Stimulated *In Situ* Removal of U(VI) from a Uranium-Contaminated Aquifer

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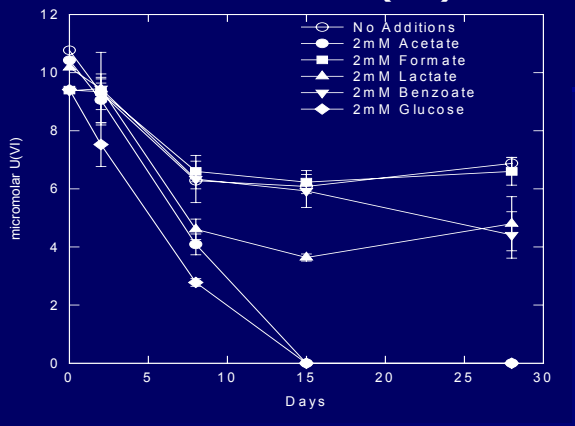
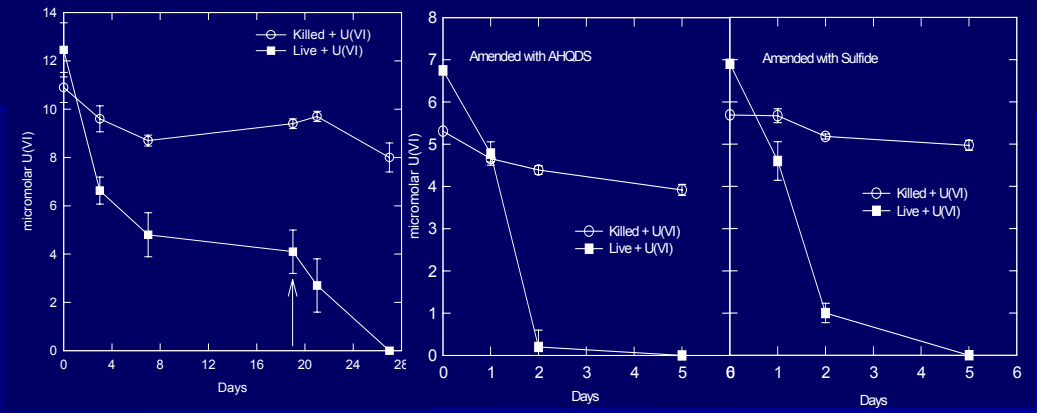
Laboratory Studies

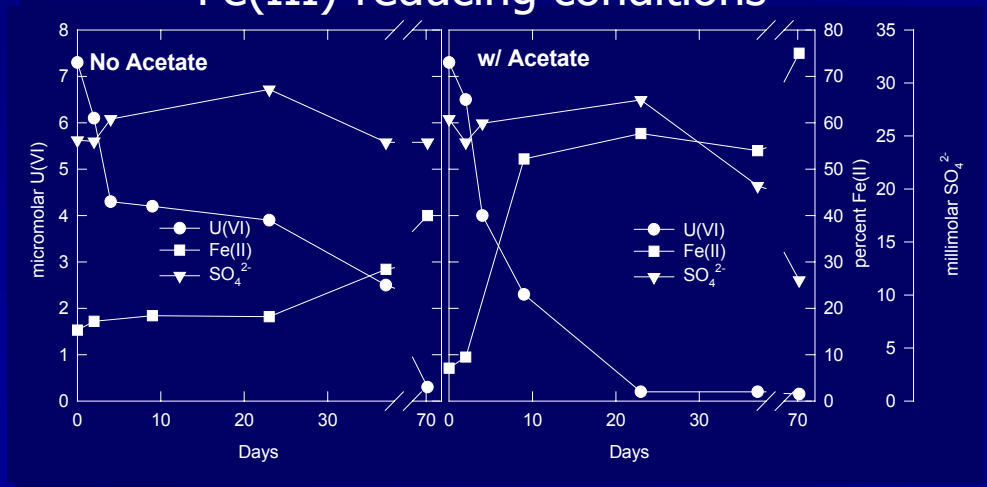
Acetate stimulates loss of soluble U(VI)



Stimulated loss of U(VI) is biological



Stimulated loss of U(VI) occurs under Fe(III)-reducing conditions



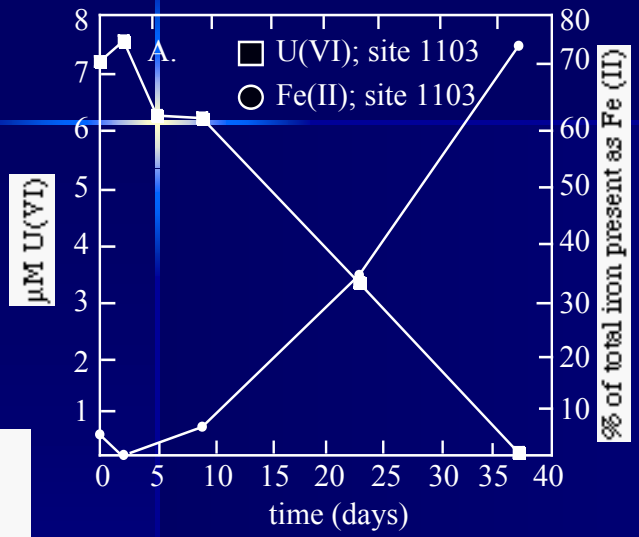
- Depletion of nitrate is a pre-requisite for stimulated loss of U

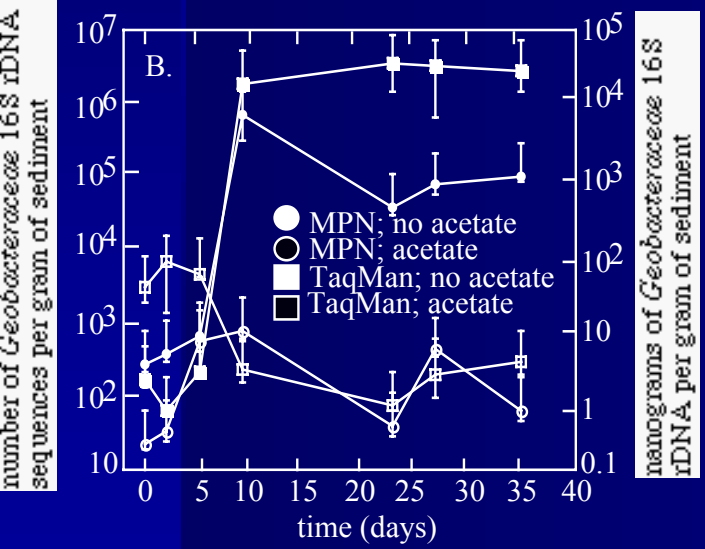
Finneran, K.T., Anderson, R.T., Nevin, K.P., Lovley, D.R. 2002, *Soil and Sed. Contam.* 11:339-357

Finneran, K.T., Housewright, M.E., Lovley, D.R., 2002, *Environ. Microbiol.* 4: 510-516.

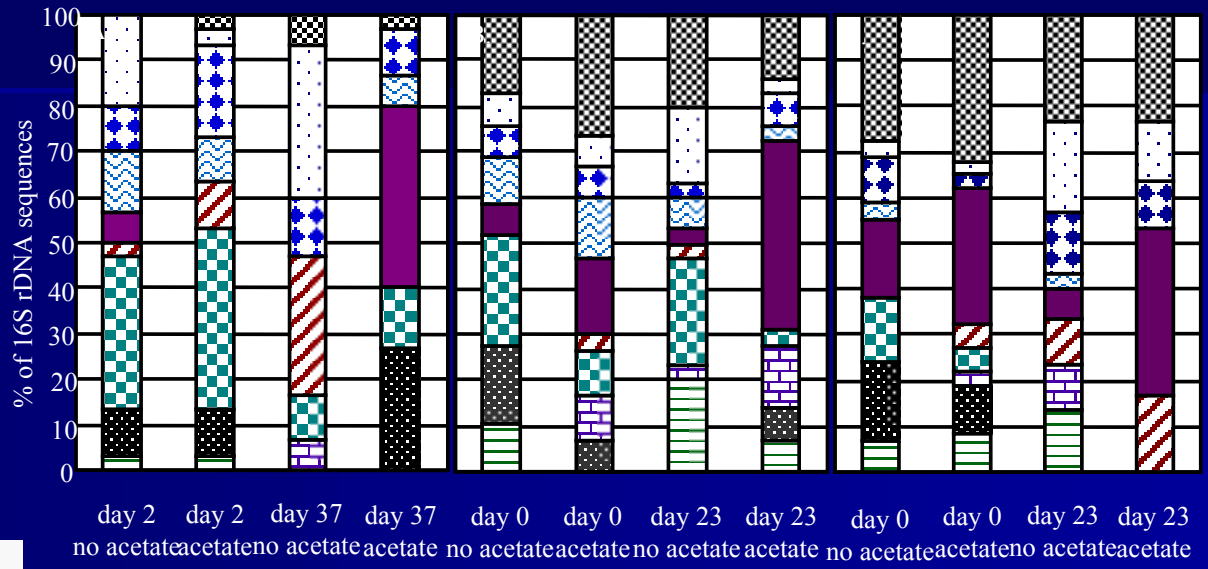
Detection and Evaluation of *Geobacteraceae*

Population Increase





Enrichment of *Geobacteraceae*



Relative proportions of organisms in clone libraries from the three different sites. 3A. site 1103; 3B. site 857; 3C. site 853. Firmicutes; Clostridium/Bacillus; Cytophagales; Geobacteraceae; other deltaproteobacteria; gammaproteobacteria; Azoarcus; other betaproteobacteria; alphaproteobacteria; other.

Holmes, D.E., Finneran, K.T., O'Neill, R.A., Lovley, D.R., 2002, *Appl. Environ. Microbiol.* 68:2300-2306

Laboratory Sediment Incubations

1) Acetate addition to aquifer sediments stimulates loss of soluble U(VI).

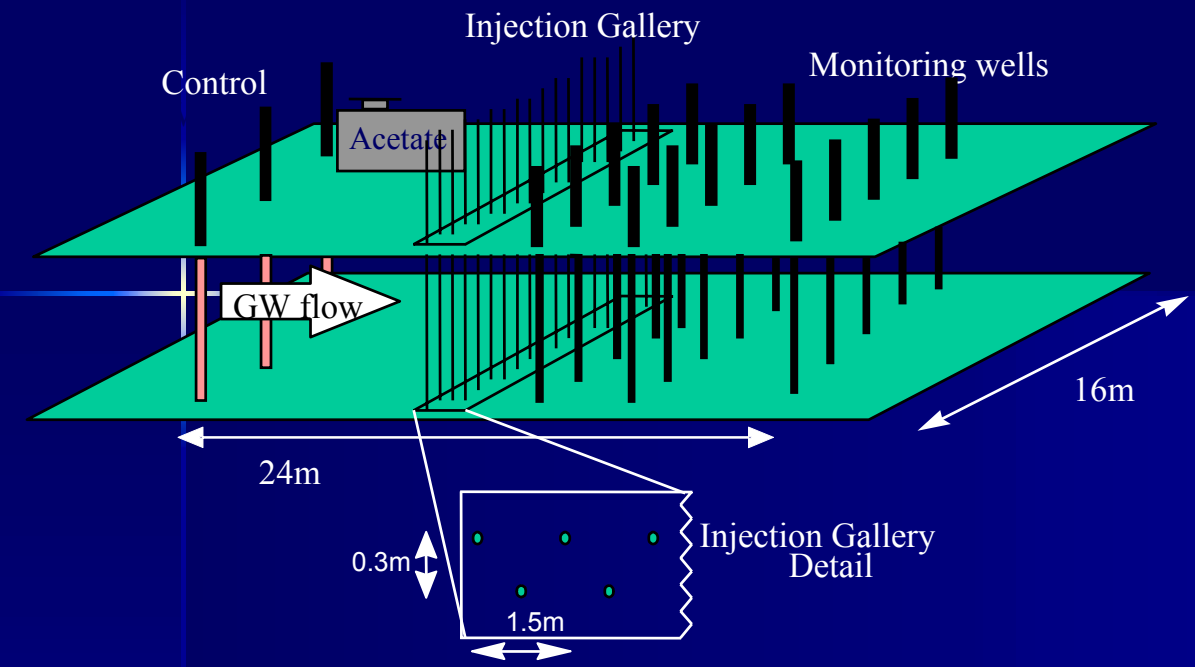
2) Stimulated loss of U(VI) in sediments is a biological process.

