Uranium Reactive Transport in the Hanford 300 Area Vadose Zone-Aquifer-River System

Steve Yabusaki

Yilin Fang
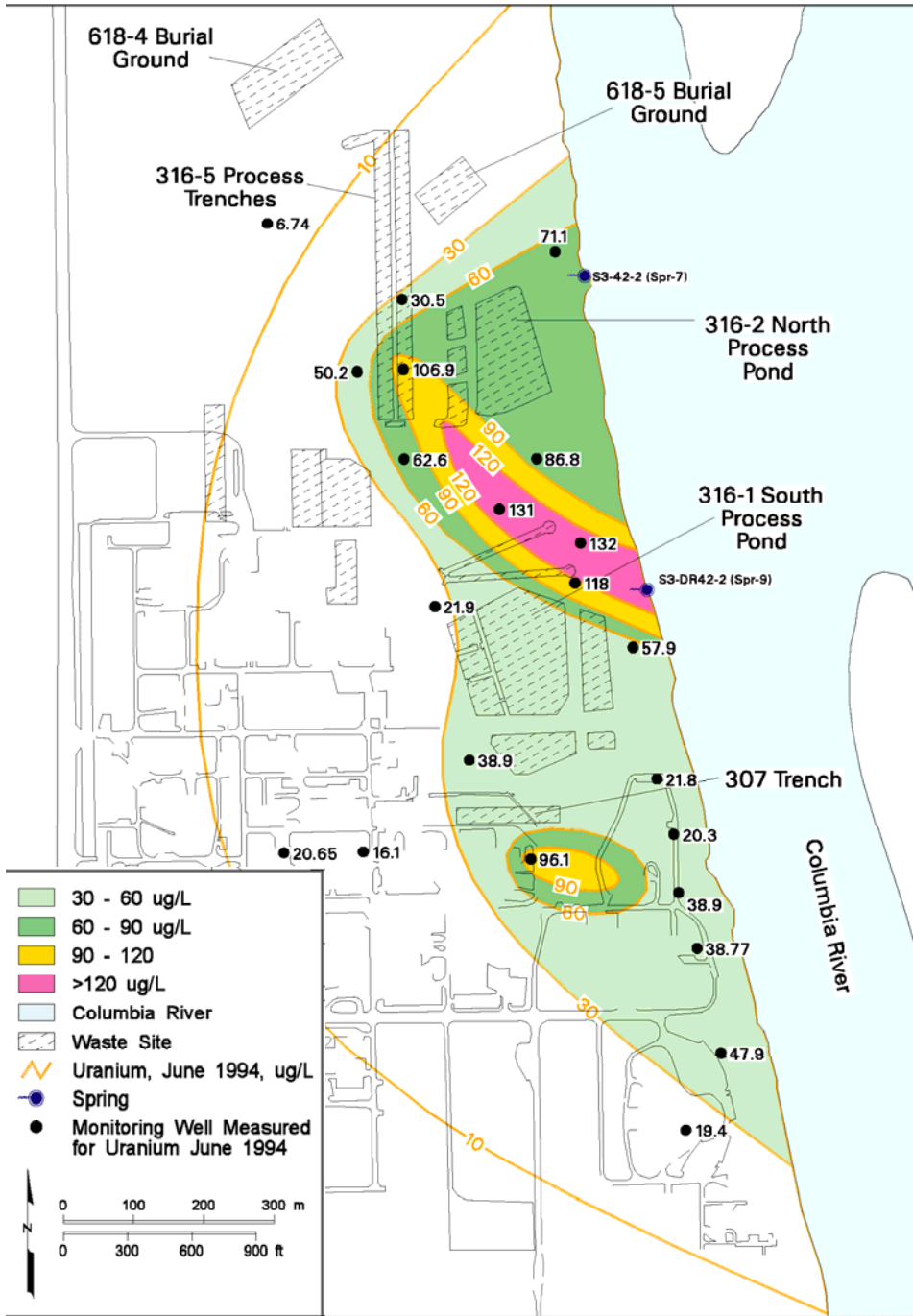
Scott Waichler

Pacific Northwest National Laboratory

1993 Conceptual Model
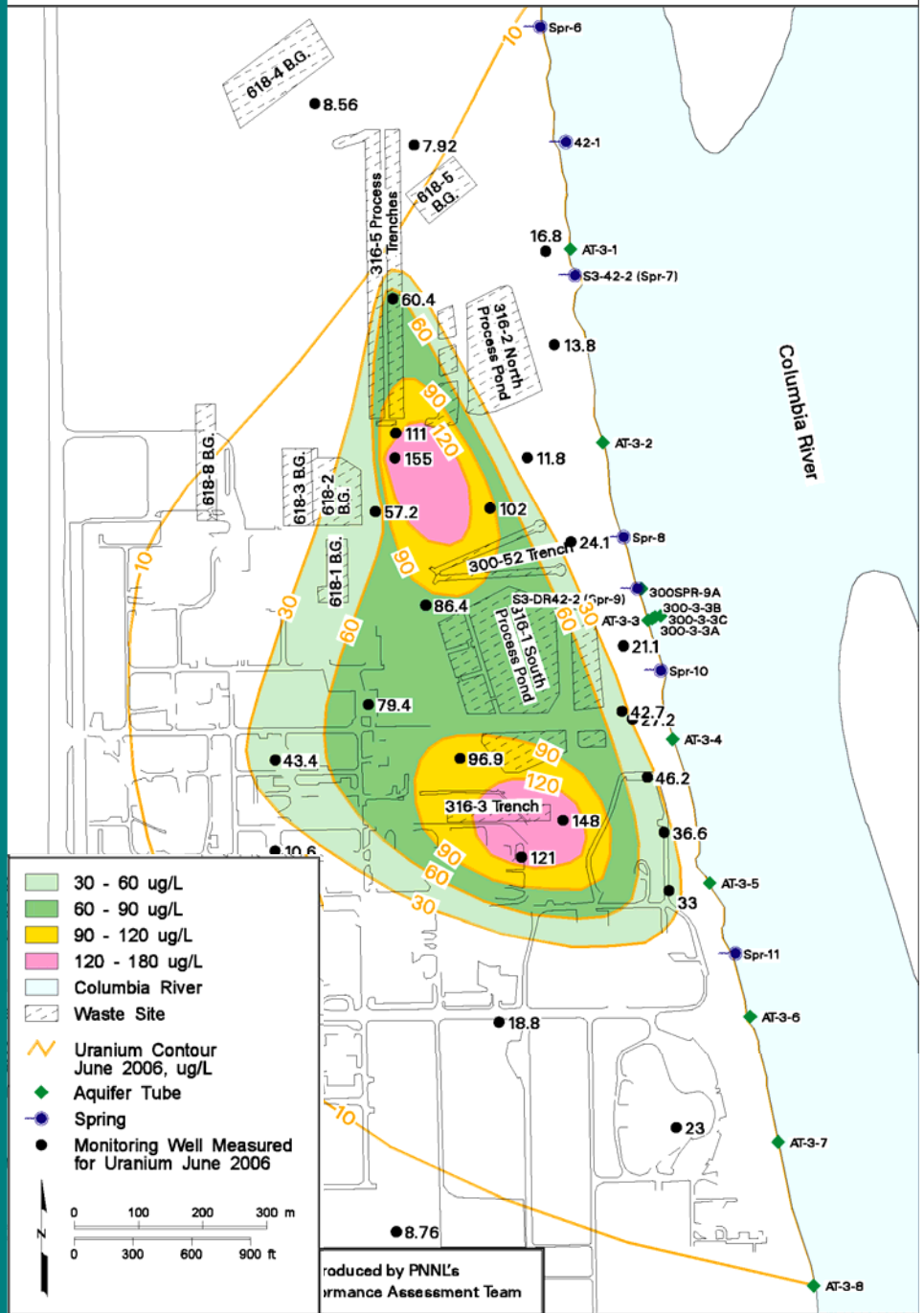
Modeling Assumptions in Phase I Remedial Investigation

▶ 3-D saturated unconfined aquifer; **vadose zone not modeled**

- Flow field driven by **monthly** changes in river stage fluctuations
- Uranium mobility controlled by "best estimate" **constant K_d** ~1-2 ml/g

