FRC workshop
2002

FIELD SCALE EVALUATION OF BIOSTIMULATION FOR REMEDIATION OF URANIUM-CONTAMINATED GROUNDWATER

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The Oak Ridge S3 ponds

A legacy of the Cold War: 32 years of atomic waste

- **Uranium**
- **Nitric and sulfuric acid**
- **Chlorinated solvents**
- **Heavy metals**

How to get rid of it?

- **Dump into an unlined pond**
- **Cover with a parking lot**

Tributary 1 to Bear Creek

QuickTime™ and a TIFF (Uncompressed) decompressor are needed to see this picture.

PRIMARY OBJECTIVE

- **Evaluate rates and mechanisms of microbially-mediated reduction of uranium in a highly heterogeneous field setting.**

U(VI) is converted to U(IV)

$UO_2(CO_3) + H^+ + 2e^- = UO_2 + HCO_3^-$ E°' = +0.105 V

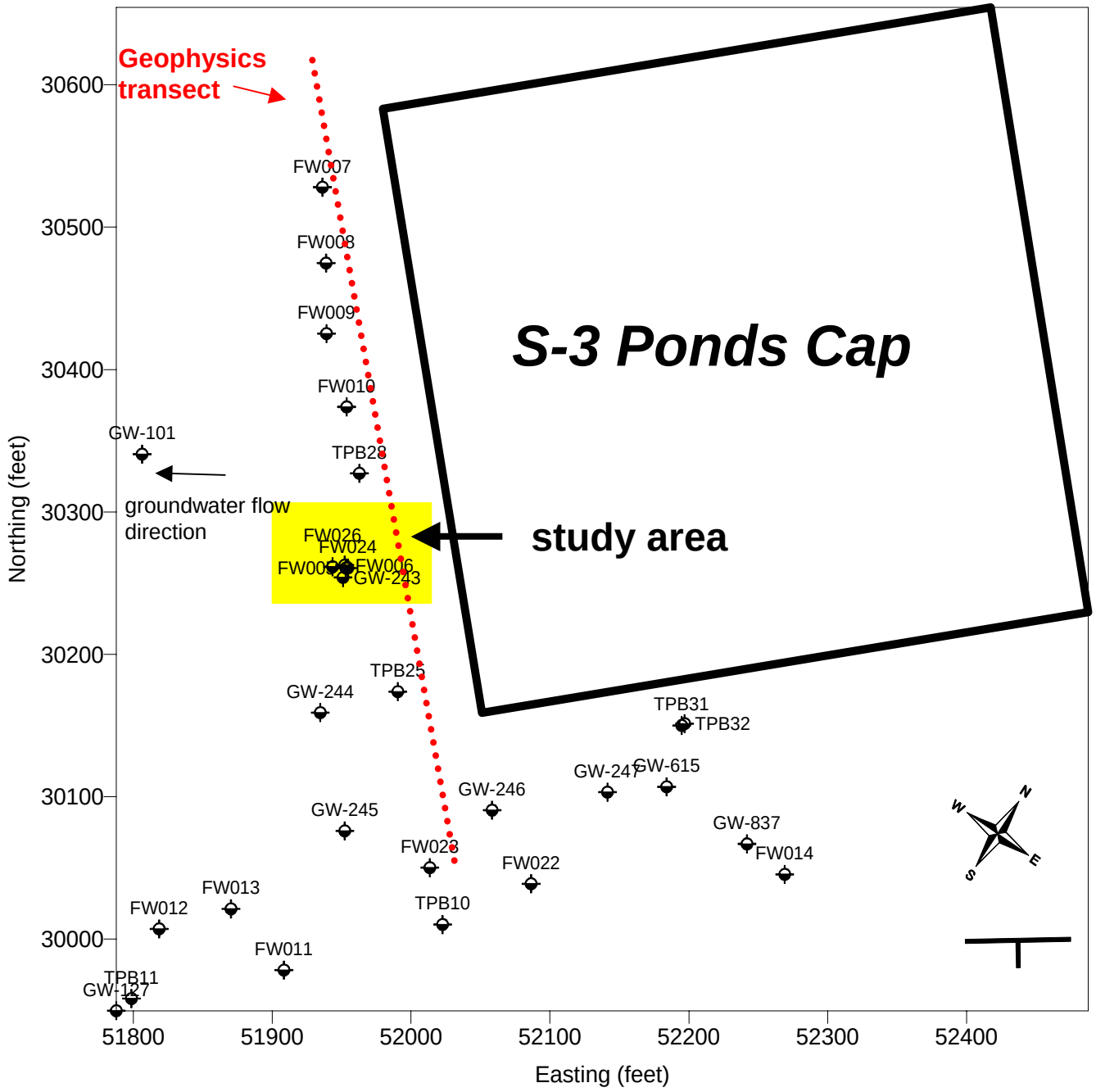
Good thing: a few electrons goes a long ways - 119 mg U/ meq

Bad thing: Nitrate is the preferred electron acceptor. It inhibits U(VI) reduction. Moreover, the products of partial denitrification (NO_2^-, N_2O) oxidize U(IV) (Senko et al., 2002). Partial denitrification is common at low pH.

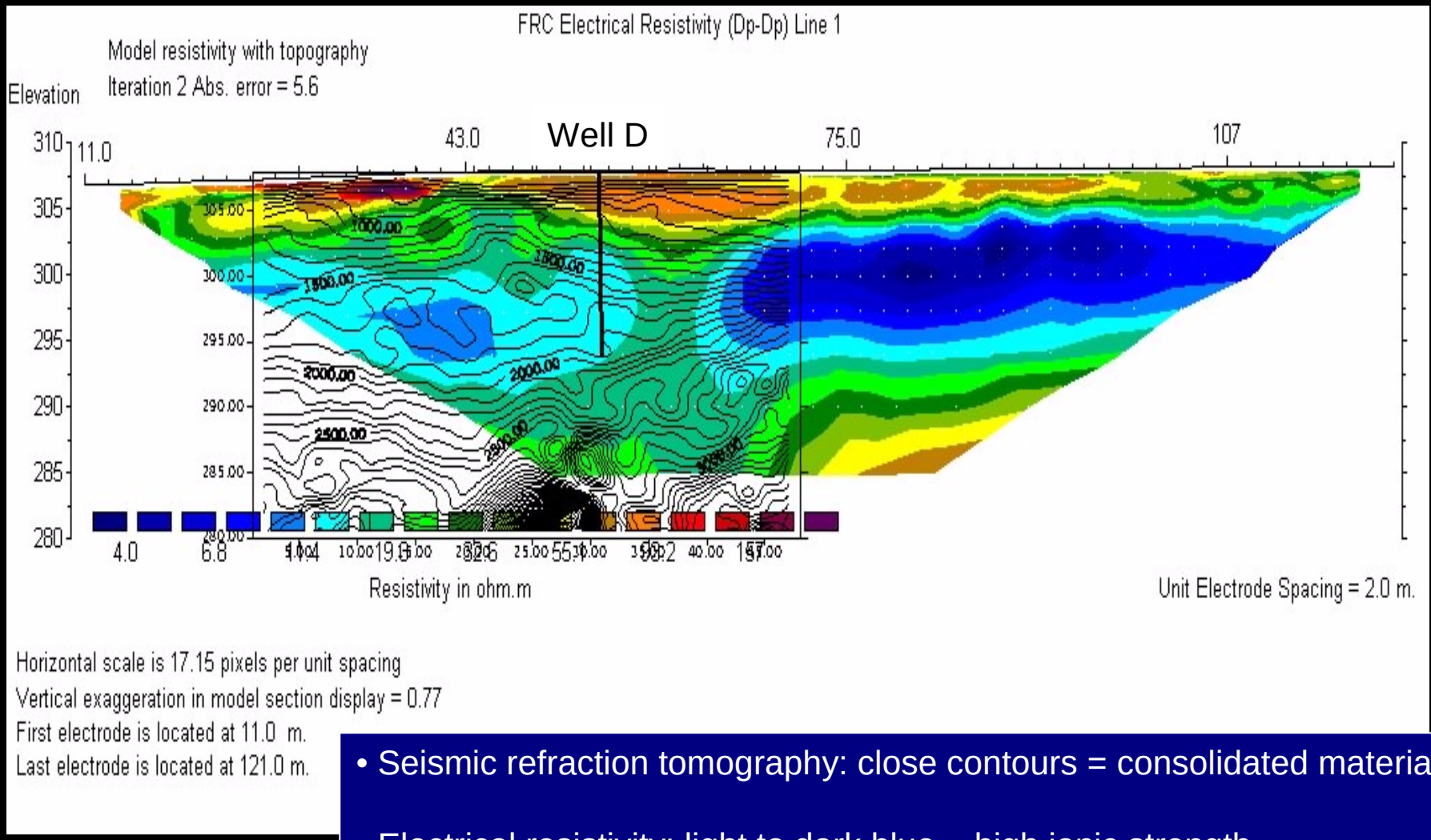
PHASE 1: SITE CHARACTERIZATION

PHASE 2: SITE CONDITIONING

PHASE 3: BIOSTIMULATION


Geophysics transect
S-3 Ponds Cap
study area
groundwater flow direction
FW007
FW008
FW009
FW010
GW-101
TPB23
FW026
FW024
FW006
GW-243
TPB25
GW-244
TPB31
TPB32
GW-247
GW-615
GW-246
GW-245
GW-837
FW014
FW023
FW022
FW013
FW012
TPB10
FW011
TPB11
GW-127
30600
30500
30400
30300
30200
30100
30000
Northing (feet)
51800
51900
52000
52100
52200
52300
52400
Easting (feet)
N
W
E
S

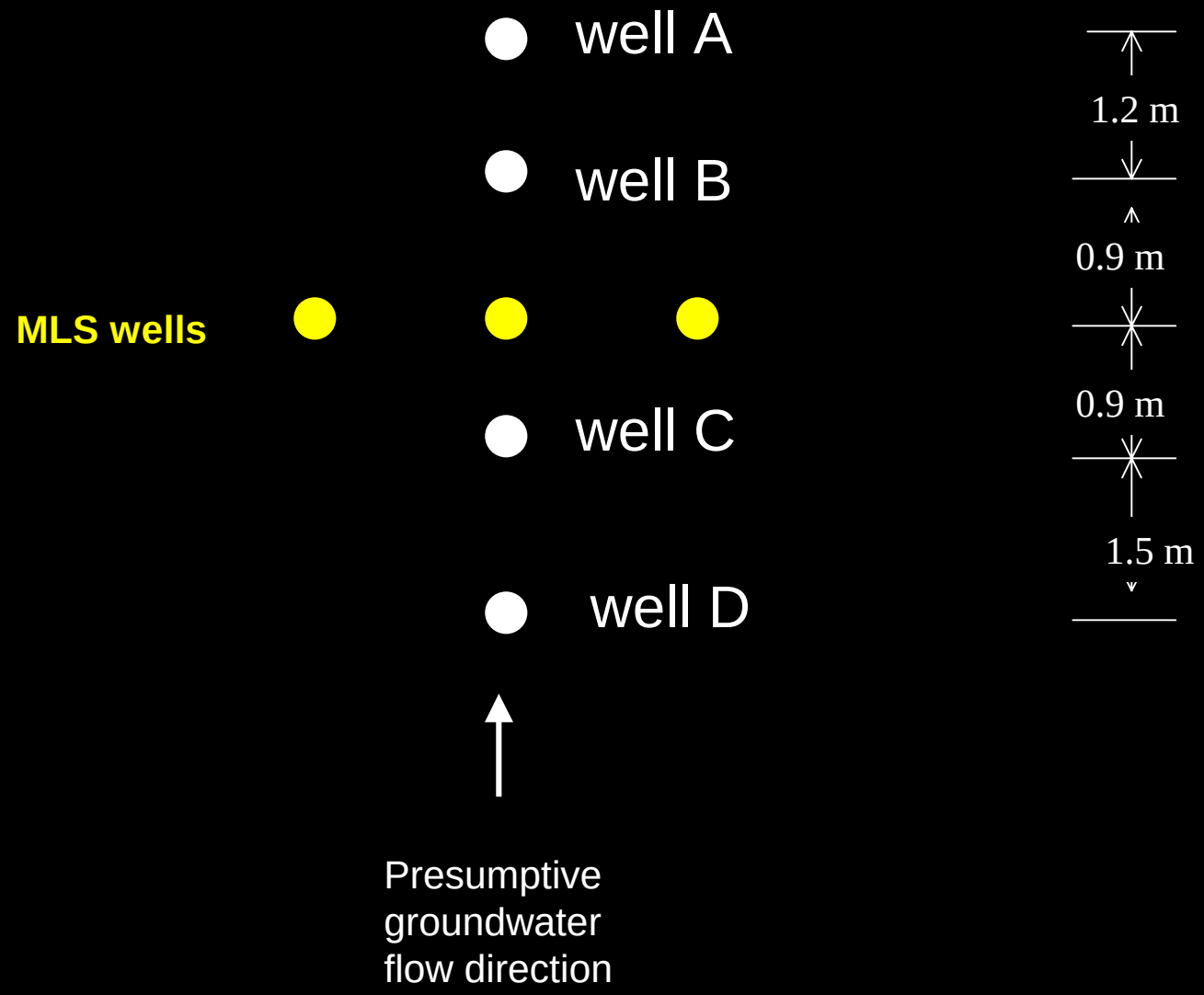
Geophysics used to identify probable areas of contaminant transport



