PNNL-SA-60382

Reactive Transport Modeling of Uranium Surface Complexation and Mass Transfer in the 300 Area Hydrologic System

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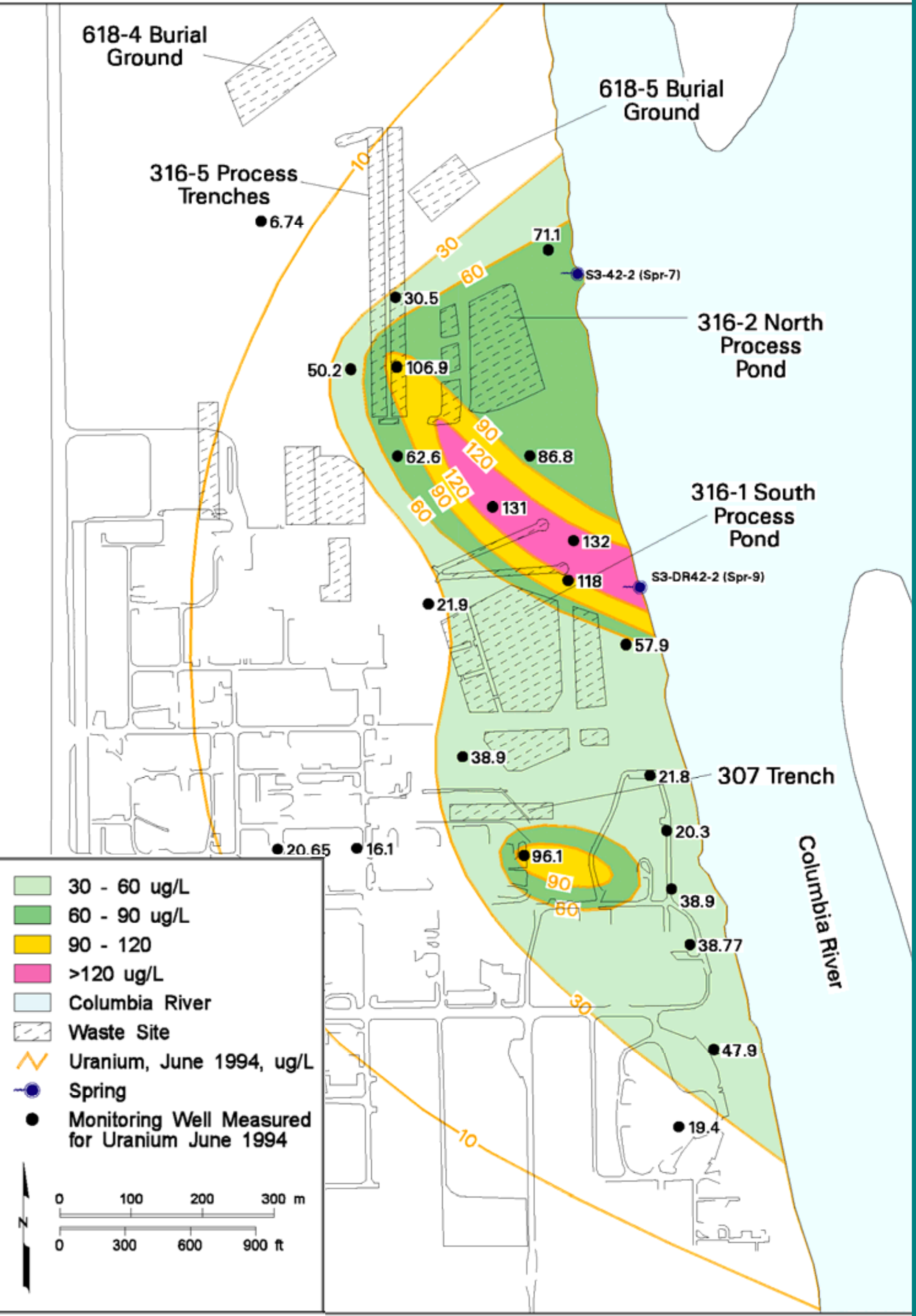
Hanford 300 Area IFC Project Meeting
April 29, 2008
Richland, Washington

Shaded 300 Area Uranium, June 1994



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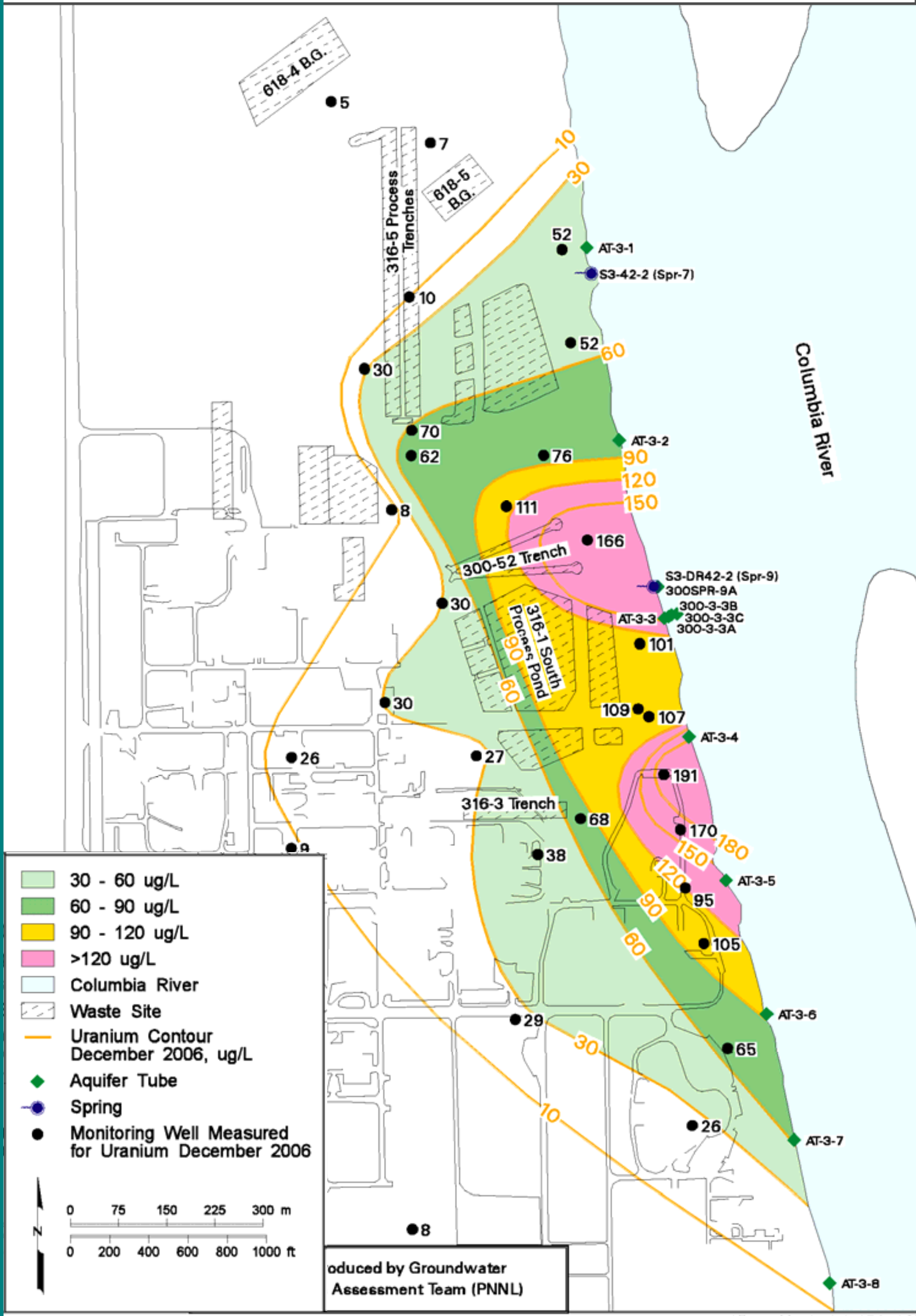
Shaded 300 Area Uranium, December 2006



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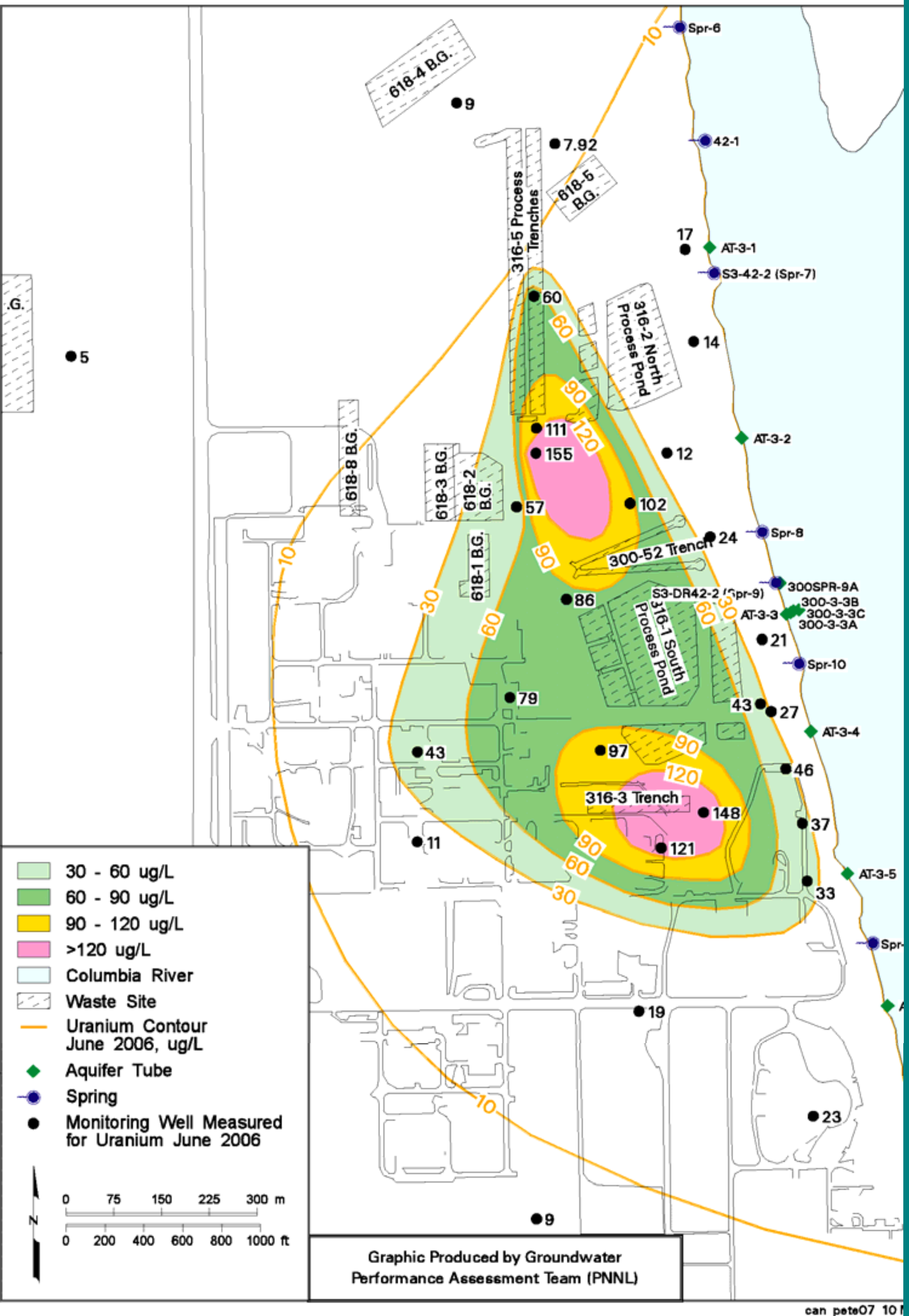
Hanford 300 Area Uranium Plume

