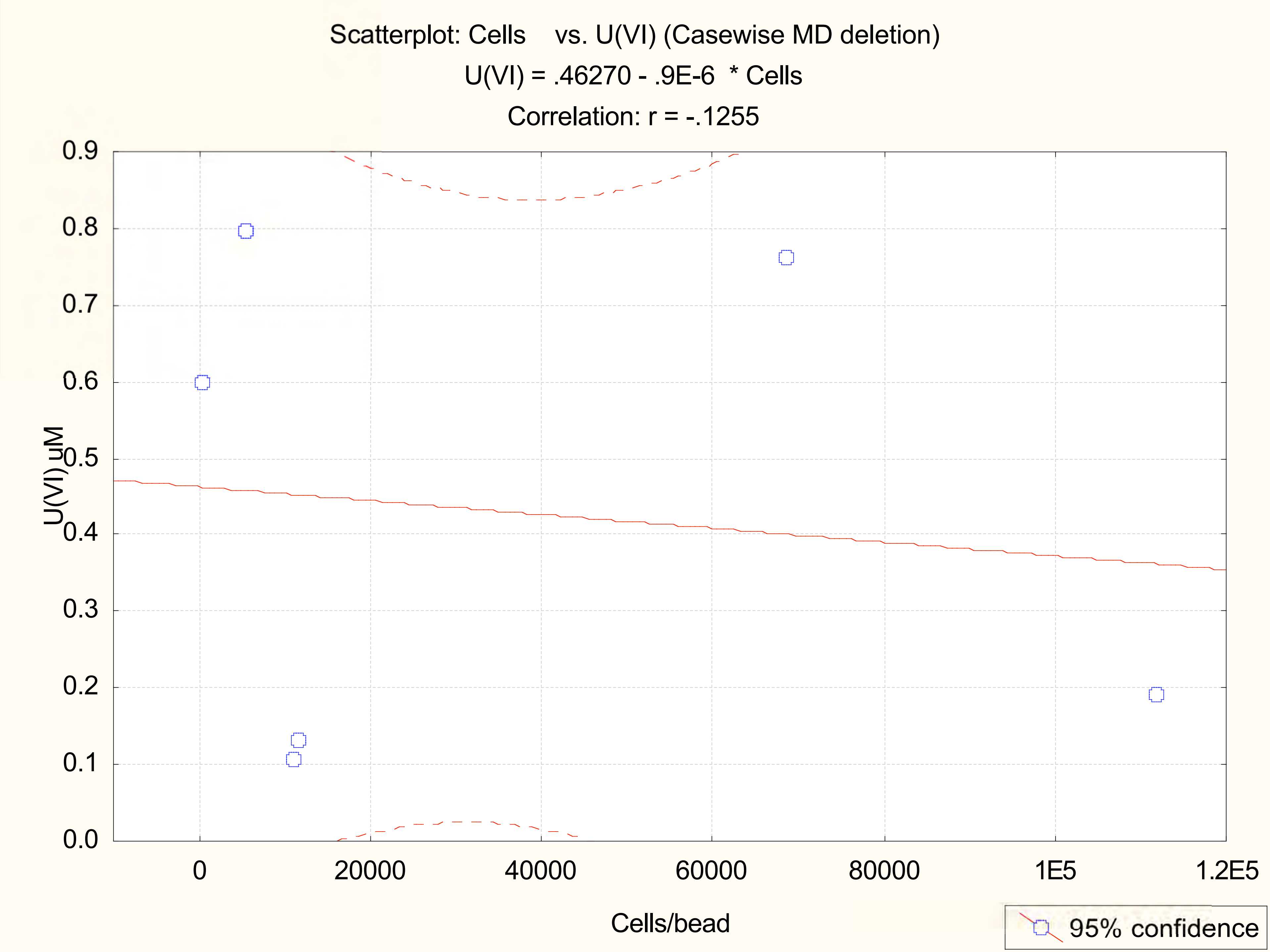
- Amendment of acetate to the subsurface removes U(VI) from groundwater by direct enzymatic reduction to U(IV)
- Loss of U(VI) is sustained much longer than expected, >1.5 years locally in the system
- Sustained loss post-amendment does not appear to be controlled by microbial biomass alone
- Mechanisms for sustained loss will be addressed by a field experiment in 2005, and by on-going and proposed lab studies examining reoxidation of U(IV) and redox impact to U(VI) sorption using Rifle sediments