- Seismic refraction tomography: close contours = consolidated material
- Electrical resistivity: light to dark blue = high ionic strength
- Both sets of data agree with auger penetration and geochemistry

Doll, 2001

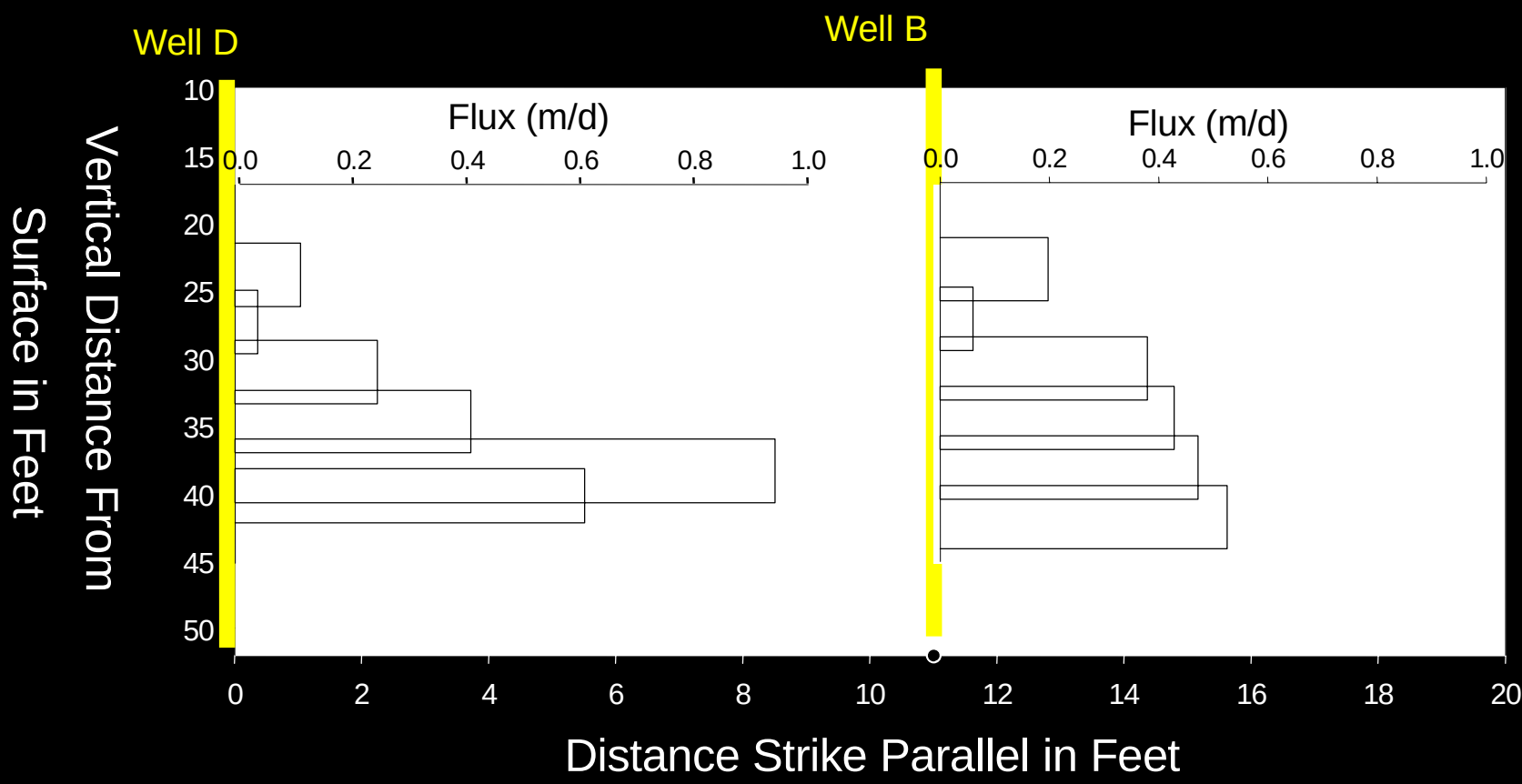
Well configuration



Can you find the FRC science advisor?

I see his shoes, but where is his head?

Groundwater Flux at FRC Area 3

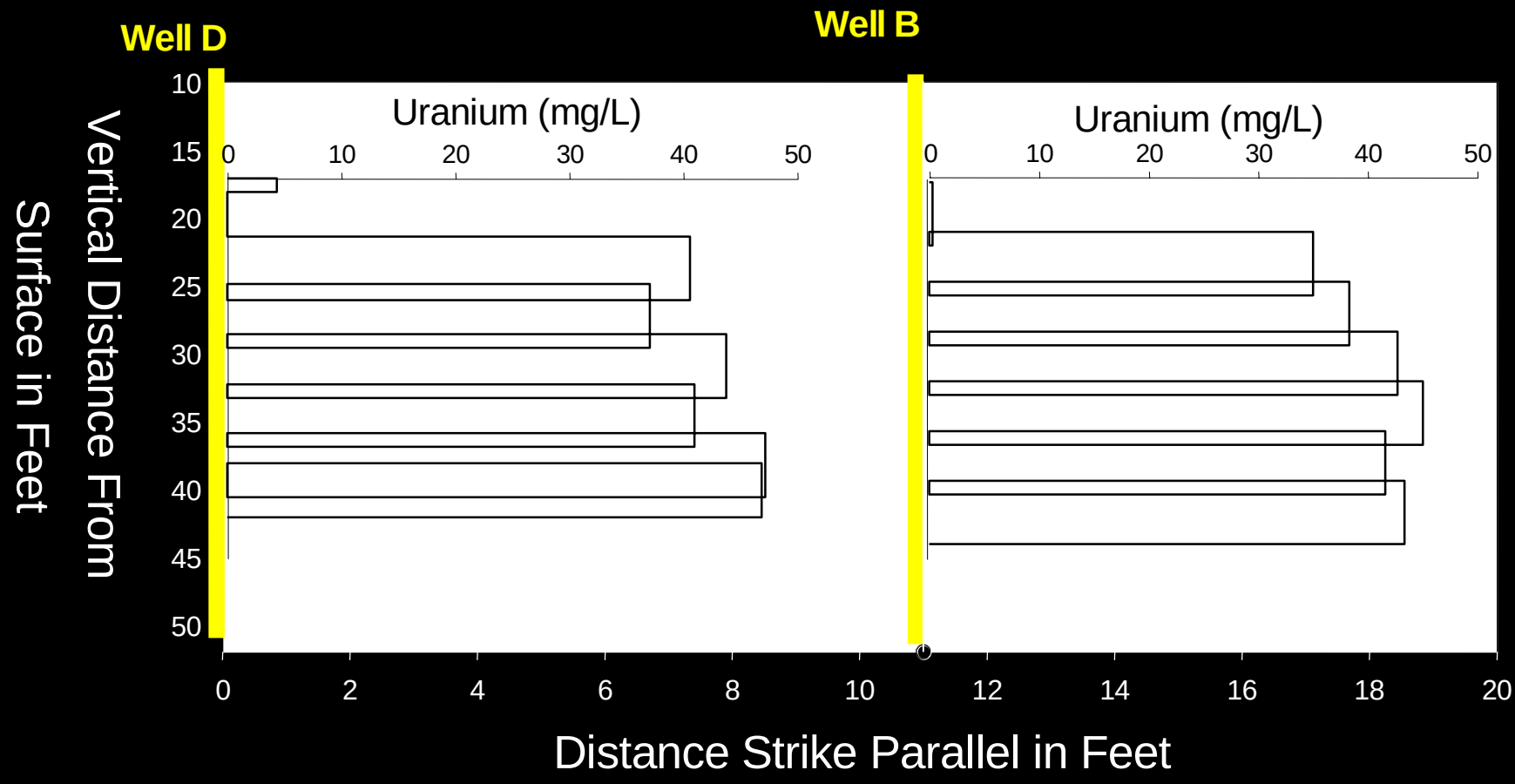


- **90-95 % of groundwater flow is within the 30 to 50 ft. depth interval. These results are consistent with independent measurements using a borehole flowmeter.**

- **Groundwater flux within this interval is on average 0.5 m/d.**

- **Consistent data for each borehole suggest flow is strike parallel.**

Groundwater Uranium at FRC Area 3

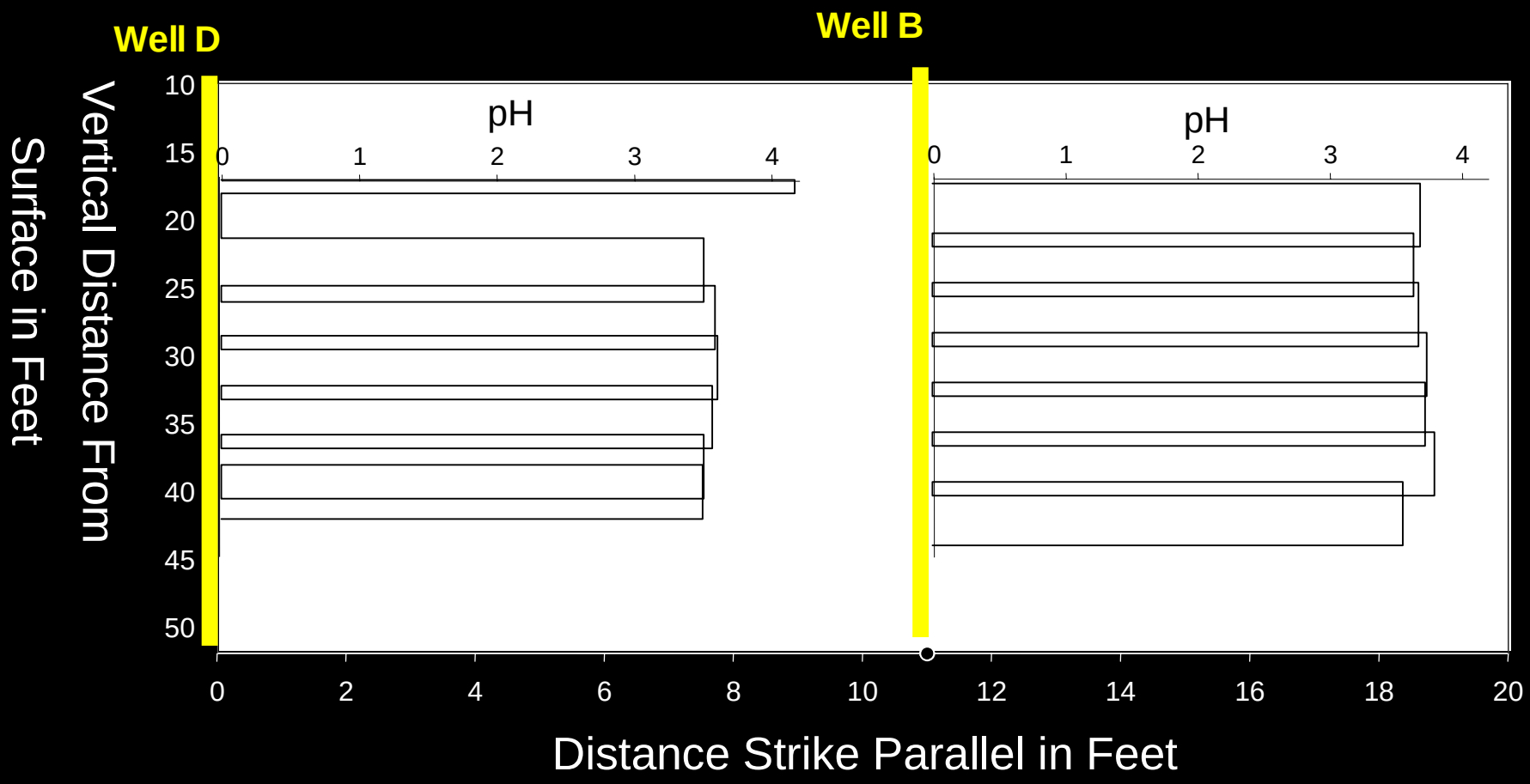


- **Groundwater concentrations of U in the fast flowing zone are very high with average values above 40 mg/L. Pumping at 1.4 lpm (achieved at Well D) gives a U mass flow rate of 81 g/d or 29 kg/yr.**