▶ No interaction between aquifer and river

▶ No interaction between aquifer and vadose zone

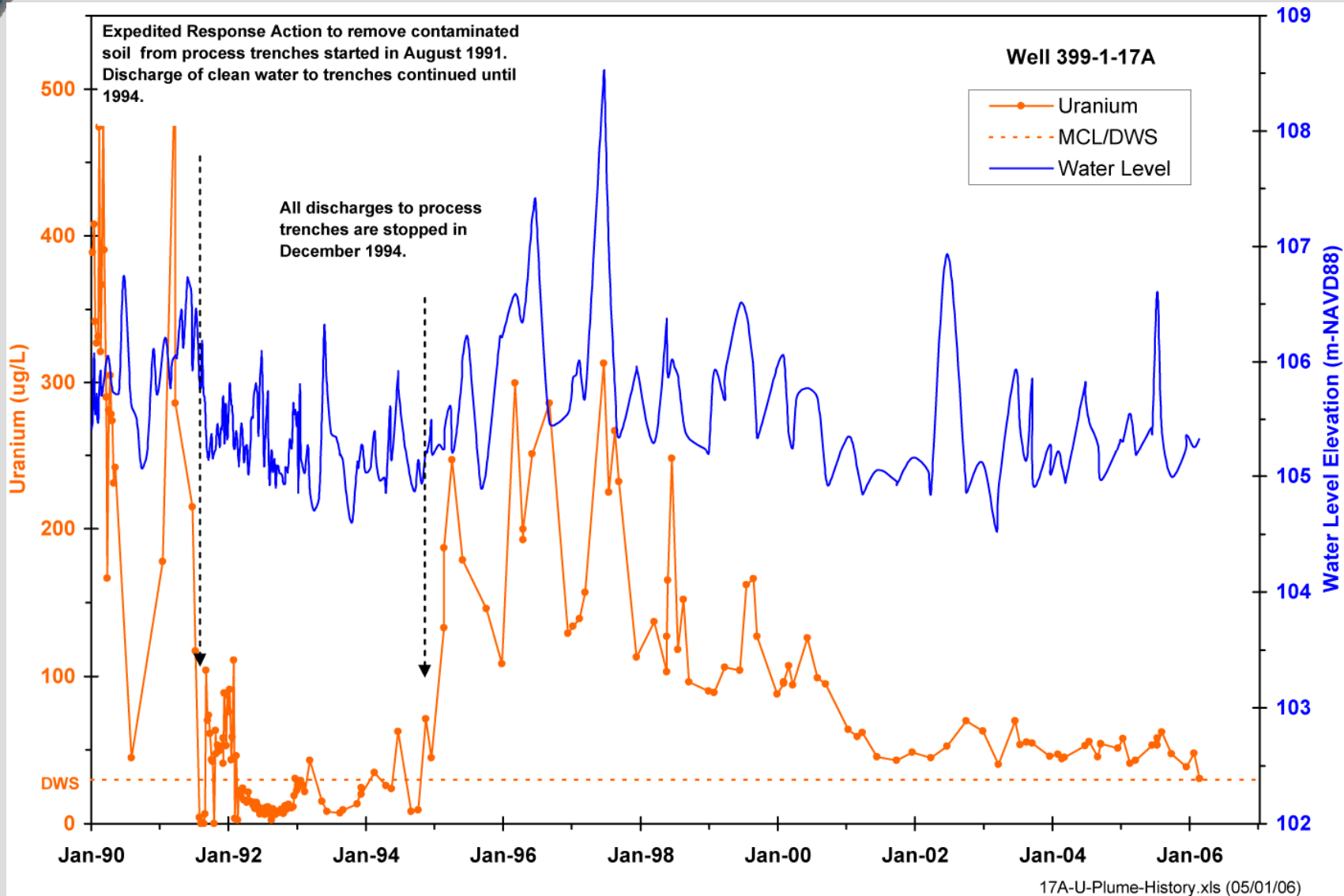Final Prediction: U < 20 ug/L in **3 to 10 years** by natural flushing

Battelle

Shaded 300 Area Uranium, June 1994

618-4 Burial Ground

618-5 Burial Ground

316-5 Process Trenches

● 6.74

71.1
S3-42-2 (Spr-7)

● 30.5

316-2 North Process Pond

● 50.2   ● 106.9

62.6   ● 86.8

● 131

316-1 South Process Pond

● 132

118   S3-DR42-2 (Spr-9)

● 21.9

● 57.9

● 38.9

● 21.8   307 Trench

● 20.3

● 20.65   ● 16.1

96.1

● 38.9

● 38.77

● 47.9

● 19.4

Columbia River

Contour labels: 10, 30, 60, 90, 120, 90, 60

Legend
- 30 - 60 ug/L
- 60 - 90 ug/L
- 90 - 120
- >120 ug/L
- Columbia River
- Waste Site
- Uranium, June 1994, ug/L
- Spring
- Monitoring Well Measured for Uranium June 1994

0   100   200   300 m
0   300   600   900 ft

N

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Shaded 300 Area Uranium, June 2006

● Spr-6

618-4 B.G.

● 8.56

● 7.92   ● 42-1

316-5 Process Trenches

618-5 B.G.

● 16.8   AT-3-1

S3-42-2 (Spr-7)

● 60.4

316-2 North Process Pond

● 13.8

618-8 B.G.   618-3 B.G.

618-2 B.G.

618-1 B.G.

111   ● 11.8   AT-3-2

155

● 57.2   ● 102

24.1   Spr-8

300-52 Trench

300SPR-9A

● 86.4   S3-DR42-2 (Spr-9)   300-3-3B

AT-3-3   300-3-3C

316-1 South Process Pond   300-3-3A

● 21.1

Spr-10

● 79.4   ● 42.7.2

● 27.2   AT-3-4

● 43.4   ● 96.9   ● 46.2

316-3 Trench   ● 36.6

● 148

121

● 10.6   ● 33   AT-3-5

Spr-11

● 18.8

AT-3-6

● 23   AT-3-7

Columbia River

Contour labels: 10, 60, 90, 120, 90, 60, 30, 10

Legend
- 30 - 60 ug/L
- 60 - 90 ug/L
- 90 - 120
- 120 - 180 ug/L
- Columbia River
- Waste Site
- Uranium Contour June 2006, ug/L
- Aquifer Tube
- Spring
- Monitoring Well Measured for Uranium June 2006

0   100   200   300 m
0   300   600   900 ft

N

● 8.76

Produced by PNNL's
Performance Assessment Team

AT-3-8

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Aquifer Water Levels and Uranium Concentrations

