Isotopic tracers for waste-fluid tracking and fluid-soil interactions: Hanford, WA

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Project Objectives

- Use natural isotopic variations of Sr, O, D, C, U, and Nd as monitors of subsurface processes
- Estimate long-term infiltration rates through the vadose zone
- Track lateral migration of waste fluids in VZ
- Document extent of silicate/carbonate dissolution by waste fluids and natural recharge
- Develop baseline knowledge for assessment of impacts of future remediation activities
- Understand Sr, U migration and budgets
- Explore possible use of Fe, Ca, and Cr isotopes

Isotopic system sensitivities

- O, D: Conservative water tracers, evaporation
- Sr: Soil dissolution, fluid flux, Sr exchange
- U: Soil dissolution, surface area
- Nd: Colloidal transport; migration of strongly sorbed species

Role of characterization

- Accurate assessment of inventory, distribution and movement of contaminants
- Improved predictive methods for flow and transport
- Improved design of remediation systems
- Improved design of and monitoring strategies for chemical treatment technologies

Addressing Hanford needs

- *RL-SS29-S: Effect of Subsurface Heterogeneities on Chemical Reaction and Transport*
- *RL-SS27-S: Rates of Coupled Abiotic and Biogeochemical Reactions Involving Contaminants in Hanford Subsurface*
- *RL-SS26-S: Reaction Rates for Key Contaminant Species and Complexes in Site-Specific Groundwater*
- *RL-SS35-S: Use of Chemical Surrogates for Contaminant monitorin*
- *AL-09-01-28-SC-S: Scientific Basis for Vadose Zone Monitoring Systems*
- *AL-09-01-14-SC-S: Vadose Zone Flux Rates*

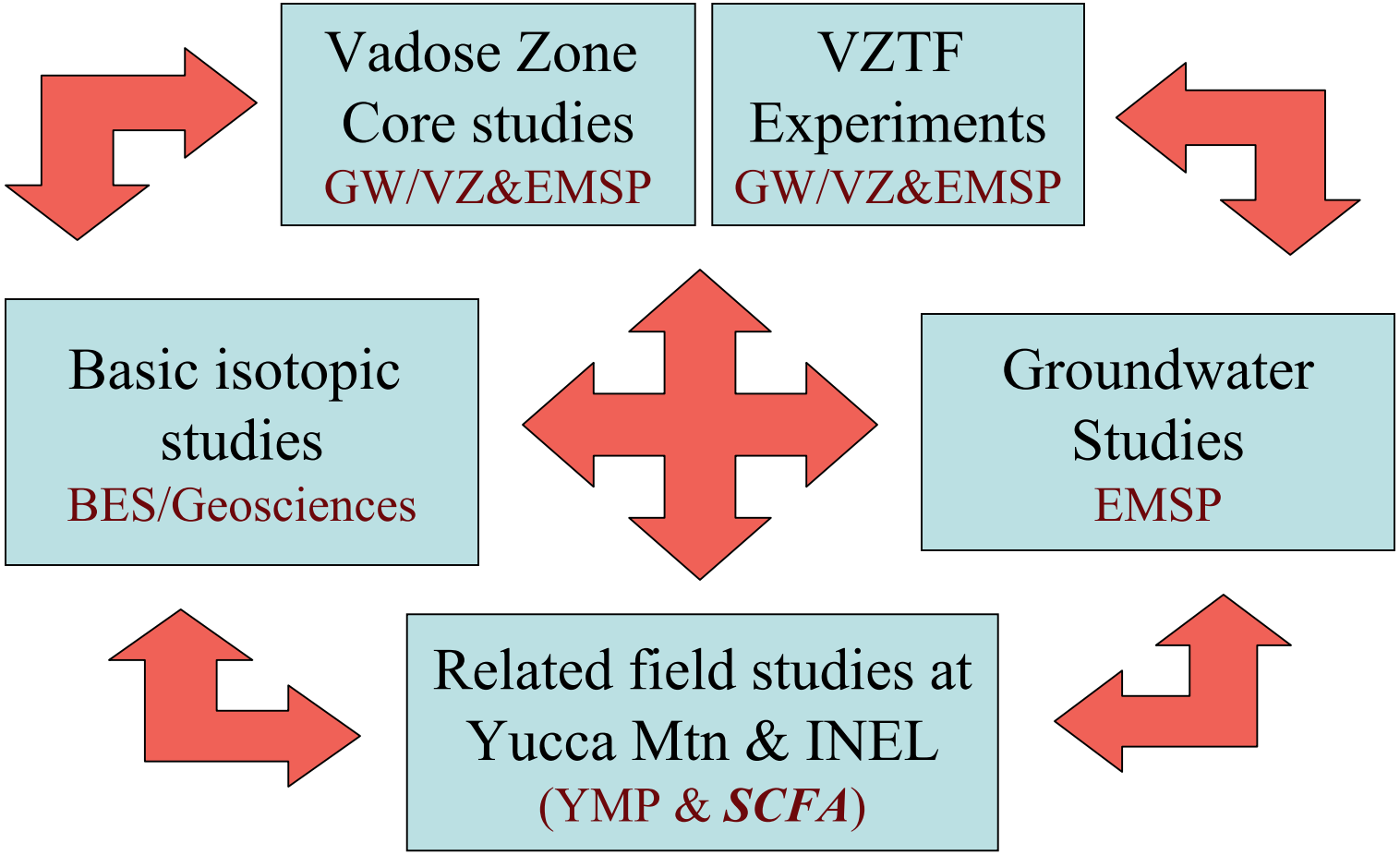
Needs identified by the Hanford GW/VZ Integration Project

- *Understand, quantify and develop descriptions of reactions and interactions between contaminants of concern and vadose zone sediments*
- *Understand, quantify and develop descriptions of contaminant transport in the vadose zone.*
- *Provide means to delineate contaminant plumes in the vadose zone and relate plume distribution to the distribution of geochemical and hydrogeological properties*

Project structure

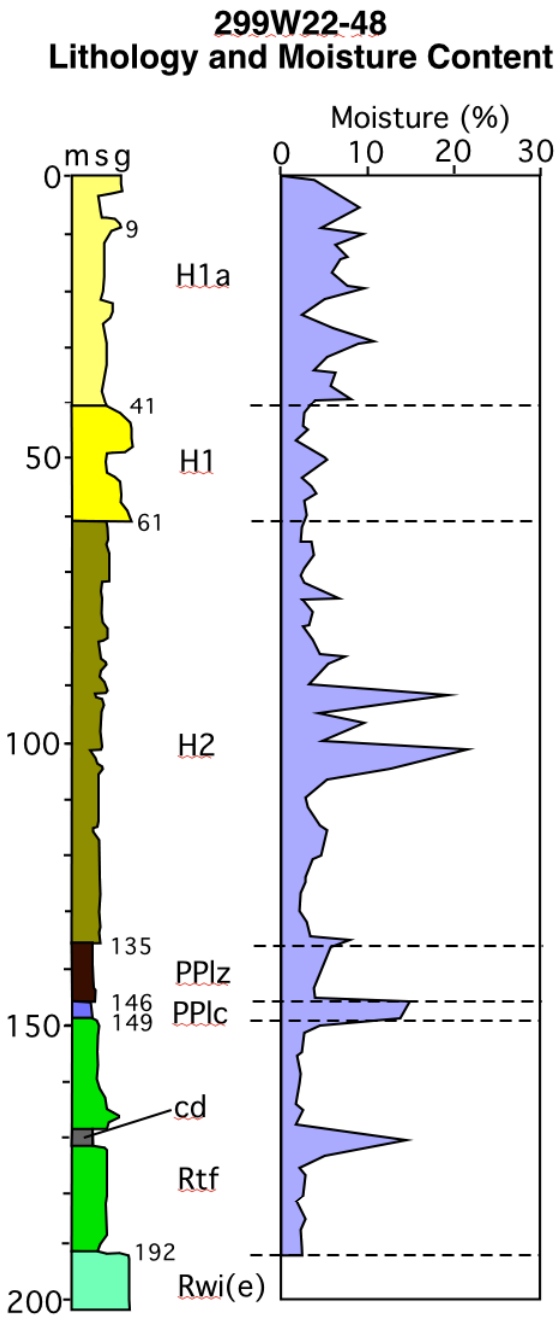
- Groundwater samples provided by the Hanford Groundwater Monitoring Program (Evan Dresel, PNNL)
- Vadose Zone core and water samples supplied by Hanford GW/VZ Field Investigations
- Isotopic measurements made at LBNL and UCB
- Other isotopic and chemical measurements made at PNNL can be used for collaborative analysis (E.Dresel J. Evans, J. Serne)

Interrelationships between EMSP, SCFA, BES-Geosciences and Hanford GW/VZ Project at LBNL for isotopic studies



Studies of Vadose Zone Core from Hanford 200 West Area

- Measurements made of bulk soils, DI leaches, acid leaches and extracted waters
- Information gained on
  - Isotopic comp of VZ waters (O,D,Sr,U)
  - Infiltration flux averaged over long time period (100's - 1000's years)
  - Soil weathering rates (U,Sr)
  - Exchange pool of Sr to retard migration