- **Consistent data for each borehole suggest flow is strike parallel.**

- **The vertical extent of the U plume is consistent with geophysical resistivity data.**

Groundwater pH at FRC Area 3

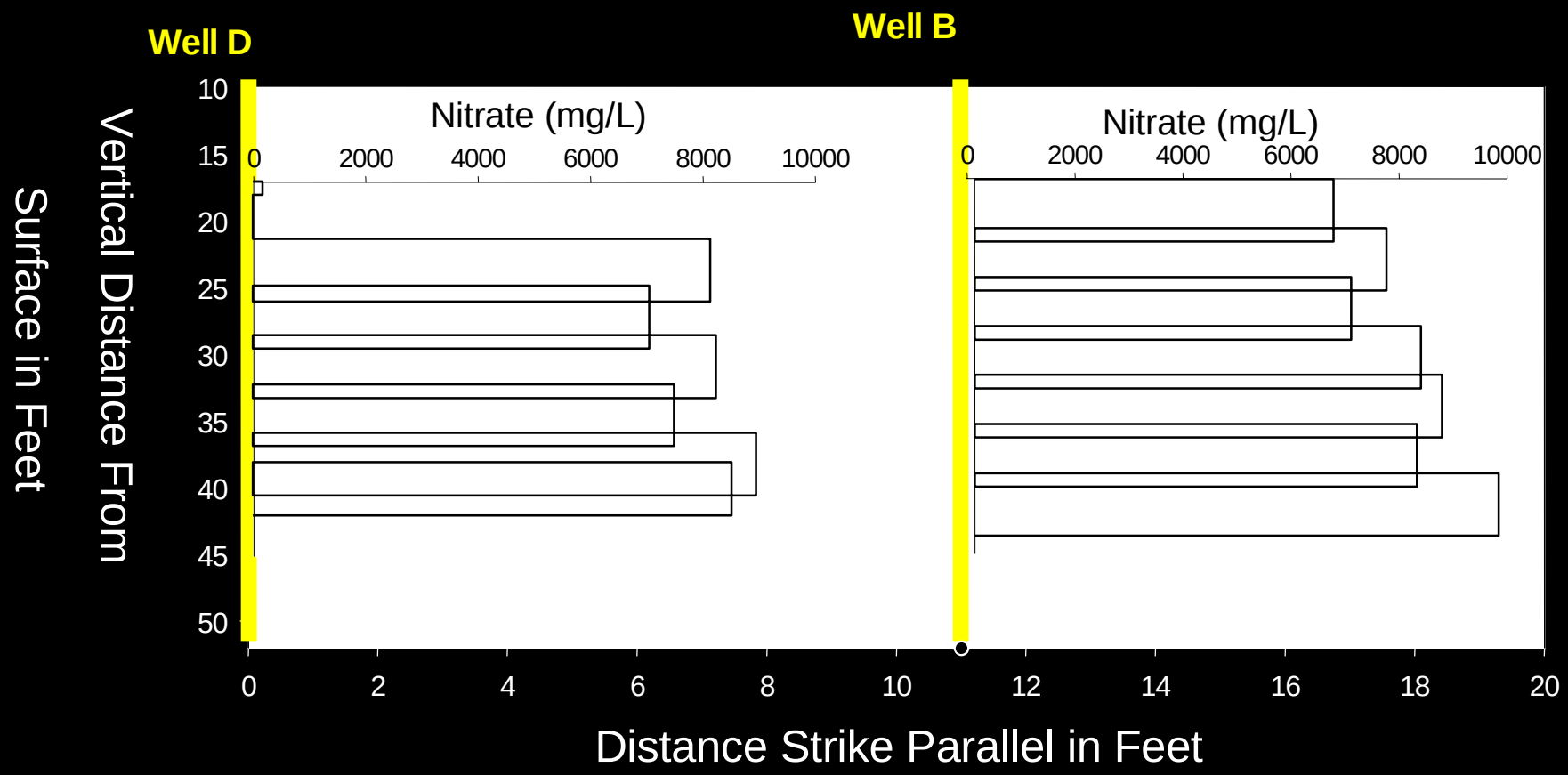


- **Groundwater pH is consistently low (e.g. ~3.5) and highly buffered.**

- **Unconfined groundwater degasses CO_2 since the soil solid phase is carbonate rich and buffered near 6.5 to 7.**

- **The low pH is not conducive to U sorption on the solid phase which is consistent with downhole *in situ* detection of U using a NaI detector. Maximum U sorption was noted from 10 to 20 ft. with less sorption occurring in the fast flowing 30 to 50 ft. interval.**

Groundwater Nitrate at FRC Area 3

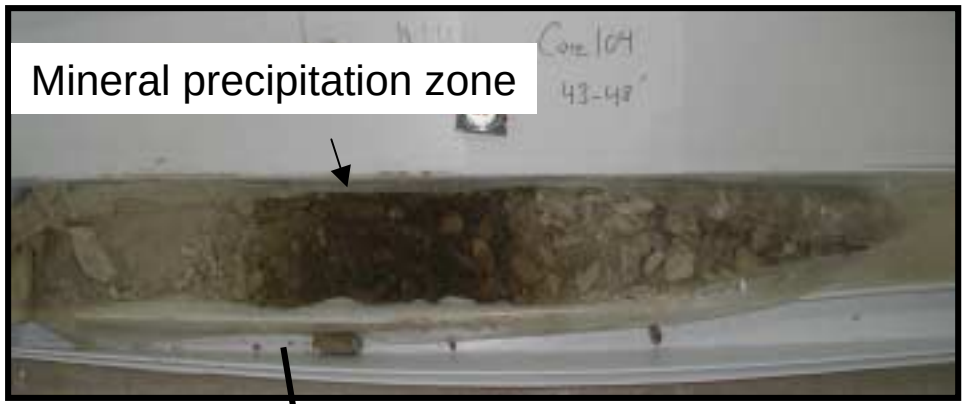


- **Average nitrate concentrations in the groundwater are near 8 g/L. The vertical extent of the plume is consistent with co-contaminant U and geophysical resistivity data.**

Undisturbed column from Area 3 treatment zone (42 ft. depth)

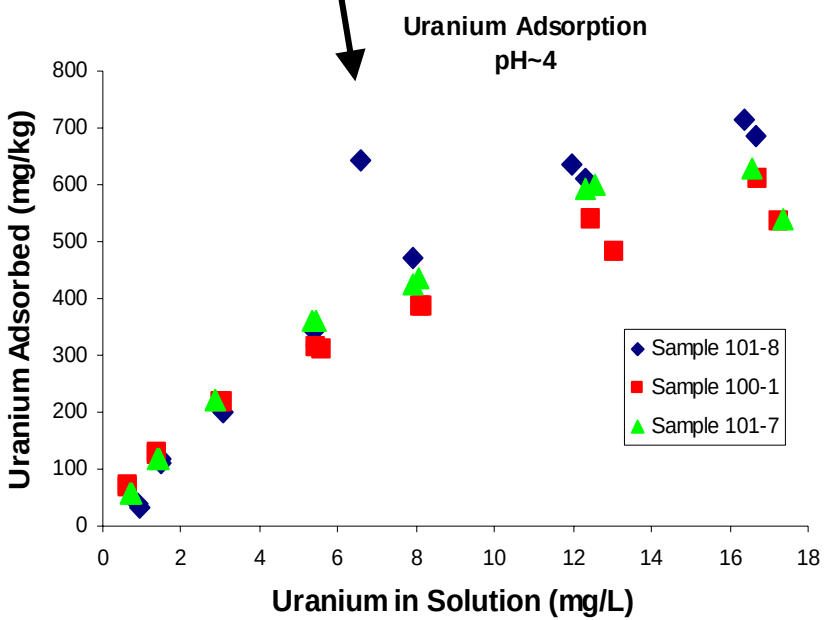
Experiments designed to quantify solute mass transfer kinetics, uranium reactivity, and propensity for bioreduction under dynamic flow conditions.

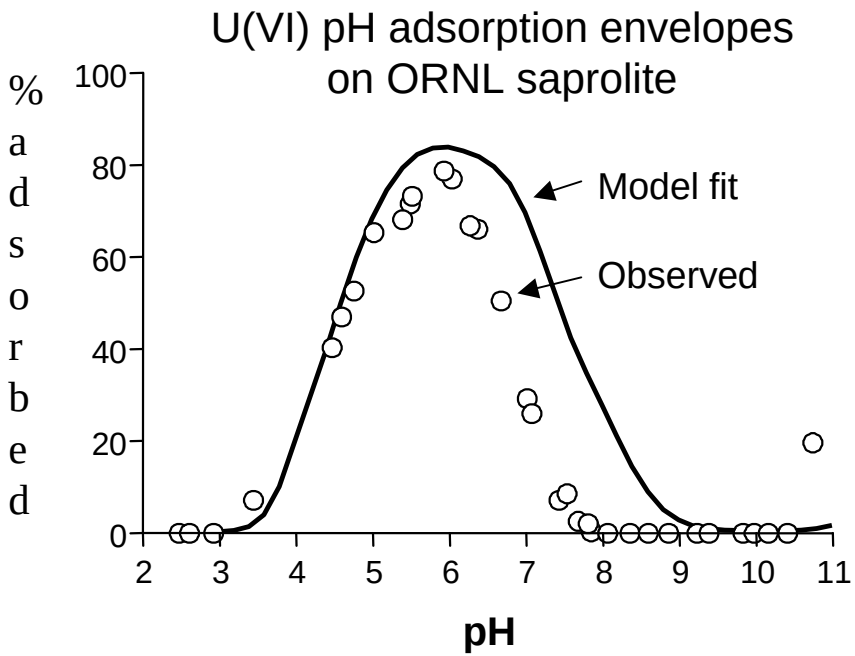
Uranium adsorption on Area 3 treatment zone soils



Concentration dependent U sorption on FRC soils.

U sorption is strongly pH dependent.





Key groundwater quality parameters at Well D.

Inorganic Constituents	Concentrations	Organic Constituents	Concentrations
pH	3.4-3.6		
TIC	202-401 mg/L	COD	200 mg/L*
Chloride	249-298 mg/L	TOC	65-81 mg/L
Sulfate	843-1116 mg/L	2-Butanone	69-84 µg/L
Nitrate	7500-8963 mg/L	Acetone	340-700 µg/L
Nitrite	Low		
Uranium	42-51 mg/L	Chloroform	34-36 µg/L
Technetium-99	35-40 nCi/L (80-89 dpm/ml)	Tetrachloroethene	2100-3300 µg/L
Ni	11.5-14 mg/L	Trichloroethene	94-130 µg/L
Cd	0.45 mg/L		
Al	541±47 mg/L	1,1,2-trichloro-1,2,2-trifluoroethane	1200-1500 µg/L
Ca	931±74 mg/L	Methylene chloride	39-42 µg/L
Mg	174±11 mg/L	Citric acid	~6 mg/L #
Mn	130±9 mg/L		
Sb	<0.003 mg/L		
Cr	0.17 mg/L		
Pb	0.03 mg/L		
Se	0.02 mg/L		

Neutralize

Remove as N_2

Precipitate at pH 5

Precipitate at pH 7-8

volatile

* estimated value: a measurement is needed.

values for MLS FW 100, 40' depth.