- Remediation and Closure Science Project funded by DOE-EM through Fluor-Hanford
- Update the 300 Area conceptual model to explain the persistence of the uranium groundwater plume
- Approach: test laboratory-derived uranium process models in field-scale flow settings
- Modeling studies target uranium-contaminated sediments in
  - upper vadose zone
  - water table fluctuation zone
  - aquifer – river interaction zone

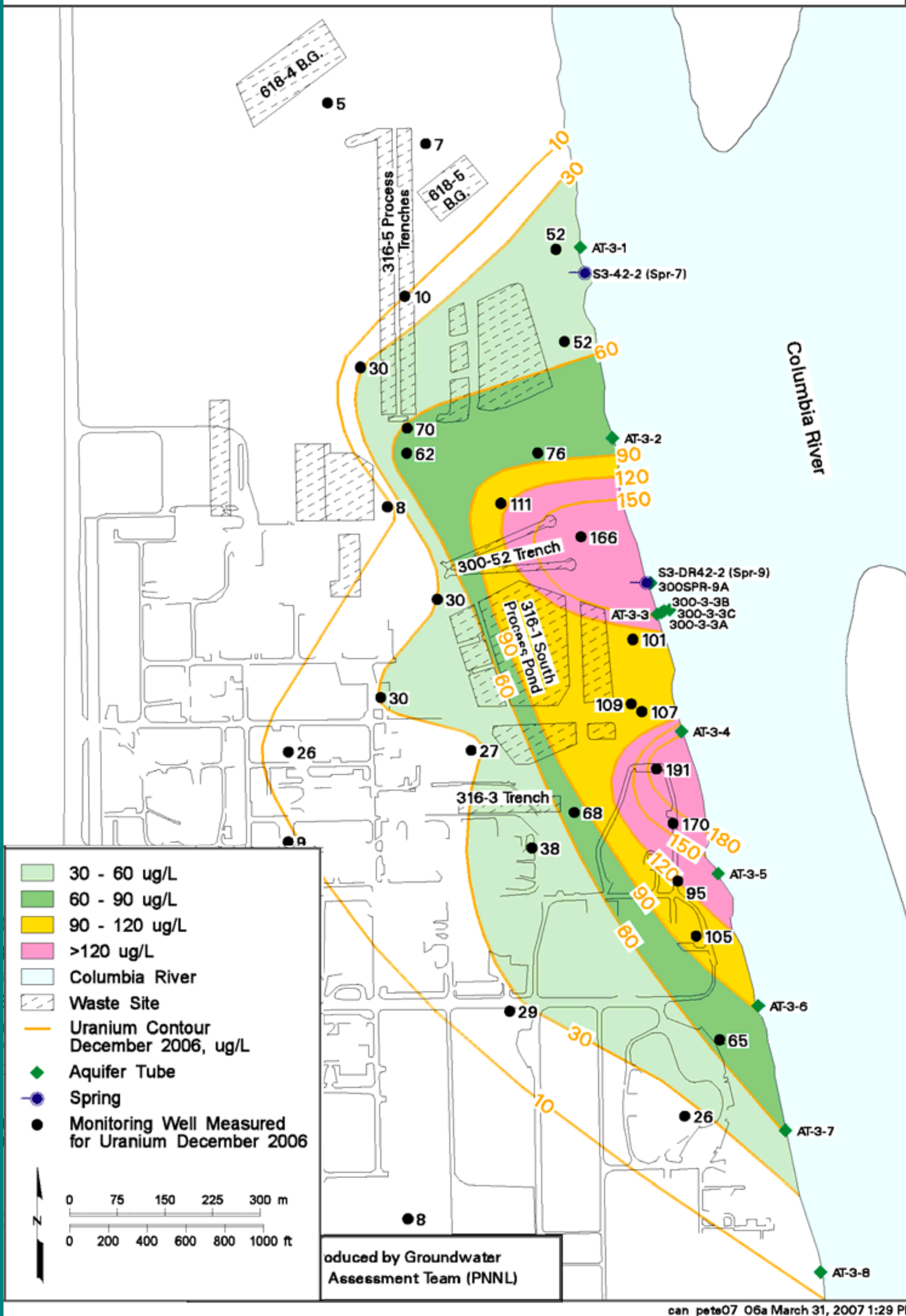
Columbia River Stage

- 300 Area
  - 0.5 m mean daily range in river stage
  - 3 m mean annual range in river stage
  - 0.14 m mean head drop from 1.1 km inland
  - ~1500 m/d hydraulic conductivity
- Groundwater impacts
  - Diurnal cycles of high GW flow with reversals
  - Seasonal extent and magnitude of river water mixing zones
  - Uranium mobility dependent on degree of mixing and time scales of transport
- Redistribution of solutes and uranium above the average water table
  - Inland transport driven by high river stage
  - Persistence in the lower vadose zone

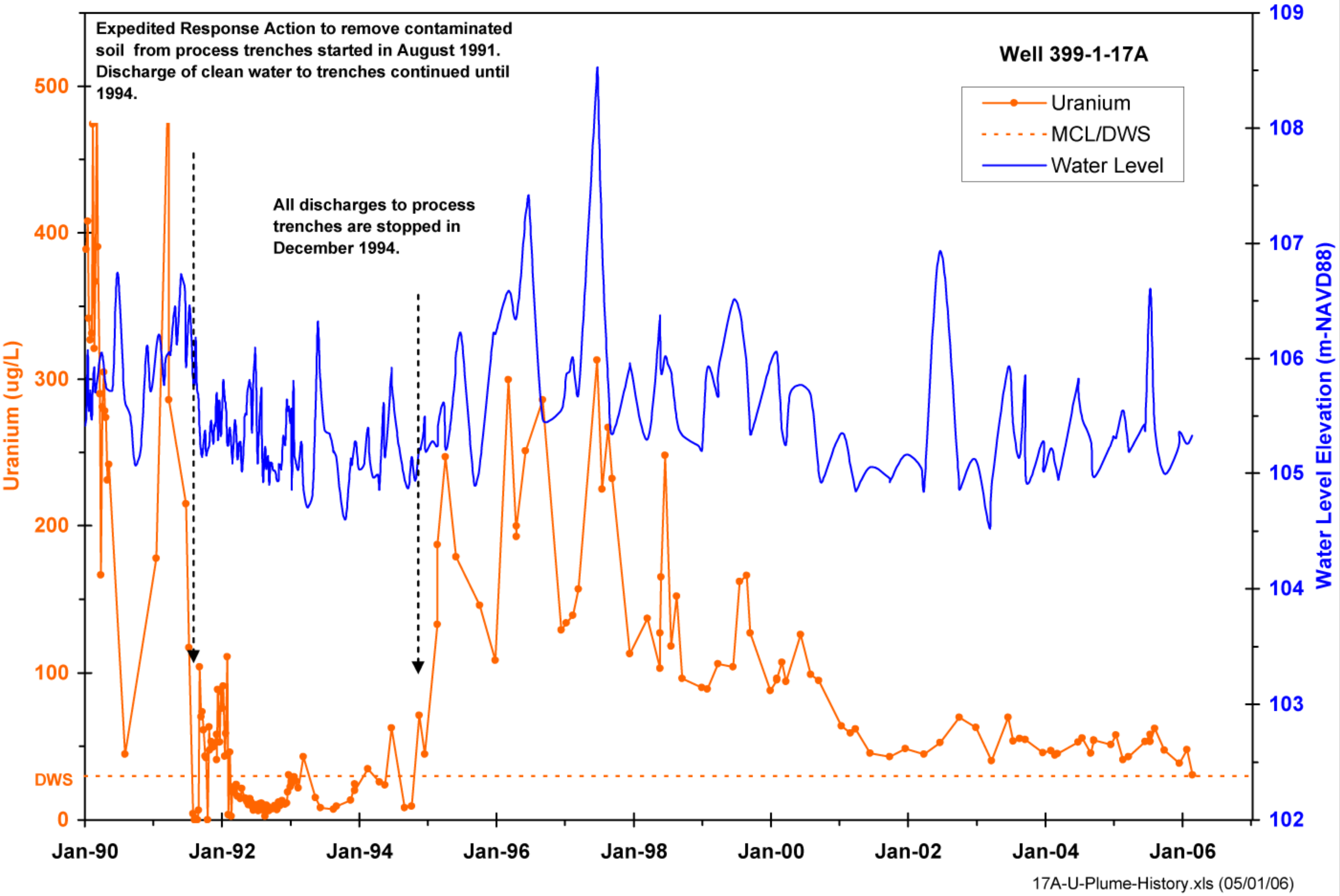
300 Area Uranium, June 2006



300 Area Uranium, December 2006



Aquifer Water Levels and Uranium Concentrations



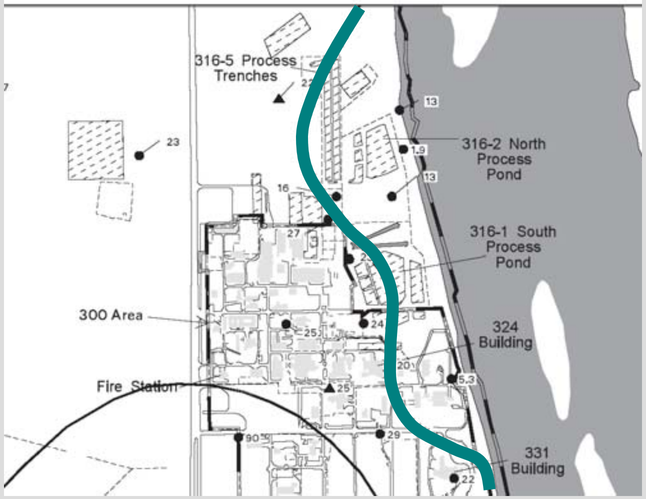
Expedited Response Action to remove contaminated soil from process trenches started in August 1991. Discharge of clean water to trenches continued until 1994.