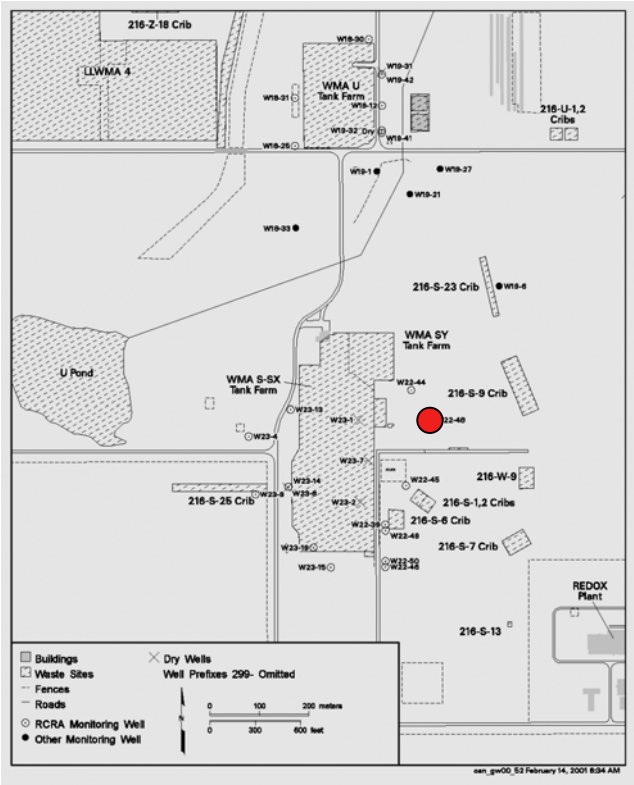


Hanford

Formation

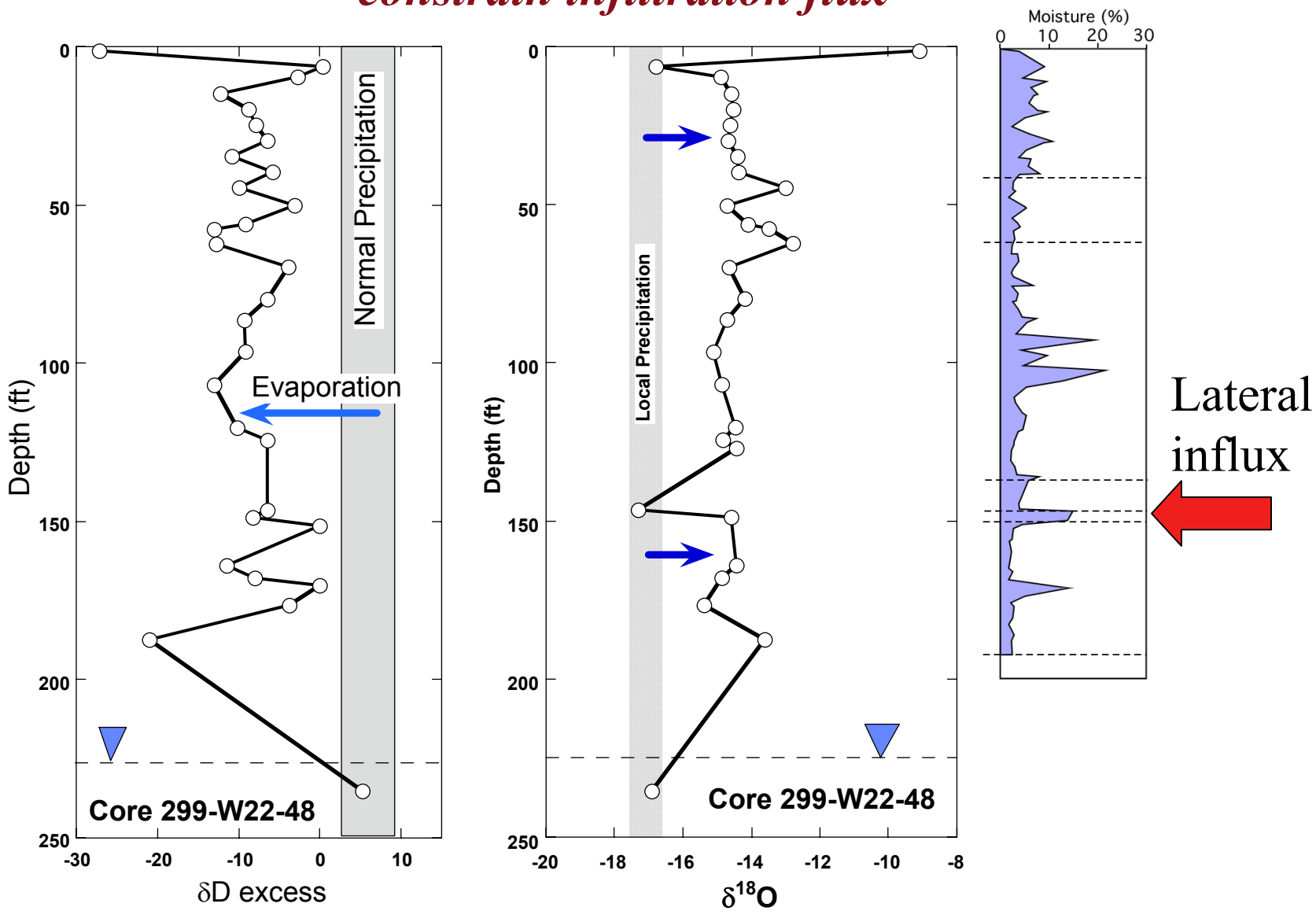
Plio-Pleistocene

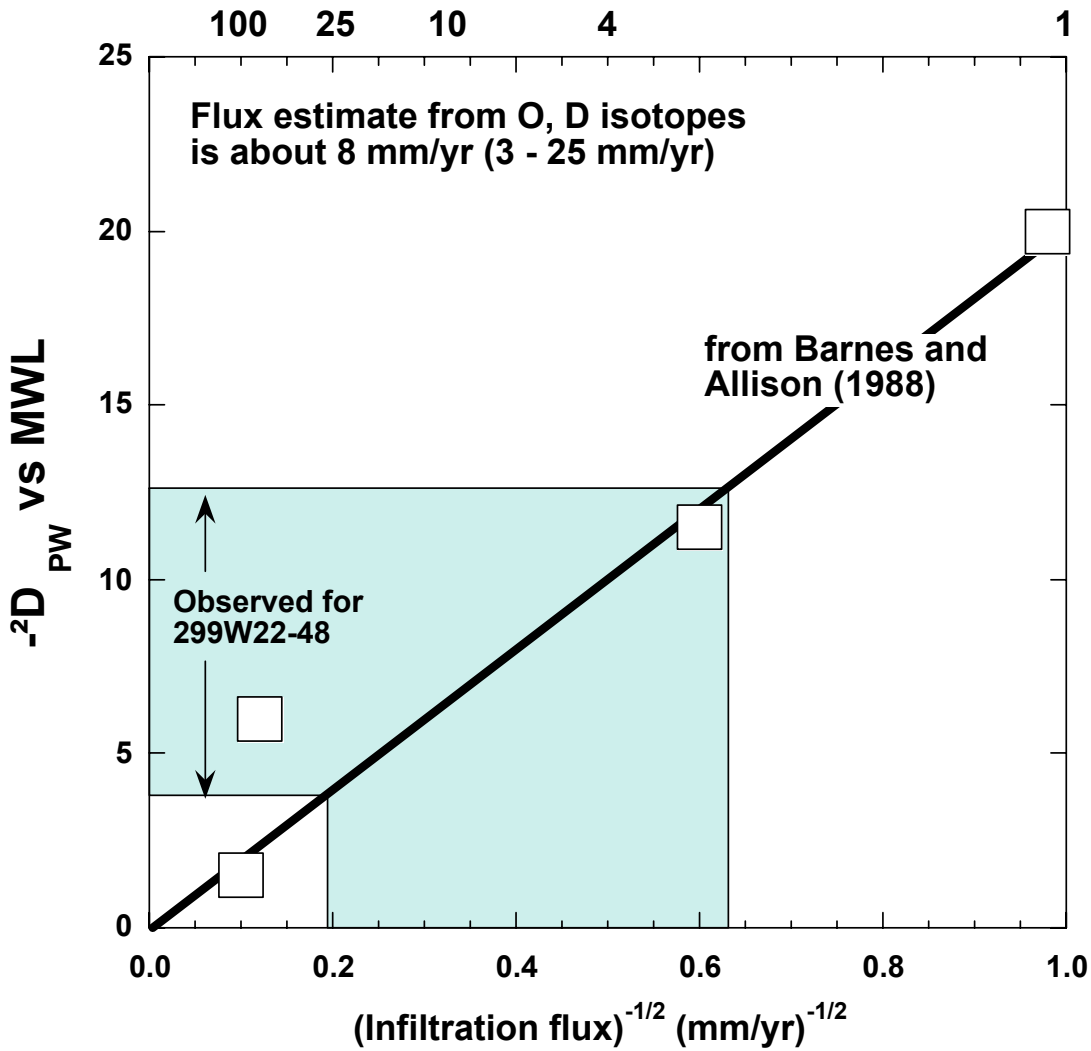
Ringold Fm.



Water Table at ≈ 230'

Stable isotope ratios label VZ water and constrain infiltration flux

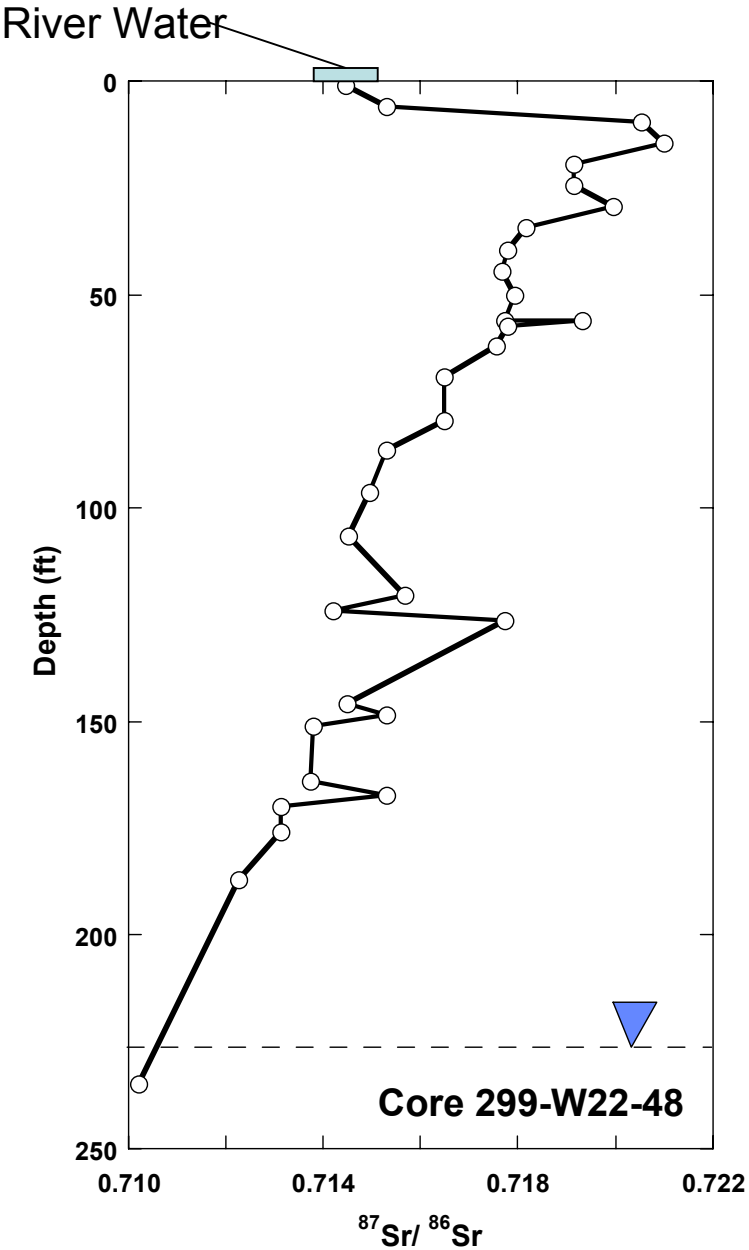


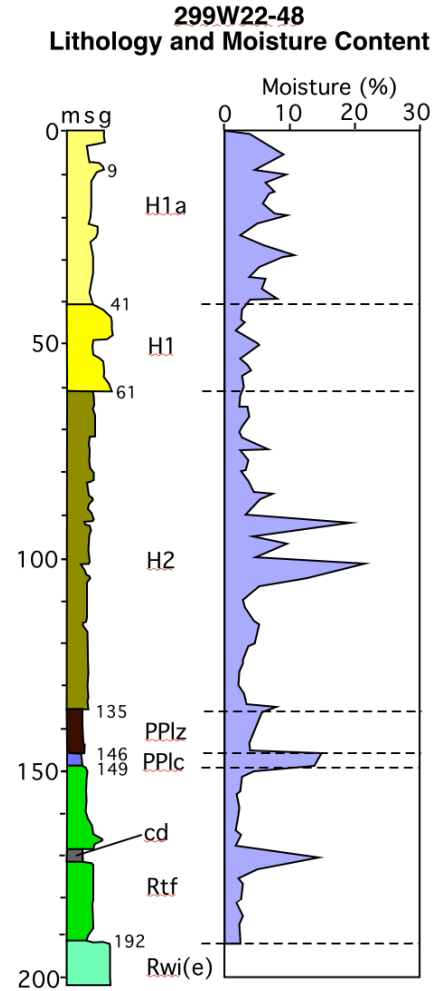


Stable isotope data suggest infiltration rates of 3-25 mm/yr. This range would represent the average for the past ≈1000 yr

(Empirical curve needs further investigation)