PHASE 2. SITE CONDITIONING

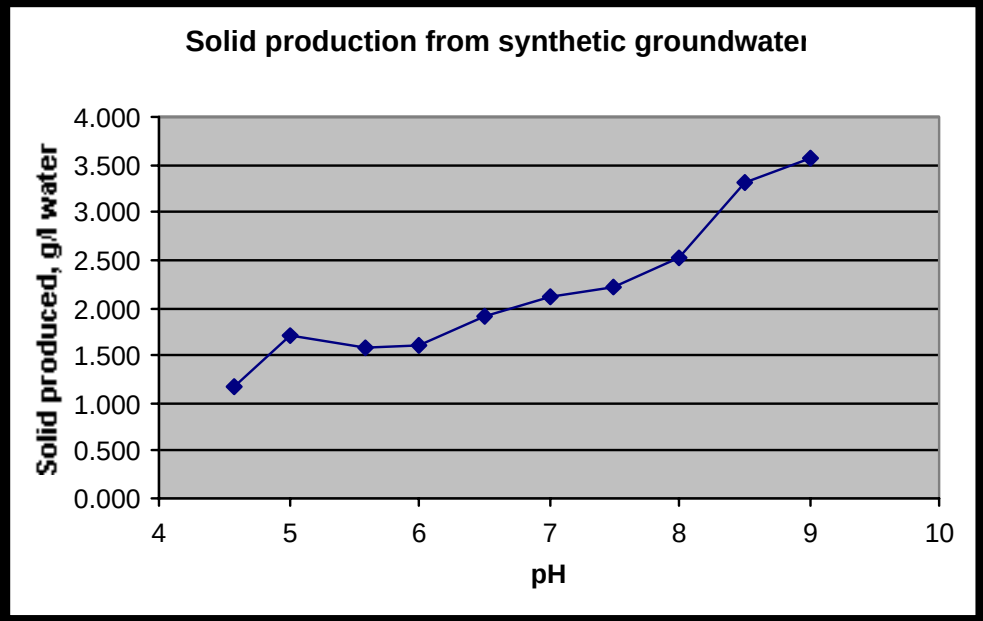
- **VOC removal**
- **pH adjustment (Al, U, Ca, Mg, Mn removal)**
- **Nitrate removal**

pH adjustment and precipitate formation

pH adjusted to 7 with Na_2CO_3

pH adjusted to 7 with KOH

pH adjusted to 7 with 50% liquid from these denitrifying batch cultures



Denitrifier cultures were grown in fed batch mode with synthetic groundwater (pH 3.4) amended with lactate-ethanol and organic P. CO_2 was periodically removed by He sparging (pH in the serum bottles: 6.8-7.2).

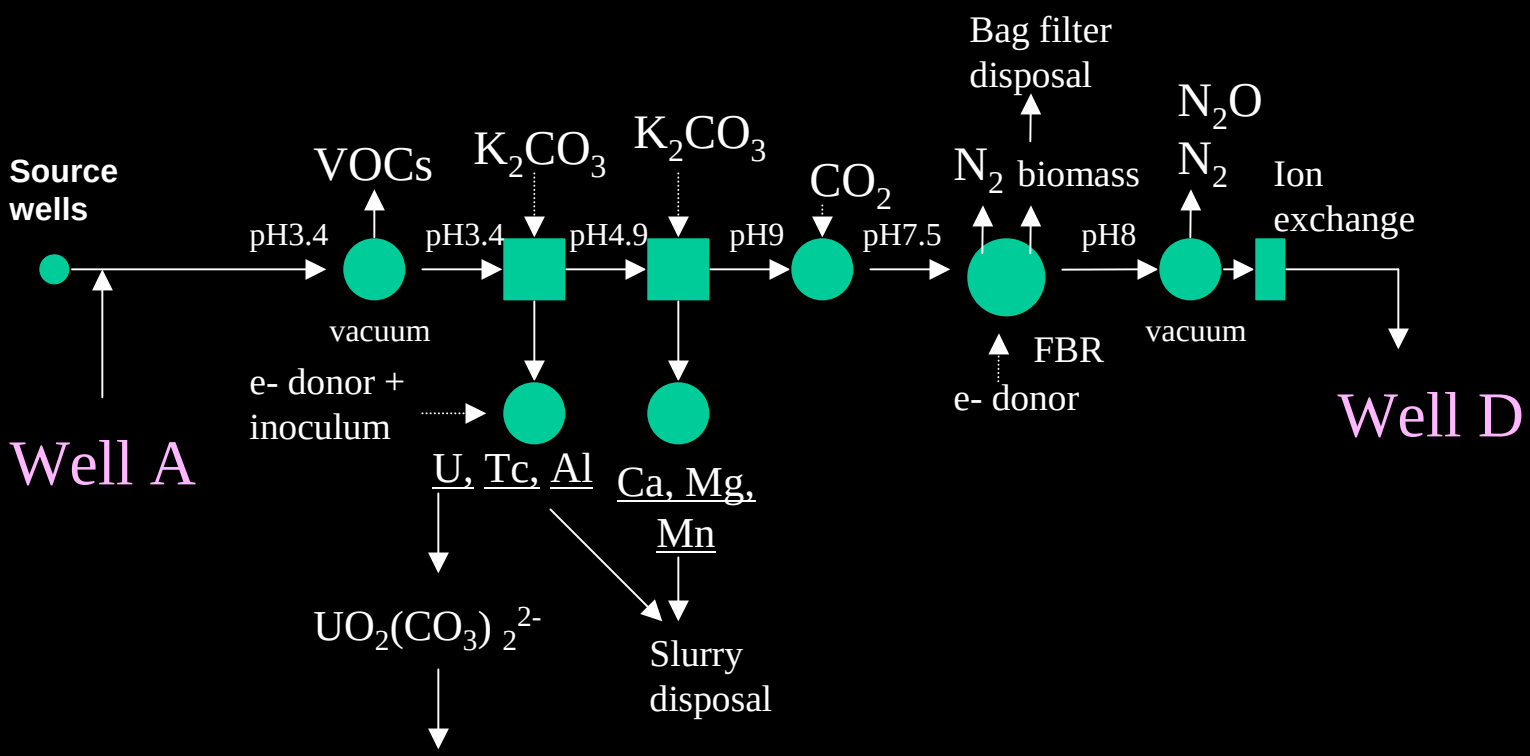
Most U(VI) precipitates along with $Al(OH)_3$ at pH~5 and resolubilizes at pH>6

pH	NO_3^-	U(VI)	^{99}Tc	Al	Ca
	----------	----------	mg/L	----------	----------
3.82	7607.6	50.44	26763.3	453.12	937.80
4.47	7936.2	27.09	9329.0	93.24	946.20
4.93	6589.4	6.01	2226.1	24.66	955.56
5.76	7981.0	3.72	1808.3	0.75	902.52
6.32	6970.1	15.55	5340.7	0.50	787.20
6.86	7966.4	23.09	7088.0	0.51	707.64
7.11	6039.3	23.86	6784.1	0.49	449.20
7.67	5909.3	28.07	8379.4	0.97	111.20
8.93	7889.4	36.65	11570.0	5.66	18.83

- Soluble U(VI)-CO_3 species exist at pH >6 - a pH regime that is conducive to microbial stimulation

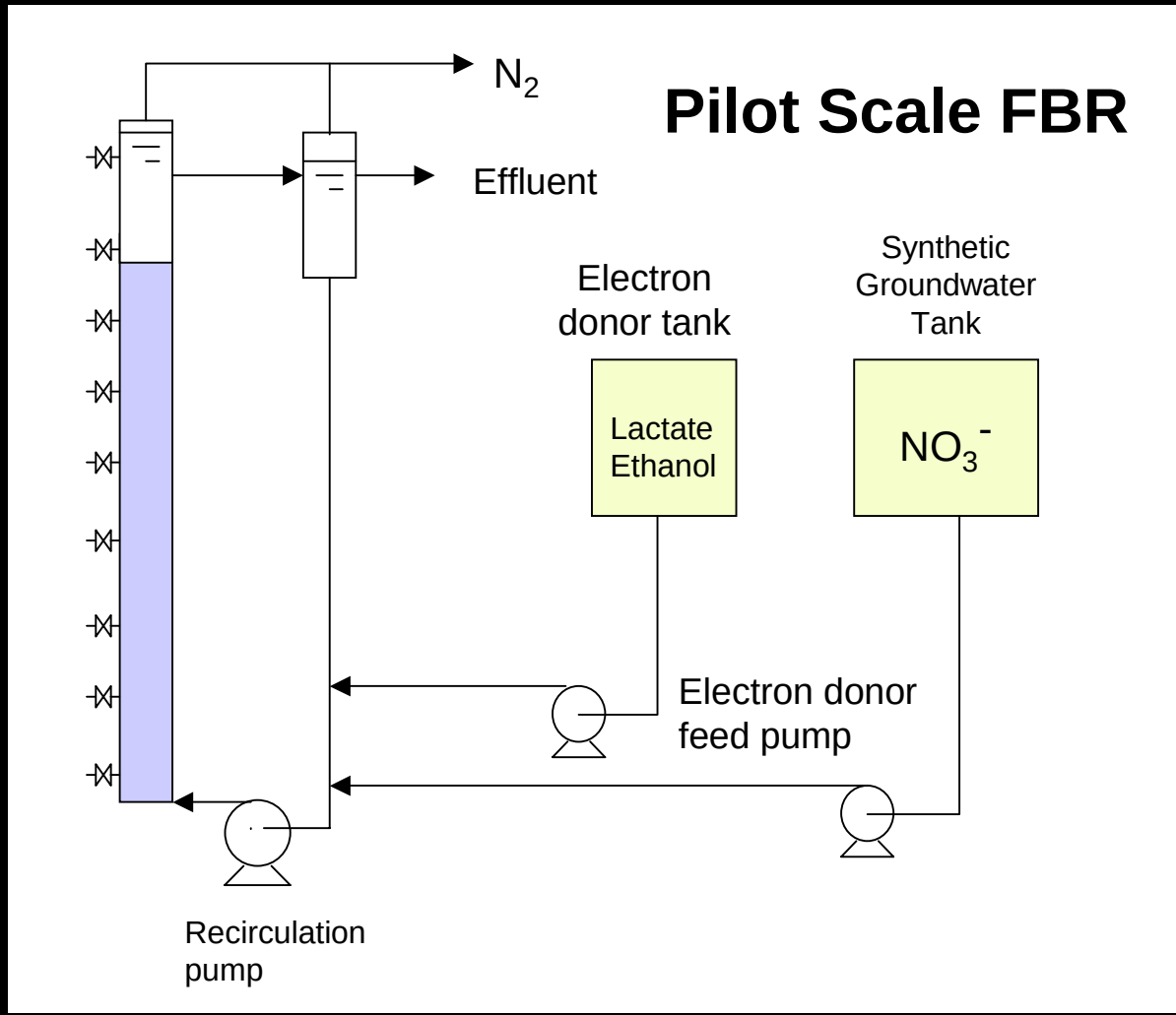
- Recall that the pH of the native soils is 6.5 to 7.0