Additional future field experiments

- High DO site (effect on reduction and reoxidation rates)
- High Nitrate site (effect of nitrate reduction on subsequent processes)
- Other electron donors (lactate, ethanol)
- Hydrogeology differences (flow rate, porosity, permeability)
- Other metals (e.g. vanadium)
- In-well electrode biocapture of uranium



Acetate/Br in Well M-08 and from injection tank
Molar Ratio of Acetate to Br
40
35
30
25
20
15
10
5
0
2/13/02
5/24/02
9/1/02
12/10/02
3/20/03
6/28/03
10/6/03
1/14/04
Date
Tank values 2003
Initial decrease ~ 62%
Tank values 2002
Well M-08
Initial decrease
~ 29%
Acetate/Br in situ
Tank Acetate/Br

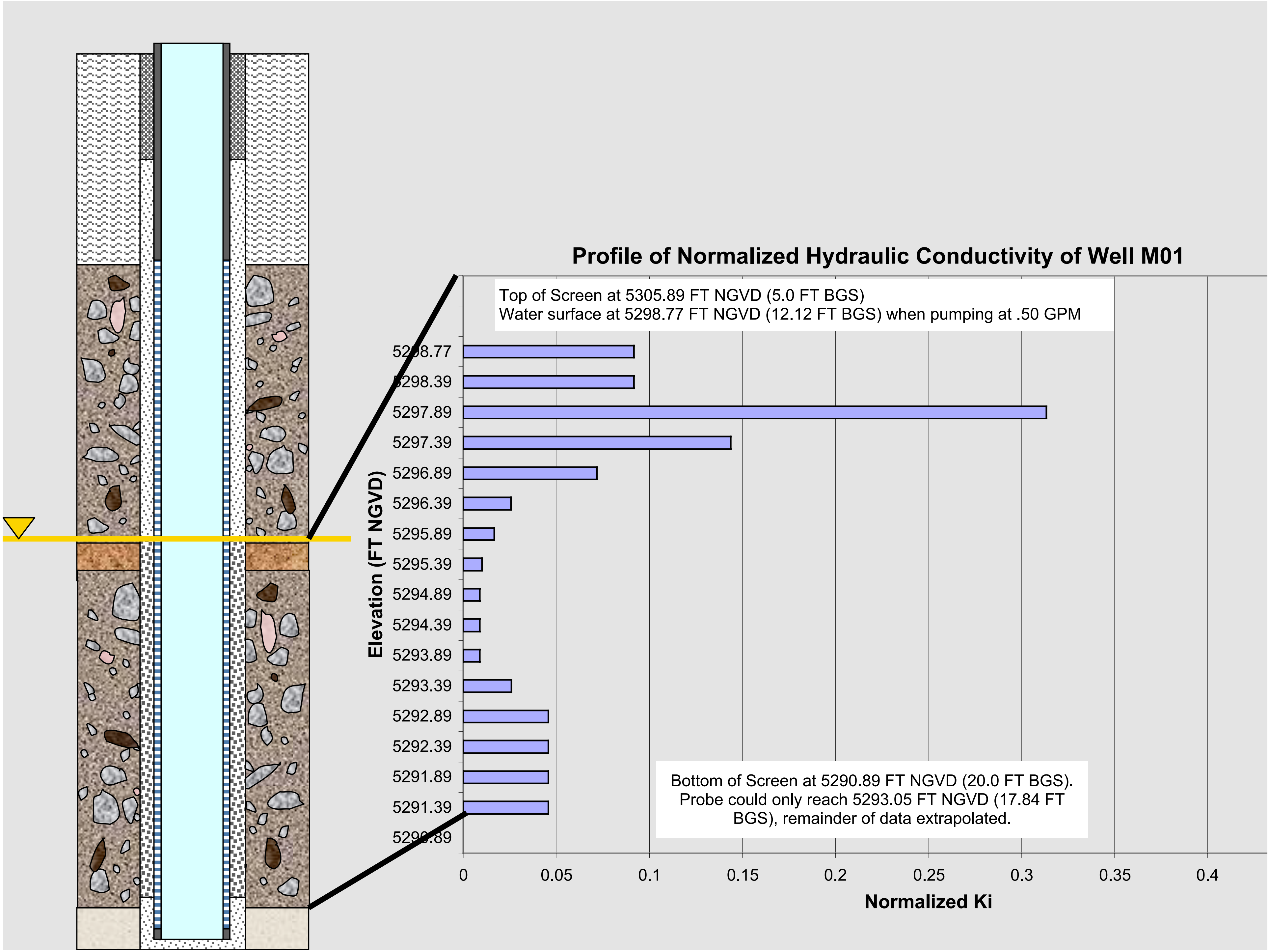

Scatterplot: Cells vs. U(VI) (Casewise MD deletion)
U(VI) = .46270 - .9E-6 * Cells
Correlation: r = -.1255
U(VI) uM
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
0
20000
40000
60000
80000
1E5
1.2E5
Cells/bead
95% confidence

Typical Groundwater Chemistry