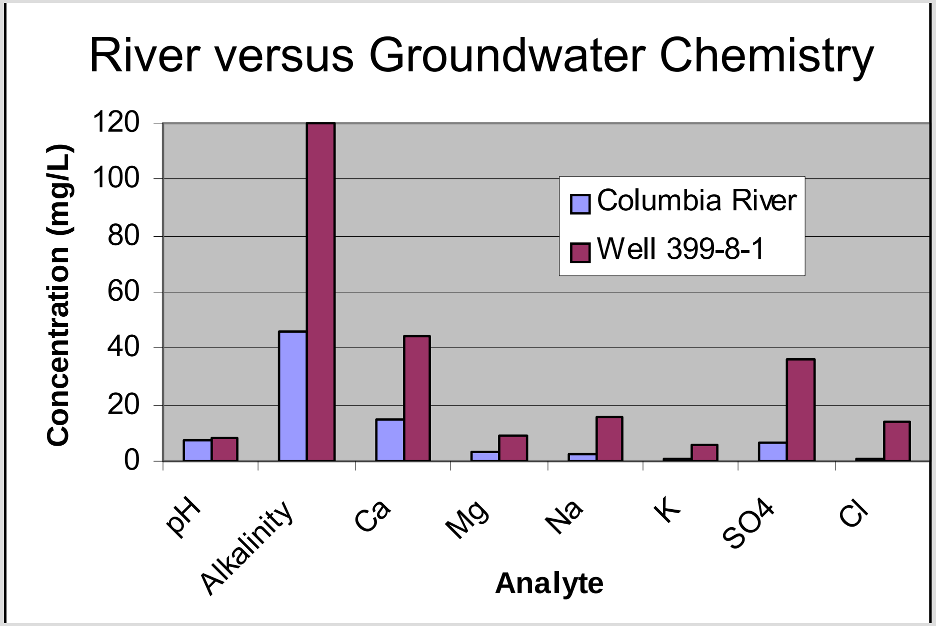
All discharges to process trenches are stopped in December 1994.

17A-U-Plume-History.xls (05/01/06)

Aquifer-River Solution Chemistry

2002 Nitrate Concentration



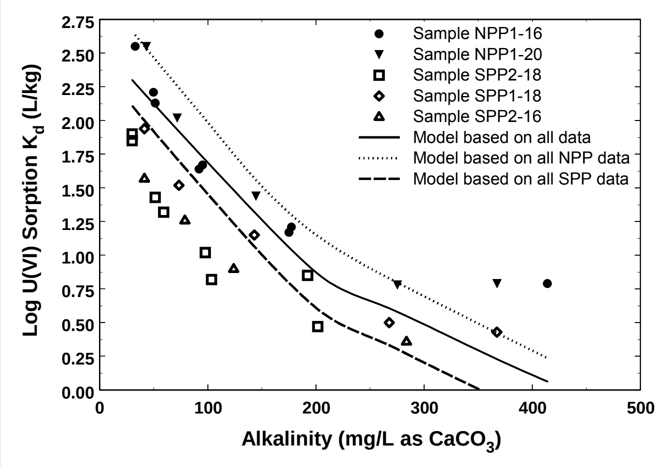

River versus Groundwater Chemistry

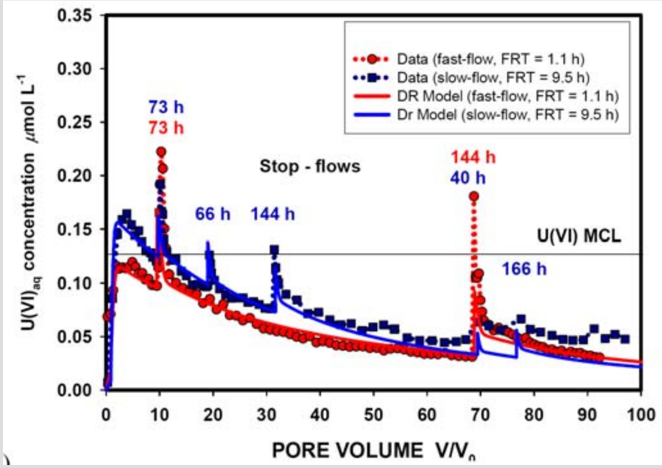
- River water influx occurs during high stage
- Prolonged seasonal high stage period allows mixing in aquifer with river water
- Significant differences in solution chemistry

Uranium Geochemistry in 300 Area Sediments

Constant K_d not consistent with experimental observations

- Uranium sorption varies strongly over the range of observed water chemistry (e.g., U, Ca, pH, alkalinity concentrations)
- Rate-limited uranium mass transfer identified in column experiments with flow rates consistent with field observations





Uranium Geochemical Process Models

- 2-reaction generalized composite surface complexation model (Bond and Davis, USGS)
  - accounts for bicarbonate concentration, sediment surface area, and aqueous U(VI) complexation (21 reactions)

$\text{SOH} + \text{UO}_2^{2+} + \text{H}_2\text{O} = \text{SOUO}_2\text{OH} + 2\text{H}^+$ Log K = −5.235

$\text{SOH} + \text{UO}_2^{2+} + \text{H}_2\text{CO}_3 = \text{SOHUO}_2\text{CO}_3 + 2\text{H}^+$ Log K = −1.033

- Multisite model with variable uranium mass transfer kinetics (Chongxuan Liu, PNNL):
  - Accounts for reaction rates and rate-limited diffusion processes
  - Distributed rate parameters were assumed to follow the Gamma statistical distribution (two parameters):

$$\frac{\partial S}{\partial t} = \sum_{i=1}^{N} \frac{\partial S_i}{\partial t}; \qquad \frac{\partial S_i}{\partial t} = \alpha_i \left[f_i(\alpha_i) K_d{}^i C - S_i \right]$$

$$f_i(\alpha_i) = \int_{\alpha_i}^{\alpha_i + \Delta\alpha_i} \frac{\beta^{-\eta} \tau^{\eta-1}}{\Gamma(\eta)} \exp\left(-\frac{\tau}{\beta} \right) d\tau$$

$K_d = 14$ ml/g

$\beta = 0.011$/h

$\eta = 0.42$

Field-Based Reactive Transport Modeling

Account for full sediment size distribution

- < 2 mm size fraction in the lab studies
  - Specific surface area: 27.2 m²/g
  - 8% of total sediment
- Preliminary assumption: gravels are unreactive
  - apportion 8% of the 2.06 kg/L field bulk density for surface complexation

Size (mm)	Mass Distribution (%)
Cobbles	
>12.5	74.5
2.0 – 12.5	17.2
Sand	
1.0 – 2.0	2.64
0.5-1.0	2.34
0.25 – 0.5	0.78
0.149 – 0.25	0.33
0.106 – 0.149	0.19
0.053 – 0.106	0.20
Silt + Clay	
<0.053	1.78