ABOVE GROUND TREATMENT



Nitrate removal by denitrification in an FBR

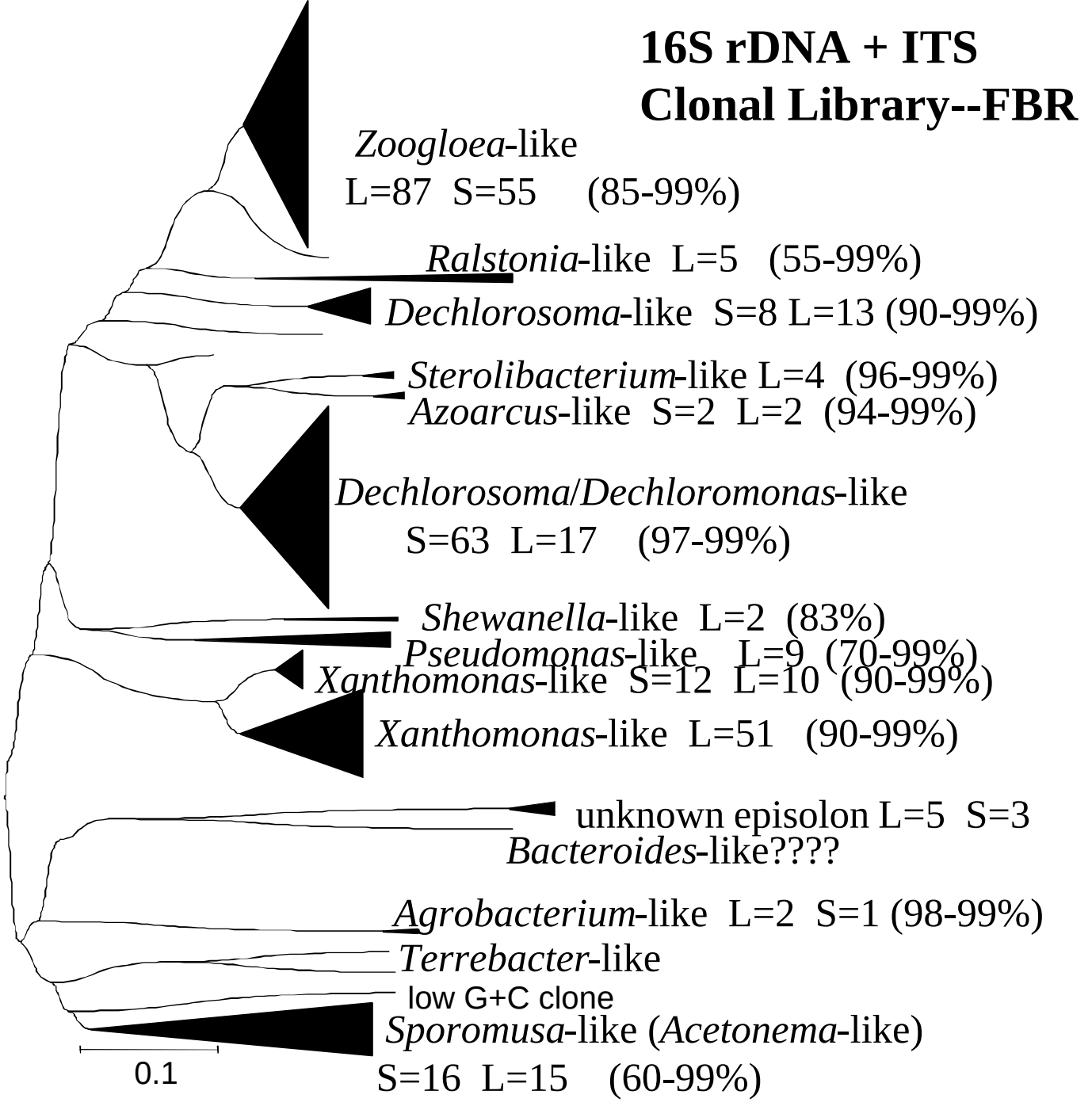
Continuously removes NO_3^- as N_2
Efficient
Cheap
Raises pH; creates bicarbonate/carbonate for U complexation
Demonstrated in two continuous pilot-scale systems (pH 7.4 and 9.2)



Pilot scale FBR

Denitrifying biofilms growing on granular activated carbon

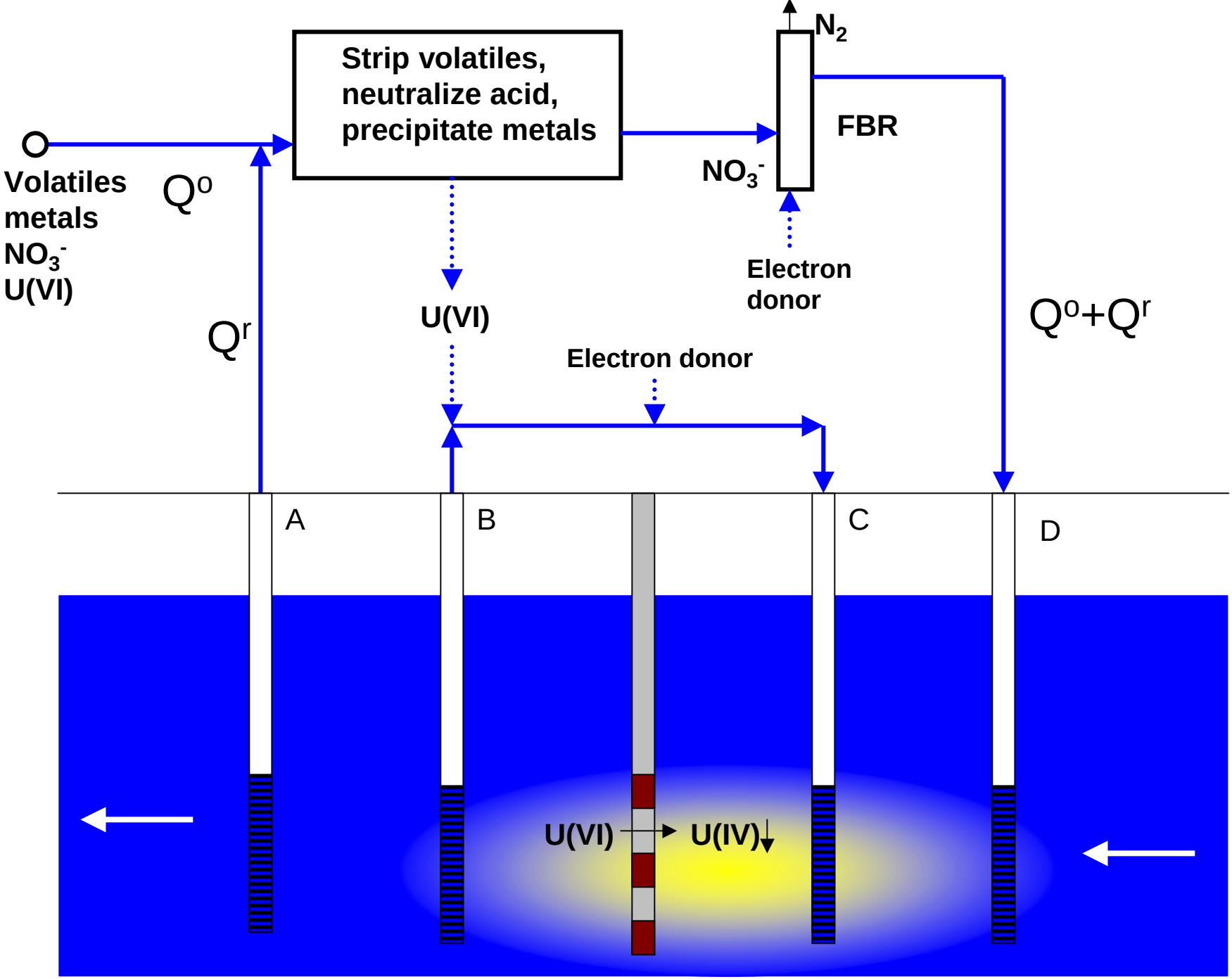
16S rDNA + ITS Clonal Library--FBR

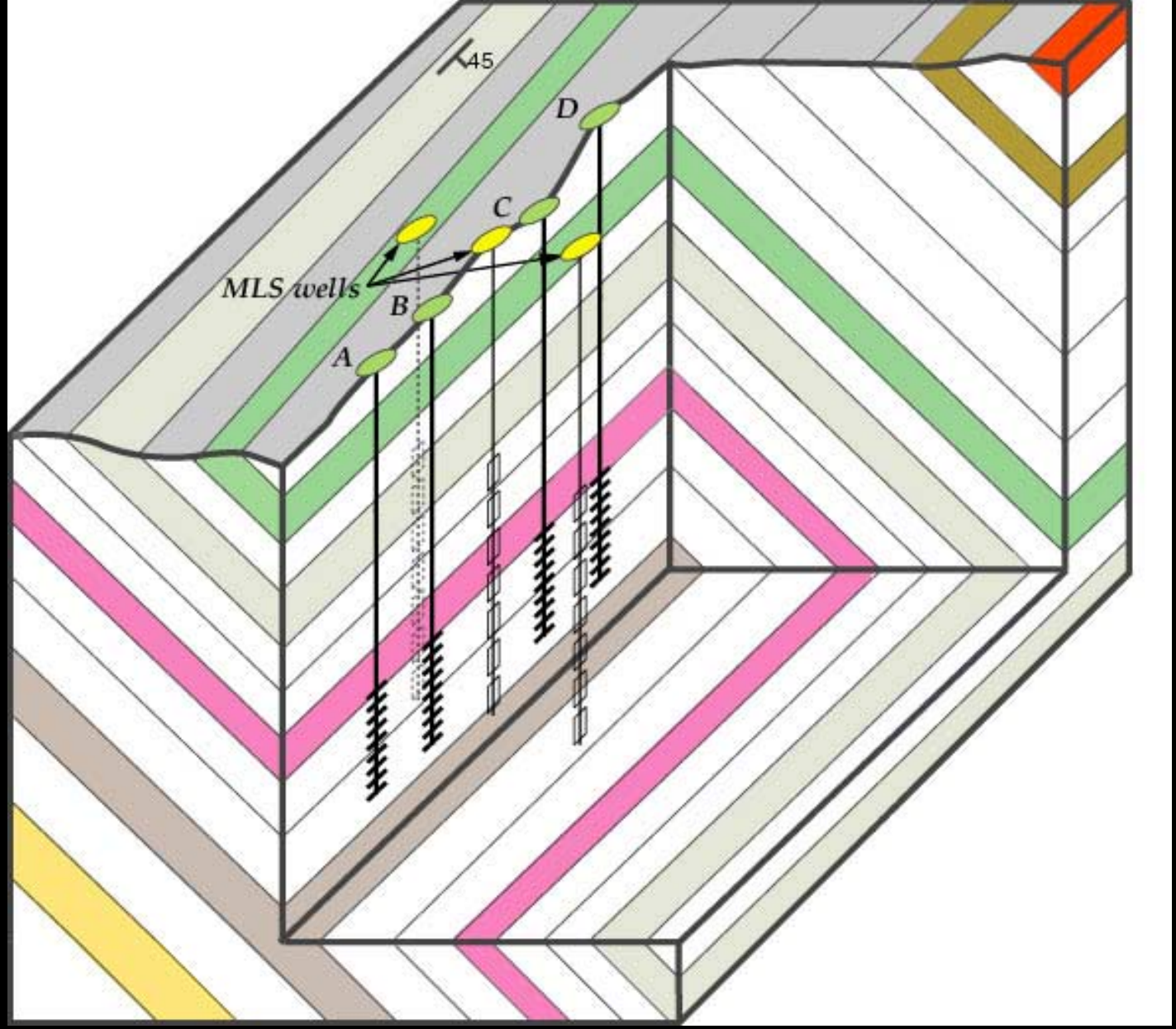


Estimated diversity: 120-140 species! (Fields & Zhou, 2002)

PHASE 3. BIOSTIMULATION

- Well configuration
- Start-up
- Intermittent lactate addition
- Management issues


Strip volatiles, neutralize acid, precipitate metals
N_2
FBR
NO_3^-
Electron donor
Volatiles
metals
NO_3^-
U(VI)
Q^o
Q^r
U(VI)
Electron donor
Q^o+Q^r
A
B
C
D
U(VI)
U(IV)



Screened Interval = 37-45’

Cross-sectional view of the injection/extraction wells and the MLS wells.