Parameter	*M-02 Prior to Biostimulation (6-20-02)*	*M-02 After Biostimulation (8/13/02)*
pH	7.06	7.23
Eh	144 mV	-41 mV
DO	0.26 mg/l	0.07 mg/l
Conductivity	2196 uS/cm	2116 uS/cm
NO_3	nd	nd
SO_4^{-2}	6.57 mM	5.25 mM
Sulfide	nd	0.78 uM
Acetate	nd	760 uM
Br	nd	253.1 uM
U(VI)	0.73 uM	0.23 uM (-68%)
Fe(II)	53.1 uM	135.1 uM (7/30/02)
DIC	2.13 mM	2.40 mM (8/1/02) +13%
DOC	0.44 mM	2.60 mM (8/1/02) +493%
Alkalinity	1.738 meq/l	2.063 meq/l (8/1/02) +19%

Typical Groundwater Chemistry (cations)

Cation	B-01 (background) Prior to Biostimulation (6-25-03)	M-02 Prior to 2003 Biostimulation (6-25-03)	M-02 After 2003 Biostimulation (8/04/03)
Al	nd	nd	nd
Ba	0.41 uM	0.45 uM	0.41 uM
Ca	5.3 mM	5.2 mM	4.1 mM (-21%)
K	0.20 mM	0.22 mM	0.20 mM
Mg	5.1 mM	5.0 mM	4.2 mM (-16%)
Mn	0.014 mM	0.019 mM	0.014 mM (-26%)
Ni	0.84 uM	0.84 uM	0.70 uM
Sr	0.038 mM	0.035 mM	0.031 mM (-11%)
V	0.021 mM	0.068 mM	nd (-94%)
Na	8.21 mM	8.28 mM	12.4 mM (+50%)
Si	0.40 mM	0.45 mM	0.44 mM