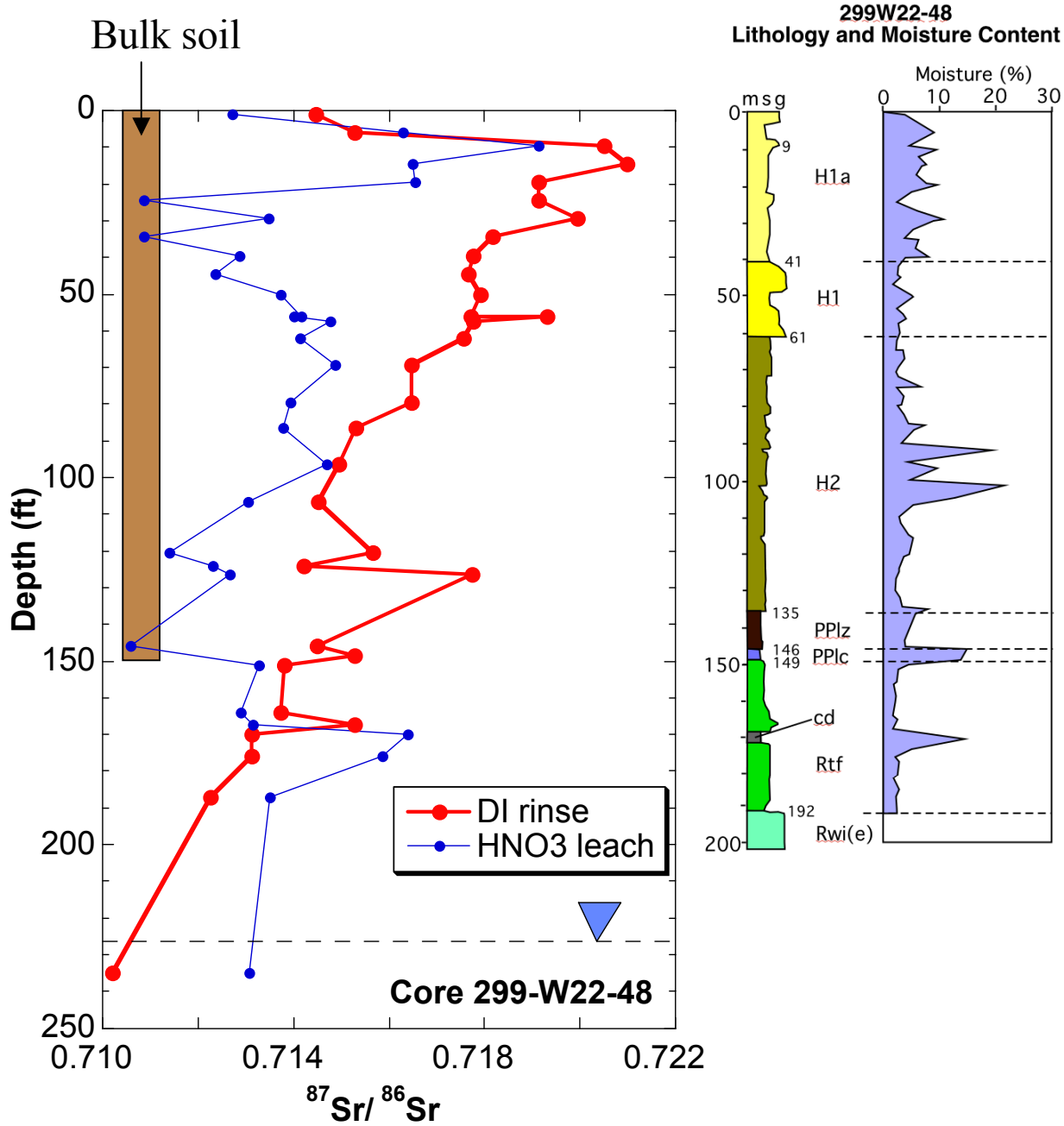
The $^{87}Sr/^{86}Sr$ values of DI water rinses shift systematically toward lower values with depth, after a peak at 4m depth.





$^{87}Sr/^{86}Sr$ values of HNO_3 rinses are generally lower than DI rinses; probably reflect calcite plus partially dissolved silicates.

Downhole shift in DI values is assumed to be due to slow dissolution of silicates and calcite.



Model for Sr isotopes in Pore Fluid

If the Sr profile represents a steady-state condition, then the differential form for the depth dependence of the pore fluid $^{87}Sr/^{86}Sr$ (denoted $r_f(z)$), is:

$$\frac{dr_f(z)}{dz} = \left[r_s(z) - r_f(z)\right]\frac{R_s[Sr]_s}{v_f[Sr]_f}$$

$r_s(z)$ = bulk $^{87}Sr/^{86}Sr$ ratio in the solid at depth z

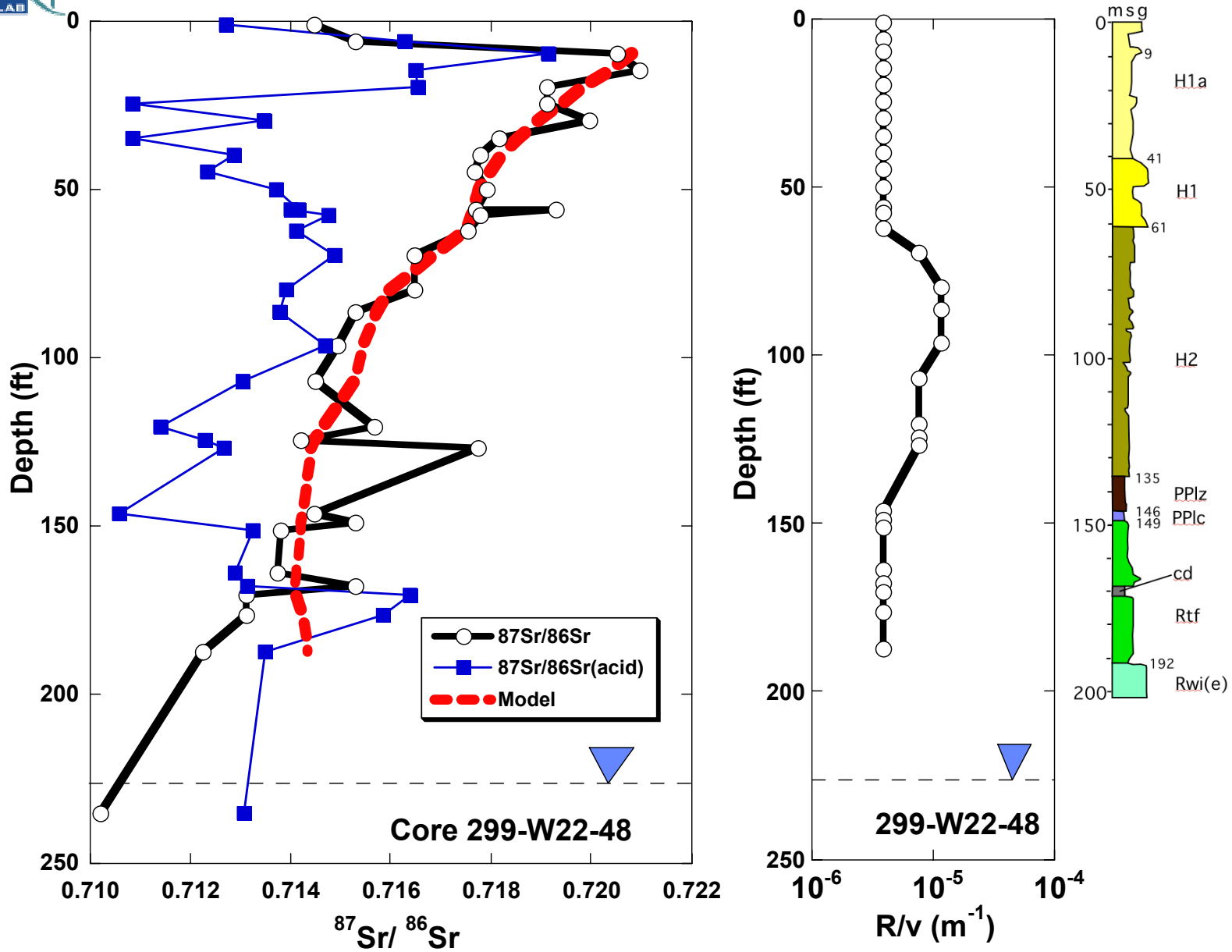
R_s = bulk dissolution (weathering) rate of the soil at depth z

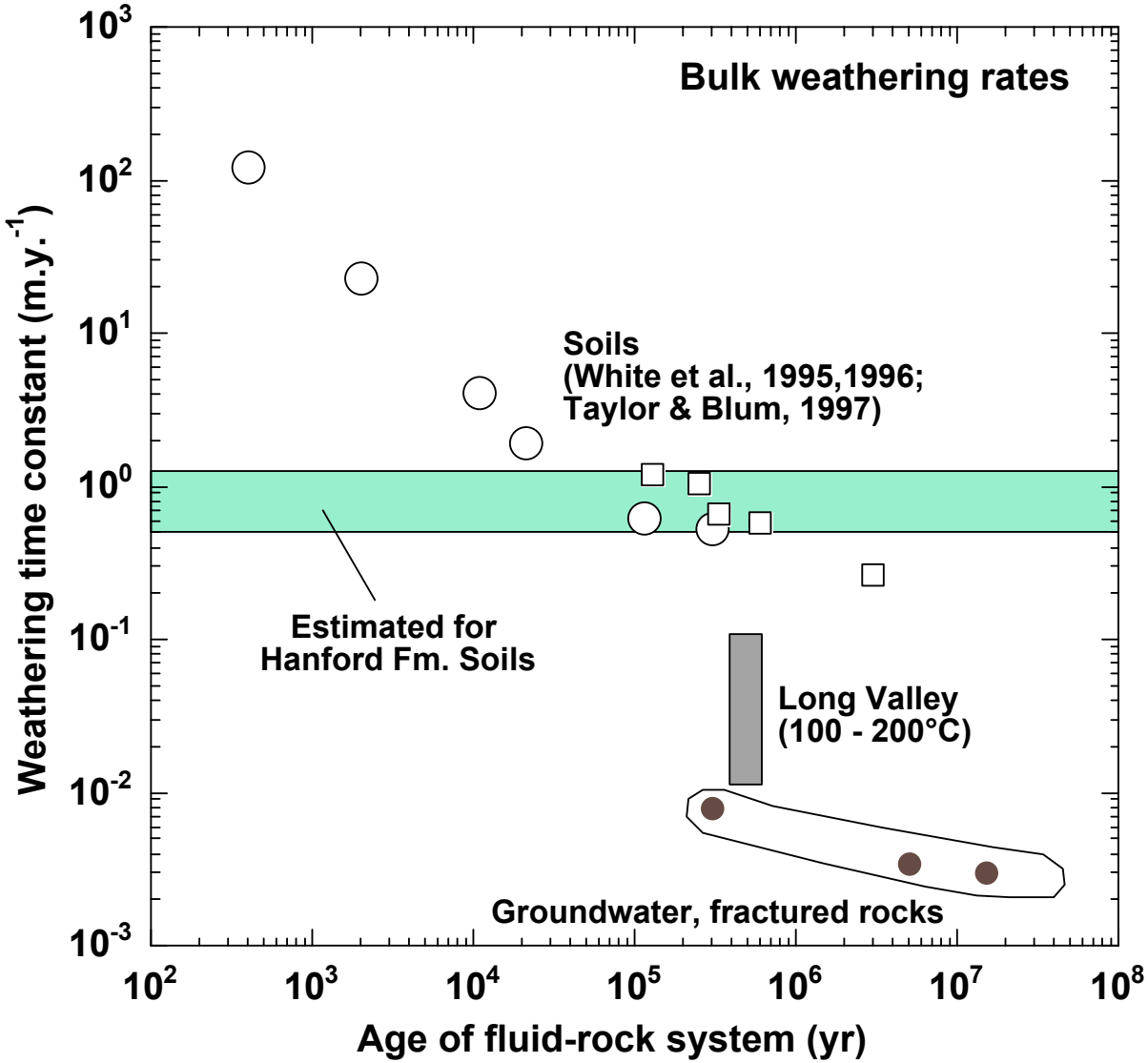
v_f = pore velocity of the fluid at depth z

$[Sr]_s$ = concentration of Sr in the soil at depth z

$[Sr]_f$ = Sr concentration in the porefluid at depth z.