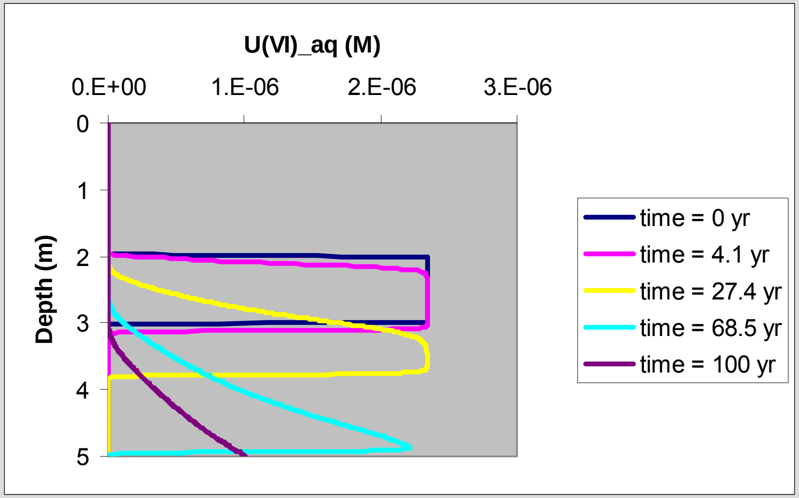
Reactions

Reaction	**log K**
$UO_2^{2+} + H_2O = UO_2OH^+ + H^+$	-5.25
$UO_2^{2+} + 2H_2O = UO_2(OH)_{2,aq} + 2H^+$	-12.15
$UO_2^{2+} + 3H_2O = UO_2(OH)_3^- + 3H^+$	-20.25
$UO_2^{2+} + 4H_2O = UO_2(OH)_4^{2-} + 4H^+$	-32.4
$2UO_2^{2+} + H_2O = (UO_2)_2OH^{3+} + H^+$	-2.70
$2UO_2^{2+} + 2H_2O = (UO_2)_2(OH)_2^{2+} + 2H^+$	-5.62
$3UO_2^{2+} + 4H_2O = (UO_2)_3(OH)_4^{2+} + 4H^+$	-11.90
$3UO_2^{2+} + 5H_2O = (UO_2)_3(OH)_5^+ + 5H^+$	-15.55
$3UO_2^{2+} + 7H_2O = (UO_2)_3(OH)_7^- + 7H^+$	-32.20
$4UO_2^{2+} + 7H_2O = (UO_2)_4(OH)_7^+ + 7H^+$	-21.9
$UO_2^{2+} + CO_3^{2-} = UO_2CO_3(aq)$	9.94
$UO_2^{2+} + 2CO_3^{2-} = UO_2(CO_3)_2^{2-}$	16.61
$UO_2^{2+} + 3CO_3^{2-} = UO_2(CO_3)_3^{4-}$	21.84
$2UO_2^{2+} + CO_3^{2-} + 3H_2O = (UO_2)_2CO_3(OH)_3^- + 3H^+$	-0.855
$Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = CaUO_2(CO_3)_3^{2-}$	25.64
$2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = Ca_2UO_2(CO_3)_3\ (aq)$	30.55
$UO_2^{2+} + NO_3^- = UO_2NO_3^+$	0.3
$UO_2^{2+} + Cl^- = UO_2Cl^+$	0.17
$UO_2^{2+} + 2Cl^- = UO_2Cl_2(aq)$	-1.1
$UO_2^{2+} + SO_4^{2-} = UO_2SO_4(aq)$	3.15
$UO_2^{2+} + 2SO_4^{2-} = UO_2(SO_4)_2^{2-}$	4.14
$SOH + UO_2^{2+} + H_2O = SOUO_2OH + 2H^+$	-5.235
$SOH + UO_2^{2+} + H_2CO_3 = SOHUO_2CO_3 + 2H^+$	-1.033

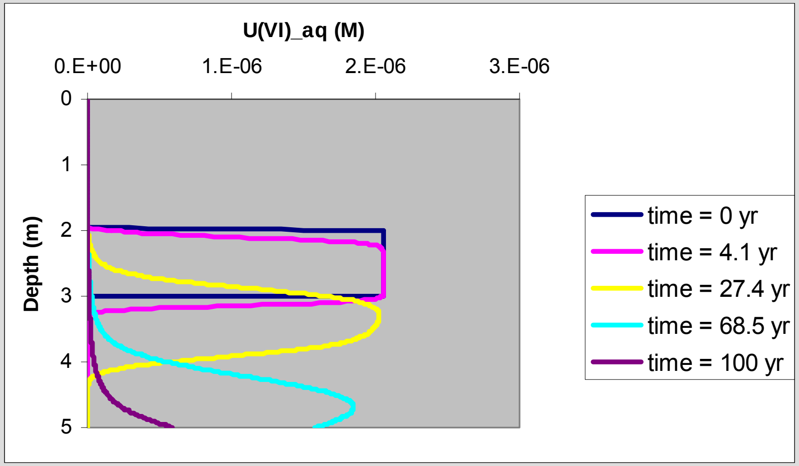
Reaction	**Log K**
$H^+ + HCO_3^- = H_2CO_3$	6.3414
$HCO_3^- = CO_3^{2-} + H^+$	-10.3249
$Ca^{2+} + HCO_3^- = CaCO_3(aq) + H^+$	-7.0088
$Ca^{2+} + Cl^- = CaCl^+$	-0.7004
$Ca^{2+} + 2Cl^- = CaCl_2(aq)$	-0.6535
$Ca^{2+} + HCO_3^- = CaHCO_3^+$	1.0420
$Ca^{2+} + NO_3^- = CaNO_3^+$	1.3
$Mg^{2+} + NO_3^- = MgNO_3^+$	1.3
$Ca^{2+} + H_2O = CaOH^+ + H^+$	-12.85
$Ca^{2+} + SO_4^{2-} = CaSO4(aq)$	2.1004
$H^+ + Cl^- = HCl(aq)$	0.6999
$H^+ + NO_3^- = HNO_3(aq)$	-1.3081
$K^+ + Cl^- = KCl(aq)$	-1.5004
$K^+ + SO_4^{2-} = KSO_4^-$	0.875
$Mg^{2+} + HCO_3^- = MgCO_3(aq) + H^+$	-7.3562
$Mg^{2+} + Cl^- = MgCl^+$	-0.1386
$Mg^{2+} + HCO_3^- = MgHCO_3^+$	1.0329
$Mg^{2+} + SO_4^{2-} = MgSO_4(aq)$	2.4125
$Na^+ + HCO_3^- = NaCO_3^- + H^+$	-9.8156
$Na^+ + Cl^- = NaCl$	-0.7821
$Na^+ + HCO_3^- = NaHCO_3\ (aq)$	0.1557
$Na^+ + H_2O = NaOH(aq) + H^+$	-14.7986
$Na^+ + SO_4^{2-} = NaSO_4^-$	0.82
$H^+ + OH^- = H_2O$	13.9911
$Sr^{2+} + HCO_3^- = SrCO_3(aq) + H^+$	-7.4703
$Sr^{2+} + Cl^- = SrCl^+$	-0.2533
$Sr^{2+} + NO_3^- = SrNO_3^+$	0.8
$Sr^{2+} + H_2O = SrOH^+ + H^+$	-13.29
$Sr^{2+} + SO_4^{2-} = SrSO_4(aq)$	2.3
$Na^+ + NO_3^- = NaNO_3(aq)$	-0.2564
$Ca^{2+} + HCO_3^- = \mathrm{Calcite}(s) + H^+$	-1.8542

1-D Unsaturated Reactive Transport Simulation

- 1-D reactive transport simulation
  - 60 mm/yr recharge results in 0.75 m/yr pore velocity
  - 5 m of vadose zone
  - 1 m of contaminated sediment in the middle
    - 30 nM/g U contaminated zone
- GC-SCM
  - Sorption front requires over 30 years to move 1 m
  - Kd = 12.4 L/kg for this solution chemistry
  - Lowest sediment contamination level results in U(VI) above MCL (0.126 uM)
- Multisite kinetic model
  - Very similar to GC-SCM result
    - Kd = 14 similar to the GC-SCM
    - impact of kinetics largely minimized by long transport time scales