Flow and Transport:
Vadose Zone – Aquifer – River System

Zone color key

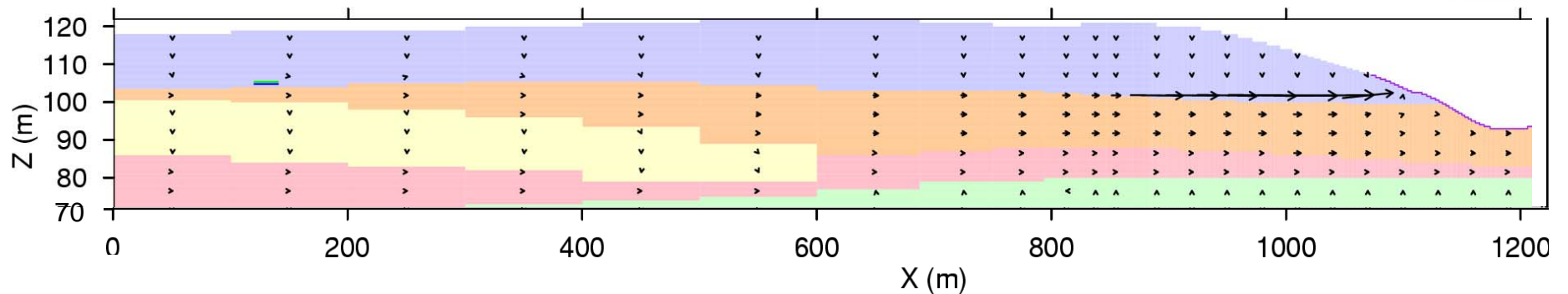| 8 | river |
7	u1
6	u5
5	u6
4	u7
3	u8
2	u9
1	basalt
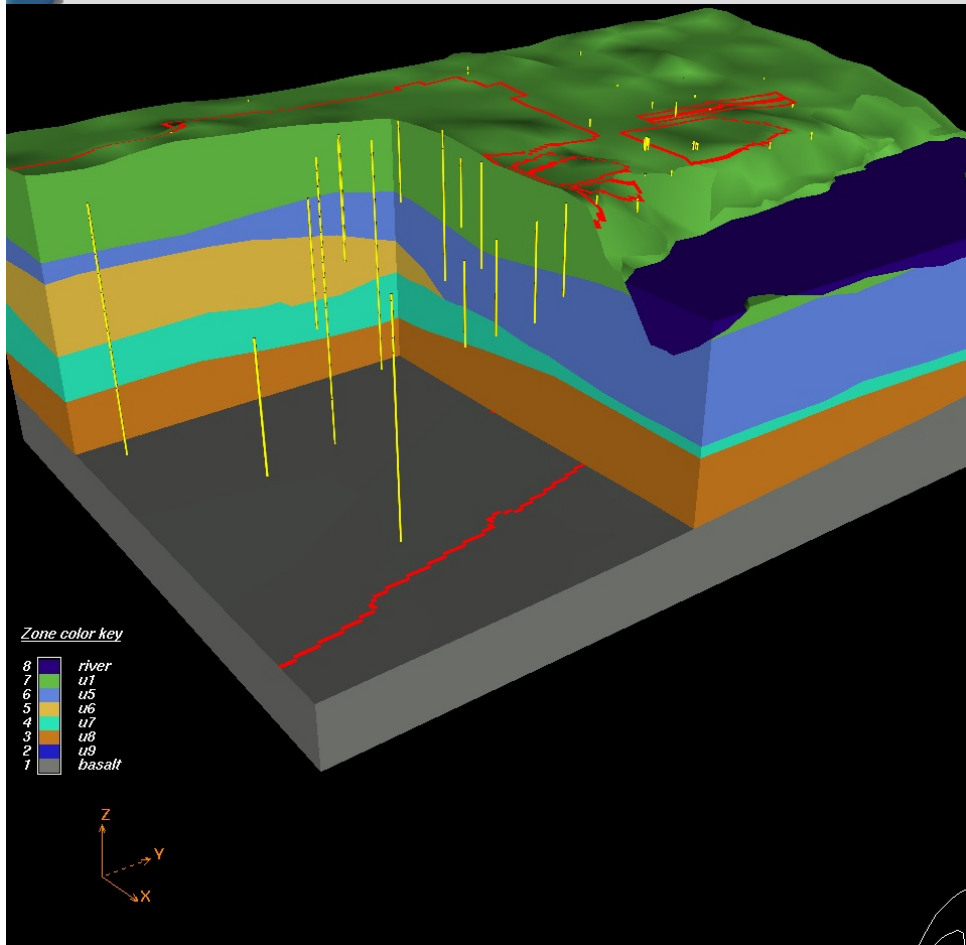
- ► 2-D and 3-D modeling with STOMP simulator

- ► Most current hydrogeology

- ► Flow and transport driven by hourly river stage fluctuations

- ► Investigate dynamics of riverbank storage and fluxes across aquifer - river interface

- ► Investigate release of uranium from contaminated vadose zone sediments due to water table fluctuations

Flow and Transport: Vadose Zone – Aquifer – River System

Case 9 STOMP Model Domain

Legend:
- Recharge boundary (green)
- Seepage face (blue)
- Defined head boundary (magenta)
- No-flux boundary (black)

Unit 1 Hanford Gravel/Sand
Unit 5 Ringold Gravel/Sand/Silt (C/E)
Unit 6 Ringold Overbank Mud
Unit 7 Ringold Gravel/Sand/Silt (B/D)
River
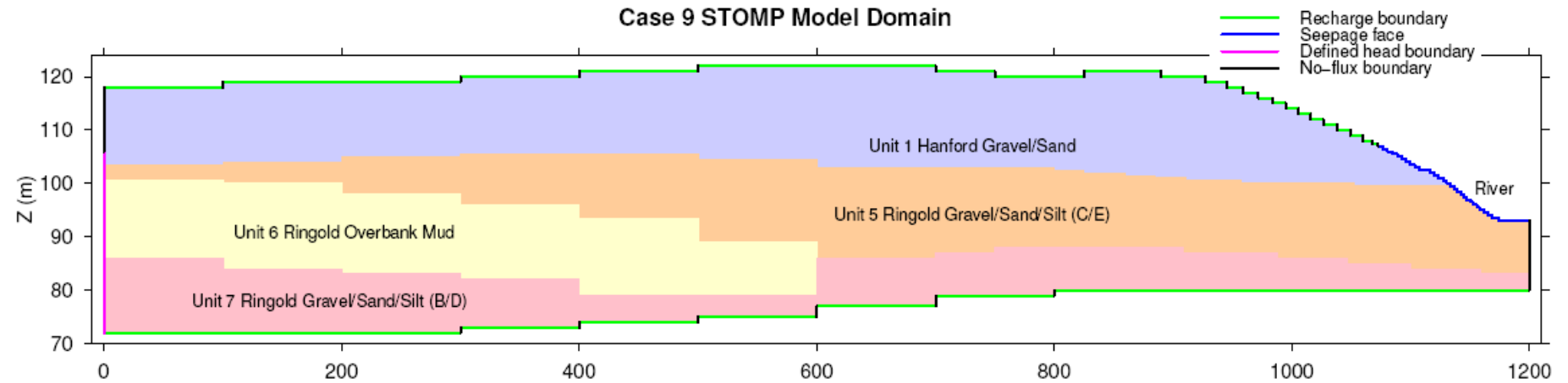
Material	$K_l^{(a)}$ (m d^{-1})	$\phi^{(b)}$	$\psi^{(c)}$ (cm)	$\lambda^{(d)}$	$\theta_r^{(e)}$
U1, Hanford Gravel/Sand	1500	0.25	23.04	0.7465	0.1471
U5, Ringold Gravel/Sand/Silt (C/E)	150	0.18	71.31	0.5193	0.1299
U6, Ringold Overbank Mud	0.01	0.18	71.31	0.5193	0.1299
U7, Ringold Gravel/Sand/Silt (B/D)	43	0.18	71.31	0.5193	0.1299
U8, Lower Ringold Mud	5e-5	0.18	71.31	0.5193	0.1299
Basalt	5e-5	0.18	71.31	0.5193	0.1299

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1992 River Stage

Legend:
- River
- River from WL_Data.xls
- Hourly 399-6-1
- Monthly 399-6-1
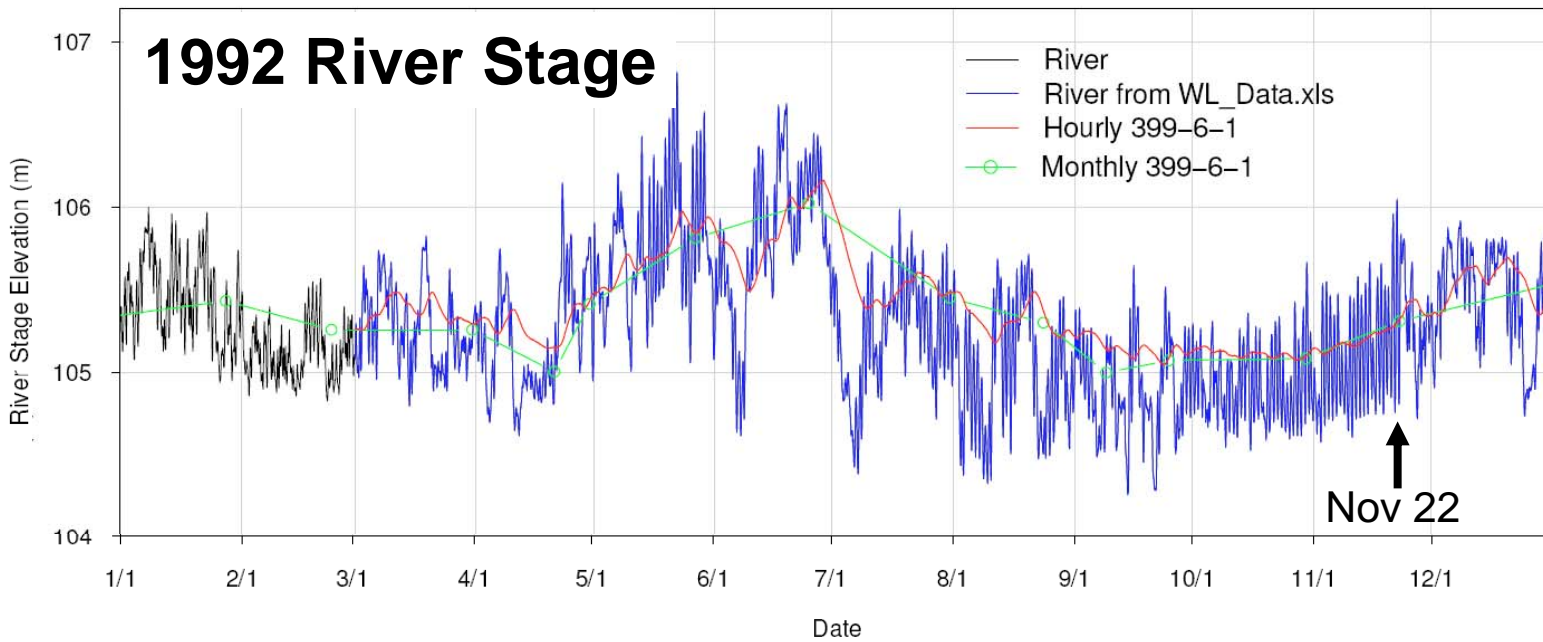
Nov 22