Data can be used to estimate R_s/v_f as function of depth

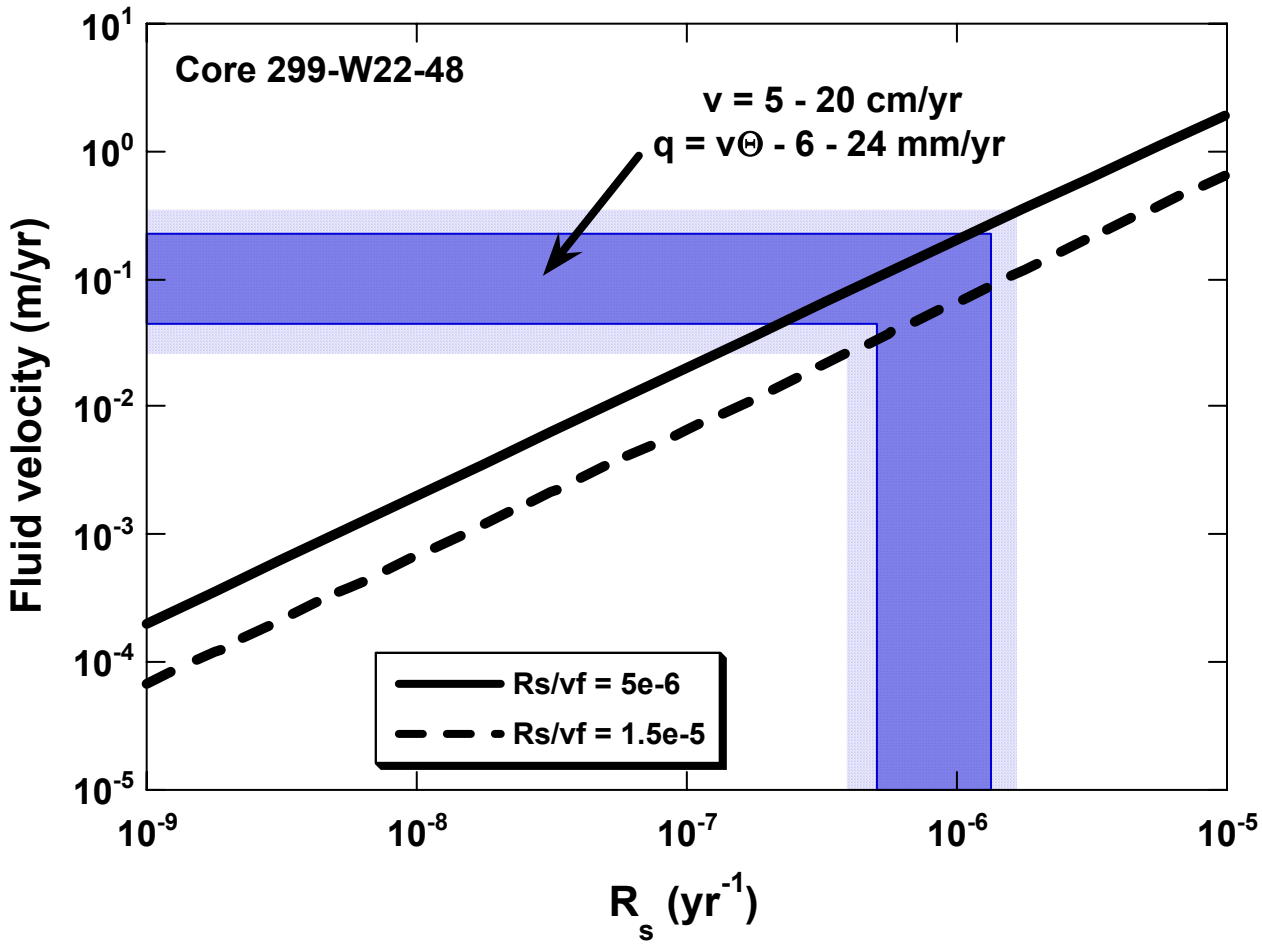

Depth (ft)
0
50
100
150
200
250
0.710
0.712
0.714
0.716
0.718
0.720
0.722
87Sr/ 86Sr
87Sr/86Sr
87Sr/86Sr(acid)
Model
Core 299-W22-48
10-6
10-5
10-4
R/v (m-1)
299-W22-48
msg
9
41
61
135
146
149
192
H1a
H1
H2
PPlz
PPlc
cd
Rtf
Rwi(e)

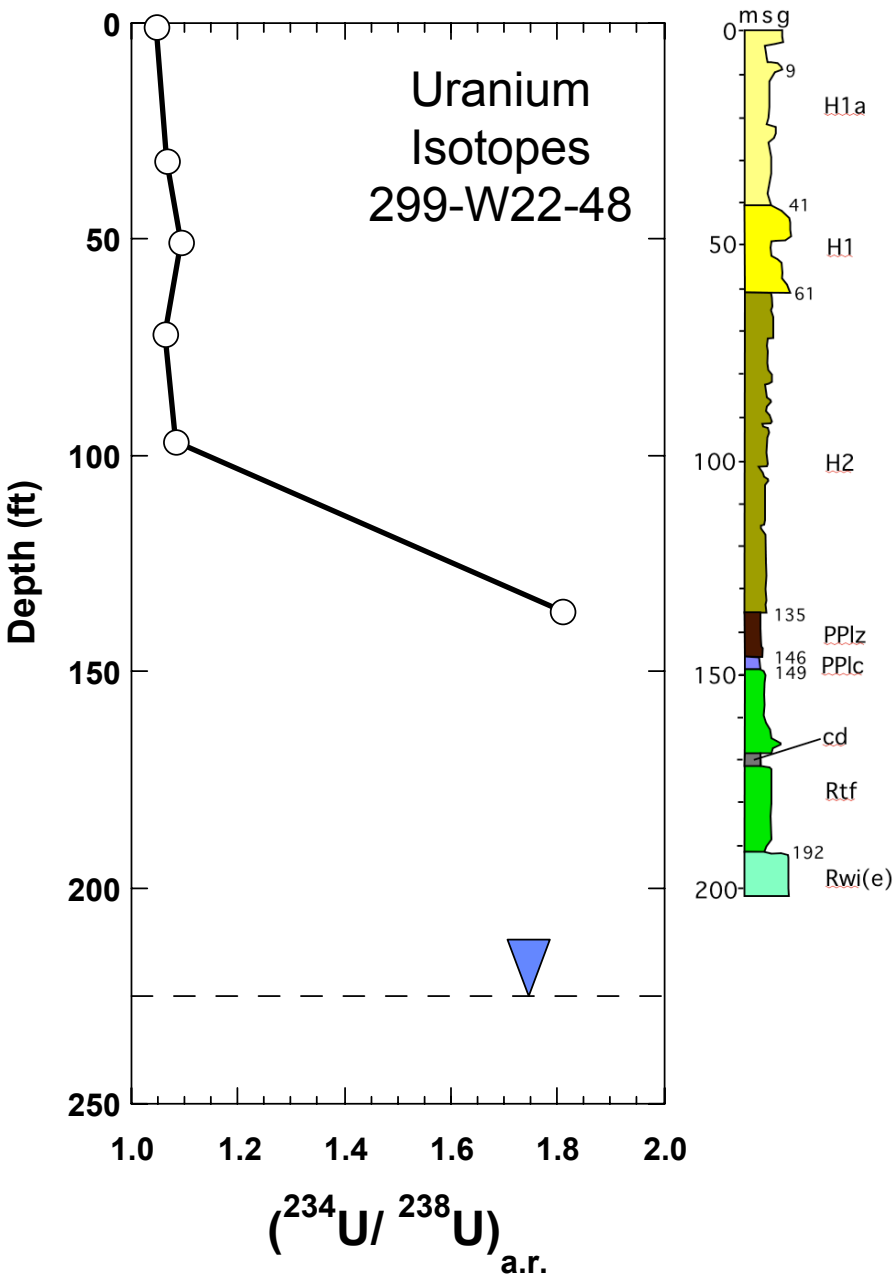


Estimate of R_s can be obtained from studies of weathering rates of soils

Values applicable to Hanford Fm. Are likely to be equal to or lower than the soil values.

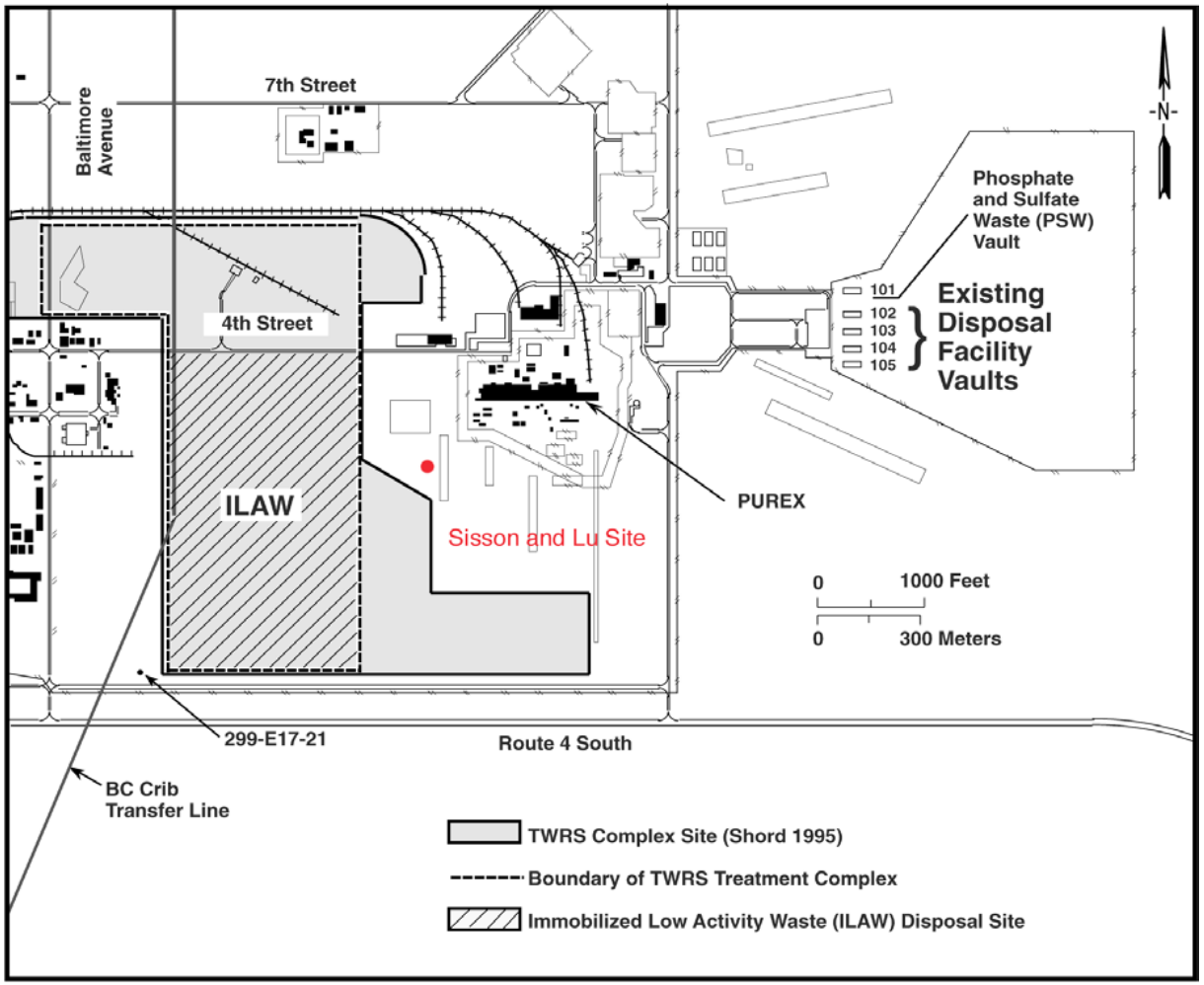
Infiltration estimate from Sr isotopes is 6 - 25 mm/yr



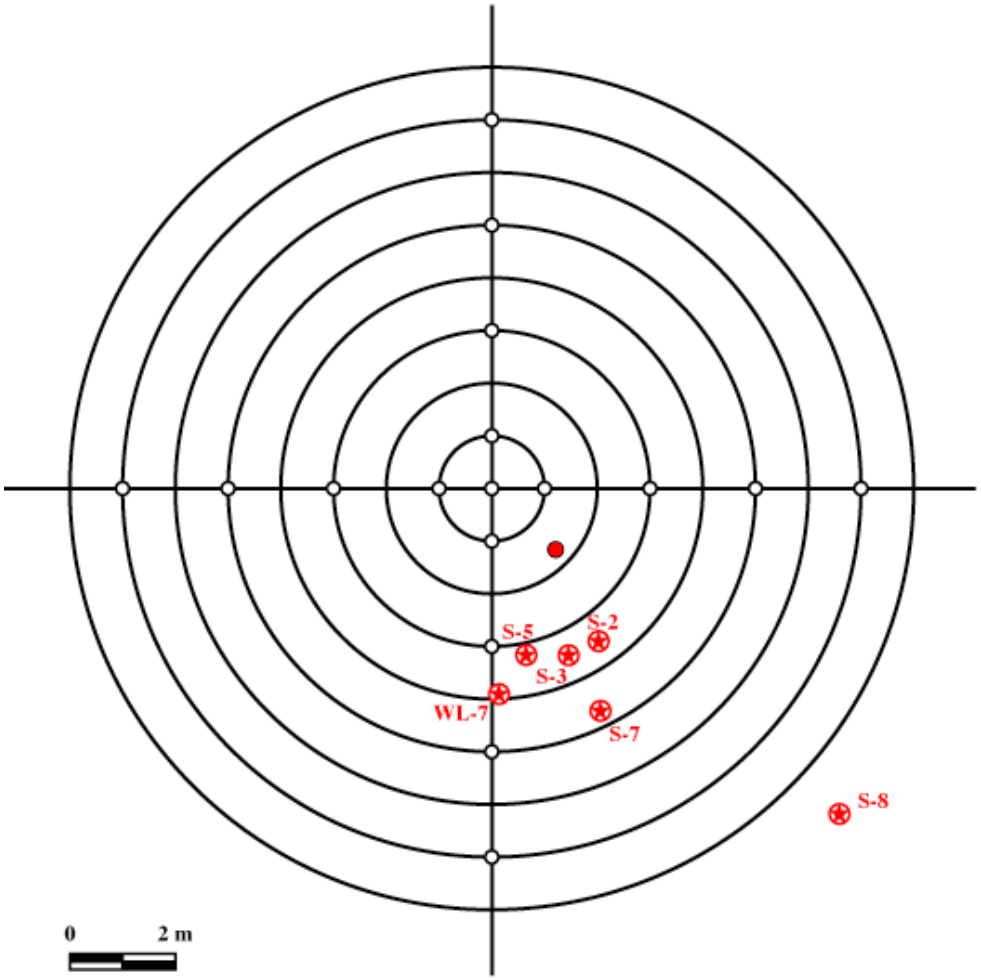


Uranium isotopes may give more information on soil weathering rates. This part of the study has just begun.