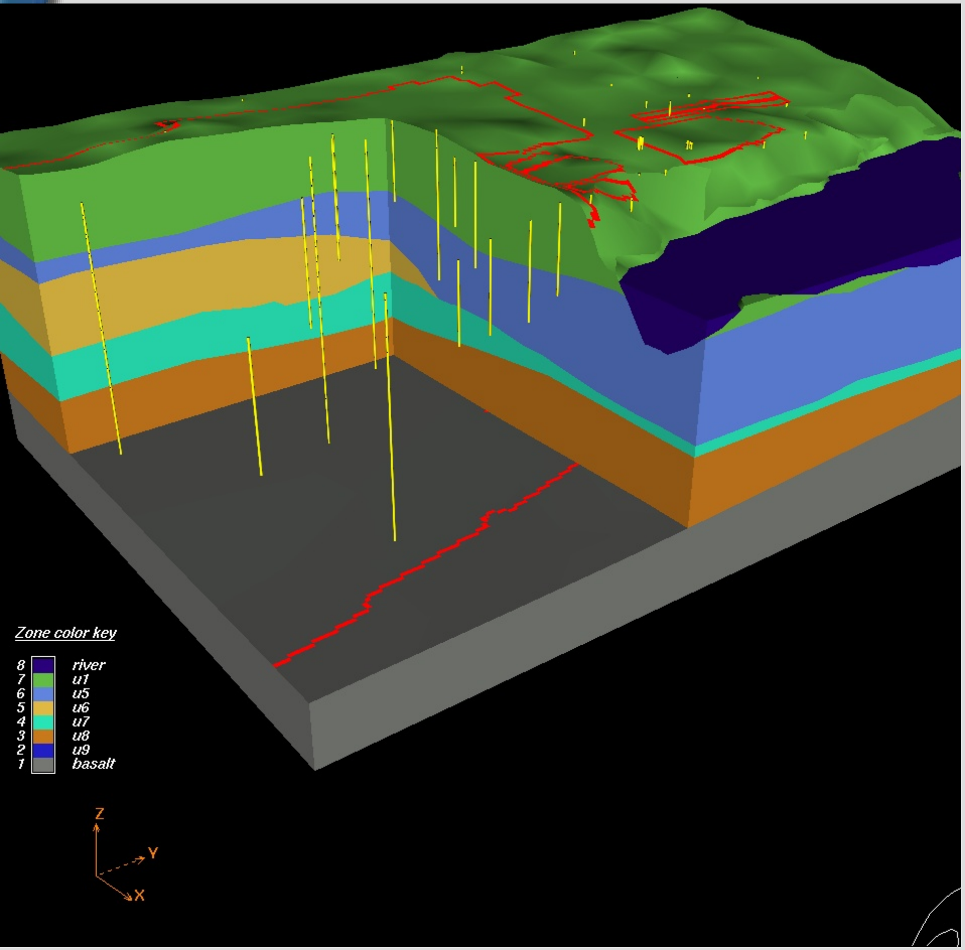


Generalized Composite SCM



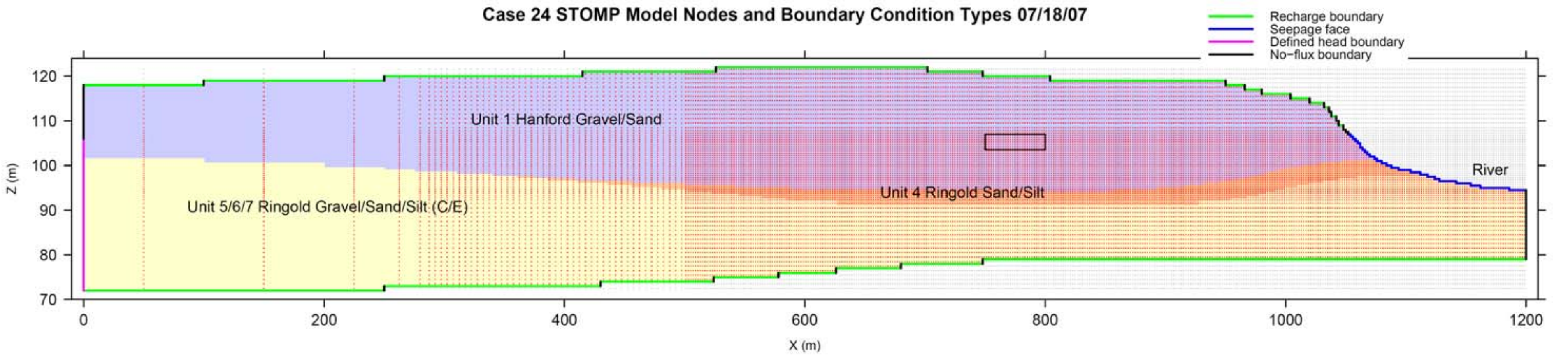
Multisite Kinetic Model

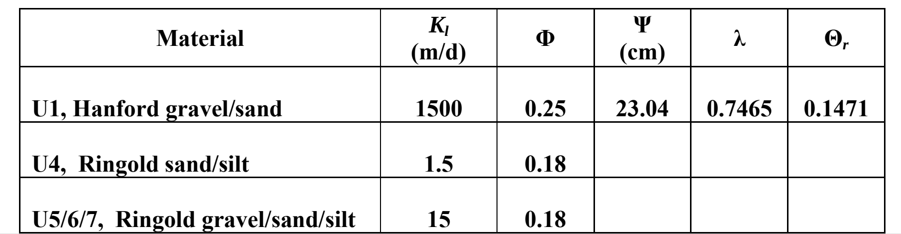
Flow and Reactive Transport: Vadose Zone – Aquifer – River System



- 2-D STOMP Modeling
  - Variably-saturated flow
  - Multicomponent geochemistry
- Investigate uranium behavior at the vadose zone – aquifer interface during water table fluctuations
- Investigate dynamics of fluxes across aquifer - river interface

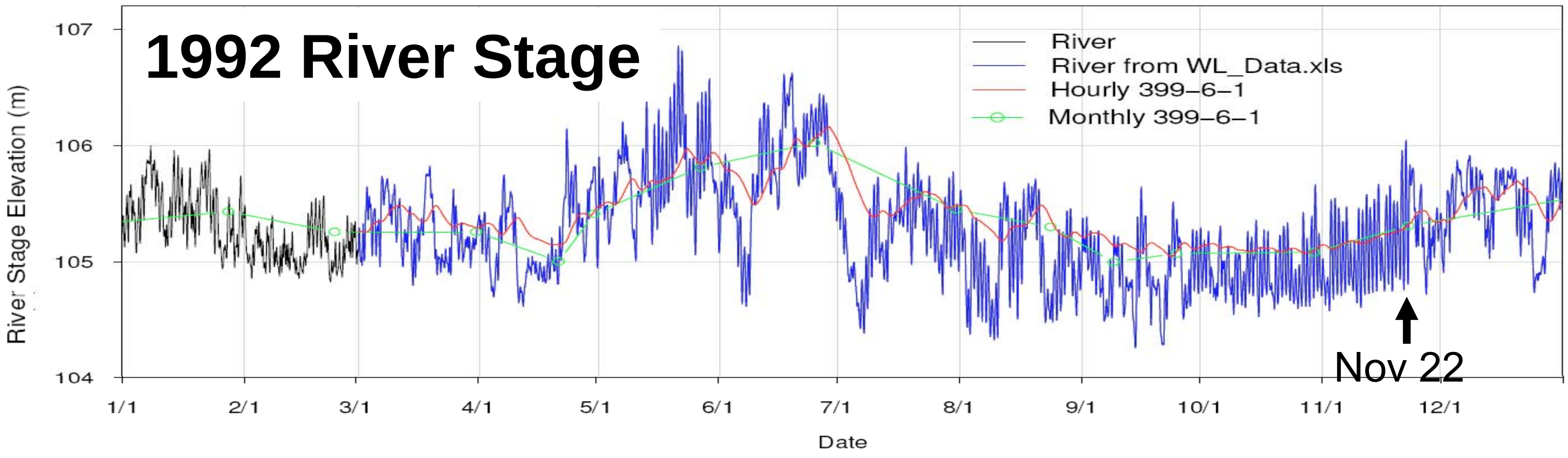
Variably Saturated Flow: Vadose Zone – Aquifer – River Hydrologic System





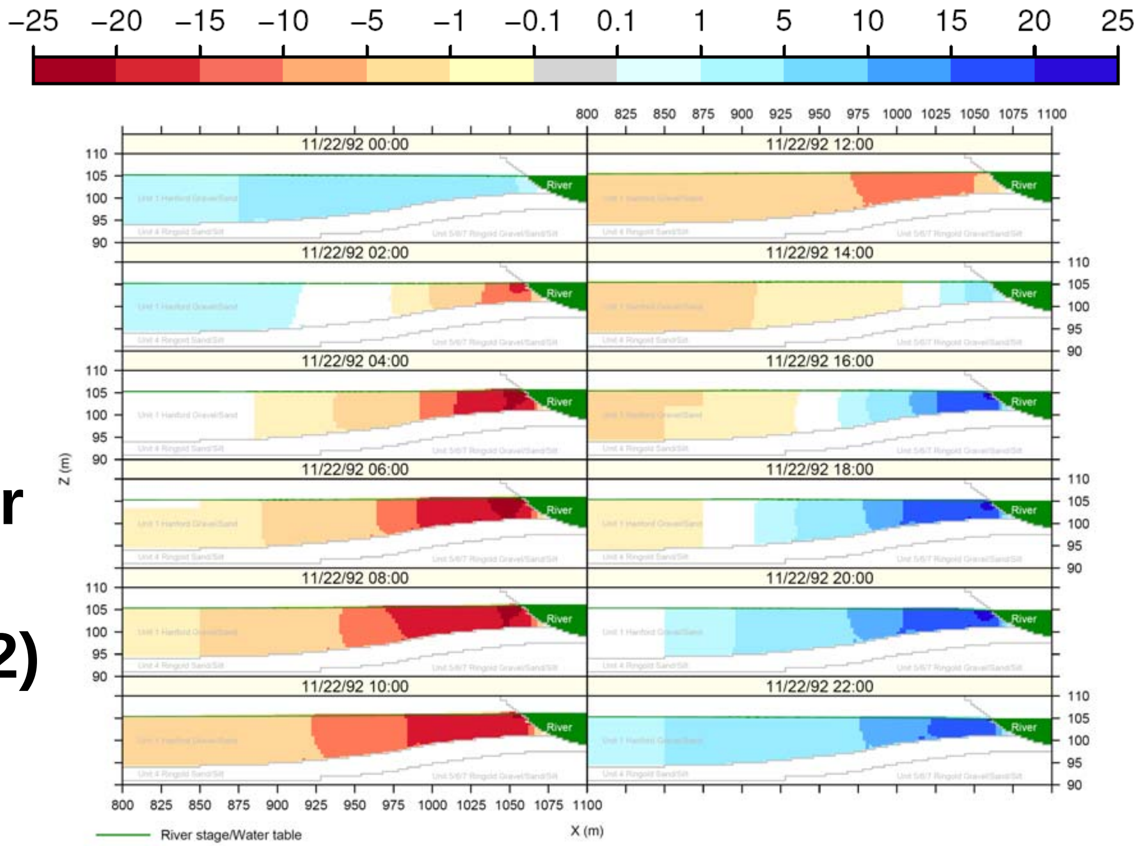
Material	K_l (m/d)	Φ	Ψ (cm)	λ	Θ_r
U1, Hanford gravel/sand	1500	0.25	23.04	0.7465	0.1471
U4, Ringold sand/silt	1.5	0.18			
U5/6/7, Ringold gravel/sand/silt	15	0.18			

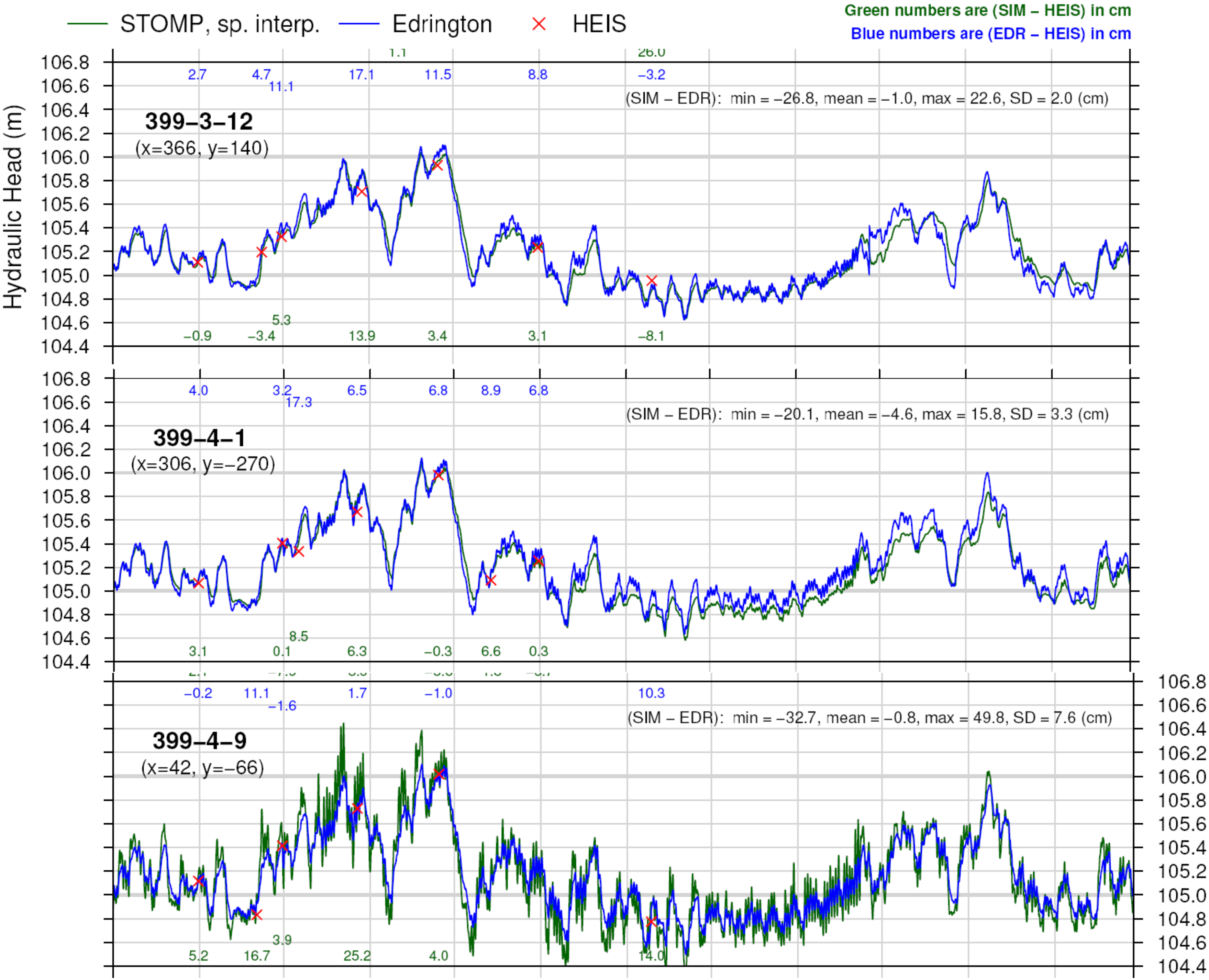
- Highly transmissive Hanford gravel overlying much less permeable Ringold units
- Hourly water levels at 3-6-1 and SWS-1
- Conditional seepage face boundary at river interface
- Recharge
  - 60 mm/yr ground surface
  - 0.9 mm/yr from basalt
- Variable grid spacing (0.5 m – 50 m): 26,268 grid cells