X-Direction Groundwater Flux (m/d) (Nov 22, 1992)
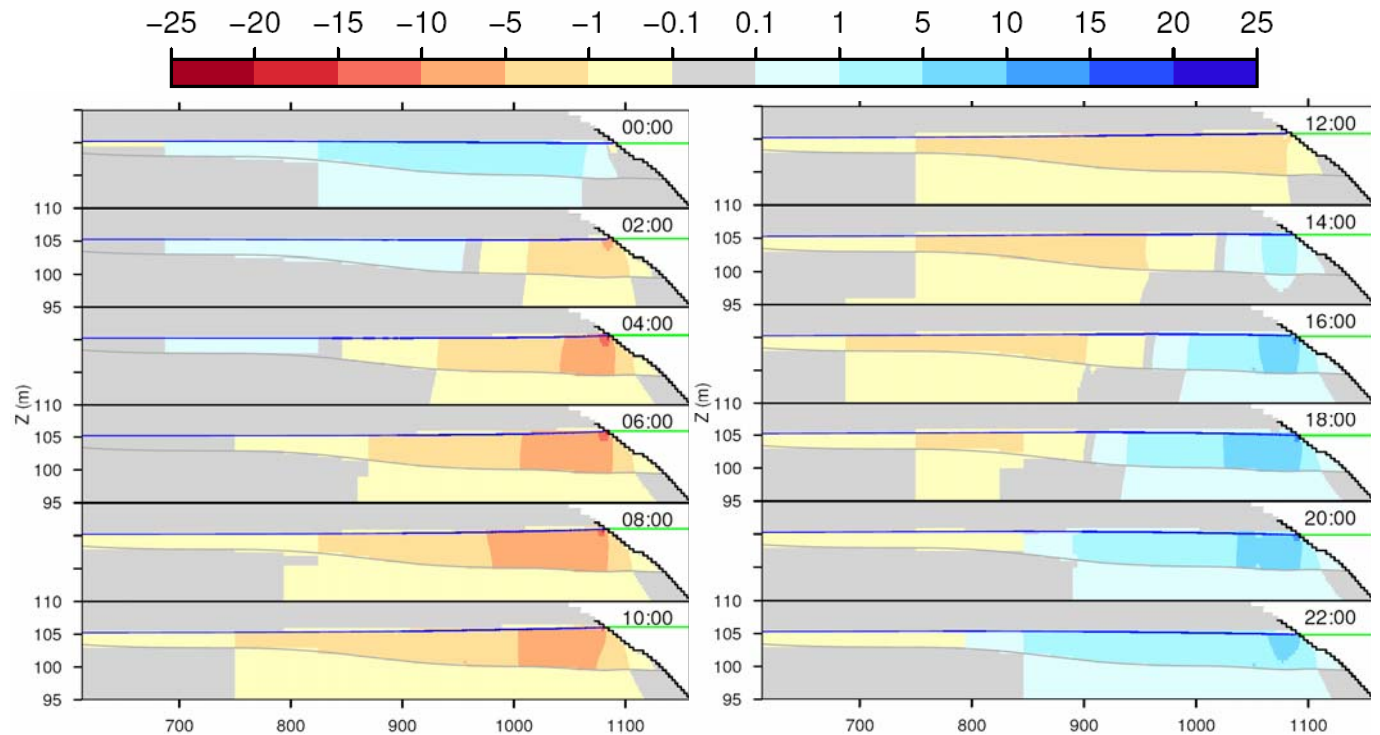
Tracer Transport
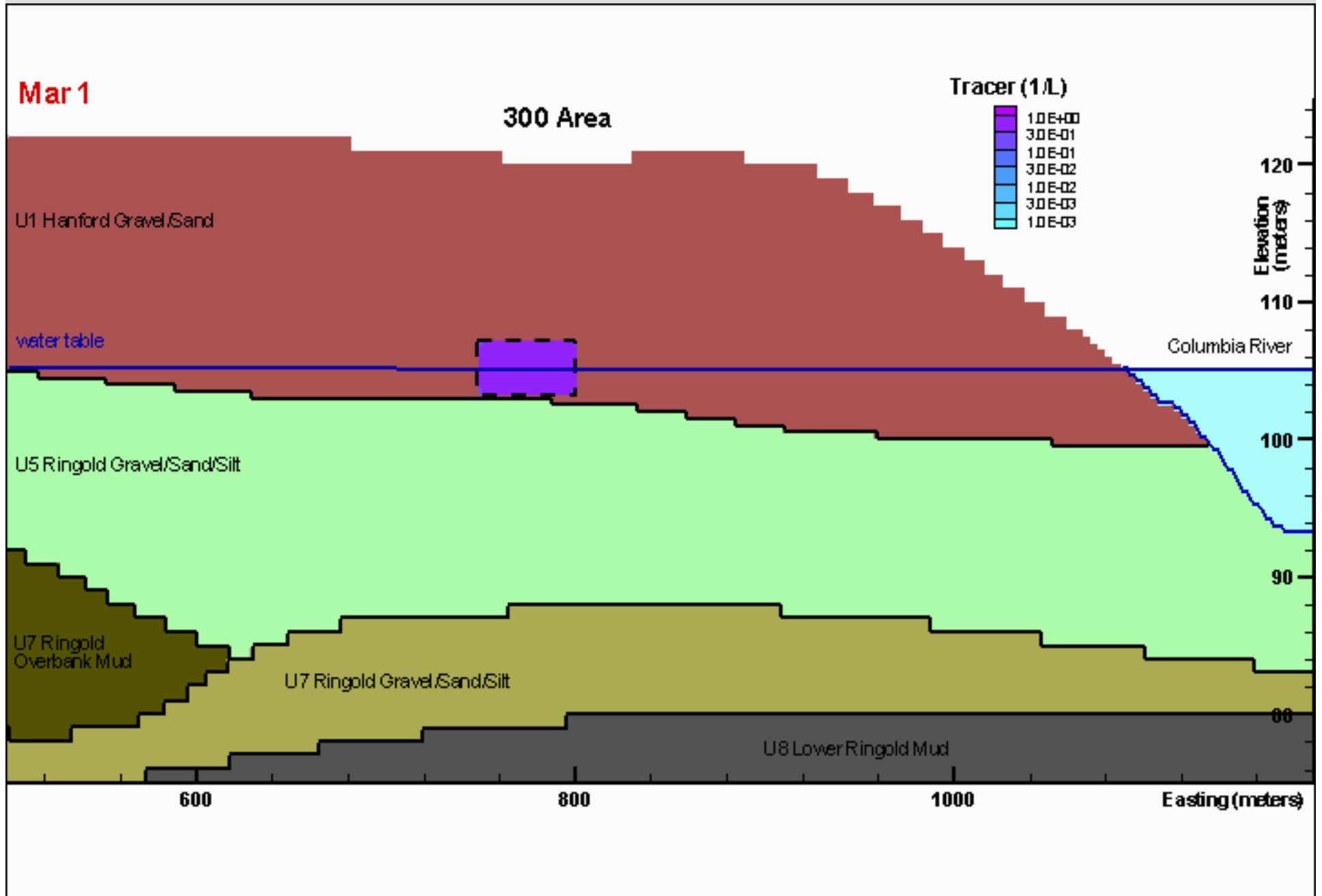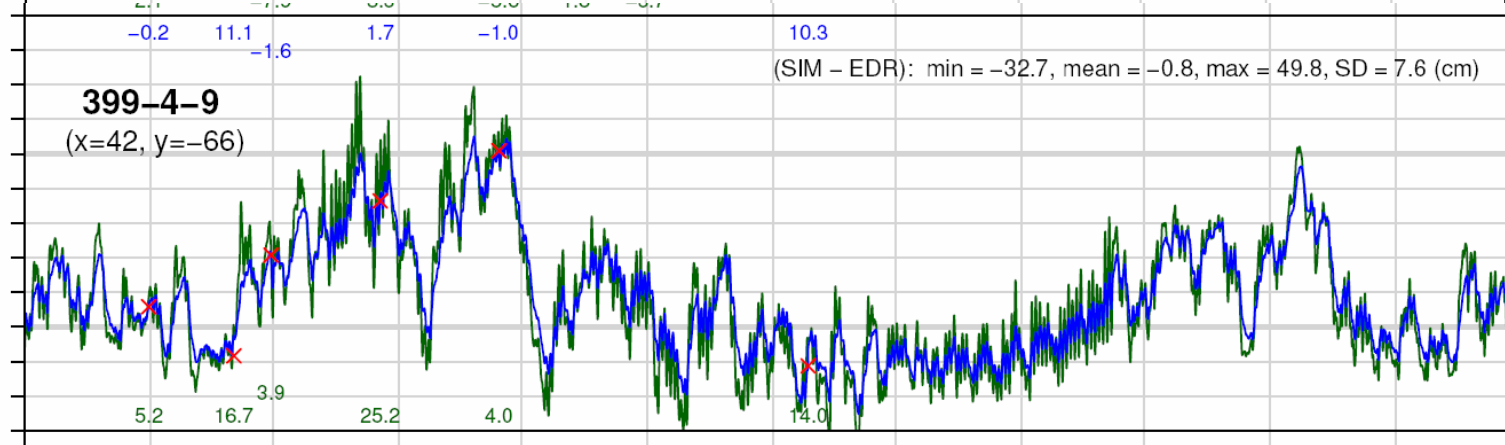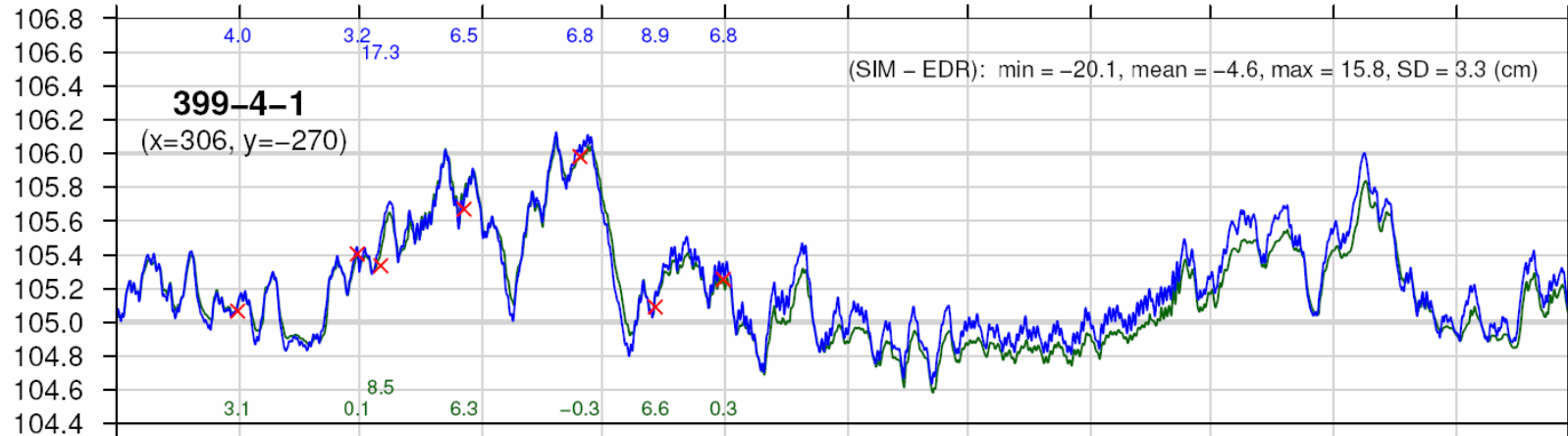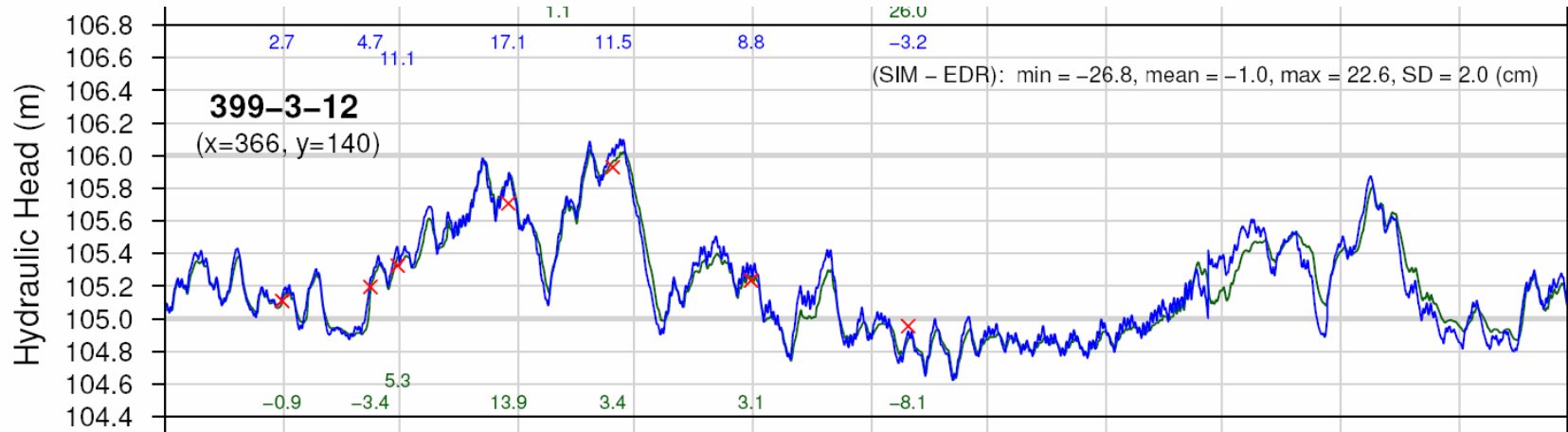
Aquifer-River Mixing Simulations