3) Loss of U(VI) from solution is associated with stimulated metal-reducing conditions in sediments.

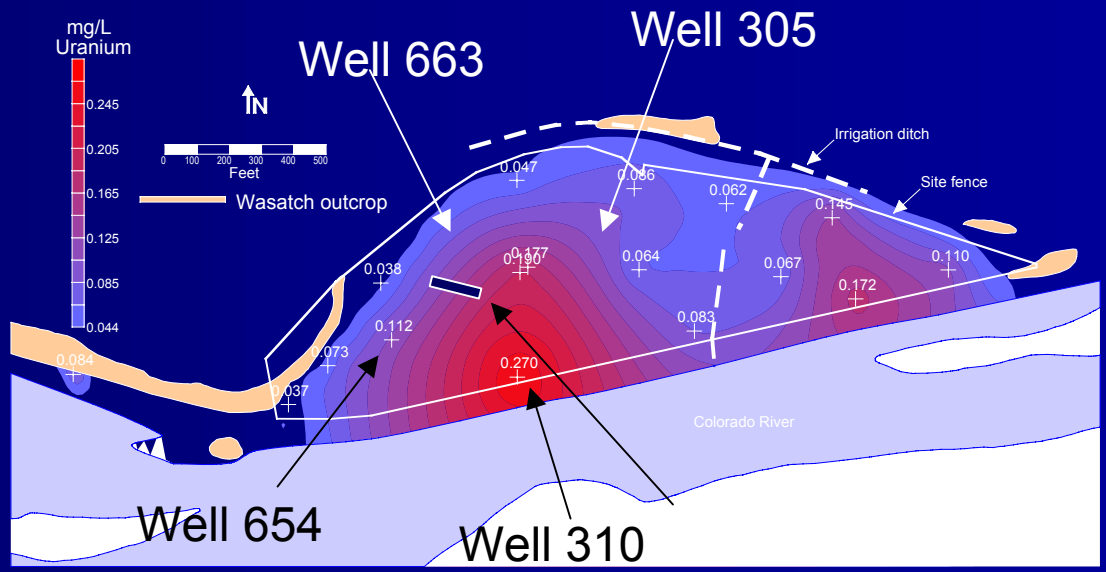
4) Stimulated loss soluble U(VI) is associated with an enrichment in the sediment microbial community of *Geobacteraceae* organisms known to reduce Fe(III) and U(VI).

5) Removal of nitrate is a prerequisite for stimulated U(VI) removal

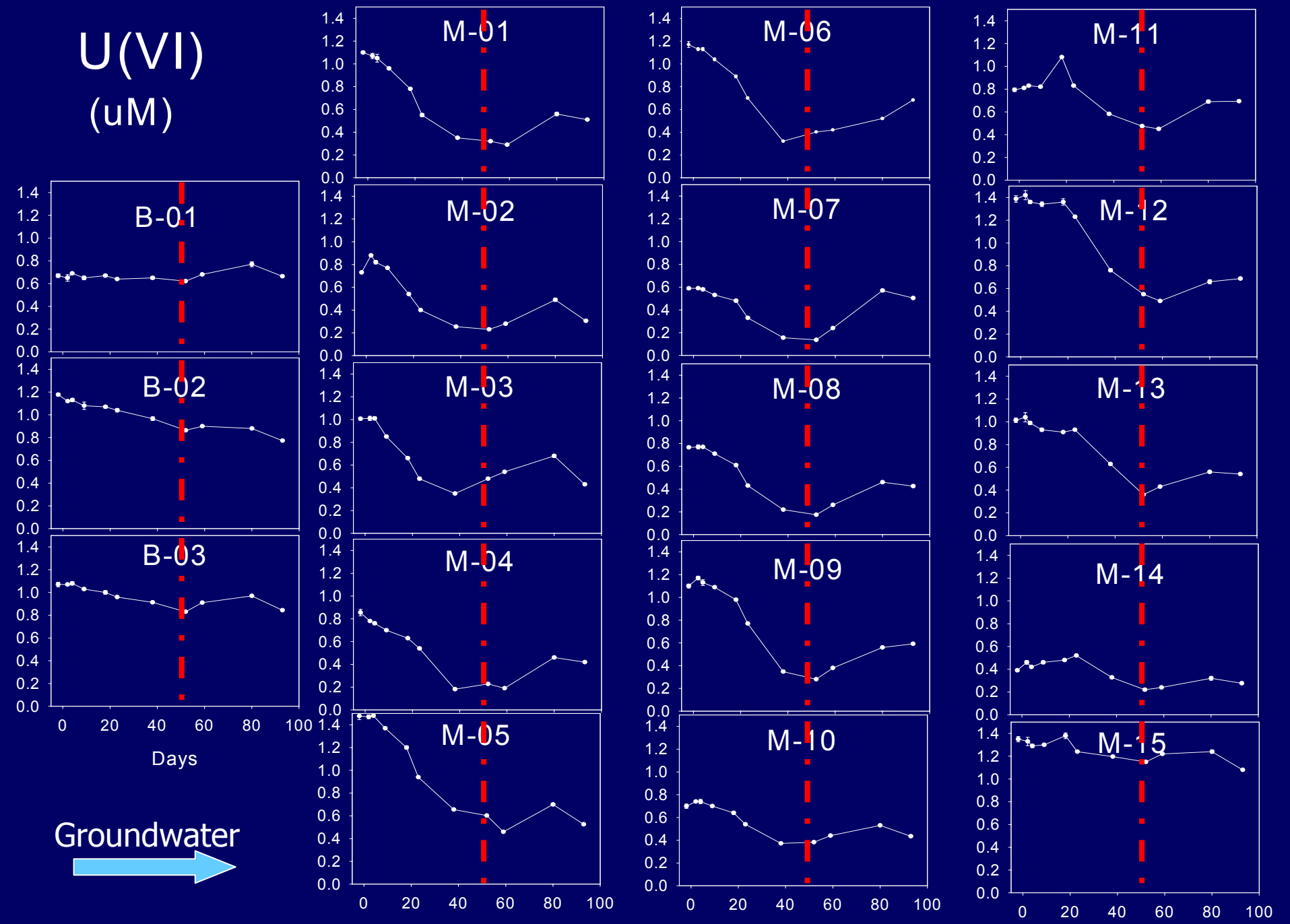
Old Rifle Test Plot



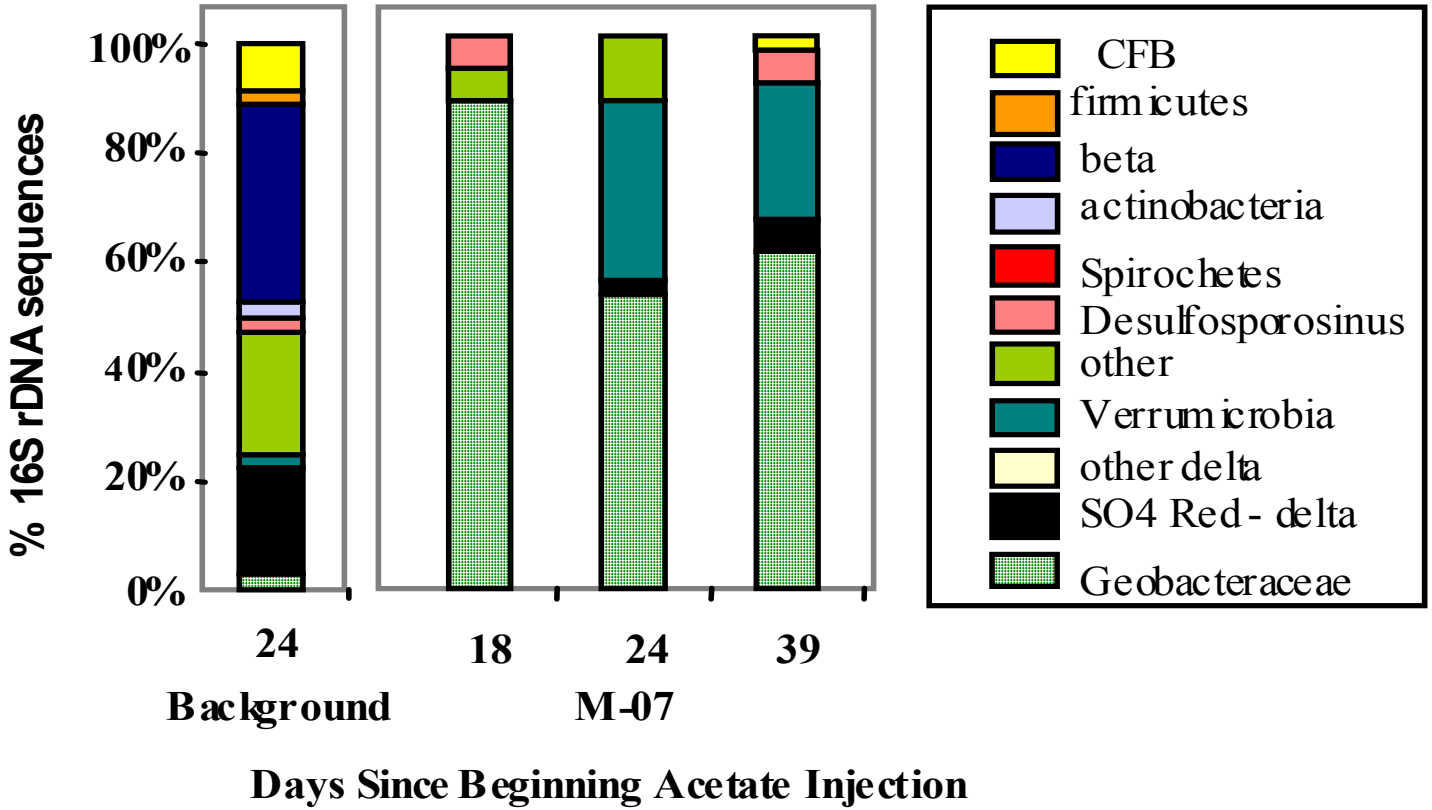
Test Plot Position within the Old Rifle Site