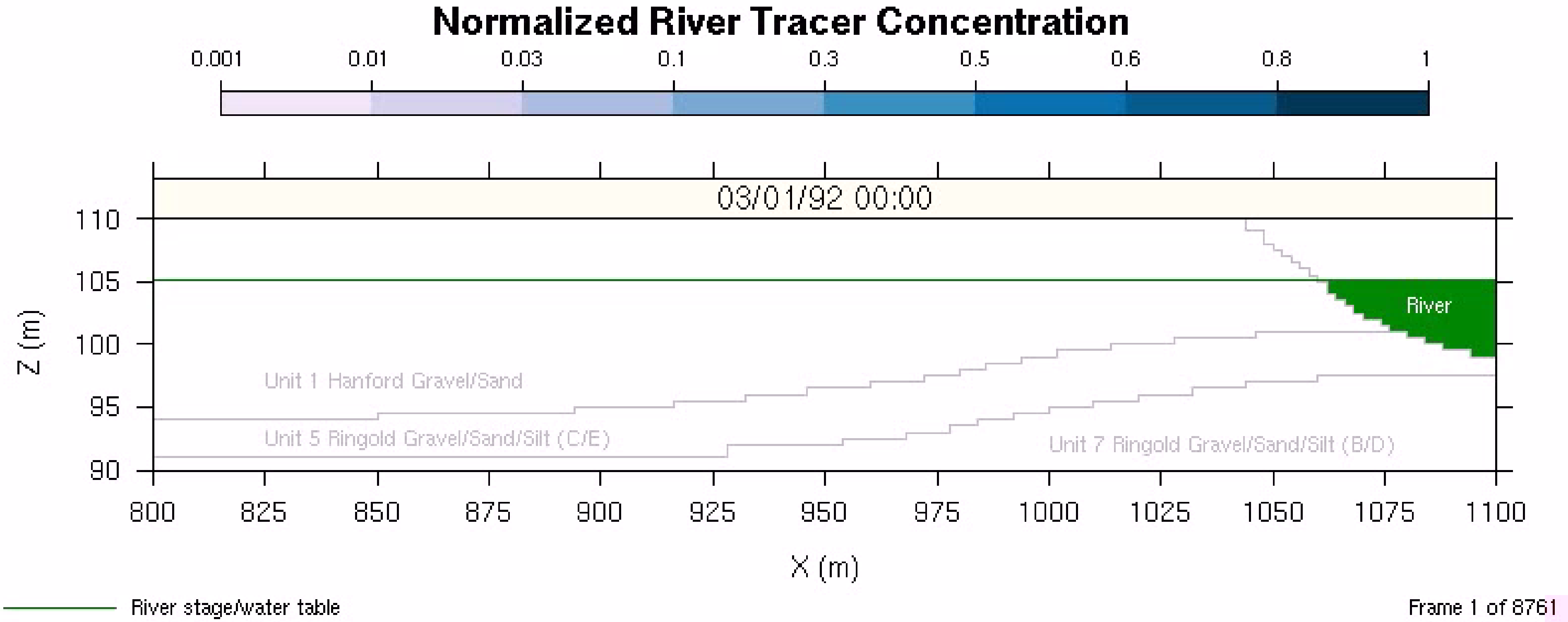
Nov 22

X-Direction Groundwater Flux (m/d) (Nov 22, 1992)

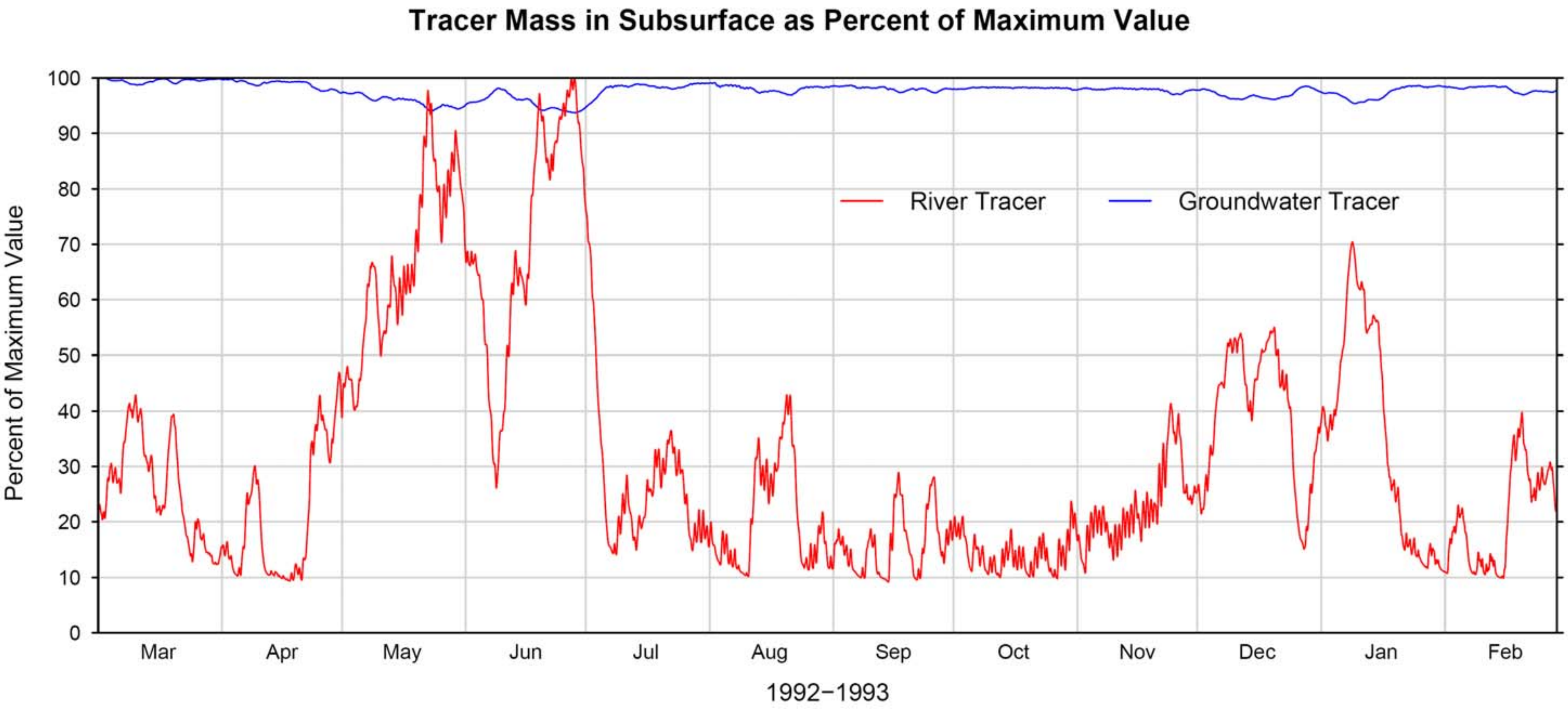



STOMP, sp. interp.
Edrington
HEIS
Green numbers are (SIM – HEIS) in cm
Blue numbers are (EDR – HEIS) in cm
Hydraulic Head (m)
399–3–12
(x=366, y=140)
(SIM – EDR): min = –26.8, mean = –1.0, max = 22.6, SD = 2.0 (cm)
2.7
4.7
11.1
17.1
11.5
8.8
–3.2
1.1
26.0
–0.9
–3.4
5.3
13.9
3.4
3.1
–8.1
399–4–1
(x=306, y=–270)
(SIM – EDR): min = –20.1, mean = –4.6, max = 15.8, SD = 3.3 (cm)
4.0
3.2
17.3
6.5
6.8
8.9
6.8
3.1
0.1
8.5
6.3
–0.3
6.6
0.3
399–4–9
(x=42, y=–66)
(SIM – EDR): min = –32.7, mean = –0.8, max = 49.8, SD = 7.6 (cm)
–0.2
11.1
–1.6
1.7
–1.0
10.3
5.2
16.7
3.9
25.2
4.0
14.0
106.8
106.6
106.4
106.2
106.0
105.8
105.6
105.4
105.2
105.0
104.8
104.6
104.4