- ► 4-year spinup period
- ► River tracer mixing zone extends ~150 m inland
- ► Averaging river stage fluctuations over daily period reduces size of mixing zone
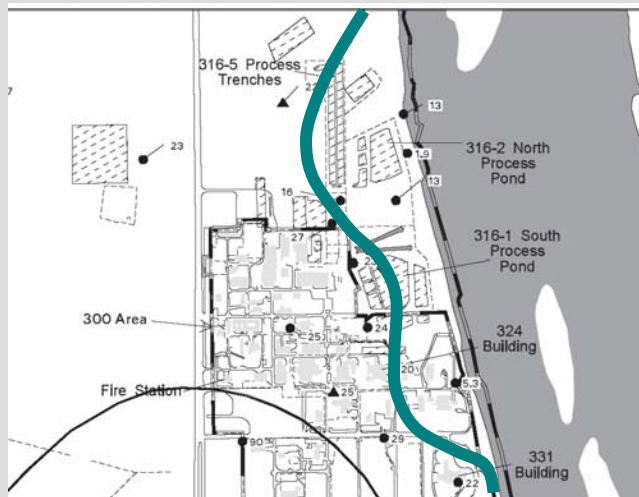- ► Monthly average essentially eliminates mixing with river water
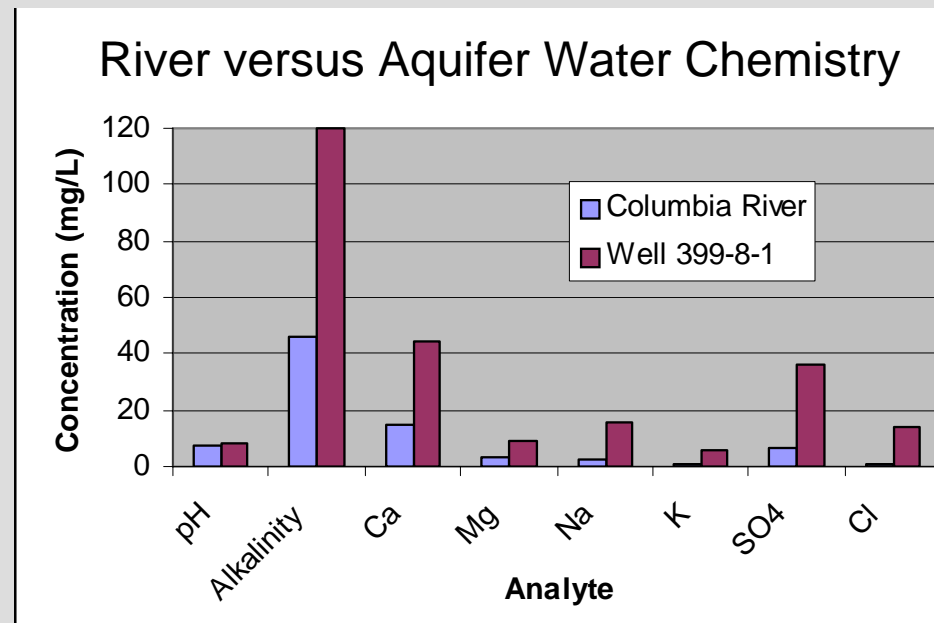