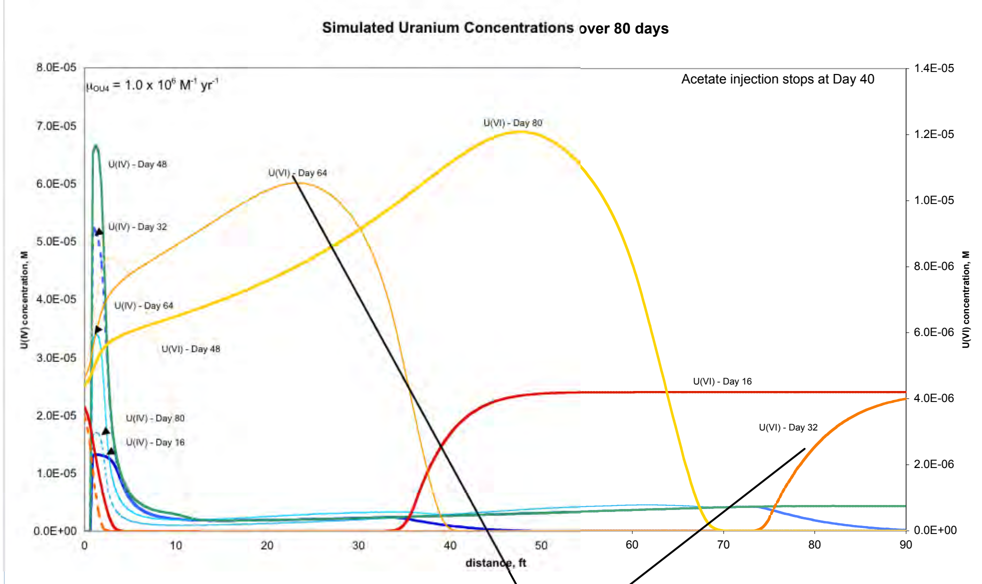


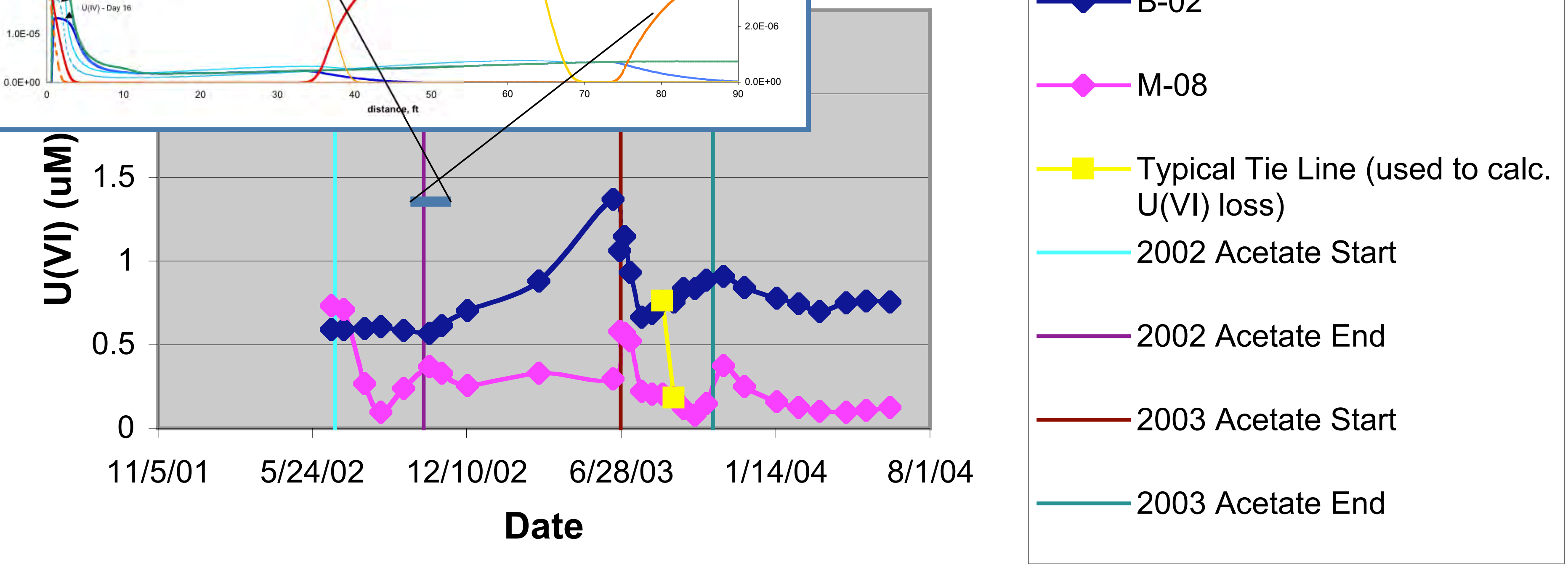
Profile of Normalized Hydraulic Conductivity of Well M01
Top of Screen at 5305.89 FT NGVD (5.0 FT BGS)
Water surface at 5298.77 FT NGVD (12.12 FT BGS) when pumping at .50 GPM
Bottom of Screen at 5290.89 FT NGVD (20.0 FT BGS).
Probe could only reach 5293.05 FT NGVD (17.84 FT BGS), remainder of data extrapolated.
Elevation (FT NGVD)
5298.77
5298.39
5297.89
5297.39
5296.89
5296.39
5295.89
5295.39
5294.89
5294.39
5293.89
5293.39
5292.89
5292.39
5291.89
5291.39
5290.89
0
0.05
0.1
0.15
0.2
0.25
0.3
0.35
0.4
Normalized Ki