Isotopic tracers for VZTF infiltration experiments

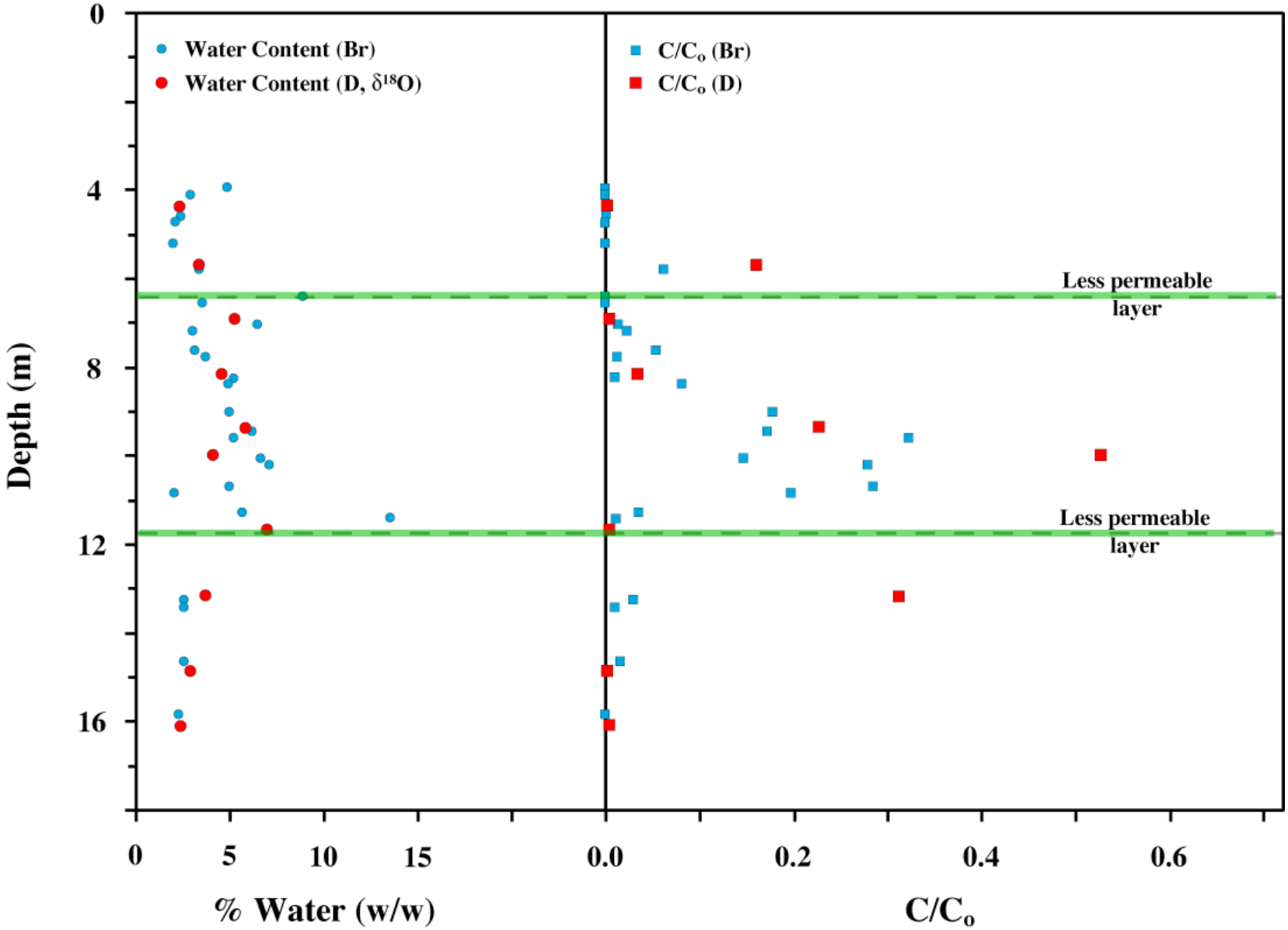


"Sisson and Lu" Site

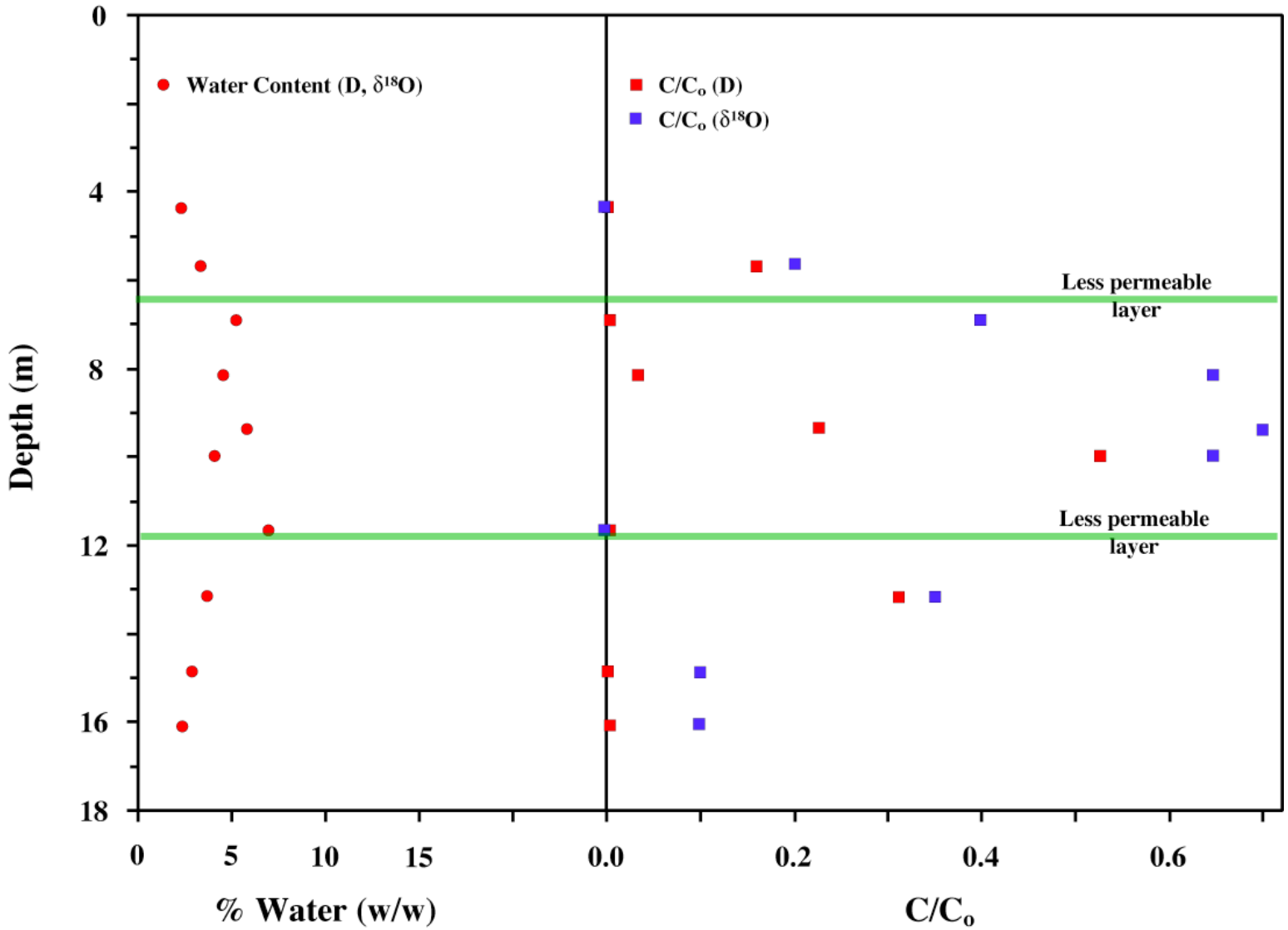


Map of the Sisson and Lu site at Hanford where the VZTFS tracer experiments are being conducted. Shown on the map are the locations of the injection well (●), boreholes where cores were taken for monitoring tracer movement (⊛), and pre-existing, steel-cased wells (○).

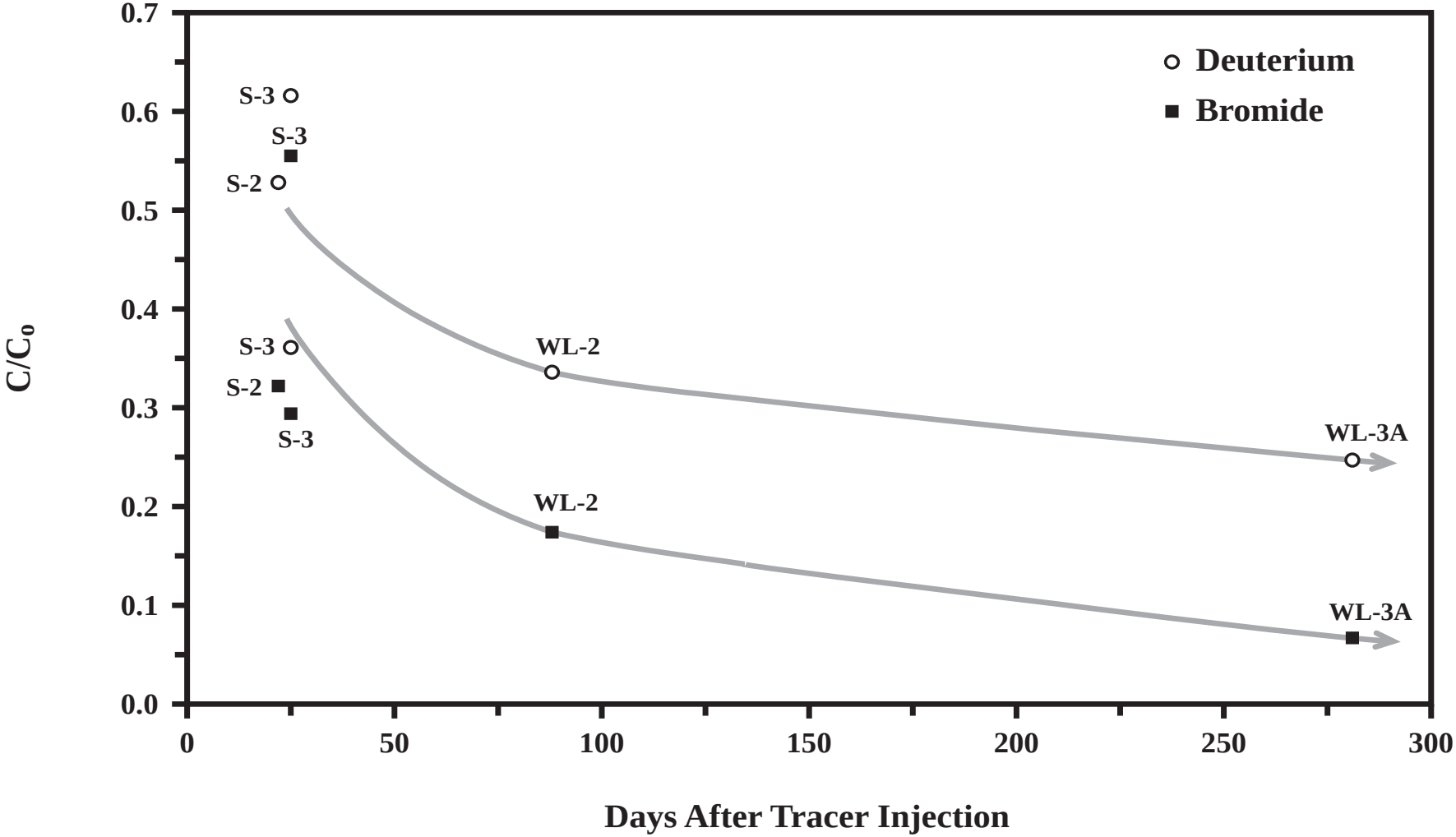
S-2 Core (~3m) 3 weeks post-injection



S-2 $\delta^{18}O$


Water Content (D, δ18O)
C/Co (D)
C/Co (δ18O)
Less permeable layer
Less permeable layer
Depth (m)
0
4
8
12
16
18
0
5
10
15
0.0
0.2
0.4
0.6
% Water (w/w)
C/Co