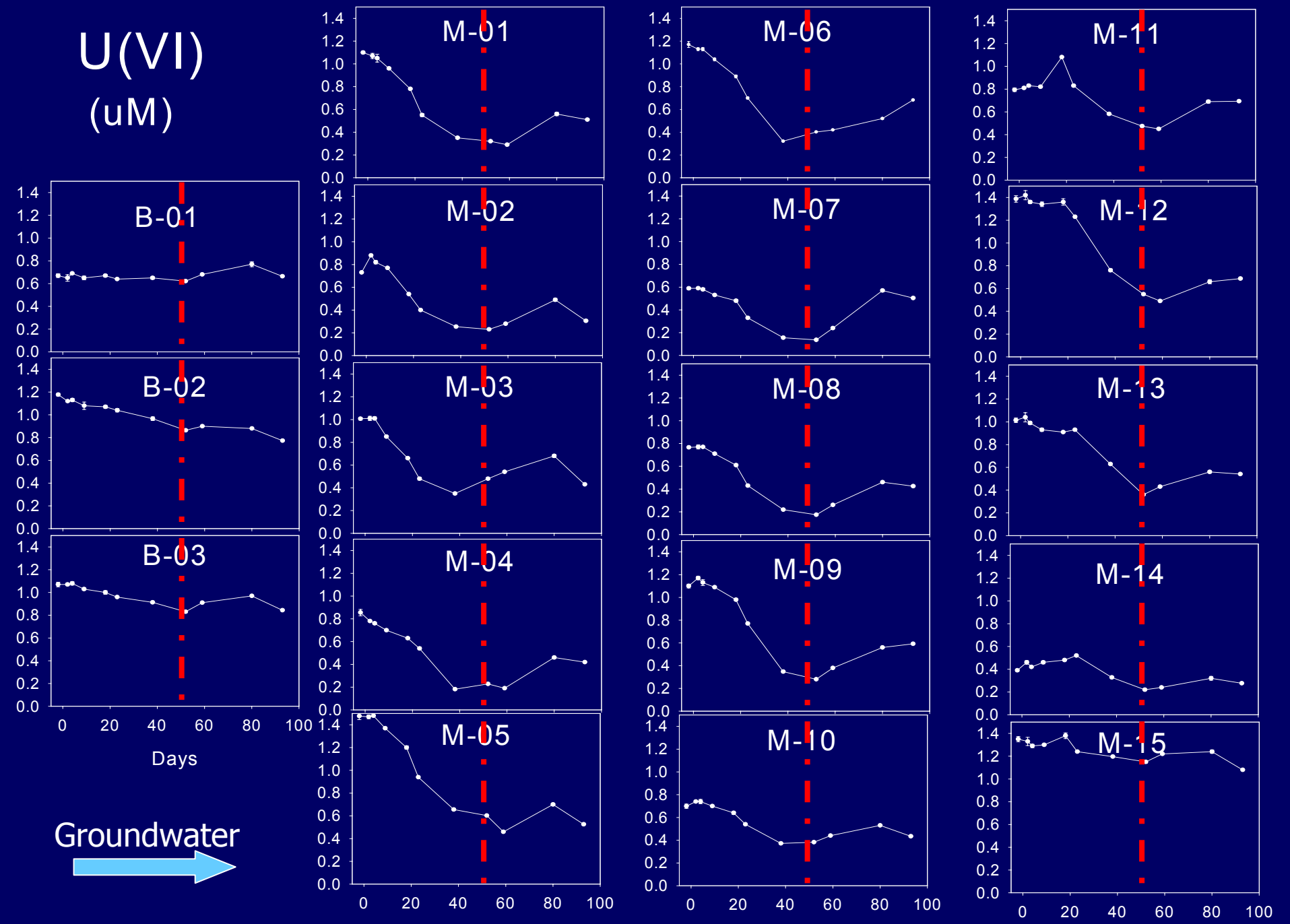


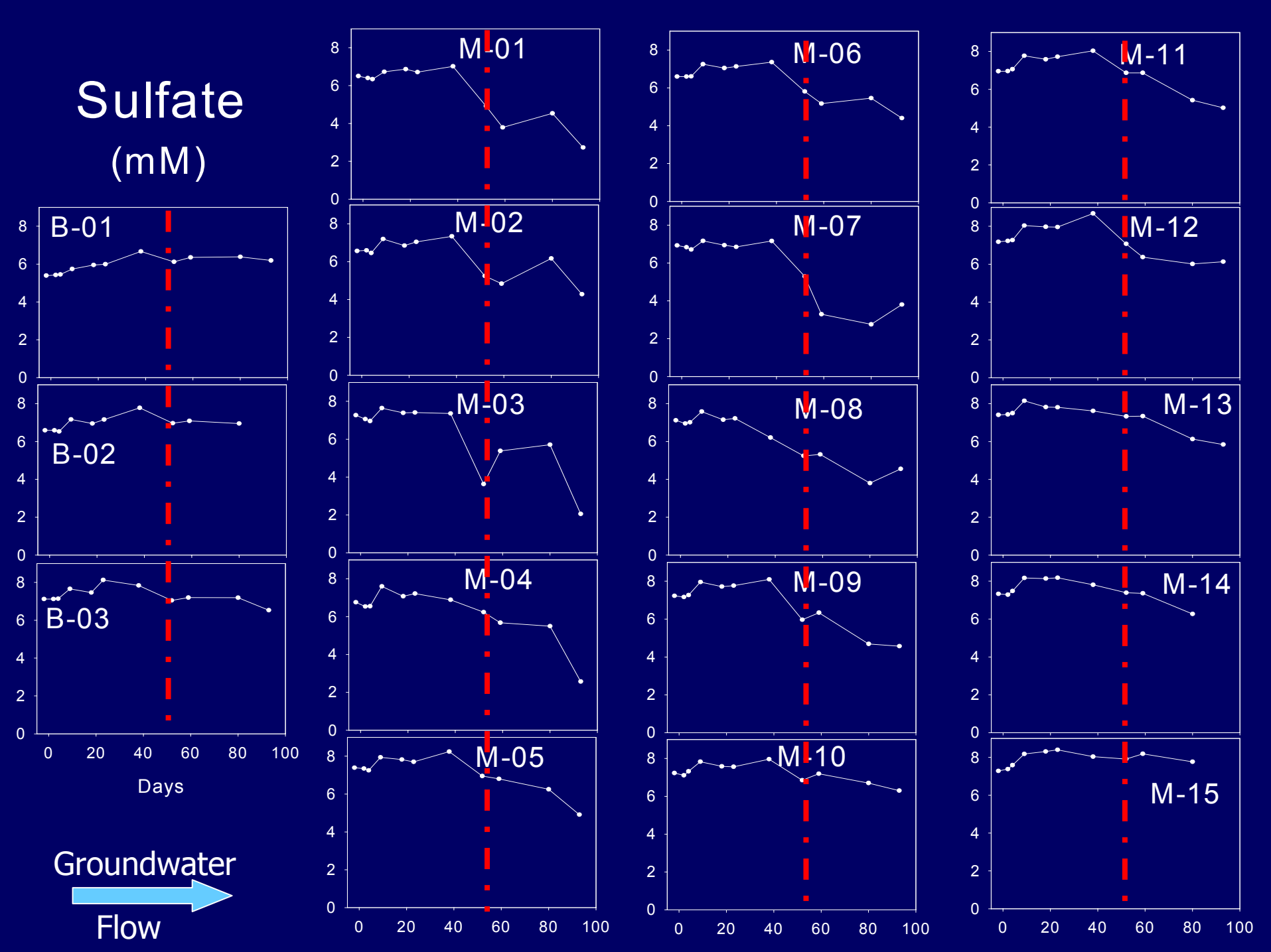
Placement of injection gallery


U(VI)
(uM)
B-01
B-02
B-03
M-01
M-02
M-03
M-04
M-05
M-06
M-07
M-08
M-09
M-10
M-11
M-12
M-13
M-14
M-15
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
20
40
60
80
100
Days
Groundwater