Hourly BC

Daily BC

Monthly BC

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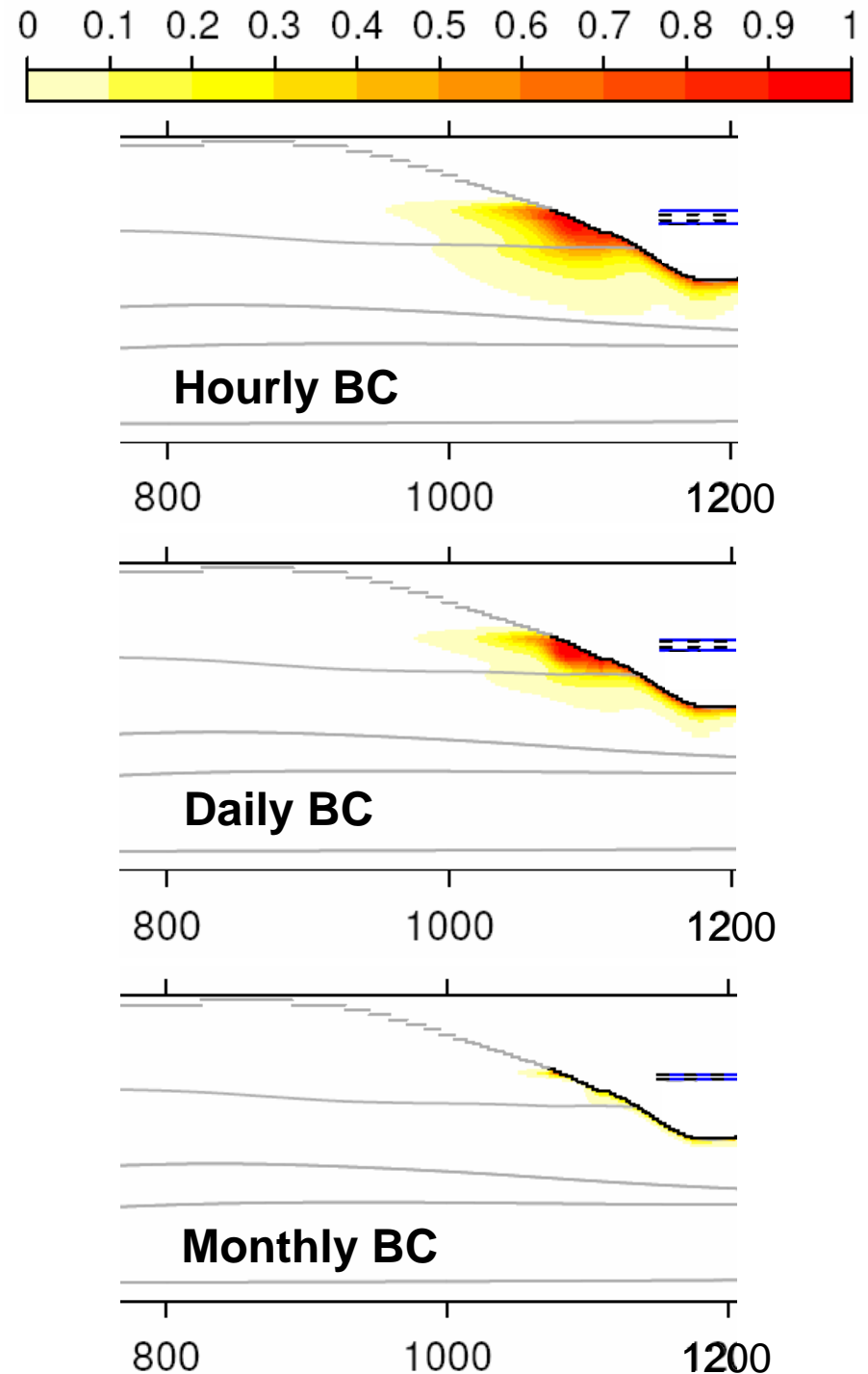
Seasonal Variation in Mixing Zone
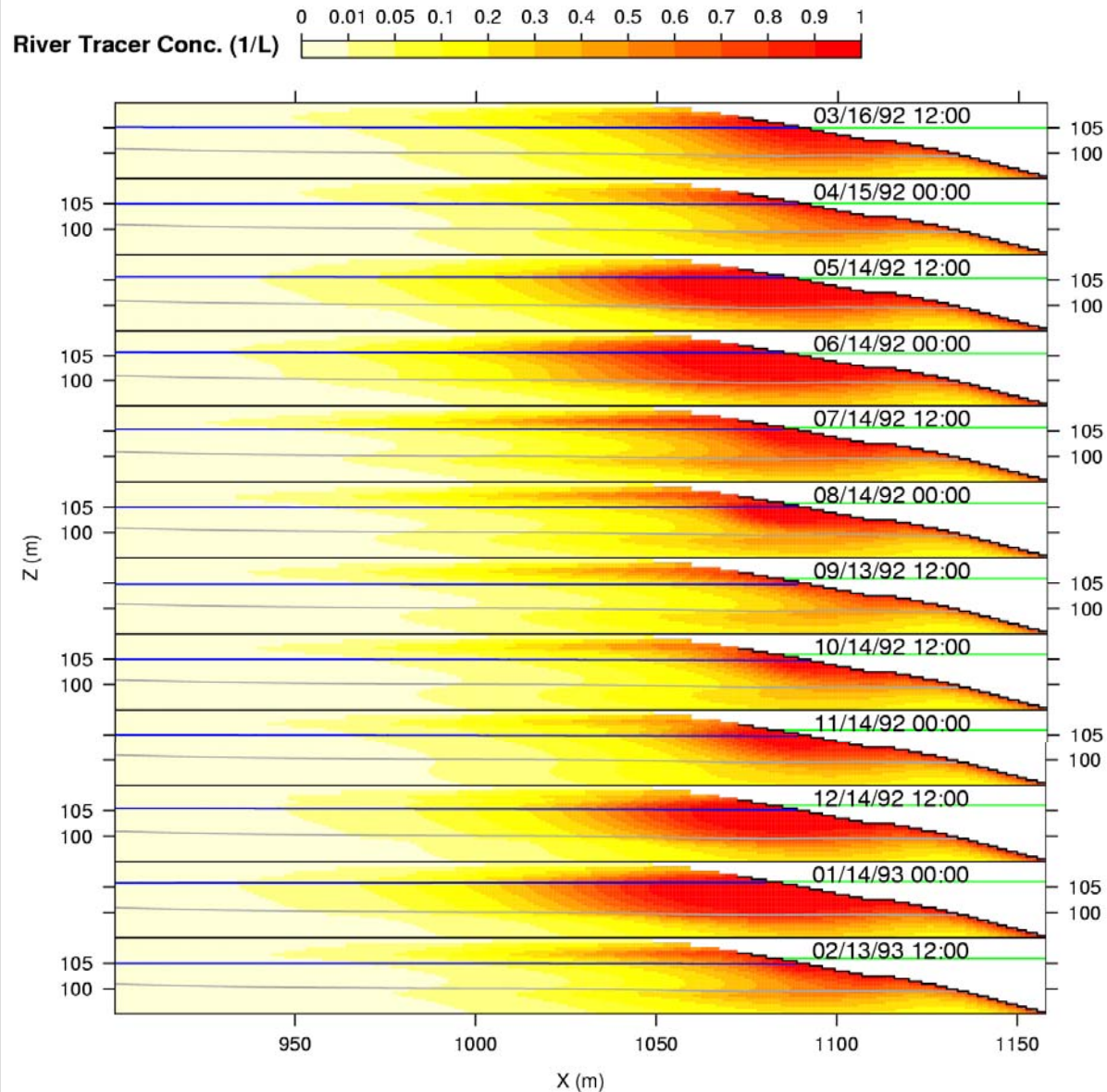
Aquifer-River Solution Chemistry