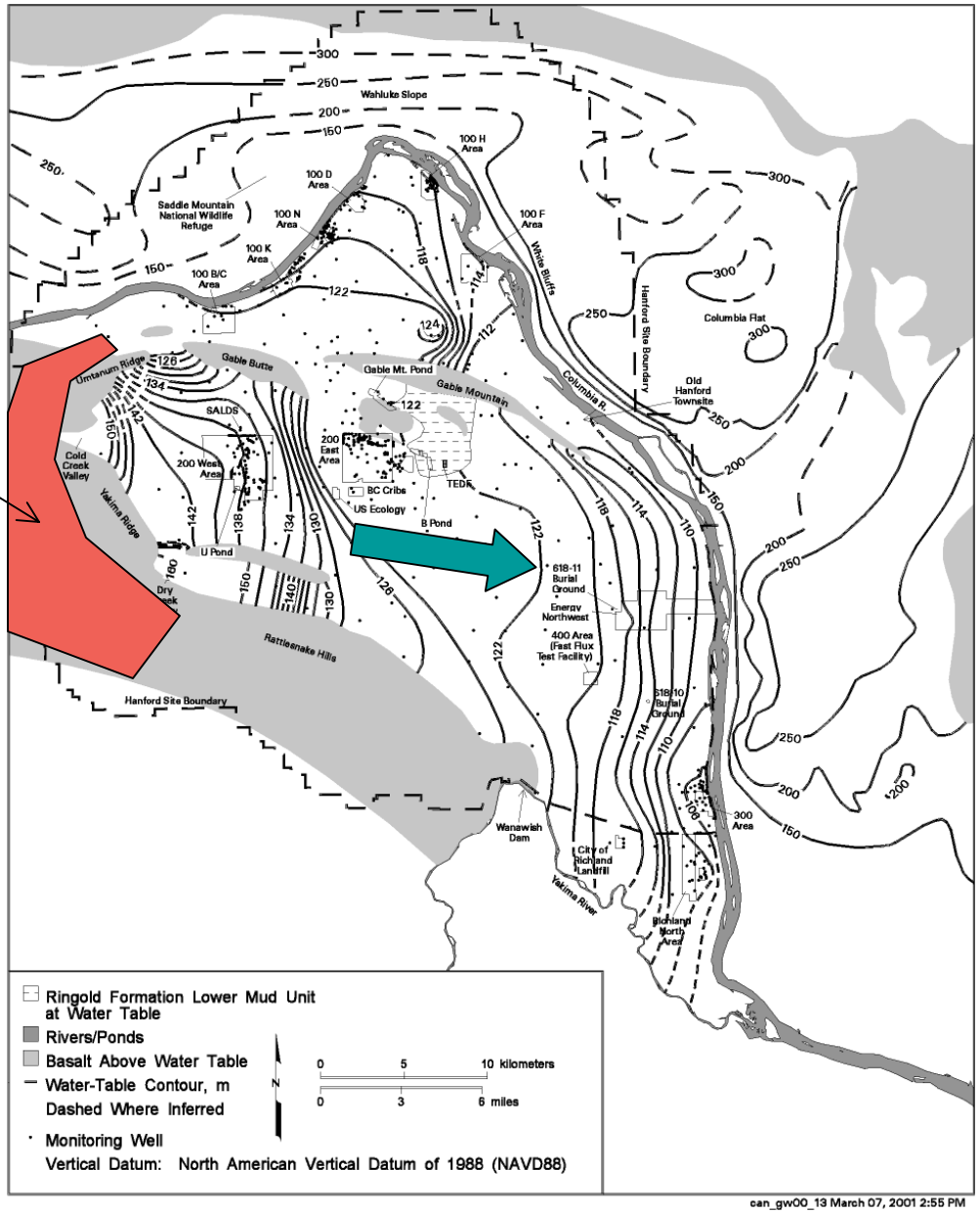
Comparative Bromide and Deuterium Concentrations over time at ~3m from Injection