Aquifer-River Interaction



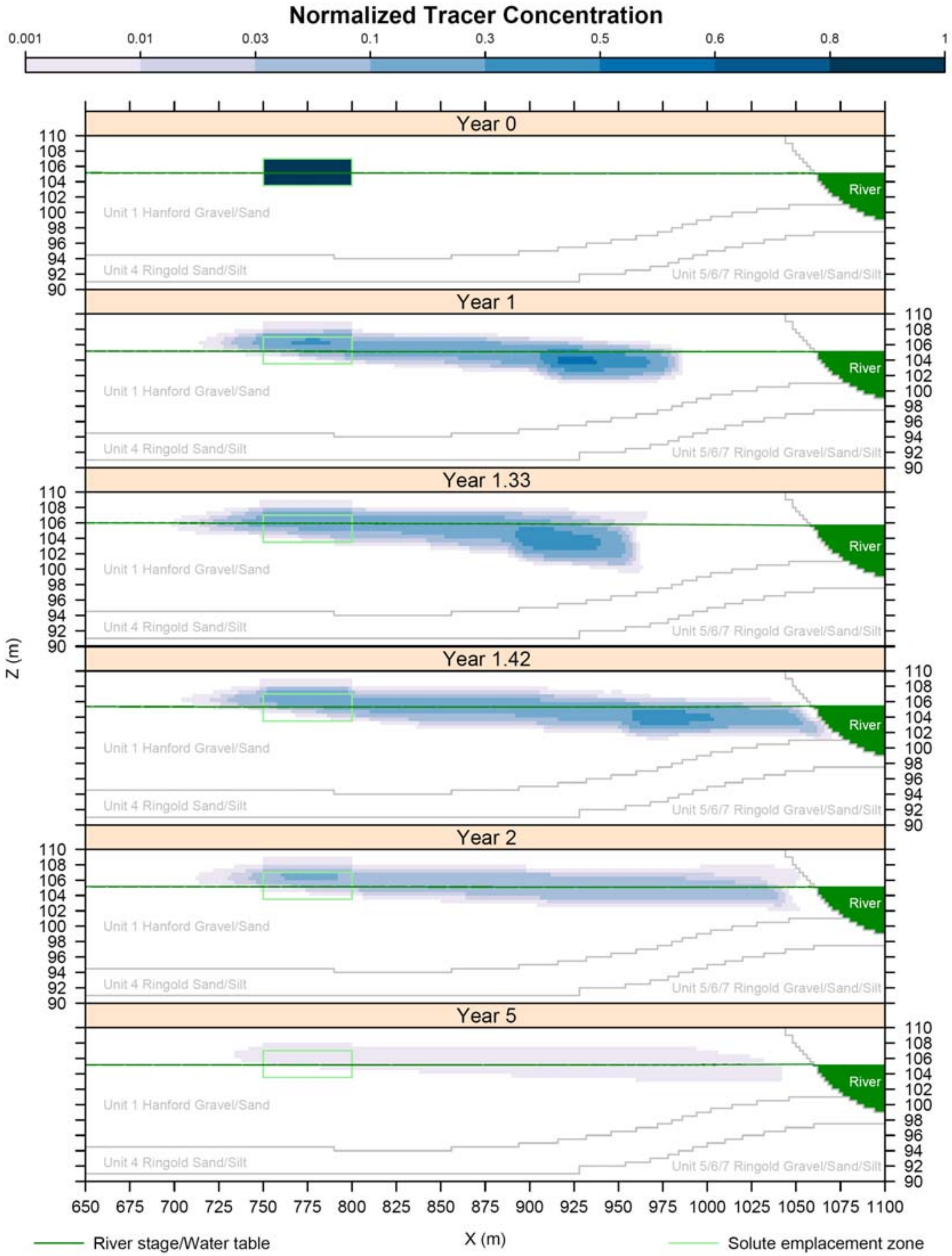
Groundwater – River Water Mixing

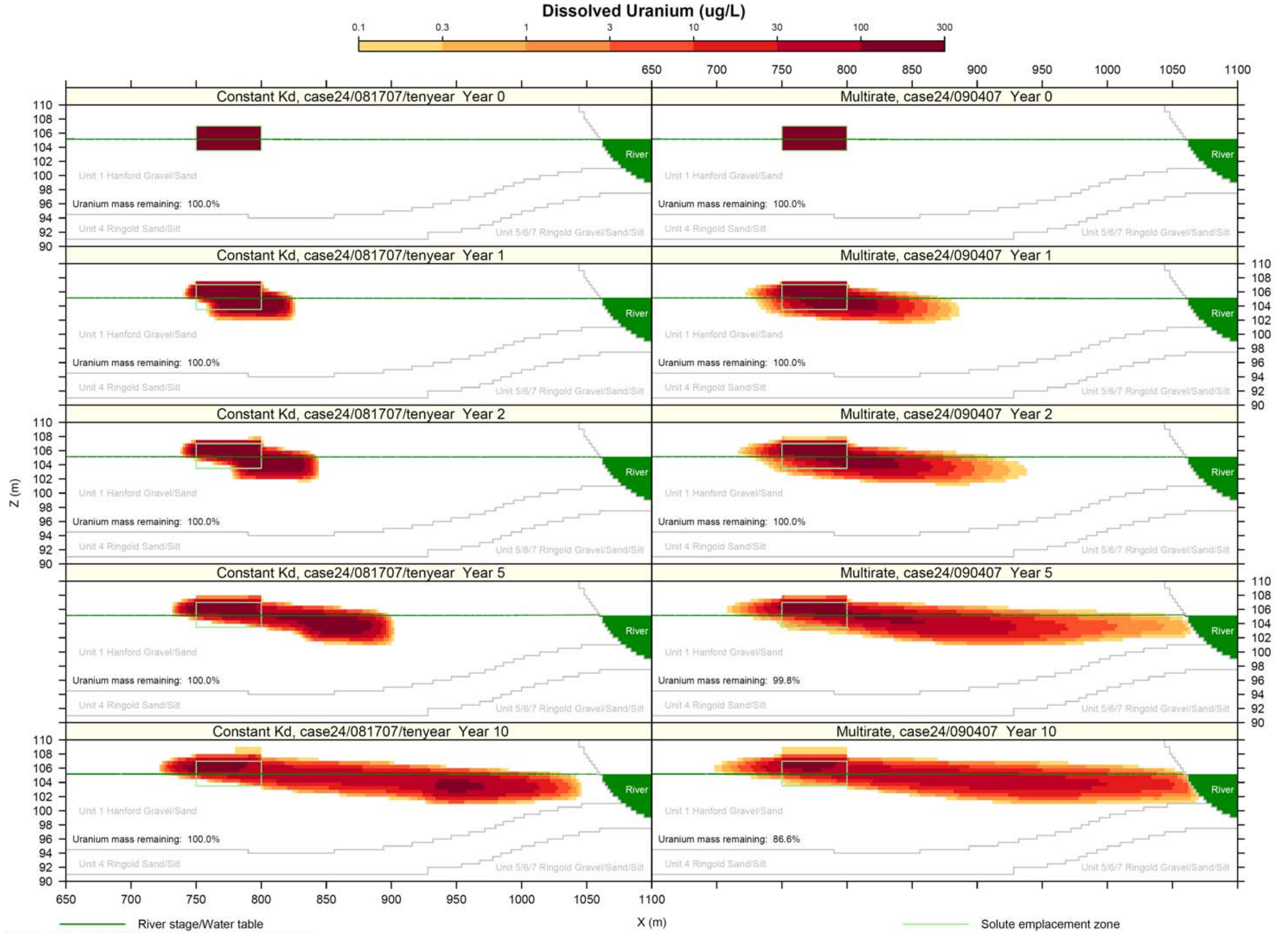


- 4 years to spin-up model for repeatable tracer behavior

Transport Simulations

- Idealized zone of initial U and tracer mass
  - 3.5 m x 50 m
  - Straddles average water table
  - 280 m from river
  - U: 300 ug/L, 0.3 ug/g
- 1st arrival: 1.2 y
- 8 years to lower tracer concentrations 1000X
- Most persistent tracer plume is above average water table