Start-up

Objectives

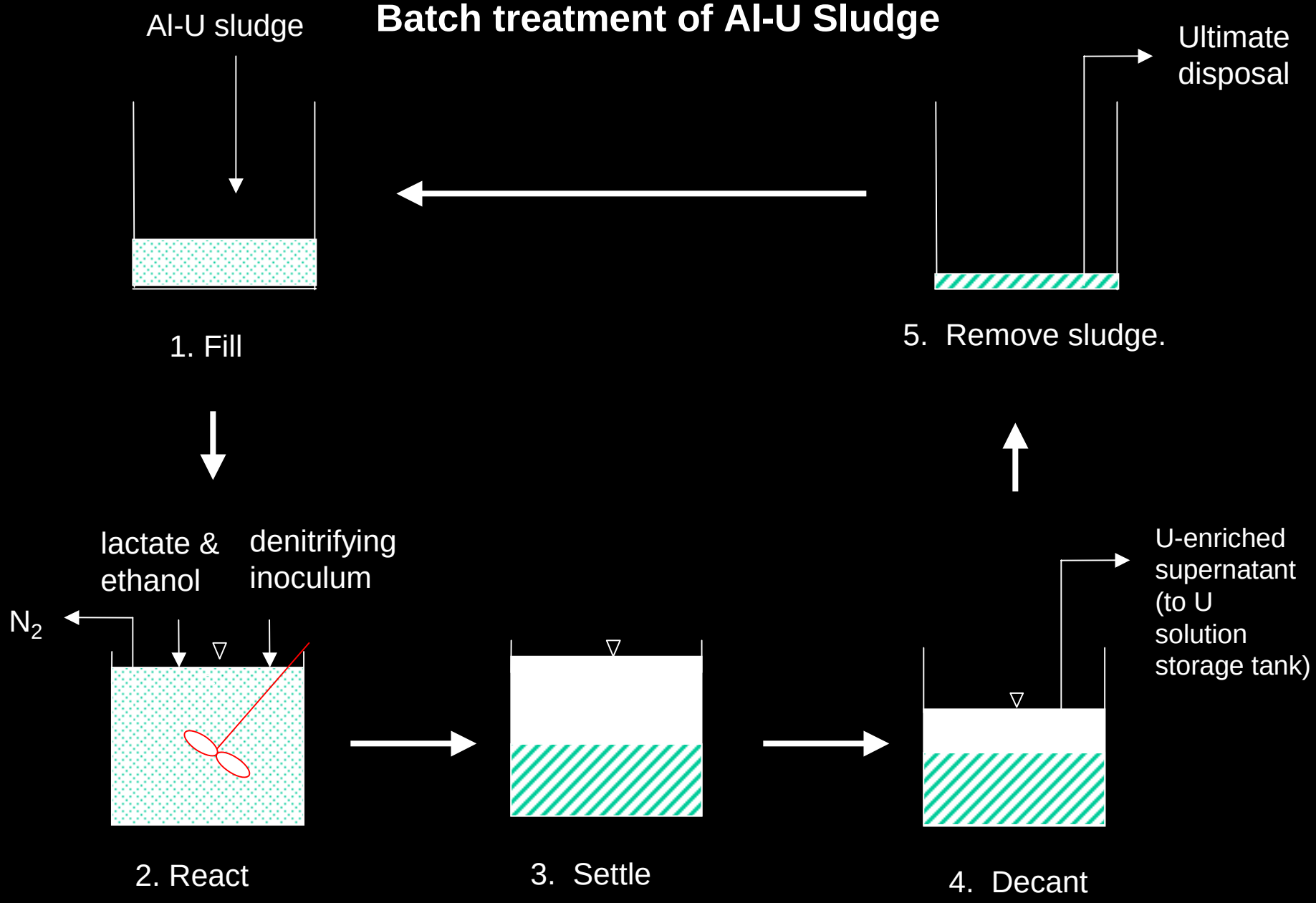
- Rapidly prepare subsurface for FBR effluent
- Avoid clogging
- Titrate acidity on soil (not much there)

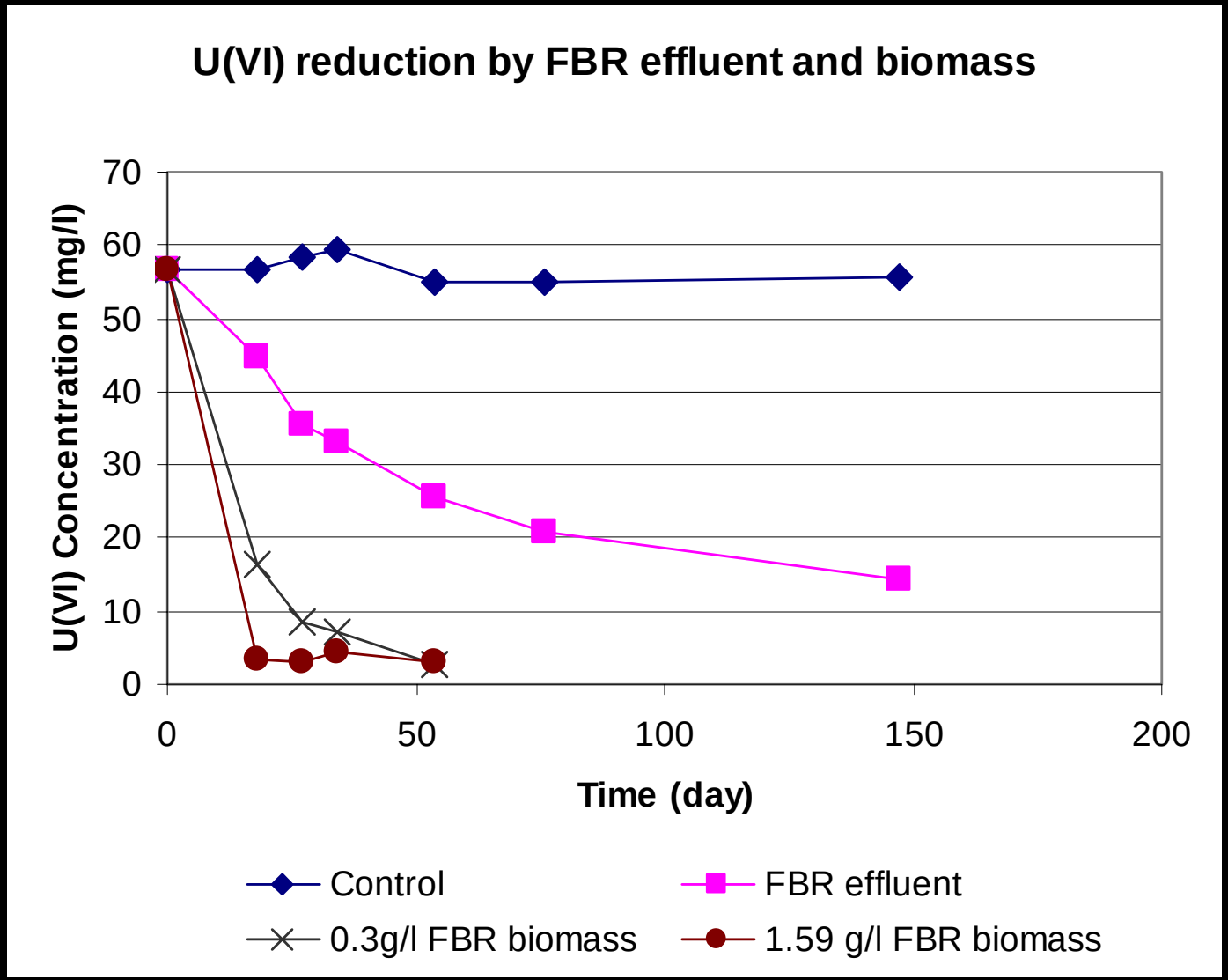
Strategy

- Treat water extracted from Well D
- Stockpile treated water (and U)
- Inject treated water at Wells B and C

First flush - pH matches groundwater
Second flush - alkalinity added

Batch treatment of Al-U Sludge





E = electron donor (ethanol + lactate) added to give an initial COD of 200 mg COD/l.

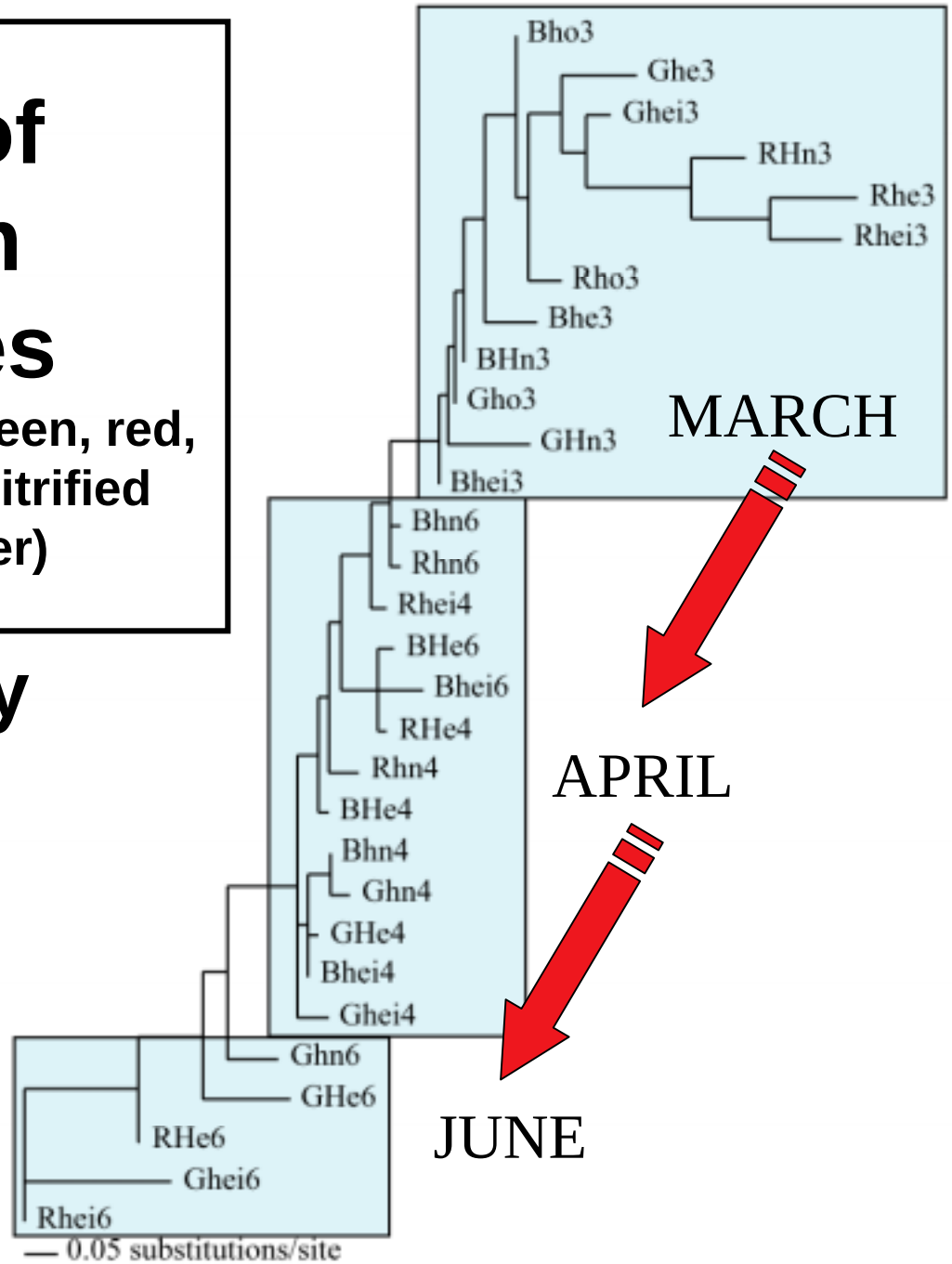
Very preliminary data for sediment + FBR effluent: ethanol looks promising…