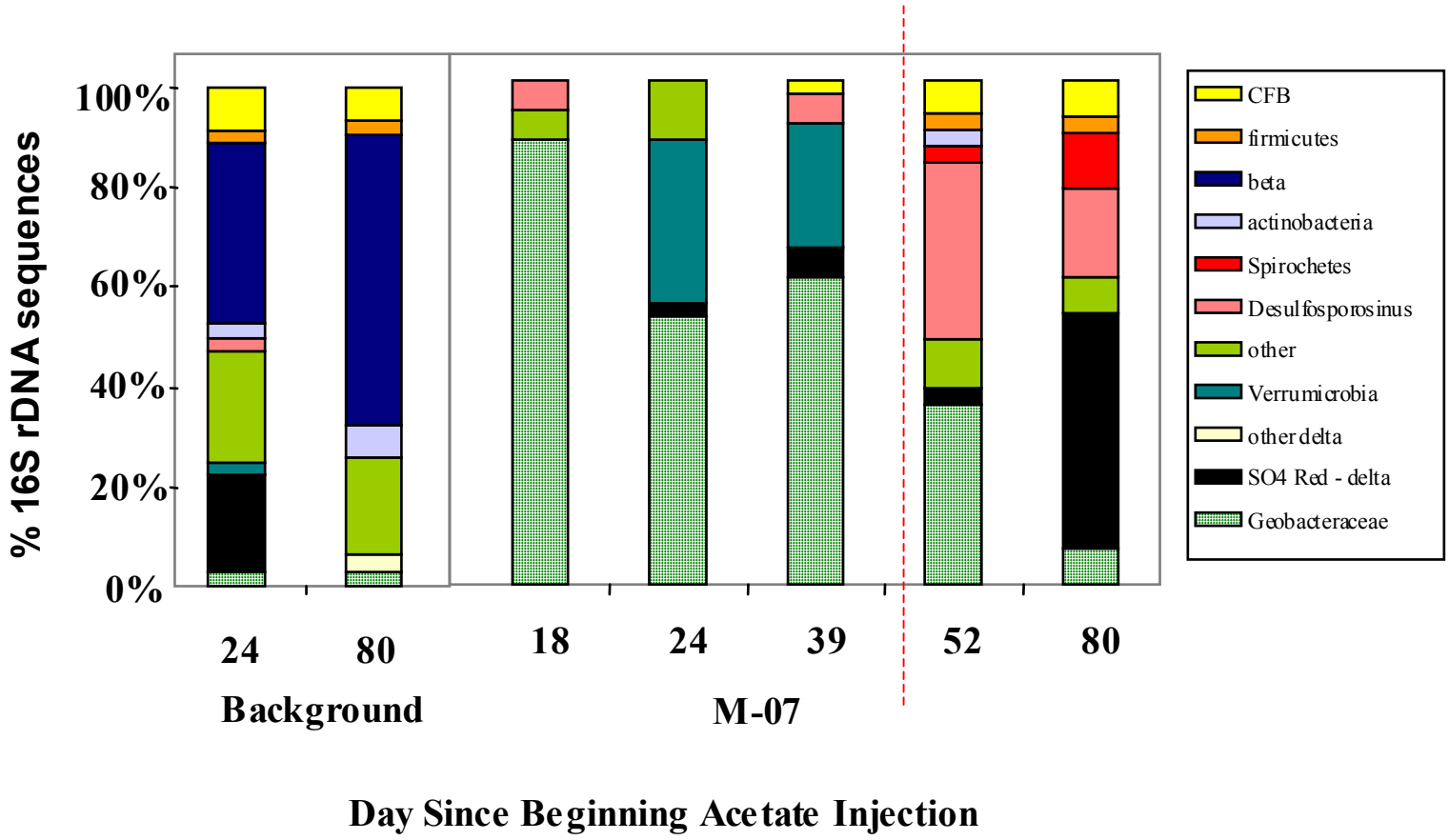
16S rDNA Clone Library Analysis

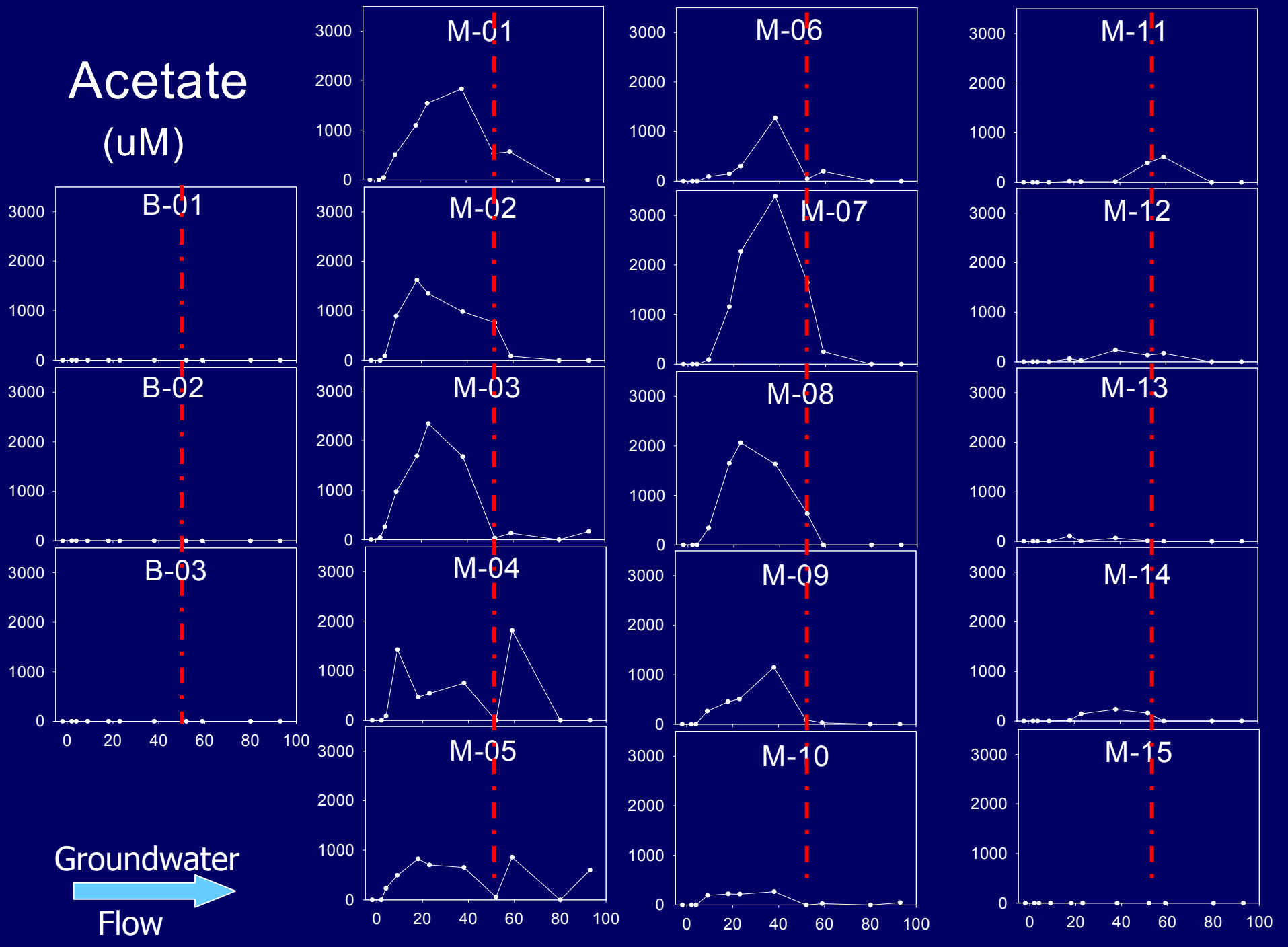



U(VI)
(uM)
B-01
B-02
B-03
M-01
M-02
M-03
M-04
M-05
M-06
M-07
M-08
M-09
M-10
M-11
M-12
M-13
M-14
M-15
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
20
40
60
80
100
Days
Groundwater

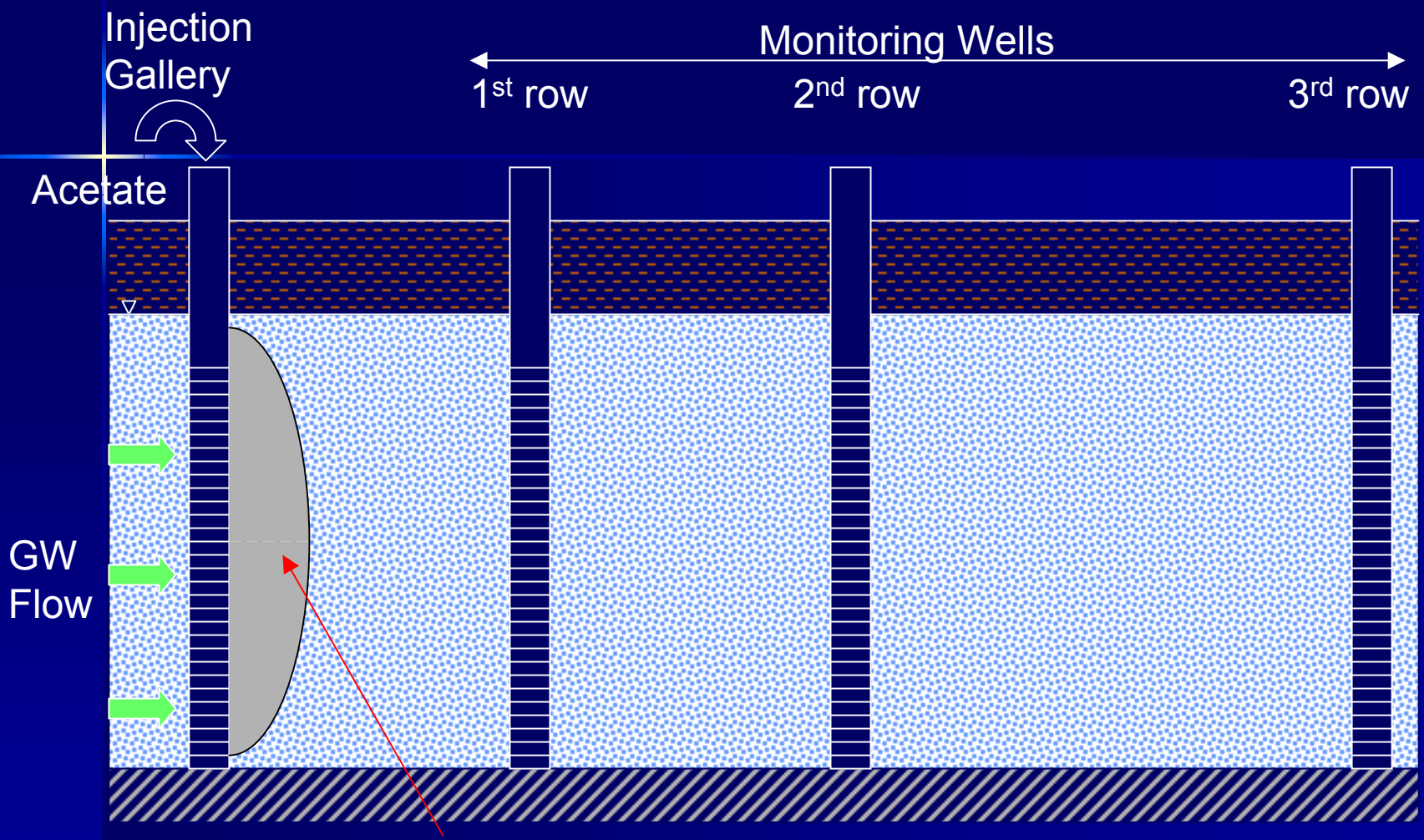

Sulfate
(mM)
B-01
B-02
B-03
M-01
M-02
M-03
M-04
M-05
M-06
M-07
M-08
M-09
M-10
M-11
M-12
M-13
M-14
M-15
0
2
4
6
8
0
20
40
60
80
100
Days
Groundwater
Flow

16S rDNA Clone Library Analysis




Acetate
(uM)
B-01
B-02
B-03
M-01
M-02
M-03
M-04
M-05
M-06
M-07
M-08
M-09
M-10
M-11
M-12
M-13
M-14
M-15
0
1000
2000
3000
0
20
40
60
80
100
Groundwater
Flow

Old Rifle Site 2002: Loss of U(VI) not sustained once sulfate reduction was stimulated



Zone of depleted Fe(III) near point of injection.
Acetate completely consumed via stimulated sulfate reduction.
Loss of U(VI) inhibited due to stimulated sulfate reduction.

Results of the 2002 *In Situ* Experiment Demonstrate:

1) Acetate addition stimulates the removal of U(VI) from the groundwater at the Old Rifle site.

2) U(VI) was removed from solution under stimulated Fe(III)-reducing conditions.

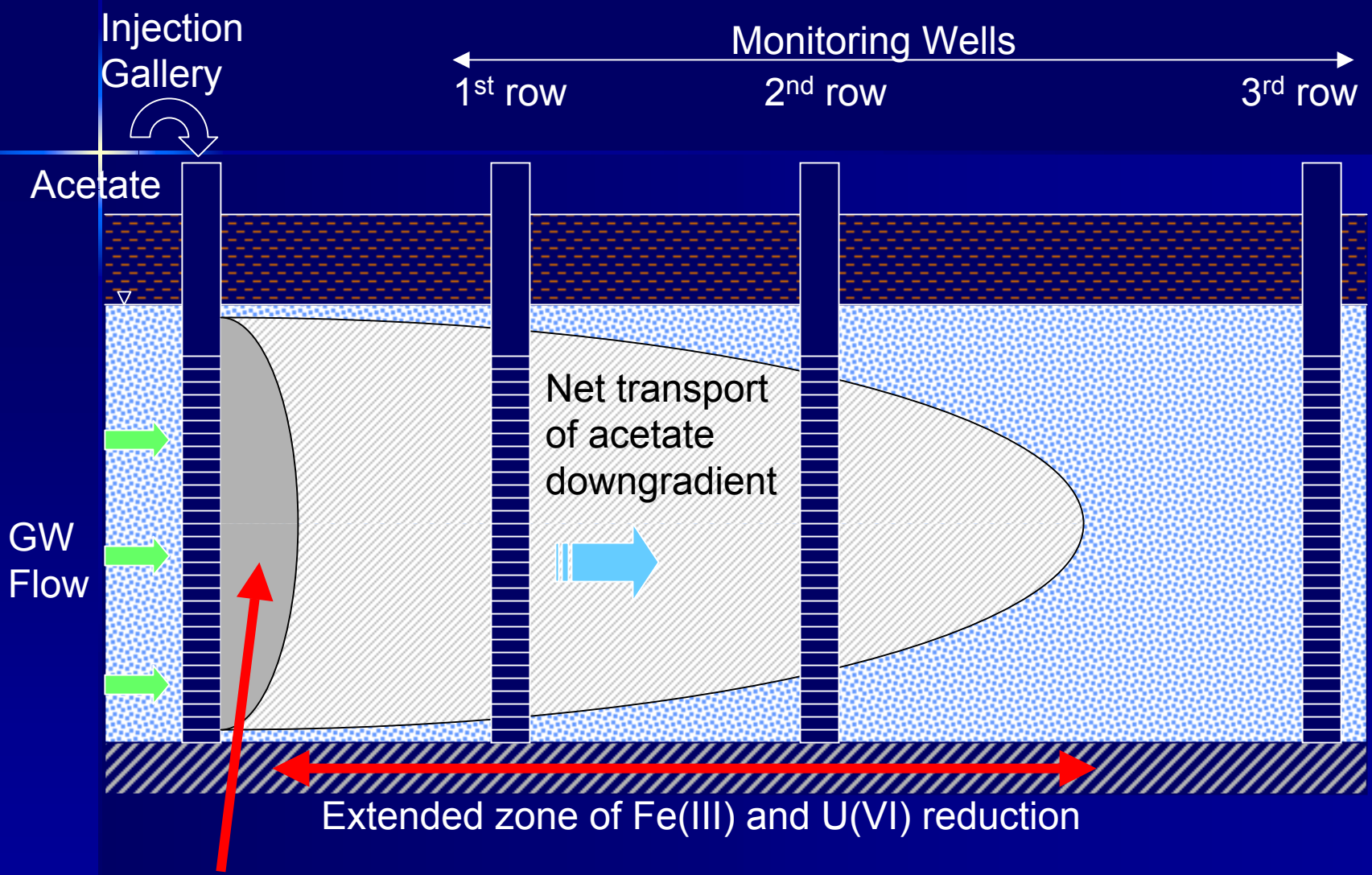
3) Molecular evidence obtained from groundwater samples indicates U(VI) removal was associated with an enrichment of *Geobacteraceae*.

4) Removal of U(VI) decreased upon the stimulation of sulfate reduction.
   - No known acetate-oxidizing sulfate reducers capable of U(VI) reduction.

5) Long term removal of soluble U(VI) from groundwater will require maintenance of Fe(III)-reducing conditions *in situ*.

Anderson, R.T. et al., 2003, *Appl. Environ. Microbiol.* 69(10): 5884-5891.