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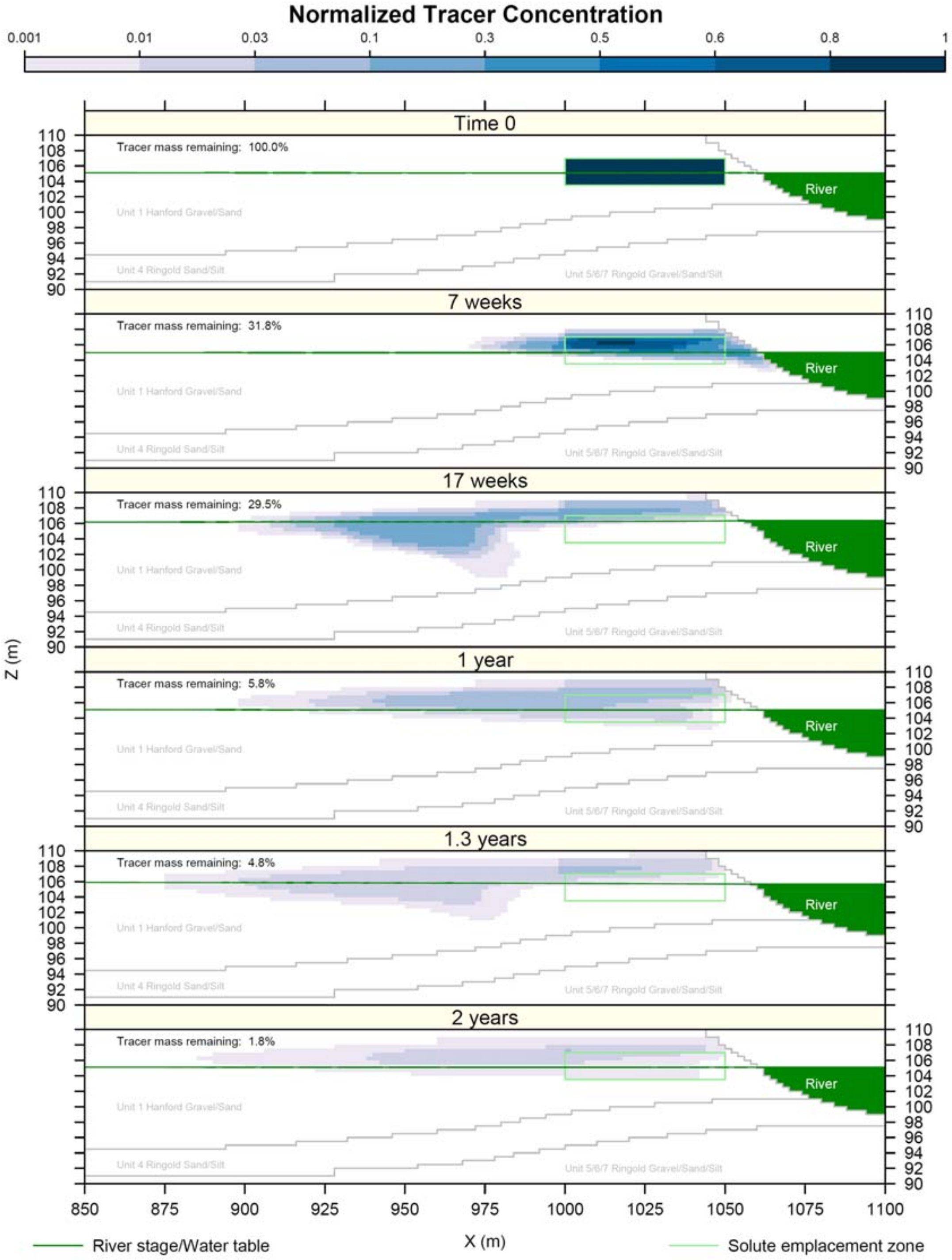
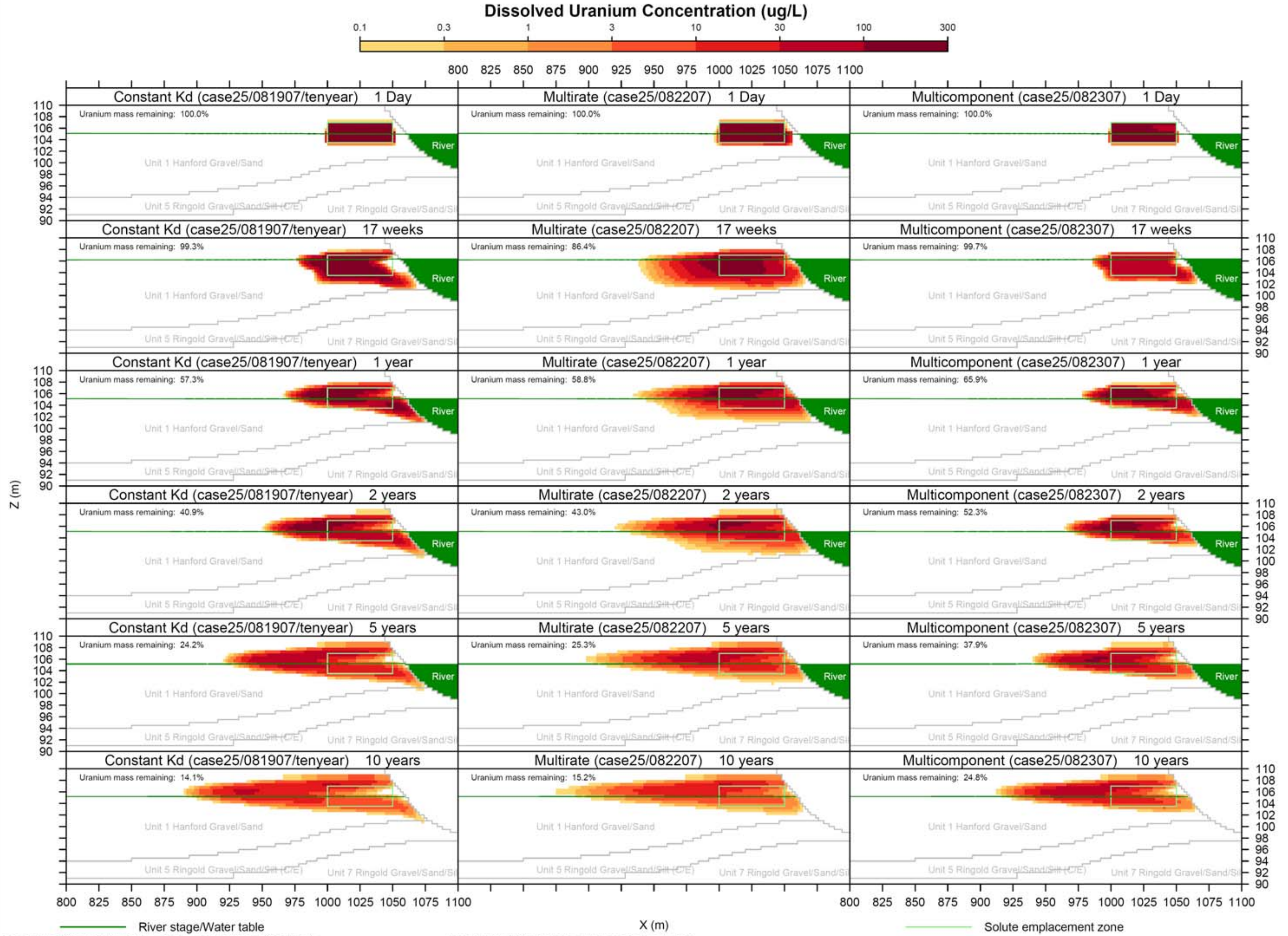
Near-River Transport

- Idealized zone of initial U and tracer mass
  - 3.5 m x 50 m
  - Straddles average water table
  - 30 m from river
  - U: 300 ug/L, 0.3 ug/g
- 90% removal of tracer in 6 months
- 0.001 contour extends 150 m inland in lower vadose zone after 2 years





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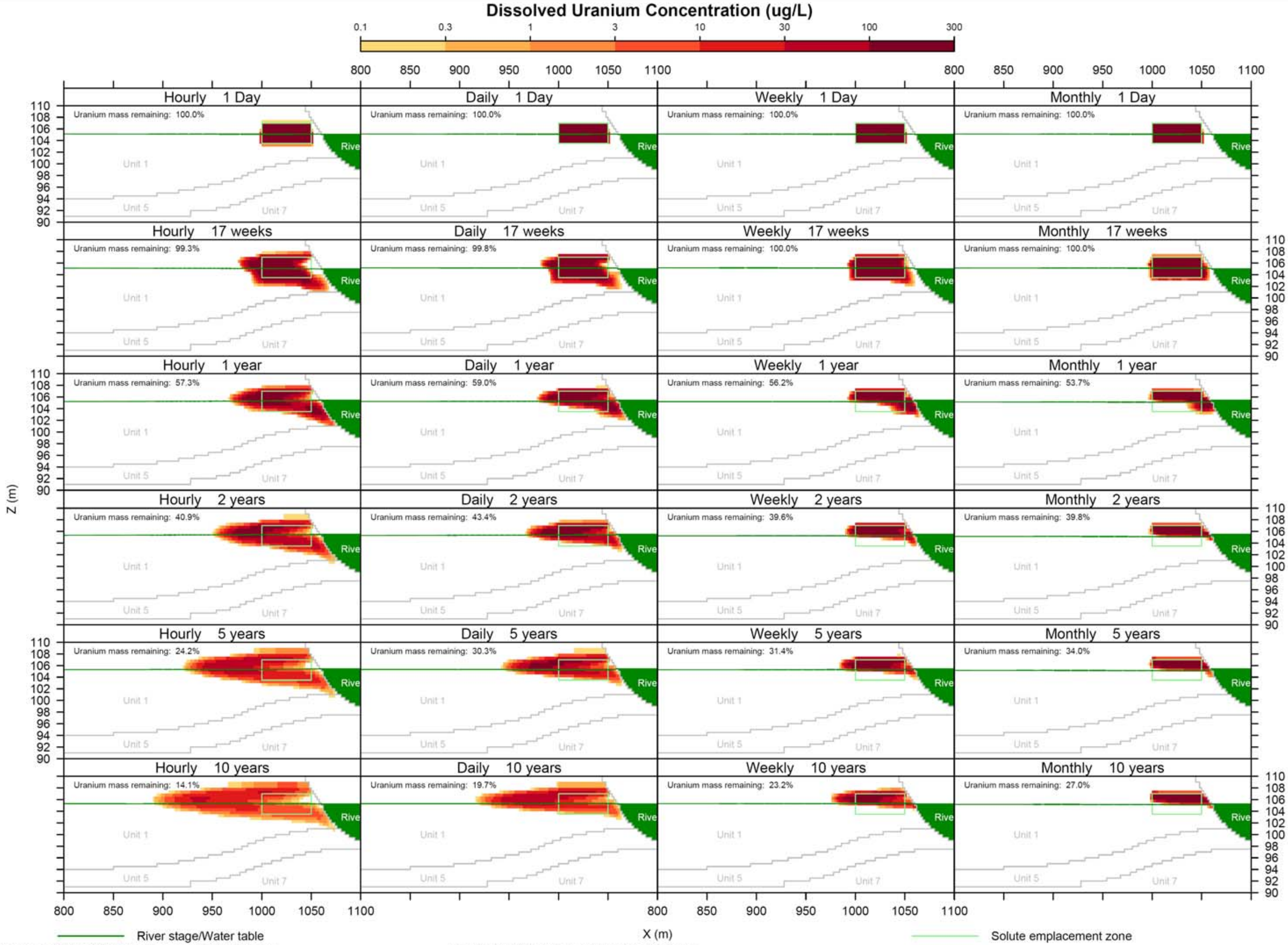
Findings

- Upper vadose zone uranium transport under natural recharge
  - U front moves slowly, once it reaches water table it can move with pore water
  - Contribution to GW depends on concentration and extent of VZ source
  - Longer transport time scales minimize the impact of rate-limited mass transfer
- River stage fluctuation has significant impacts
  - Diurnal cycles of high GW flow with reversals
    - Hourly time-stepping required to account for transport and mixing
  - Groundwater - river water mixing zones have diurnal and seasonal character
  - Diurnal and seasonally high water levels can leach uranium from lower vadose zone into the groundwater
  - Conversely, uranium can persist and be transported inland above the average water table
- Uranium mobility dependent on water chemistry, degree of mixing and time scales of transport
- Rate-limited mass transfer can significantly affect uranium mobility and fate



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