Knowledge Gaps

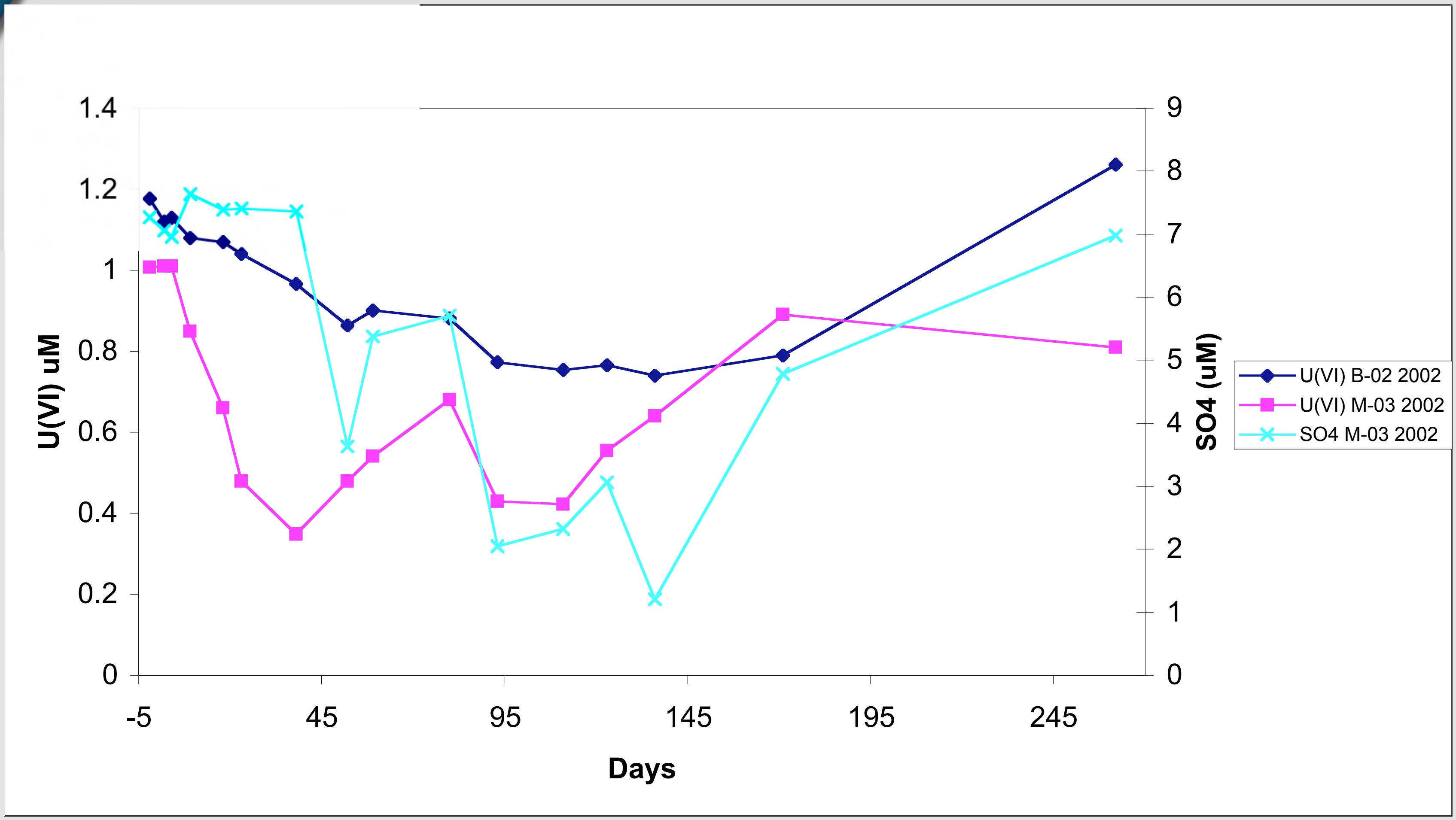
- Mechanisms for sustained U(VI) loss post-amendment
  - Effect of sulfide precipitate
  - Biomass/ongoing microbially mediated U(VI) reduction
- Competing U(VI) sorption effects
  - U(VI) released by Fe-oxide reduction
  - Sorption increased by decrease in Ca-CO_3-U(VI) complexes
- U(VI) bioreduction rates (considering sorption parameters)
- Biomass impact on reactivity
- Fe(II) sorption, bioproduction rates, surface behavior
- Overall effect of redox on U(VI) sorption (abiotic)
  - Sulfide precipitate chemistry and micro-texture
  - Scaling
  - Fe(III) reduction