Old Rifle Site 2003



Old Rifle Site 2003

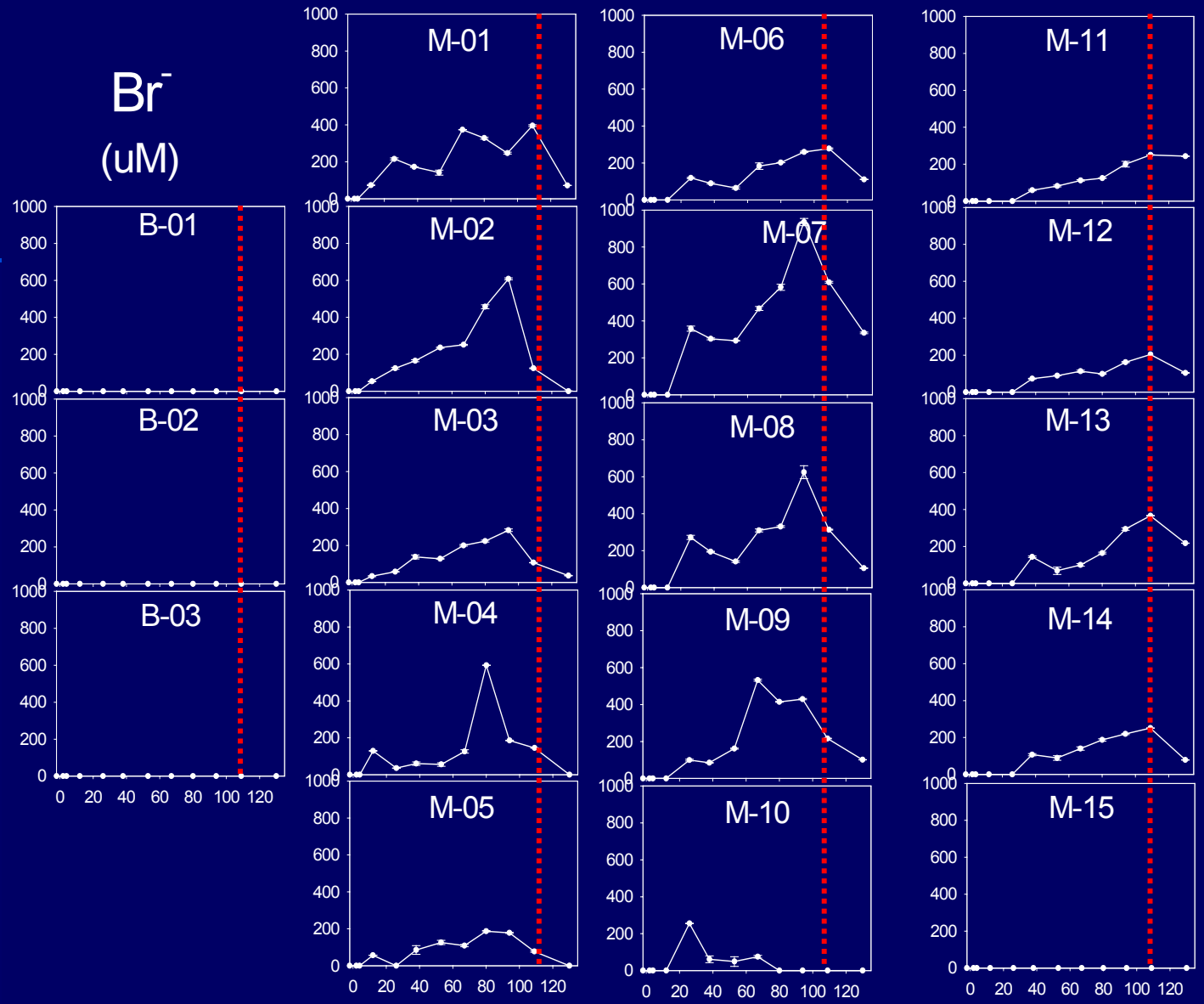
Hypothesis: Increased acetate addition ensures net transport of acetate to downgradient areas containing Fe(III) thereby sustaining metal reduction in situ.

Approach:

1) Increase the in situ acetate concentration to levels greater than the ambient sulfate concentration (>10mM).

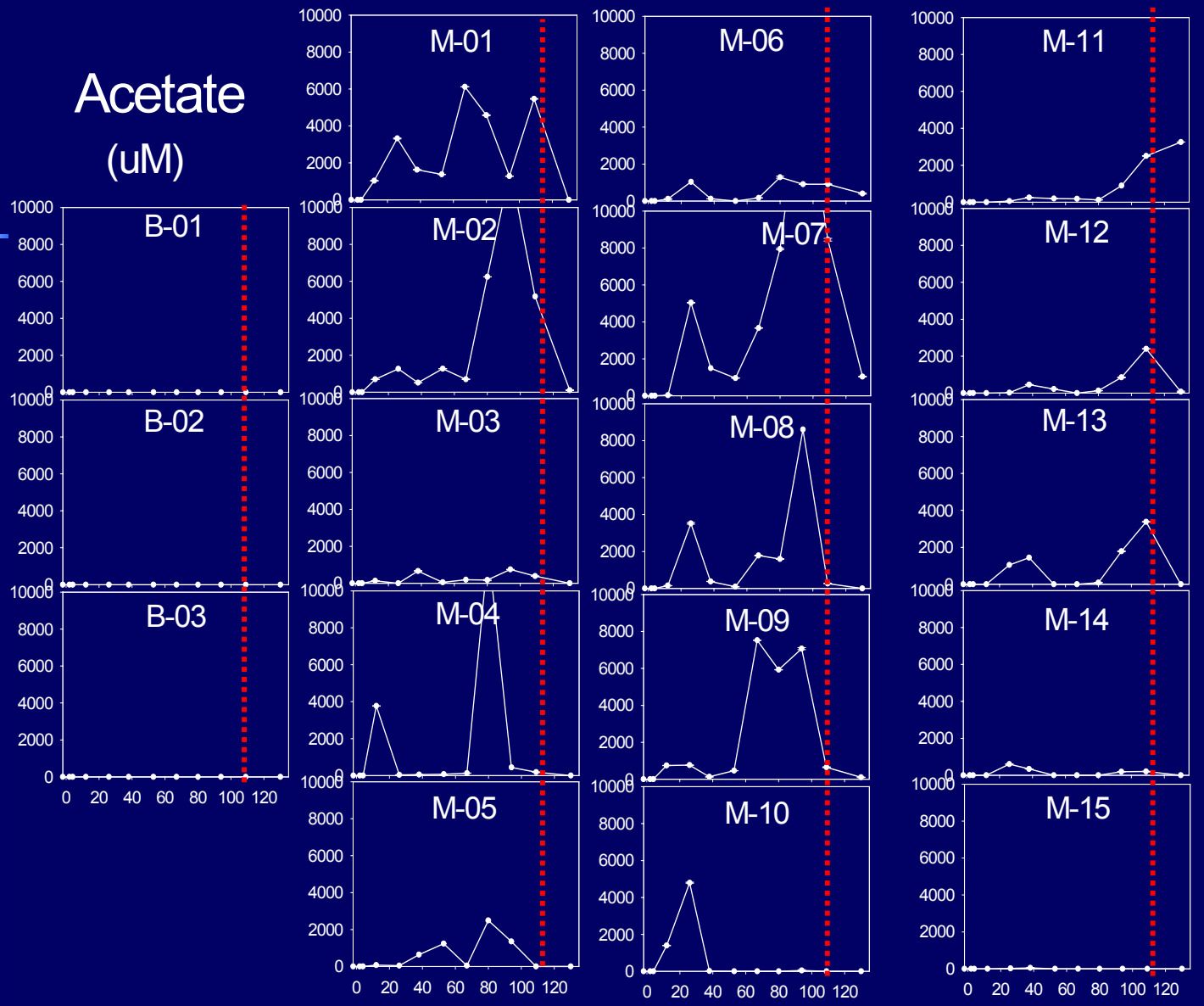
2) Monitor loss of soluble U(VI) and the progression of anaerobic conditions via groundwater and sediment sample analysis.

3) Monitor the progression of stimulated microbial processes in the groundwater and the sediments using 16S rRNA-based and PFLA-based techniques.


Br⁻
(uM)
B-01
B-02
B-03
M-01
M-02
M-03
M-04
M-05
M-06
M-07
M-08
M-09
M-10
M-11
M-12
M-13
M-14
M-15
0
200
400
600
800
1000
0 20 40 60 80 100 120