▶ River water influx occurs during high stage

▶ Prolonged seasonal high stage period allows mixing in aquifer with river water

▶ Significant differences in solution chemistry

2002 Nitrate Concentration

River versus Aquifer Water Chemistry

Uranium Geochemistry

▶ Constant K_d not consistent with experimental observations

- Uranium sorption varies strongly with transition between aquifer and river water chemistries (e.g., U, Ca, pH, alkalinity concentrations)

- Rate-limited uranium mass transfer identified in column experiments with flow rates consistent with field observations
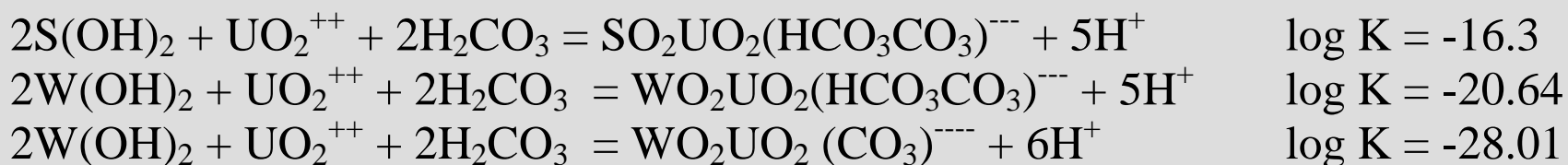
▶ Key Issues

- Uranium leaching from contaminated vadose zone sediments by water table fluctuations

- Changing uranium geochemistry during mixing and exchange of river and groundwater

Uranium Sorption

Alkalinity (mg/L as CaCO3)

Kd (L/kg)

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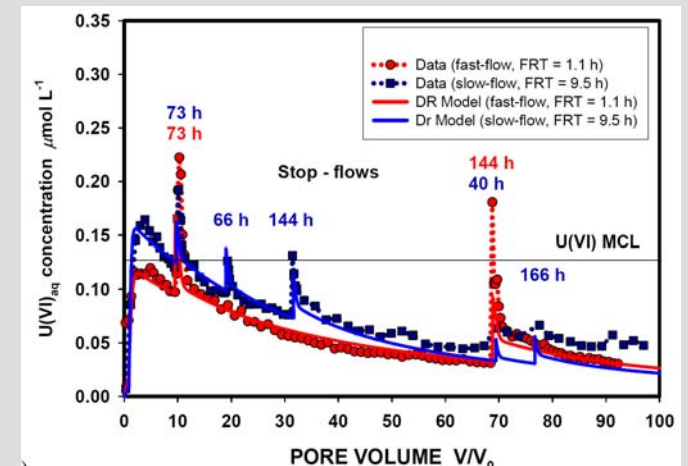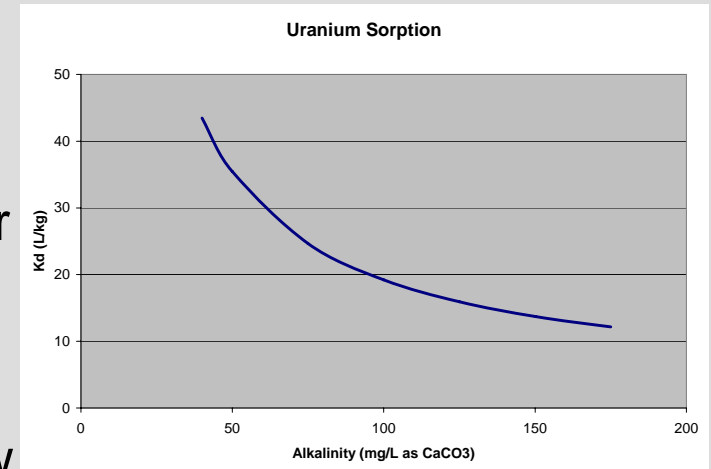
Uranium Geochemical Process Models

▶ Preliminary three-reaction generalized composite surface complexation model (Jim Davis, USGS)

- accounts for bicarbonate concentration, sediment surface area, and aqueous U(VI) complexation (21 reactions)

- 1 strong site and 2 weak site reactions:

$$2S(OH)_2 + UO_2^{++} + 2H_2CO_3 = SO_2UO_2(HCO_3CO_3)^{---} + 5H^+ \qquad \log K = -16.3$$
$$2W(OH)_2 + UO_2^{++} + 2H_2CO_3 = WO_2UO_2(HCO_3CO_3)^{---} + 5H^+ \qquad \log K = -20.64$$
$$2W(OH)_2 + UO_2^{++} + 2H_2CO_3 = WO_2UO_2(CO_3)^{----} + 6H^+ \qquad \log K = -28.01$$
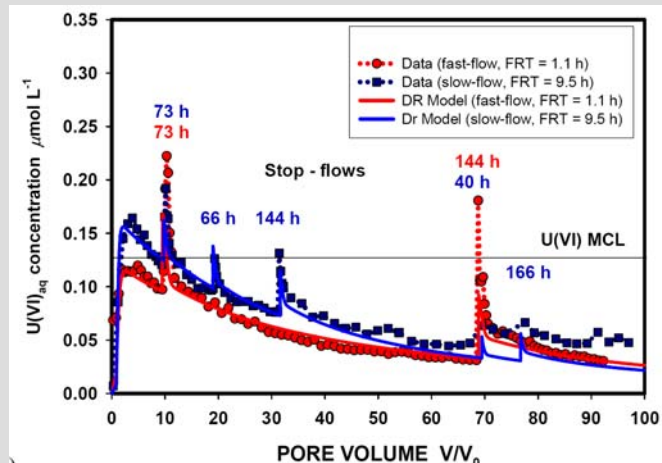
▶ Multisite model with variable uranium mass transfer kinetics (Chongxuan Liu, PNNL):

- Accounts for reaction rates and rate-limited diffusion processes

- Distributed rate parameters were assumed to follow the Gamma statistical distribution (two parameters):

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

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

Field-Based Reactive Transport Modeling

## Account for full sediment size distribution

- < 2 mm size fraction in the lab studies
  - Specific surface area: 27.2 m^2/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

Unsaturated Flow Model Parameters	Value	Units
Horizontal Hydraulic Conductivity	1500	m/d
Vertical Hydraulic Conductivity	150	m/d
Air entry pressure	23.04	cm
Brooks-Corey λ	0.7465	
Residual Saturation	0.1471	
Relative Permeability Method	Burdine	
Porosity	0.25	
Bulk Density	2.06	Kg/L
Recharge Rate	60	mm/yr
Calculated Water Content	0.08	