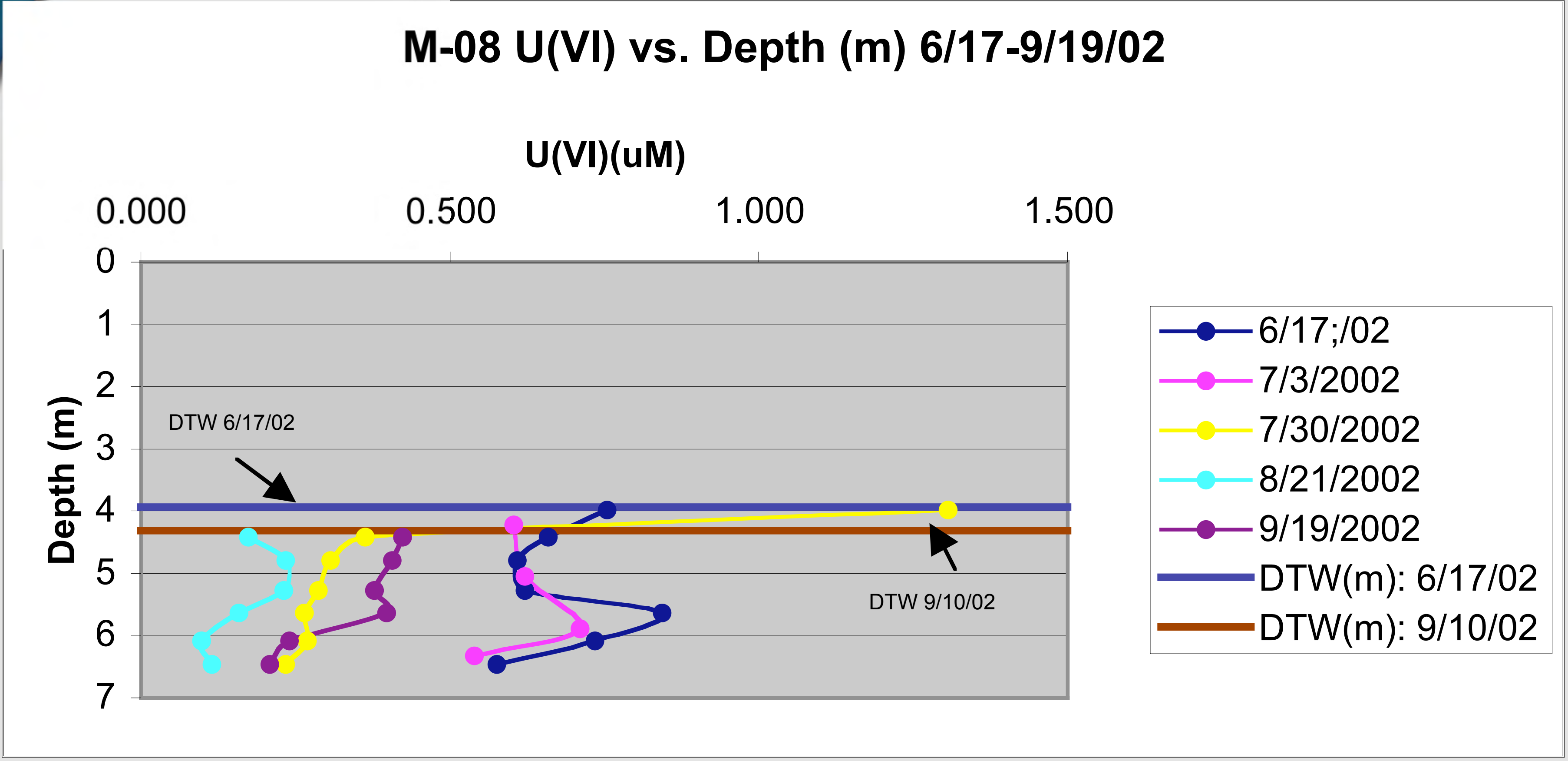
s from B-02 to M-08





2002 U(VI) and SO_4





M-08 U(VI) vs. Depth (m) 6/17-9/19/02
U(VI)(uM)
0.000
0.500
1.000
1.500
Depth (m)
0
1
2
3
4
5
6
7
DTW 6/17/02
DTW 9/10/02
6/17;/02
7/3/2002
7/30/2002
8/21/2002
9/19/2002
DTW(m): 6/17/02
DTW(m): 9/10/02

Battelle