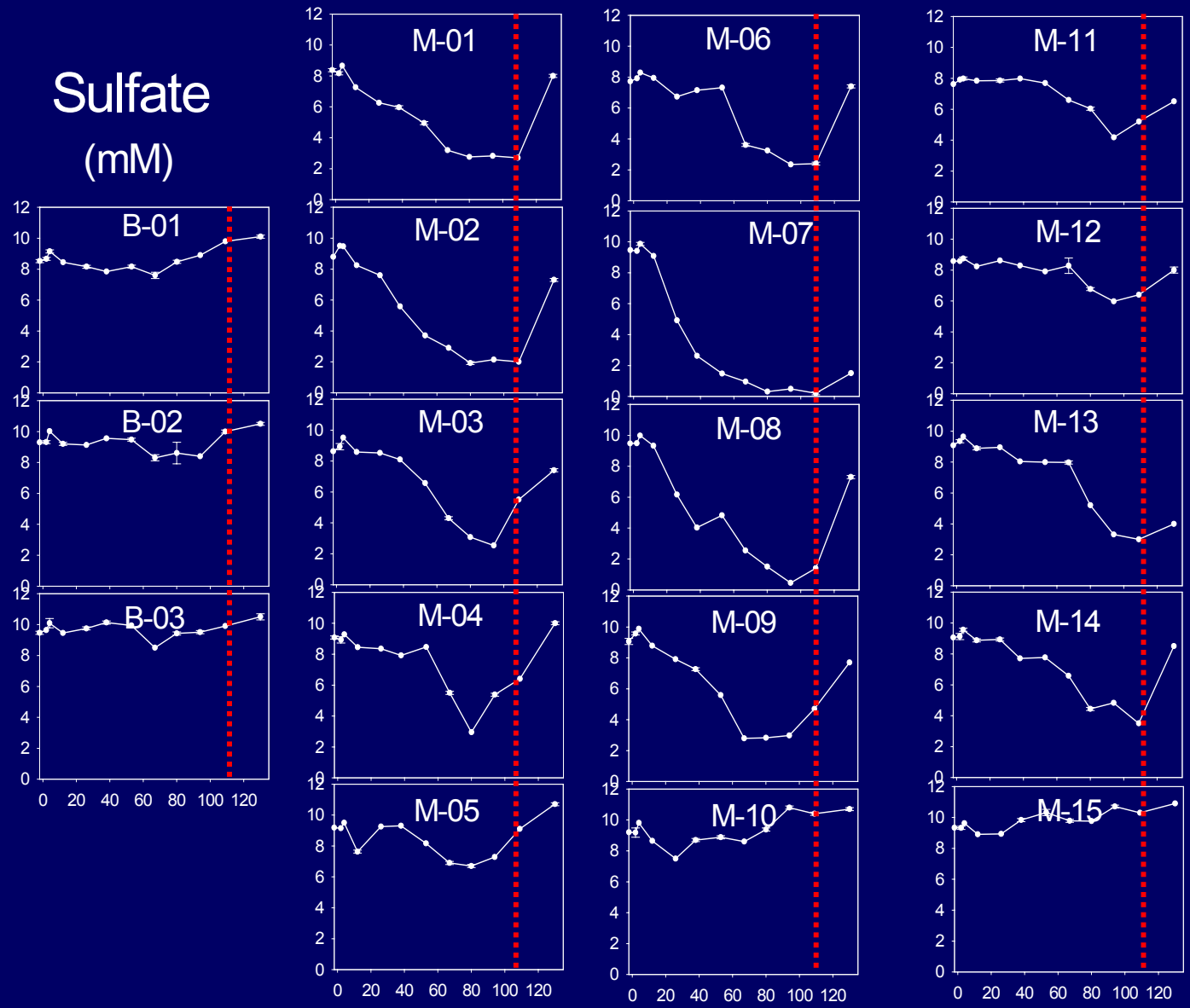
Acetate

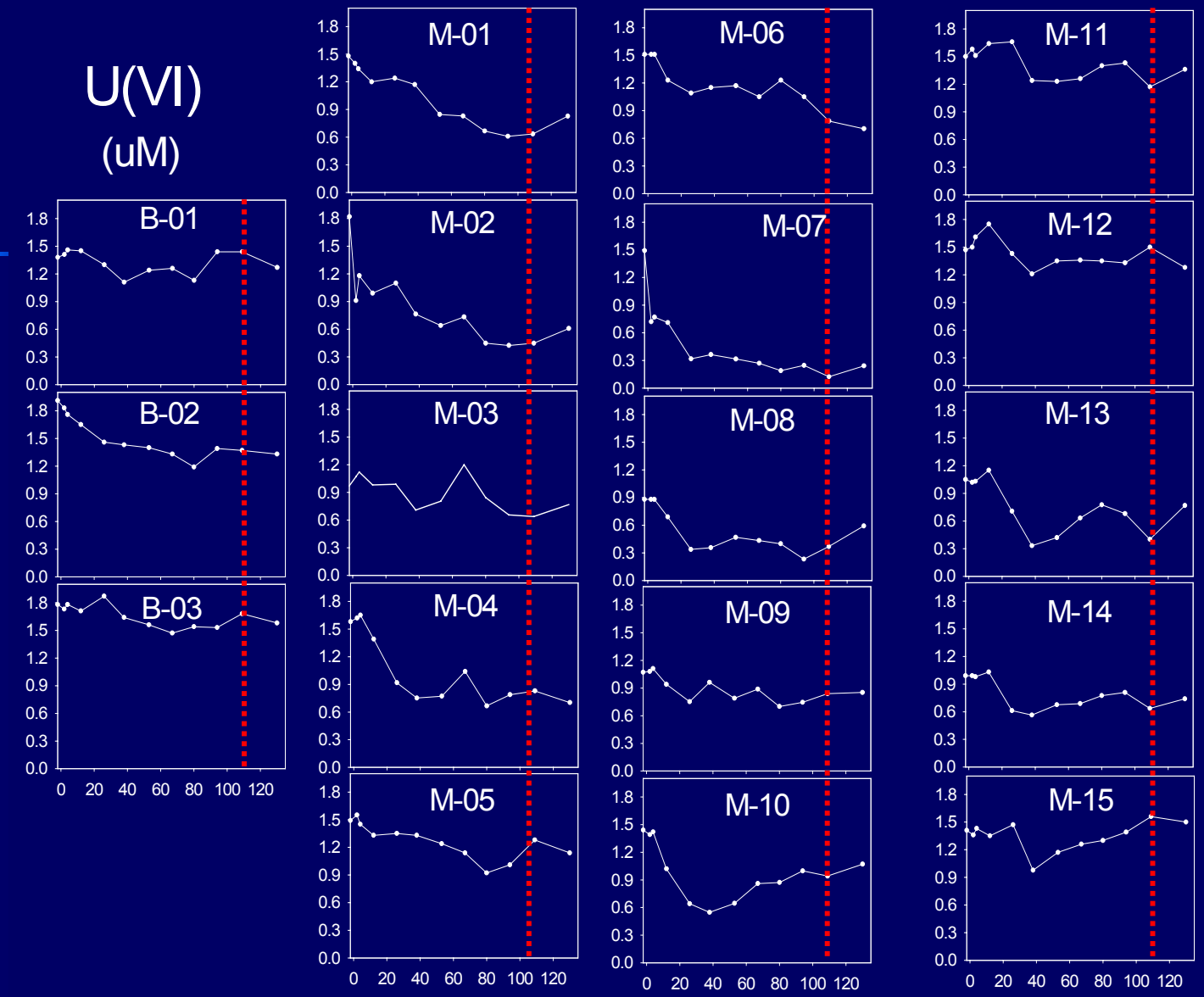
(uM)


B-01
B-02
B-03
M-01
M-02
M-03
M-04
M-05
M-06
M-07
M-08
M-09
M-10
M-11
M-12
M-13
M-14
M-15
0
2000
4000
6000
8000
10000
0 20 40 60 80 100 120

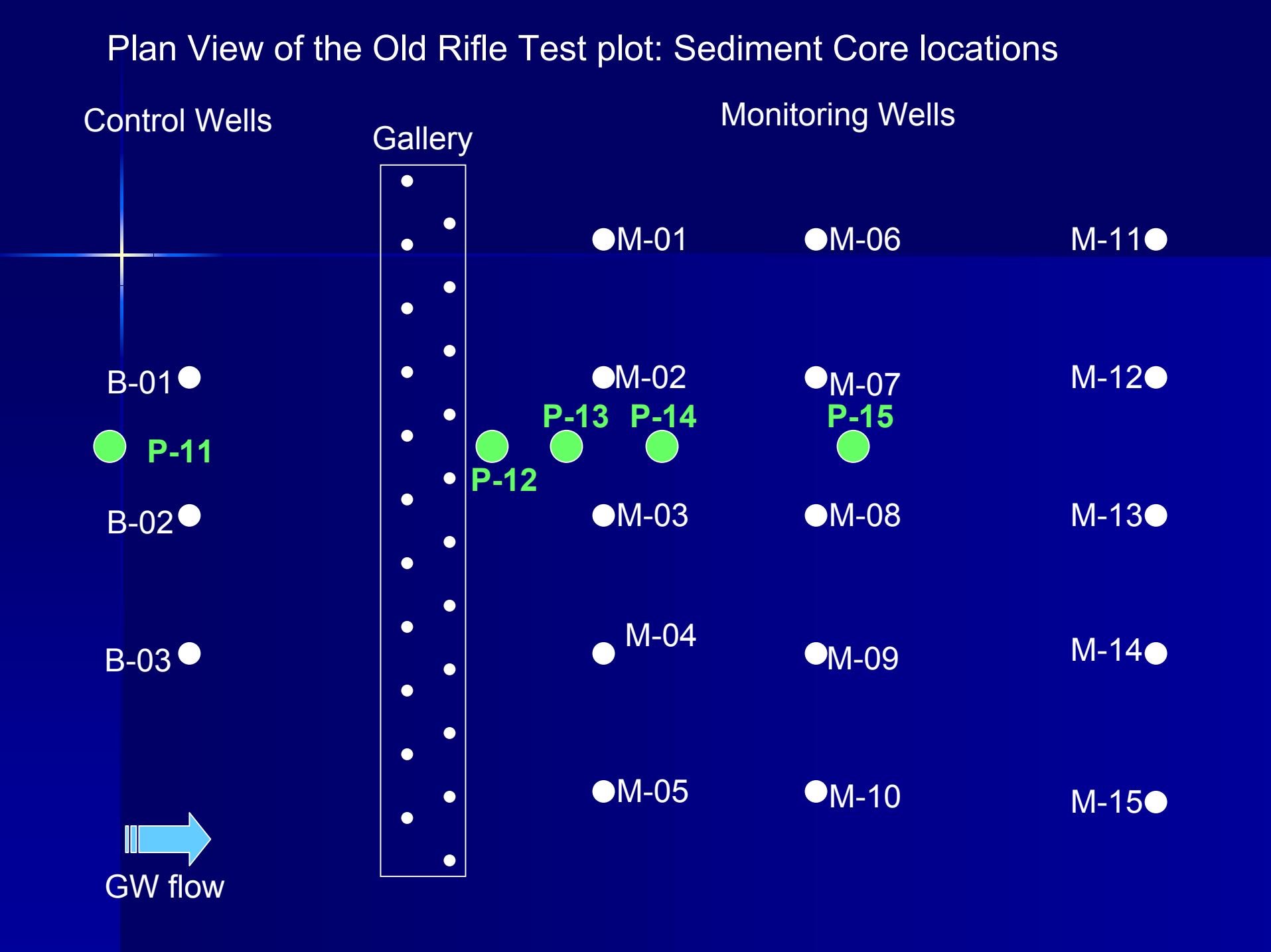
Sulfate

(mM)

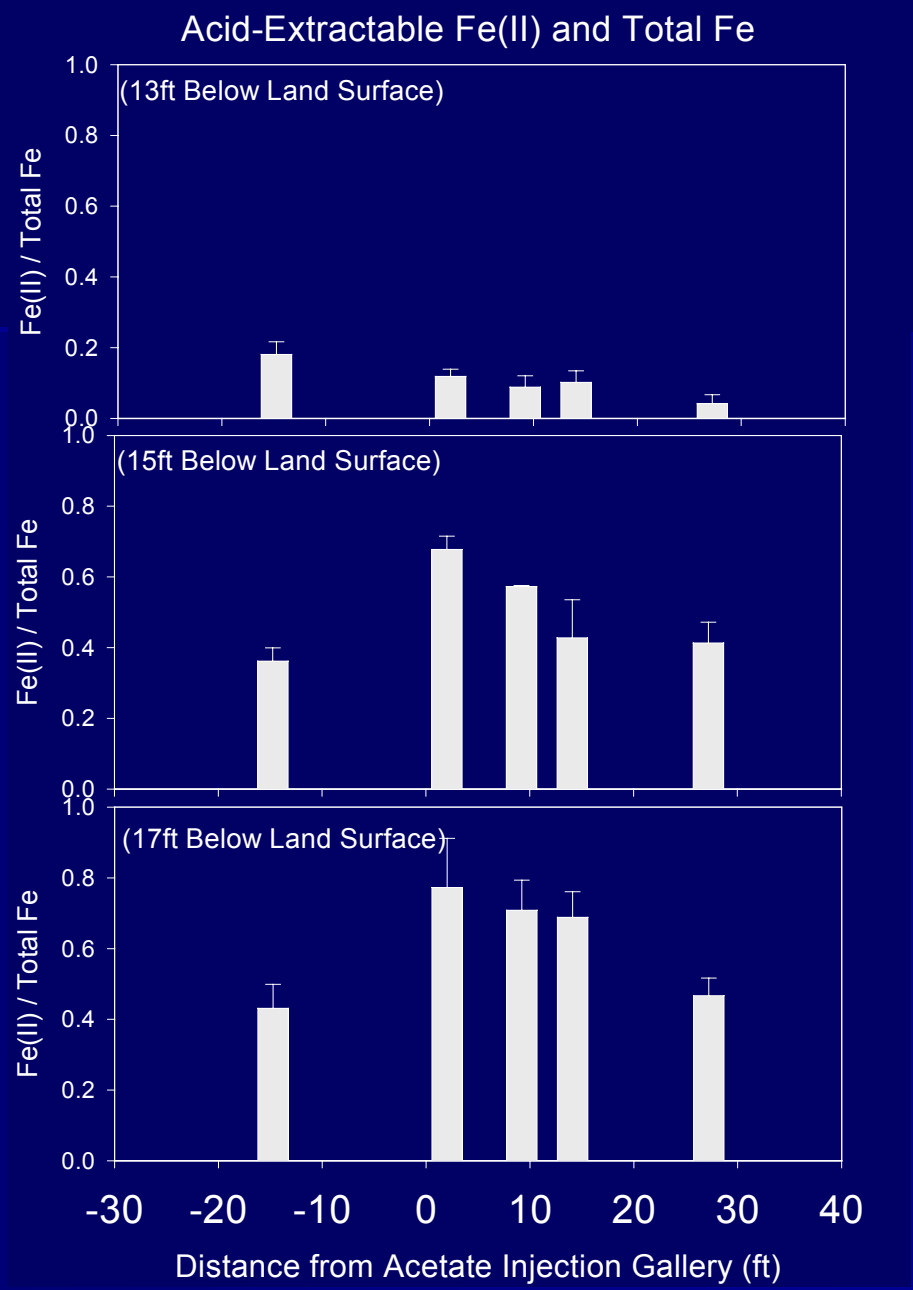

B-01
B-02
B-03
M-01
M-02
M-03
M-04
M-05
M-06
M-07
M-08
M-09
M-10
M-11
M-12
M-13
M-14
M-15
0 2 4 6 8 10 12
0 20 40 60 80 100 120


U(VI)
(uM)
B-01
B-02
B-03
M-01
M-02
M-03
M-04
M-05
M-06
M-07
M-08
M-09
M-10
M-11
M-12
M-13
M-14
M-15
0.0 0.3 0.6 0.9 1.2 1.5 1.8
0 20 40 60 80 100 120