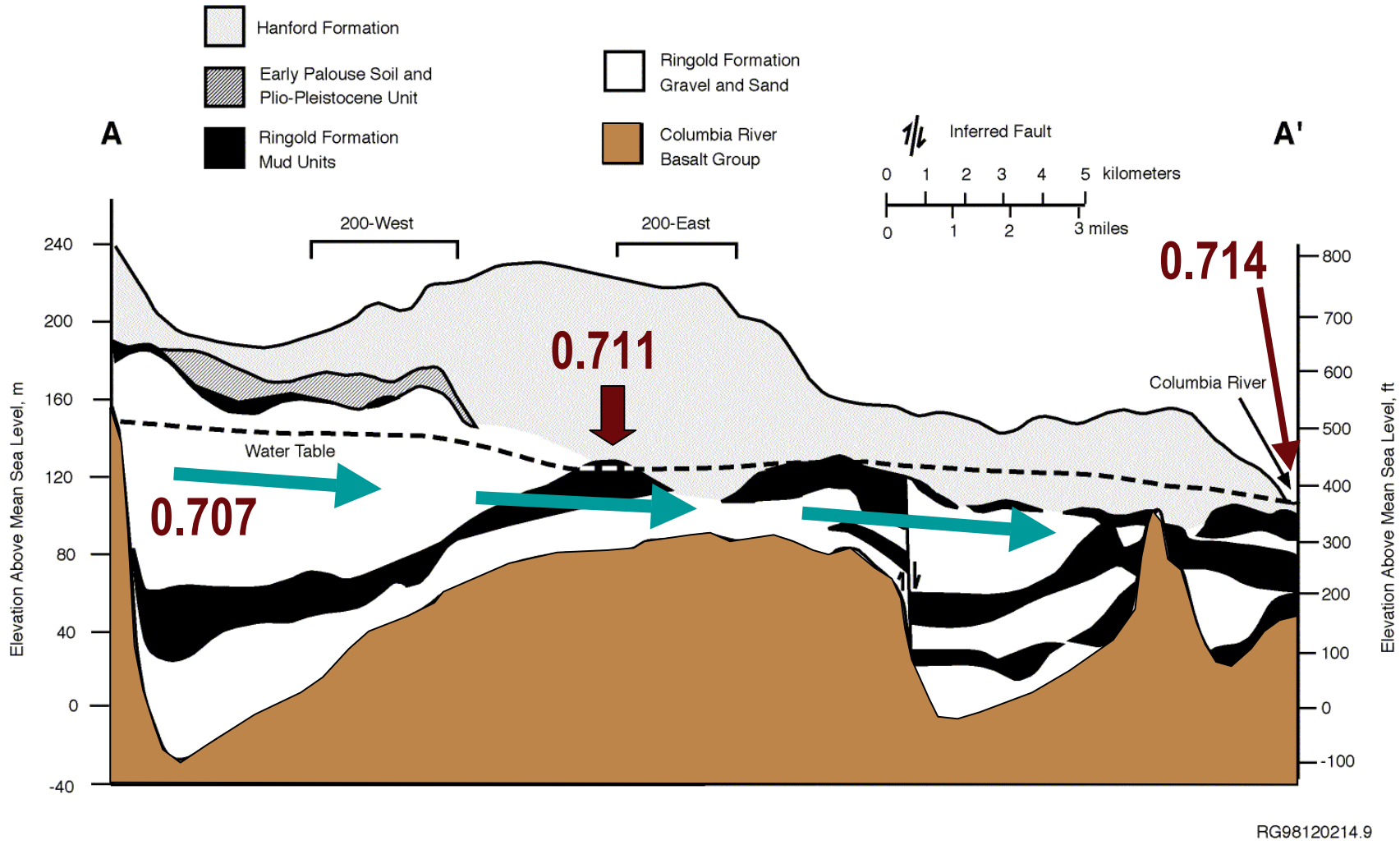


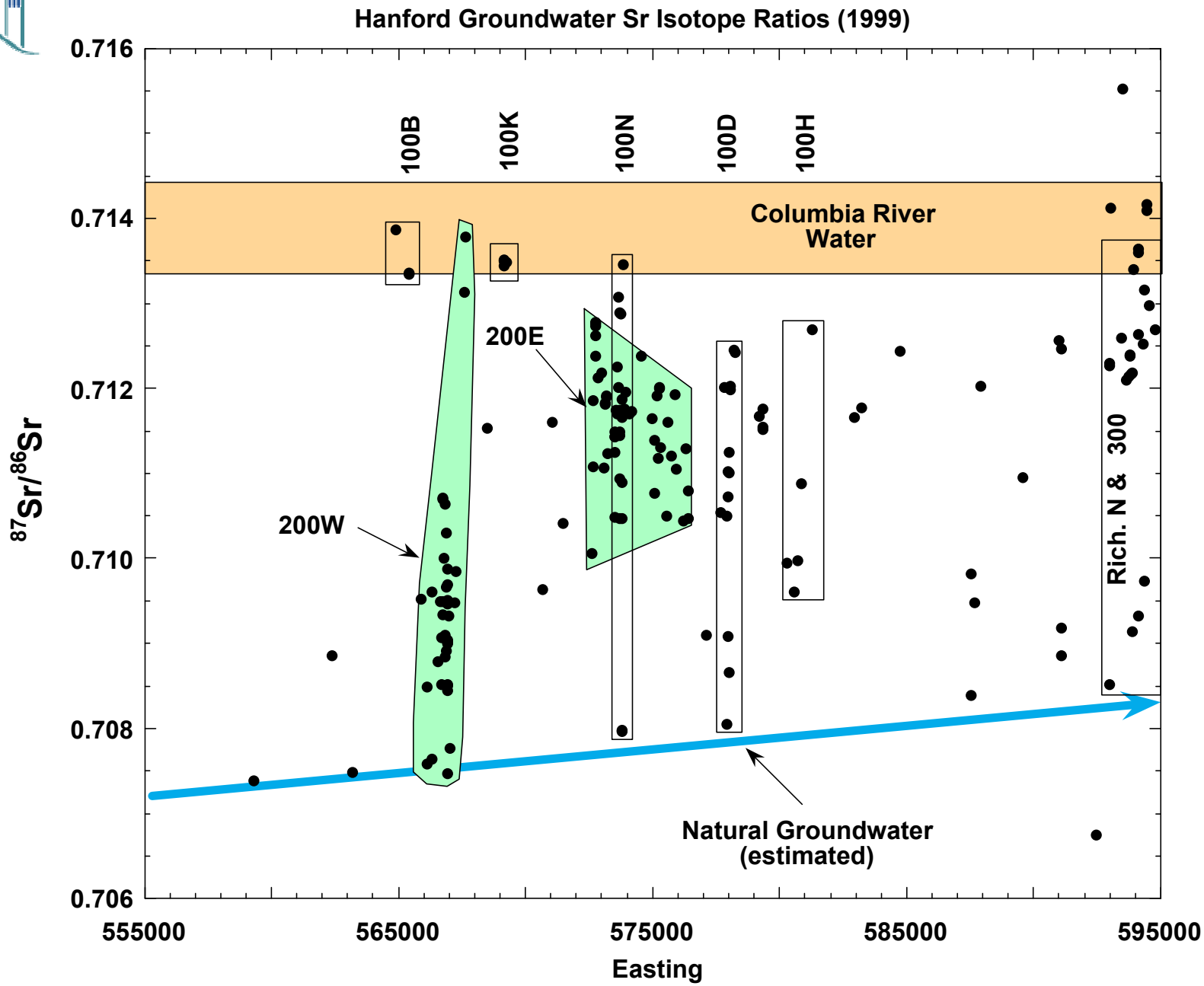
Groundwater studies

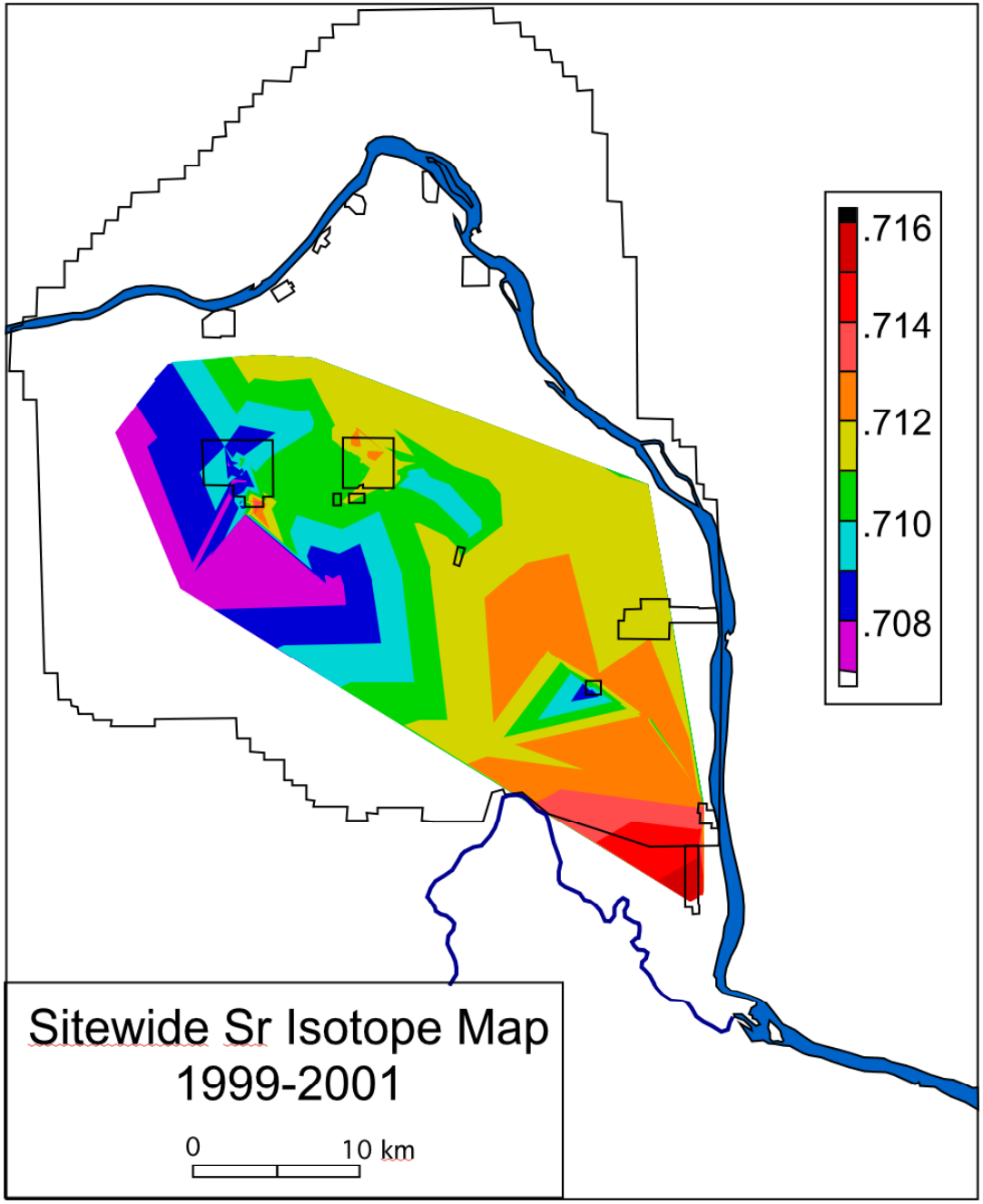
- Piggy-backed on sampling for groundwater monitoring
- Measurements of O,D,C,Sr made at Berkeley
- Measurements of other chemistry, radionuclides made at PNNL

Recharge area in basalt - low $^{87}Sr/^{86}Sr$

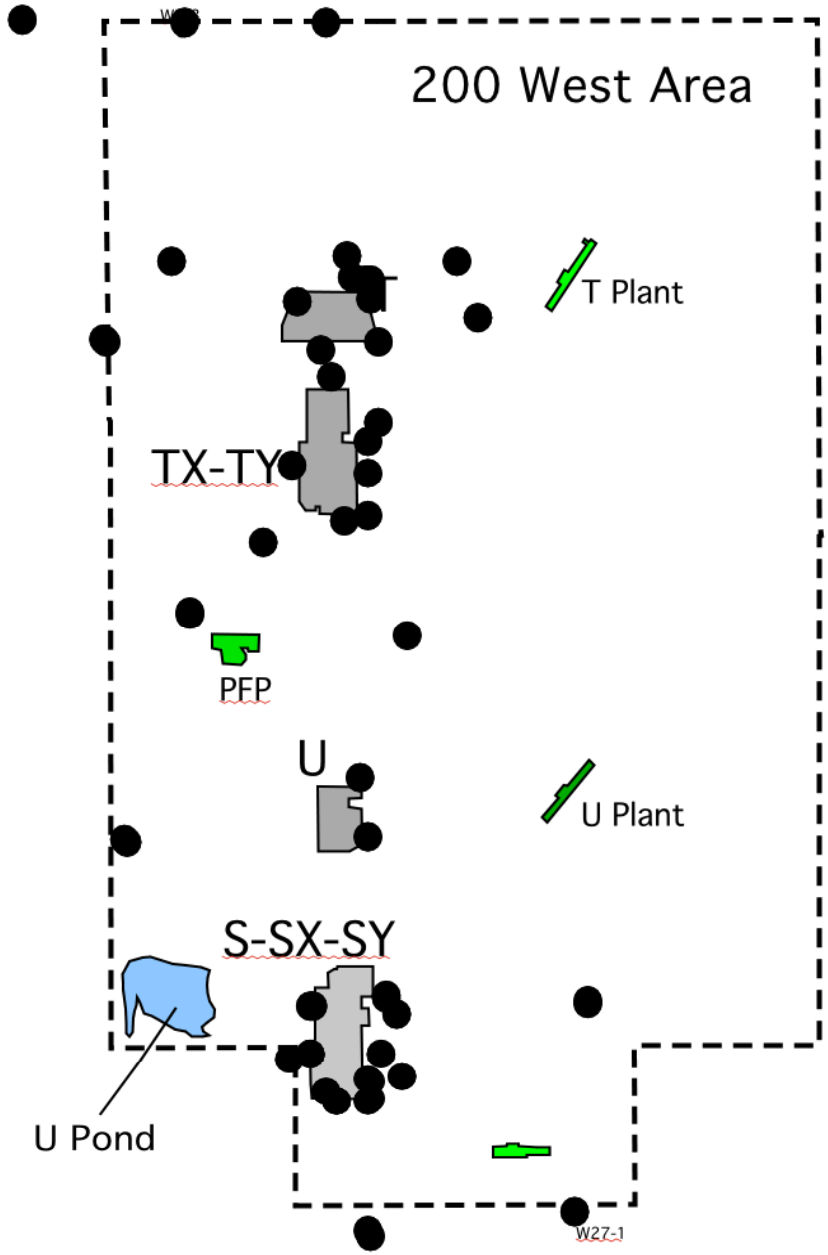



Hanford Formation
Early Palouse Soil and Plio-Pleistocene Unit
Ringold Formation Mud Units
Ringold Formation Gravel and Sand
Columbia River Basalt Group
Inferred Fault
A
A'
0 1 2 3 4 5 kilometers
0 1 2 3 miles
200-West
200-East
0.714
0.711
0.707
Columbia River
Water Table
Elevation Above Mean Sea Level, m
240
200
160
120
80
40
0
-40
Elevation Above Mean Sea Level, ft
800
700
600
500
400
300
200
100
0
-100
RG98120214.9

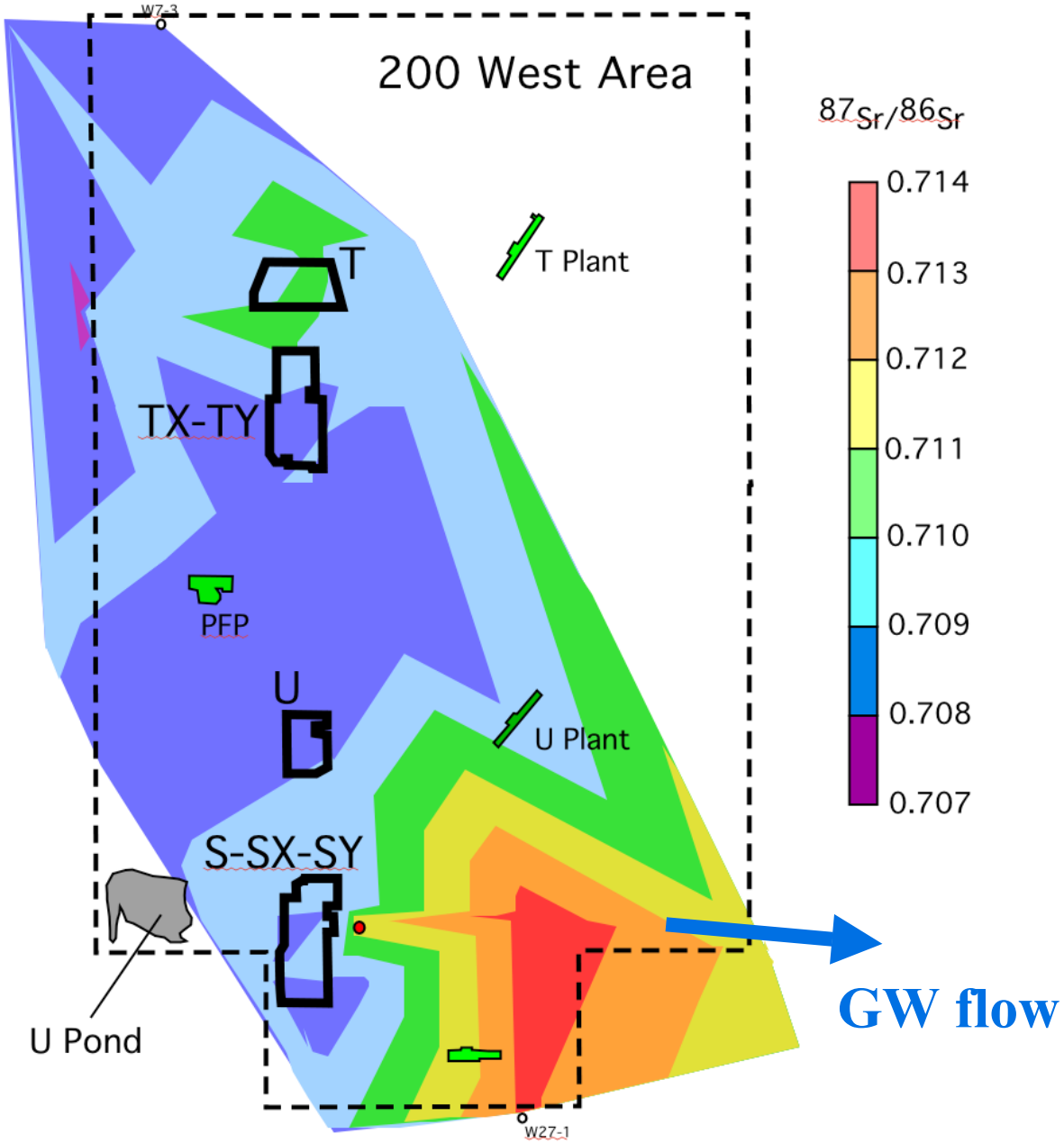

Hanford Groundwater Sr Isotope Ratios (1999)
0.716
0.714
0.712
0.710
0.708
0.706
$^{87}Sr/^{86}Sr$
555000
565000
575000
585000
595000
Easting
100B
100K
100N
100D
100H
Columbia River Water
200E
200W
Rich. N & 300
Natural Groundwater (estimated)