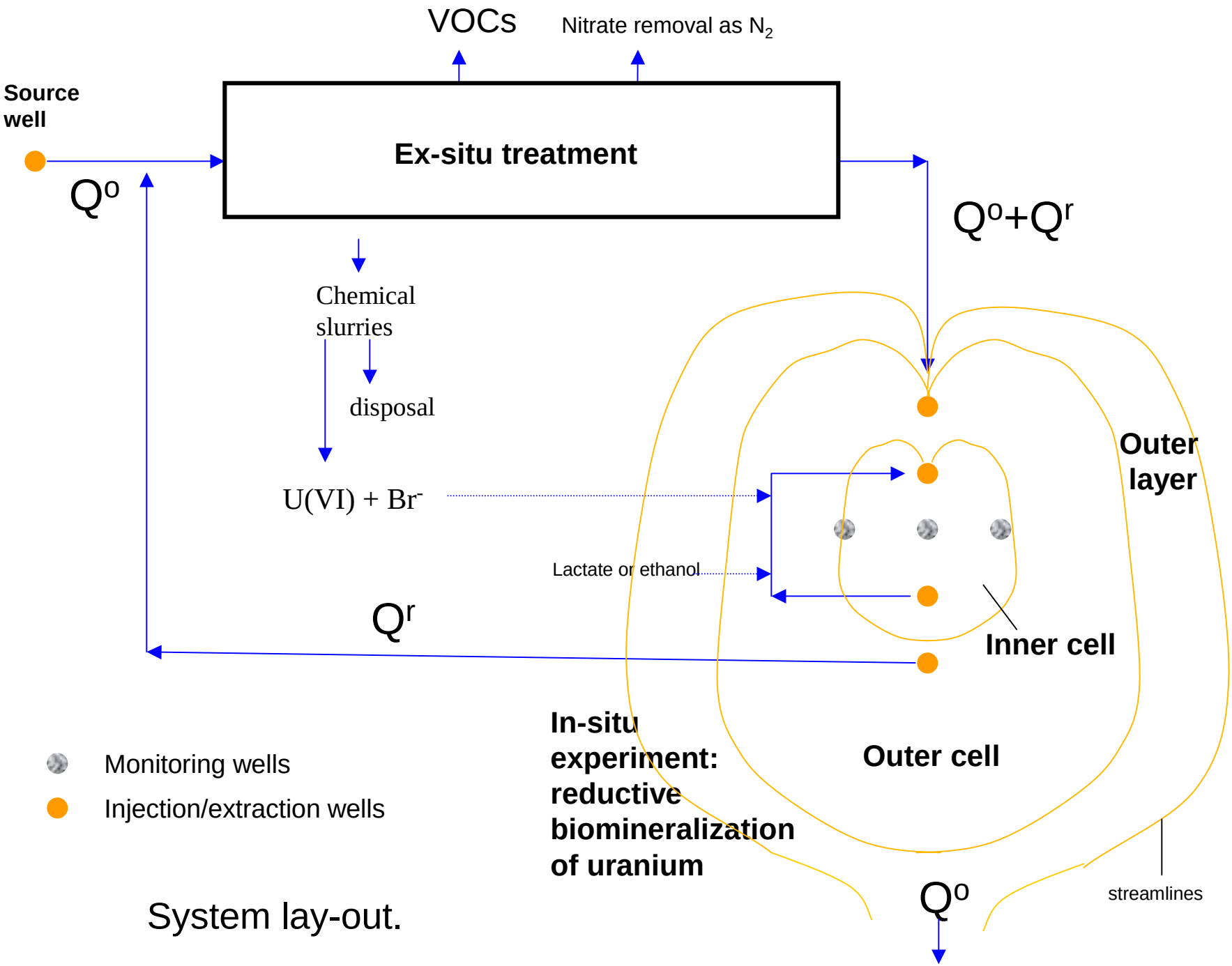
Trajectory of Microcosm Communities

(initiated with unwashed green, red, and black sediment + denitrified synthetic groundwater)

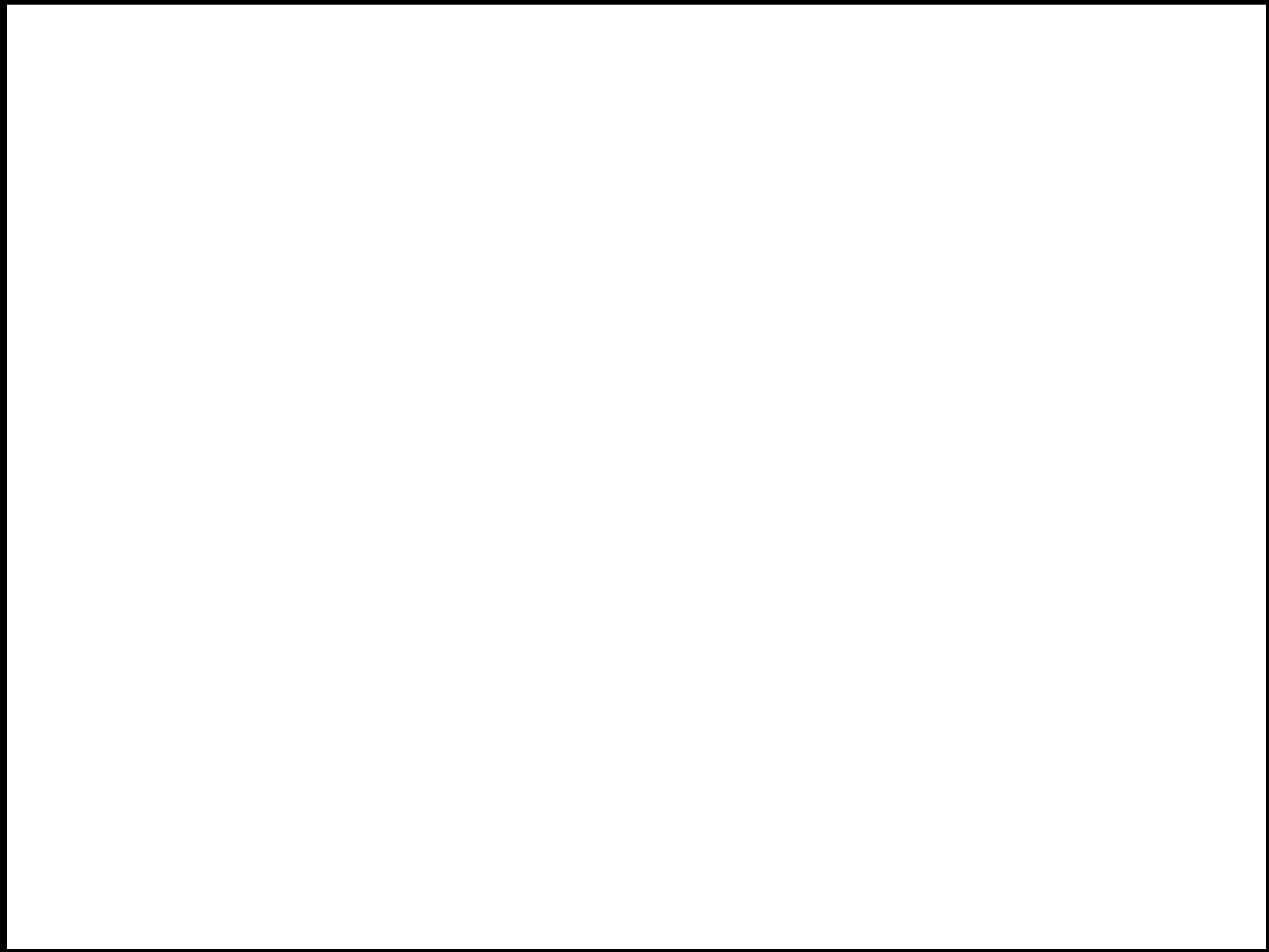
T-RFLP Community profiles compared with Neighbor Joining

(collaboration with T. Marsh)





System lay-out.