Plan View of the Old Rifle Test plot: Sediment Core locations

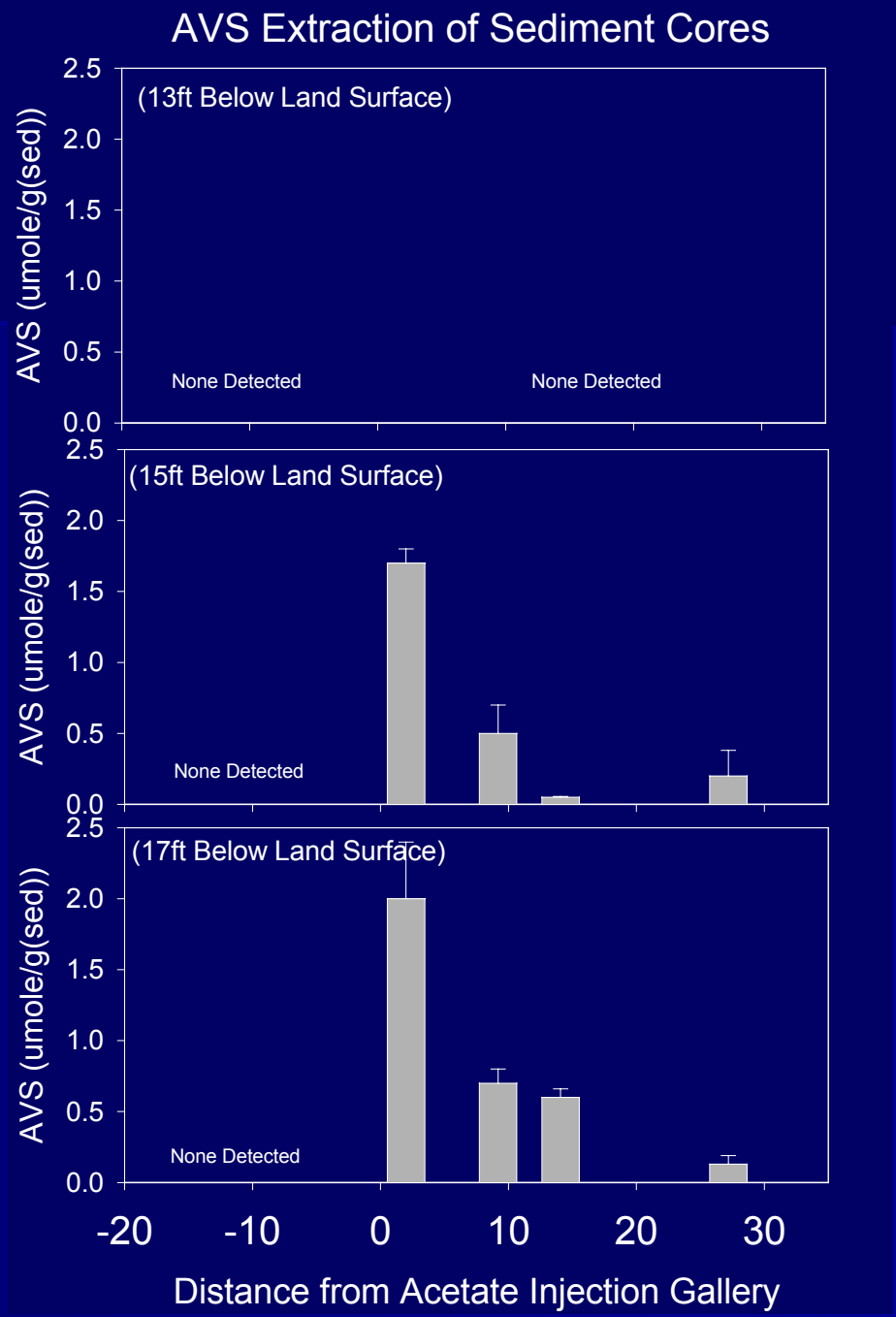


Iron Analyses of Core Samples with Depth



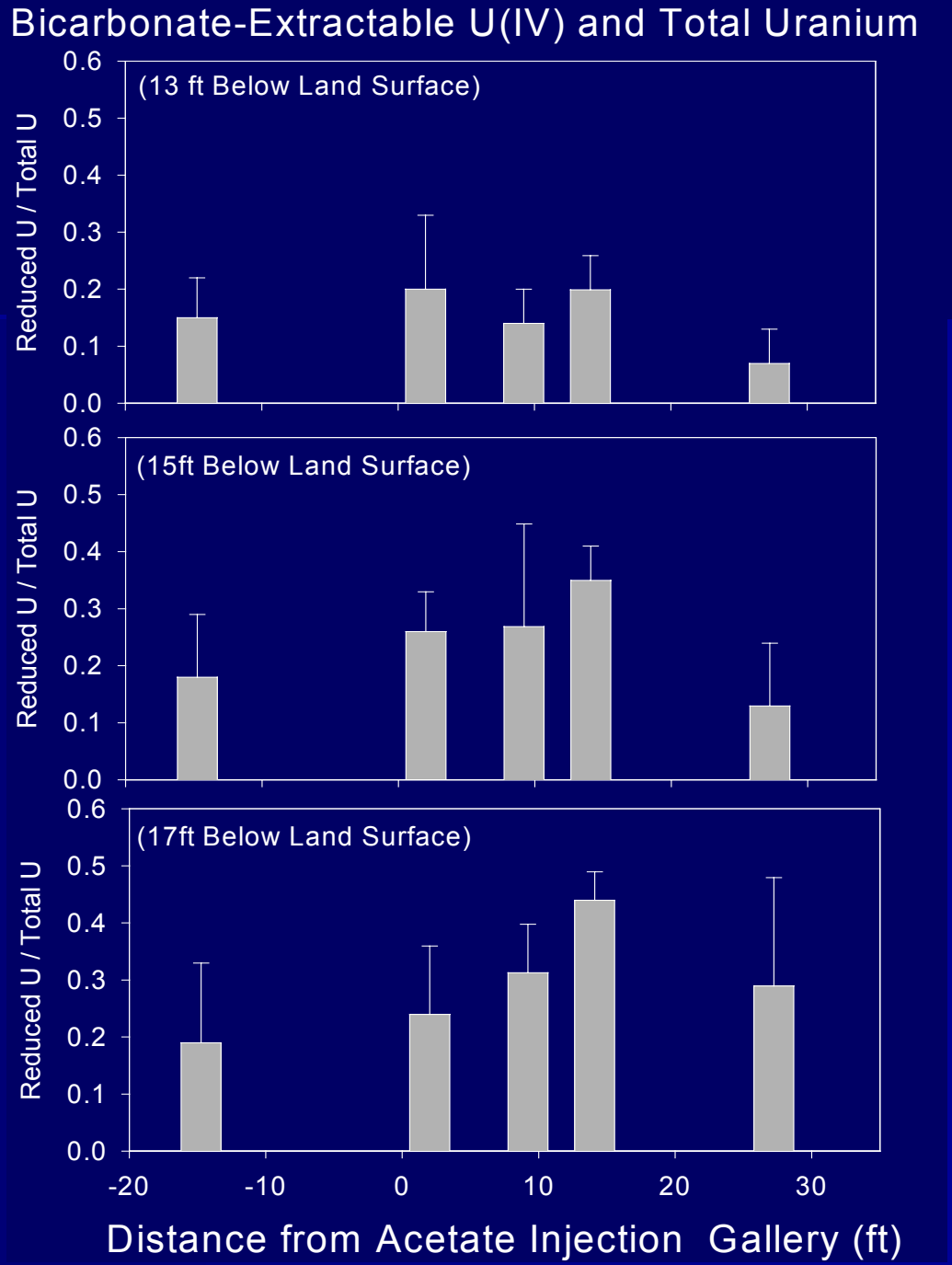
- Increased Fe(II) content with depth and proximity to injection gallery

Acid Volatile Sulfur (AVS) Extraction of Sediment Cores With Depth



- Increased sulfide content with depth and proximity to injection gallery

Extractable Uranium from Sediment Cores with Depth

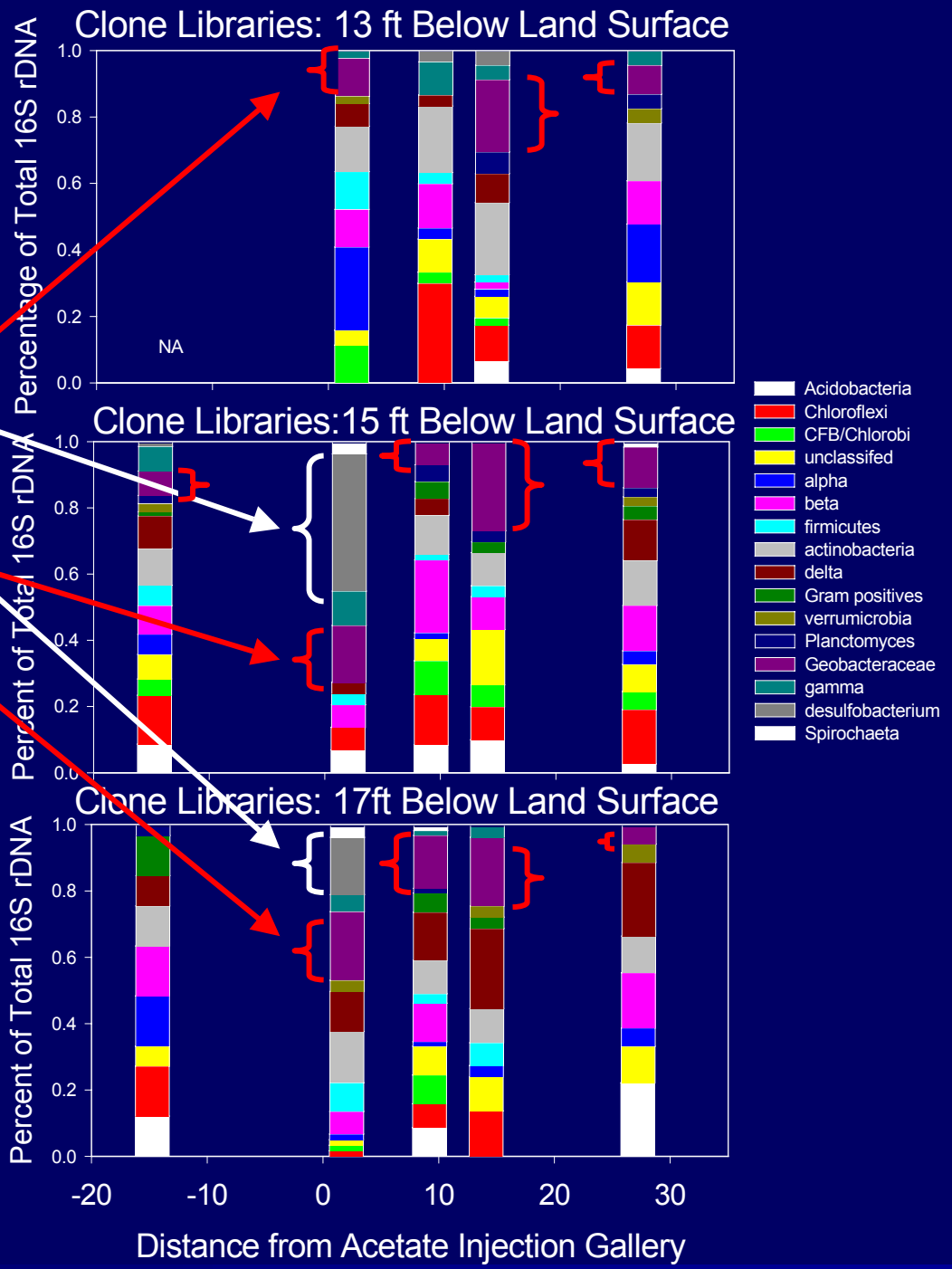


- Percentage of reduced U increases with depth and distance from acetate injection gallery.