.716
.714
.712
.710
.708
Sitewide Sr Isotope Map
1999-2001
0
10 km

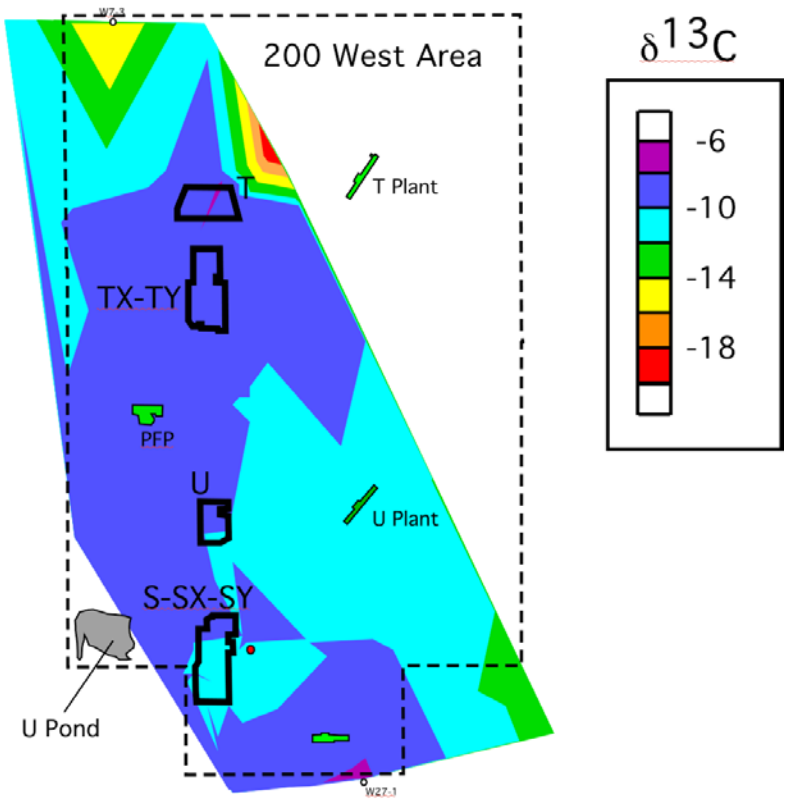
41 wells were sampled in the 200W area, most in 1999, some in 2001. Measurements of $^{87}Sr/^{86}Sr$, $\delta^{18}O$, δD, $\delta^{13}C$ have been made on most

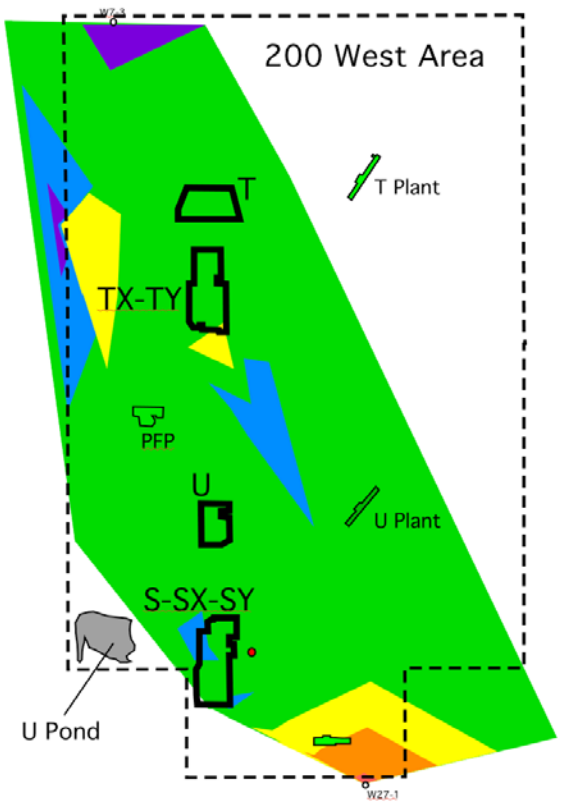


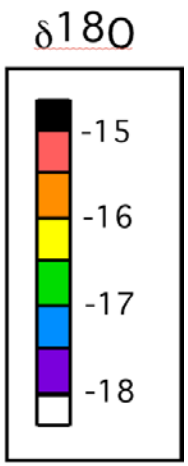
Water entering from west of 200W has the normal ratio. Ratio increases due to high recharge from VZ; probably from ponds, cribs, trenches

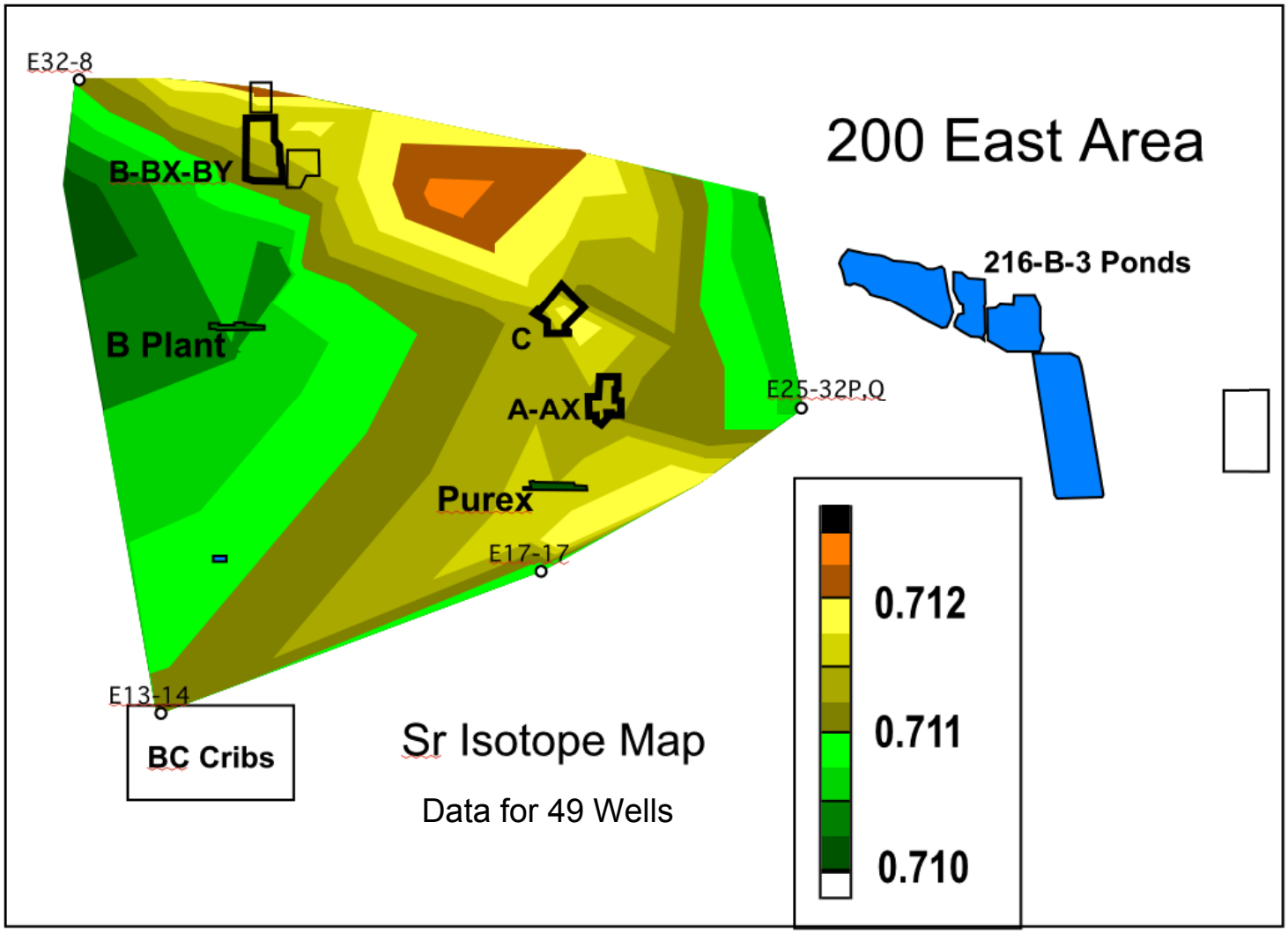


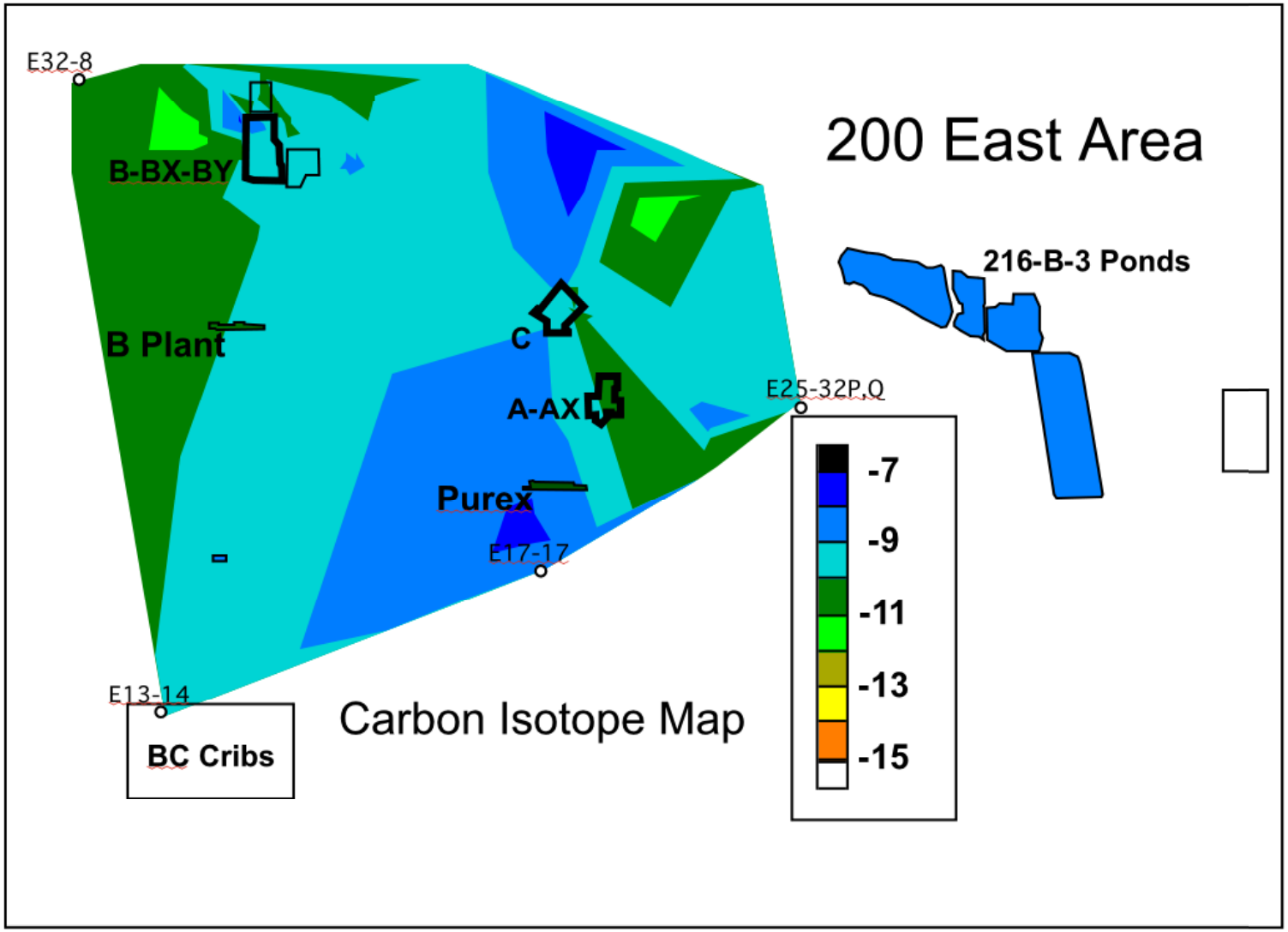
Carbon and Oxygen isotopes - 200 West








200 East Area
E32-8
B-BX-BY
B Plant
C
A-AX
Purex
E25-32P,Q
E17-17
E13-14
BC Cribs
216-B-3 Ponds
0.712
0.711
0.710
Sr Isotope Map
Data for 49 Wells


200 East Area
E32-8
B-BX-BY
B Plant
C
A-AX
Purex
E17-17
E13-14
BC Cribs
E25-32P,Q
216-B-3 Ponds
-7
-9
-11
-13
-15
Carbon Isotope Map

Conclusions (in progress)

- Sr and O/D isotopes give consistent estimates of long term average infiltration through vadose zone in area of sandy soil (1-2 cm/yr)
- O isotopes in VZ are distinct from river water and hence are a natural tracer for industrial water
- Groundwater shows effects of both natural recharge and Hanford operations in Sr, C, and O isotopes (non-contaminant monitors)
- Differences in tracer behavior for D, O vs. Br
- U isotope variations are substantial in VZ
- Overall, isotope approaches show considerable promise for improving characterization of flow and transport in VZ and groundwater