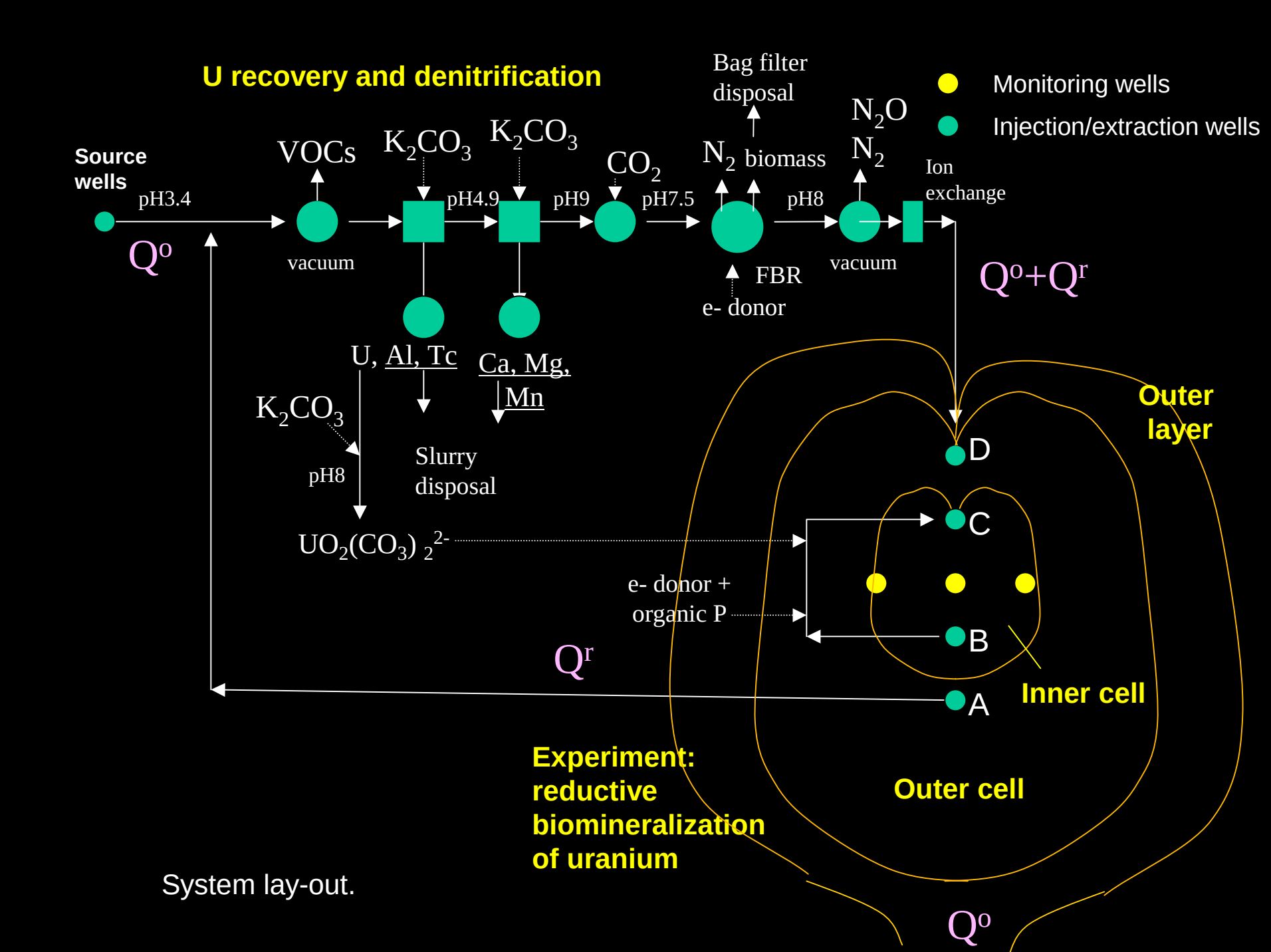
STREAM LINES FOR THE INNER AND OUTCELL

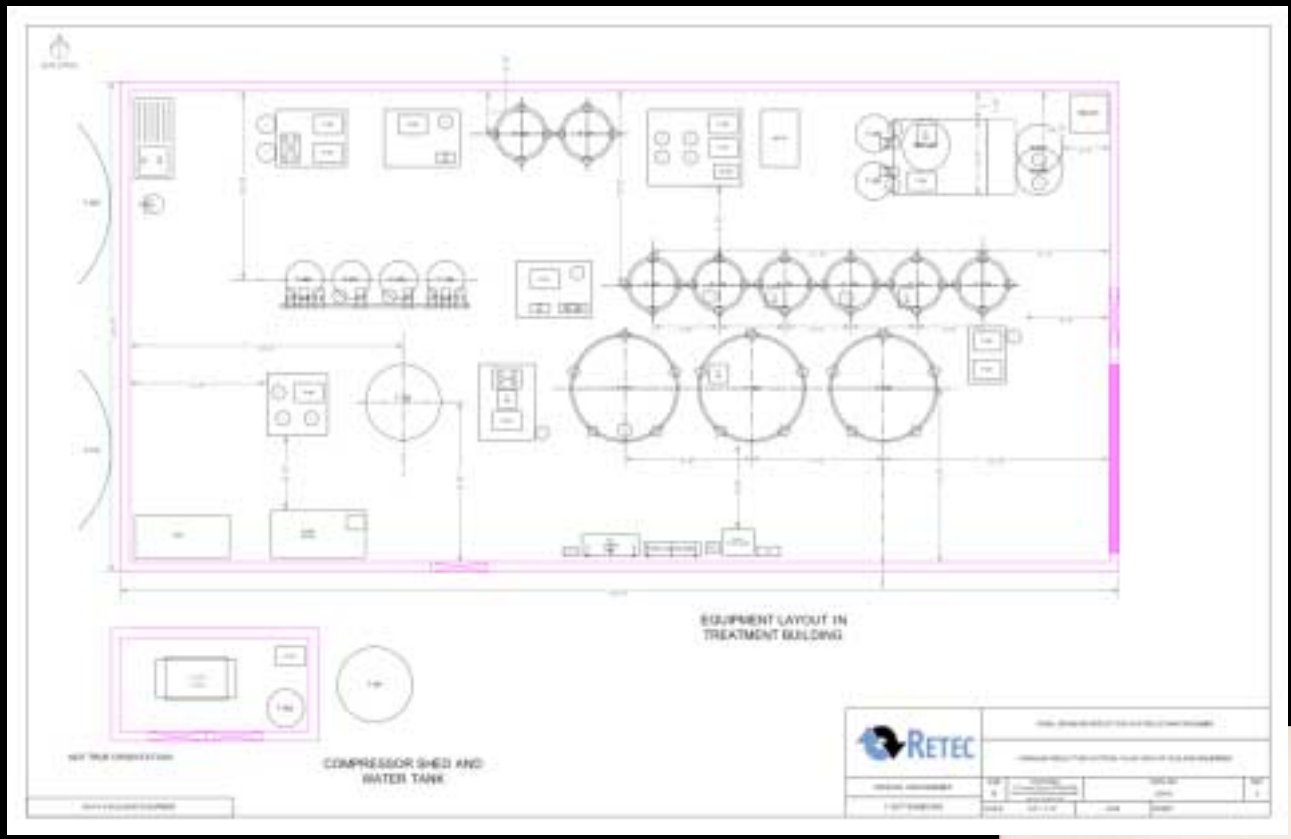
Olaf's simulation assumptions for U introduction:

1. Hydraulic conductivity =0.001 cm/s.
2. Ambient hydraulic gradient =1.5%
3. Screened interval = 2m
4. Effective porosity = 0.35
5. No sorption of U

Olaf's assumptions for biostimulation:

1. Initial sulfate = 10 mM
2. No sorption of lactate, sulfate, U(VI)
3. All biomass is immobile.
4. Initial SRB conc =1 mg/L
5. Cometabolic reduction of U(VI) to UO_2 by SRB.
6. Operational schedule:
    1. 0-10 h injection of 50 mg/L U(VI)
    2. 10h-5d no injection. Mixing of U(VI) within the inner loop.
    3. 5d-100 d Daily one hour injection of lactate at a ratio of o.23 mg lactate per mg U extracted.


U recovery and denitrification
Bag filter disposal
Monitoring wells
Injection/extraction wells
Source wells
pH3.4
VOCs
K_2CO_3
K_2CO_3
pH4.9
pH9
CO_2
pH7.5
N_2 biomass
N_2O
N_2
pH8
Ion exchange
Q^o
vacuum
FBR
e- donor
vacuum
Q^o+Q^r
U, Al, Tc
Ca, Mg, Mn
K_2CO_3
pH8
Slurry disposal
$UO_2(CO_3)_2^{2-}$
Outer layer
D
C
e- donor + organic P
B
Q^r
A
Inner cell
Experiment: reductive biomineralization of uranium
Outer cell
System lay-out.
Q^o

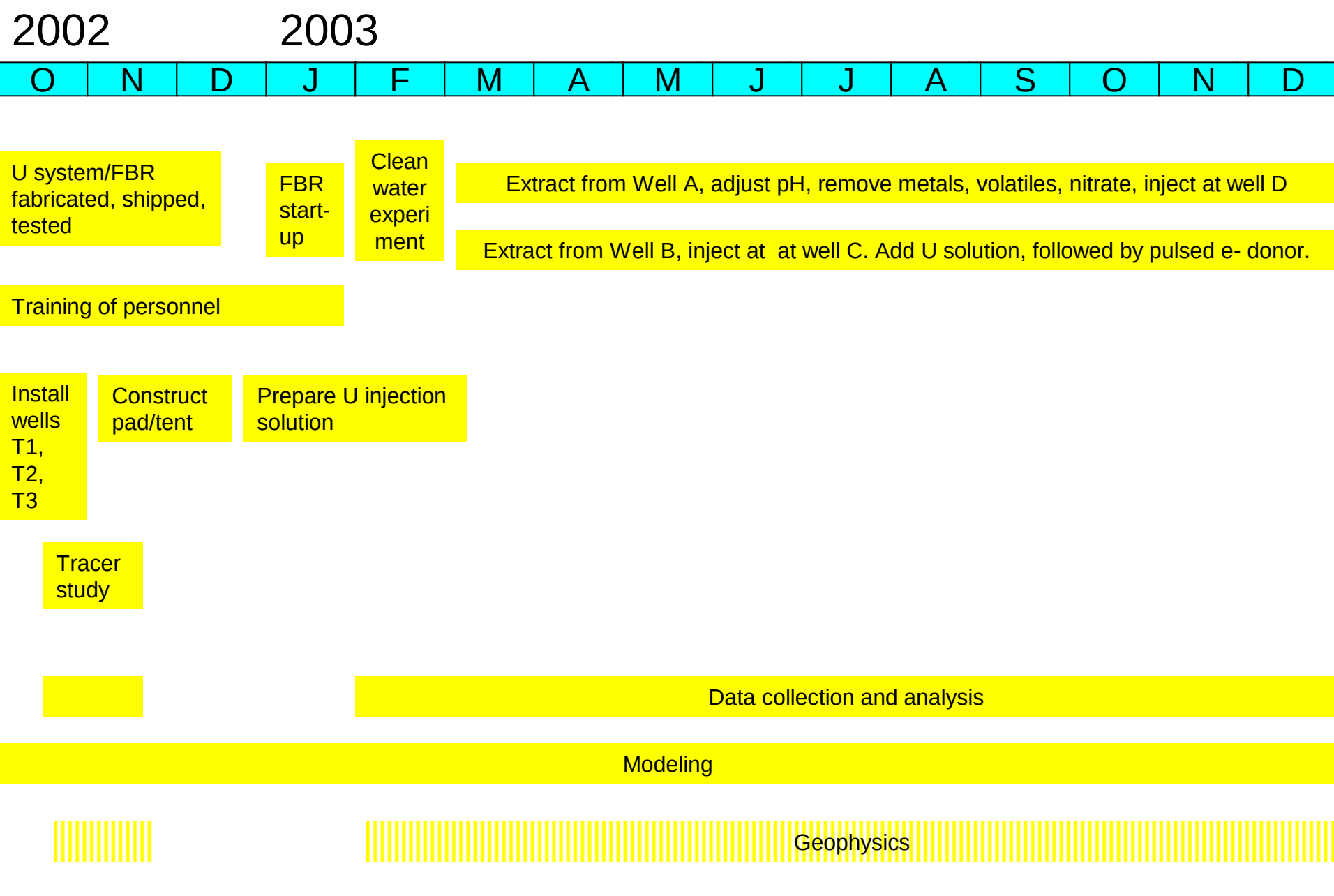

EQUIPMENT LAYOUT IN
TREATMENT BUILDING
COMPRESSOR SHED AND
WATER TANK
RETEC

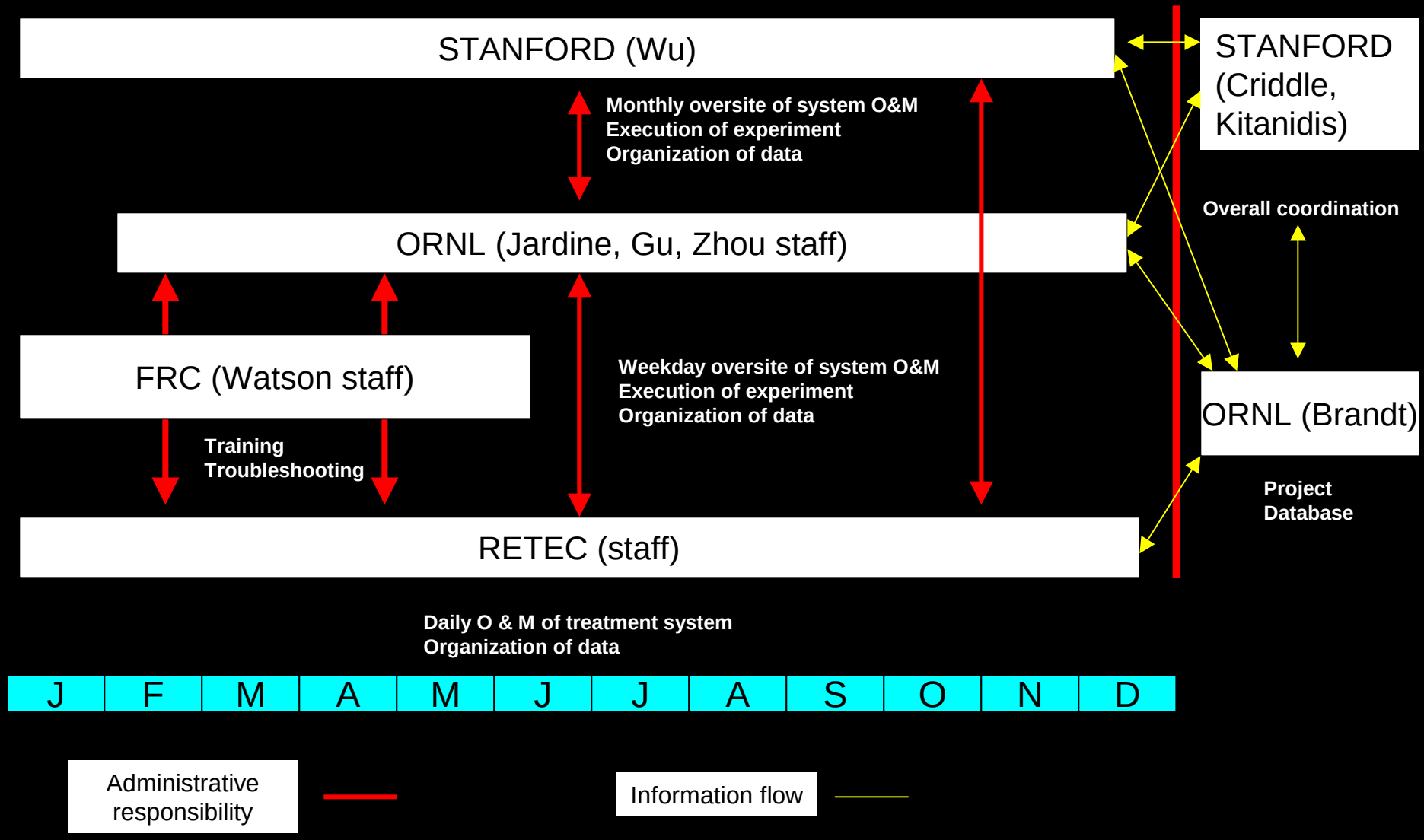
Envisioned applications…

The **ex-situ system** will be useful for remediating the source zone.

The **in-situ system** will be useful for immobilization of U at the plume periphery.

Schedule Overview





Management structure for the system operation and data management