Clone Libraries (16S rDNA) from Sediment Cores

Desulfobacterium

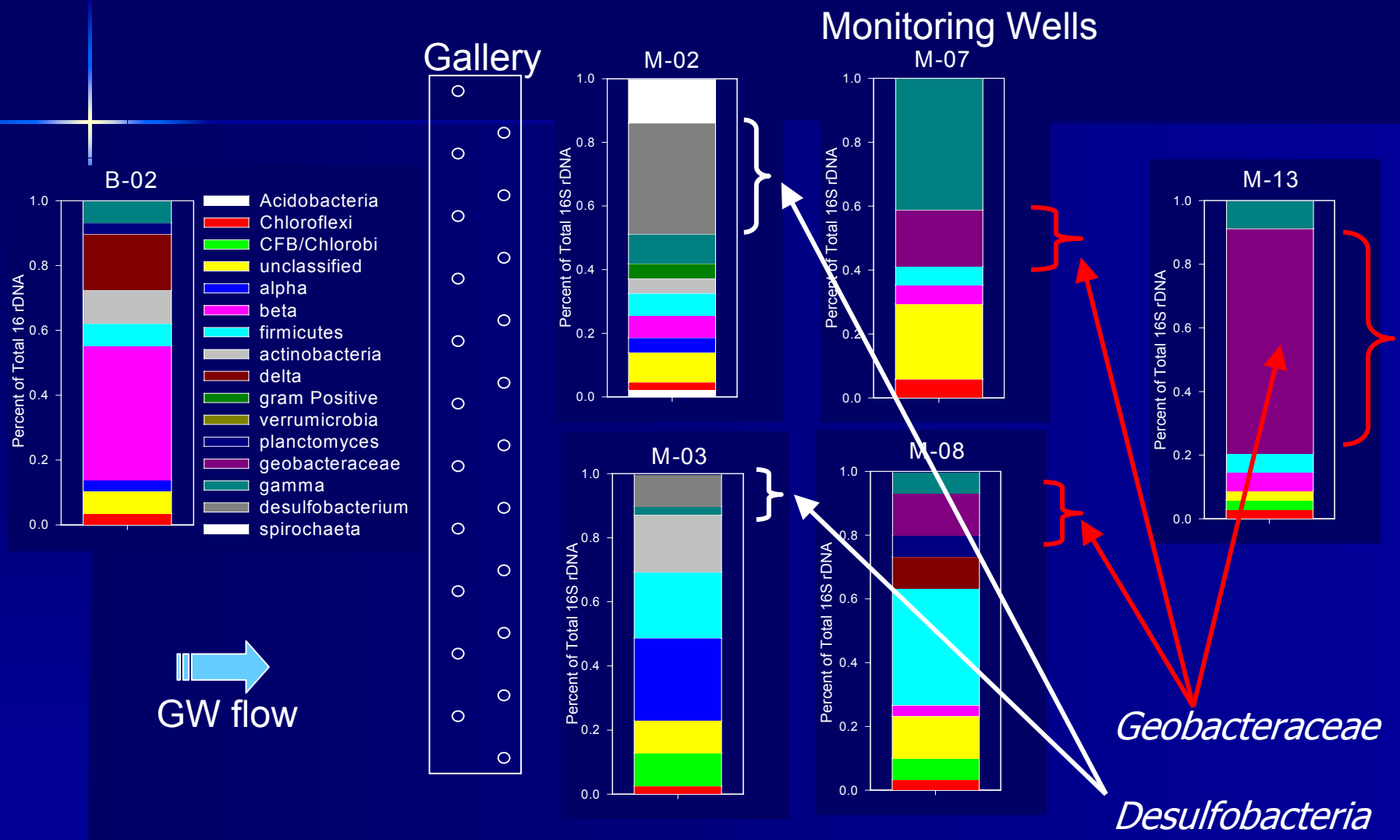
Geobacteraceae



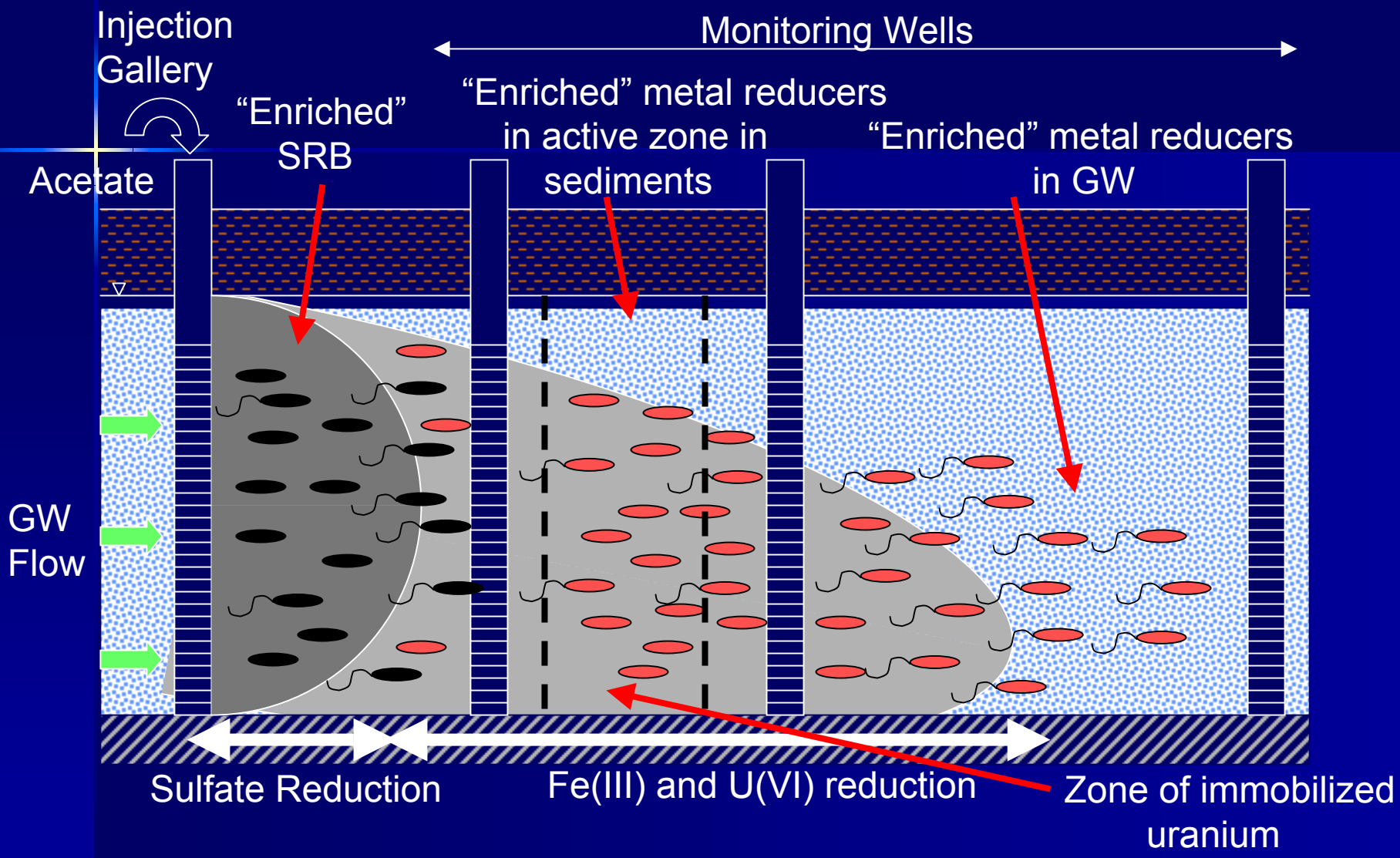
- Increases in *Desulfobacterium* and *Geobacteraceae* with depth and distance from gallery

- Increases in unclassified *delta*-Proteobacteria

Plan View of the Old Rifle Test plot: Groundwater Clone Libraries (16S rDNA)



Conceptual Summary of 16S rDNA Clone Library Data (2003)



- Prolonged loss of U(VI) due to extended area of stimulated metal reduction

Summary of 2003 Experiment

1) Acetate injection at concentrations greater than the ambient sulfate concentration extended metal-reducing conditions in the subsurface by ensuring net transport of acetate downgradient into Fe(III)-containing sediments.

2) Loss of U(VI) from groundwater was sustained in areas receiving acetate despite a stimulation of sulfate reduction.

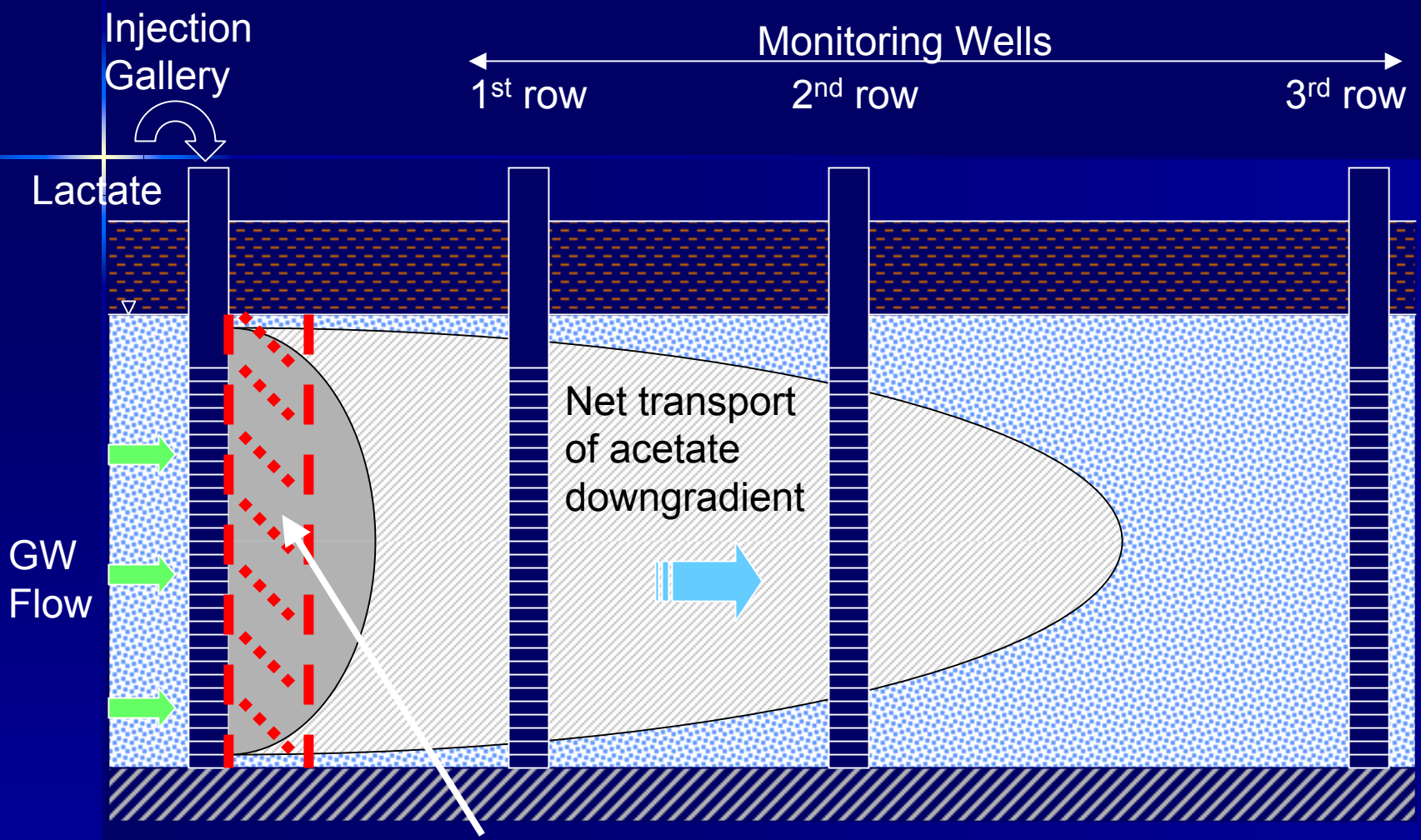
3) Enrichment of metal-reducers in sediments associated with enrichment of bicarbonate extractable U(IV).

4) The composition of the microbial community in the groundwater may not reflect the sediment community composition.

5) Acetate addition best suited for treating source zones.

- Stimulated loss of U from groundwater is progressively displaced from the source of acetate.

Old Rifle 2004: Lactate Addition



- Stable zone of U(VI) reduction under sulfate-reducing conditions
- Depends on the stimulation of *Desulfovibrio* or comparable species

Acknowledgements

University of Massachusetts
Helen A. Vrionis
Irene Ortiz-Bernad
Derek Lovley

Pacific Northwest National Laboratory
Philip E. Long
Charles “Tom” Resch

U.S. DOE UMTRA/Grand Junction, CO
Dick Dayvault
Sam Marutzky
Don Metzler

University of Tennessee
Aaron Peacock
D.C. White

….and the citizens of Rifle, CO.