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
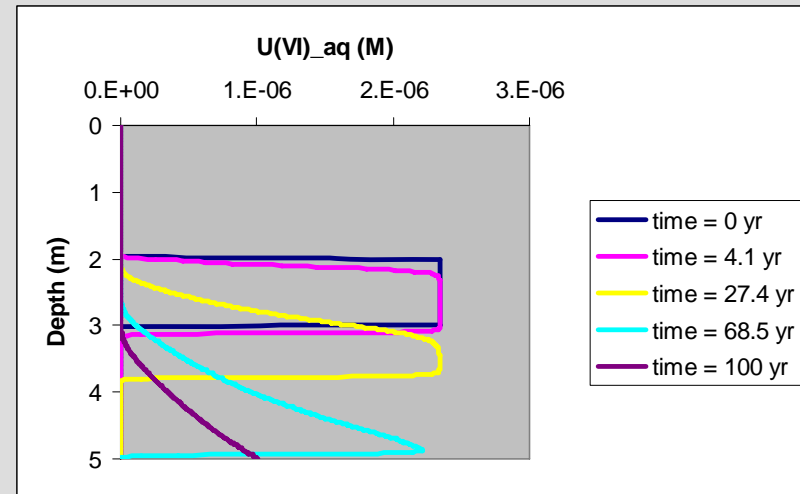
Generalized Composite SCM

Multisite Kinetic Model

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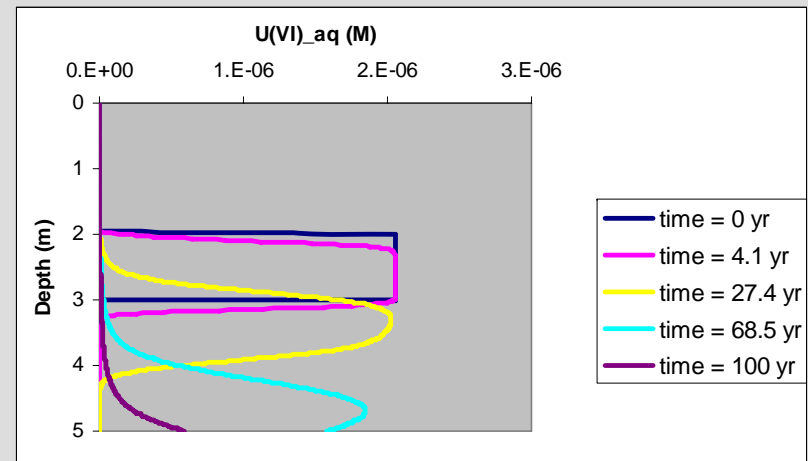
Aquifer-River Interactions

Adapt GC-SCM for the situation where the solution chemistry changes from river water to groundwater

- 1.4 m/d groundwater
- 30 nM/g U-contaminated sediments
- Initial equilibrium with river water
  - 5.76E-8 M aqueous U
  - Intrinsic Kd > 500 L/kg
- After influx of groundwater
  - Aqueous U is 2.50E-6 M
  - Intrinsic Kd = 13.5 L/kg

Solution Chemistry

Components	River water (USGS 6/1/2000)	1988 Well 399-8-3
pH	7.1	7.7
HCO3-	9.18e-4 M	2.66e-3 M
K+	1.75e-5	1.50e-4
NO3-	8.55e-6	1.73e-4
Sr++	1.23e-6	0
Na+	1.00e-4	9.87e-4
Ca++	3.74e-4	1.10e-3
Mg++	1.48e-4	4.10e-4
Cl-	3.10e-5	2.75e-3
SO4--	7.08e-5	3.25e-4

2-D Uranium Reactive Transport

► 5-year model spinup period for multicomponent reactive transport water chemistry with 0.5 h time steps

► Hypothetical source zone of U-contaminated sediments
- 50 m long by 3 m high rectangular zone centered on mean water table elevation (105 m)
- 700 ug U / L bulk volume

► Large Grid
- 26,268 (20,997 active) grid cells
- source zone 325 m from river
- model testing: multirate kinetics, equilibrium Kd

► Small Grid
- 8,512 (6,112 active) grid cells
- source zone 75 m from river
- model testing: multirate kinetics, equilibrium Kd and multicomponent

► Updated multicomponent model (Bond and Davis)
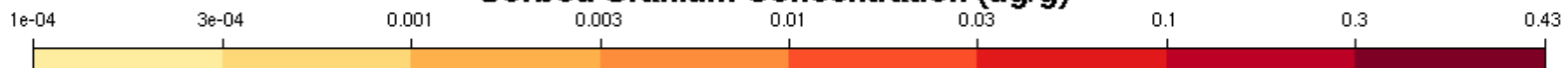- Model based on both North and South Process Pond sediments
- Single site, 2 reactions

$SOH + UO_2^{2+} + H_2O = SOUO_2OH + 2H^+$	-4.548
$SOH + UO_2^{2+} + 2H_2CO_3 = SOUO_2(HCO_3)_2^- + 3H^+$	-4.047

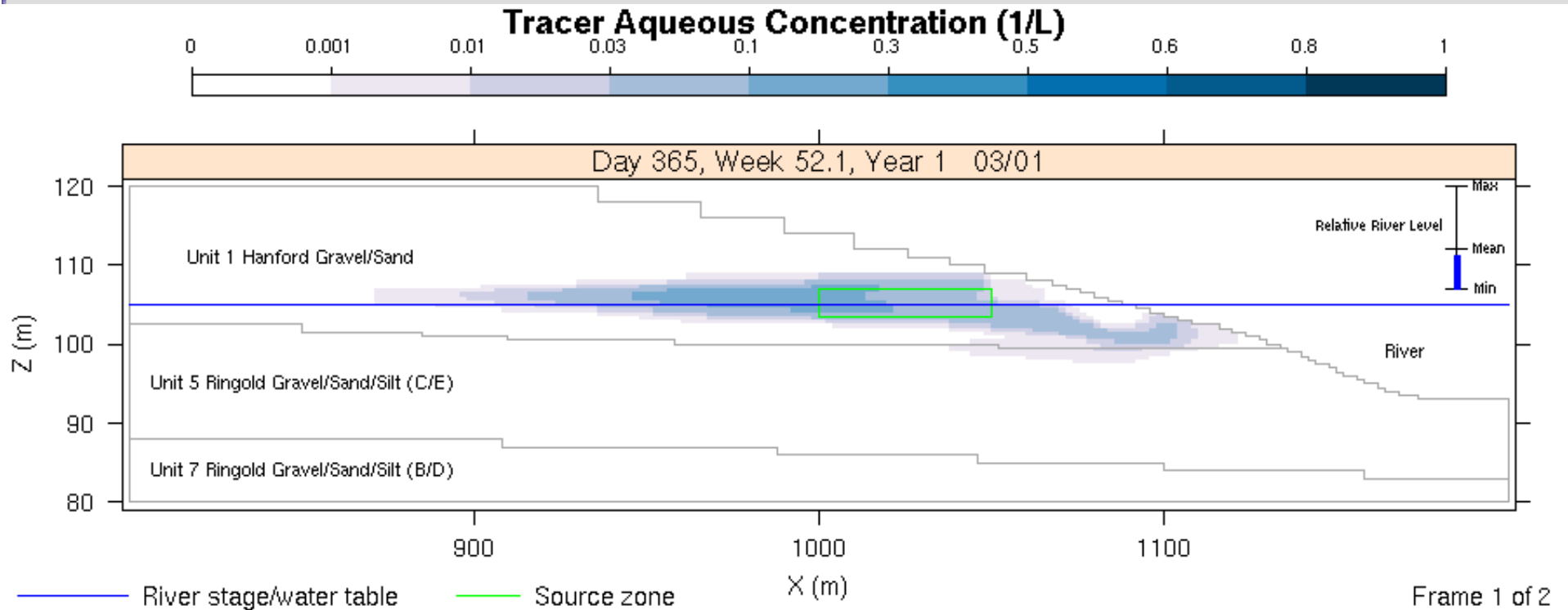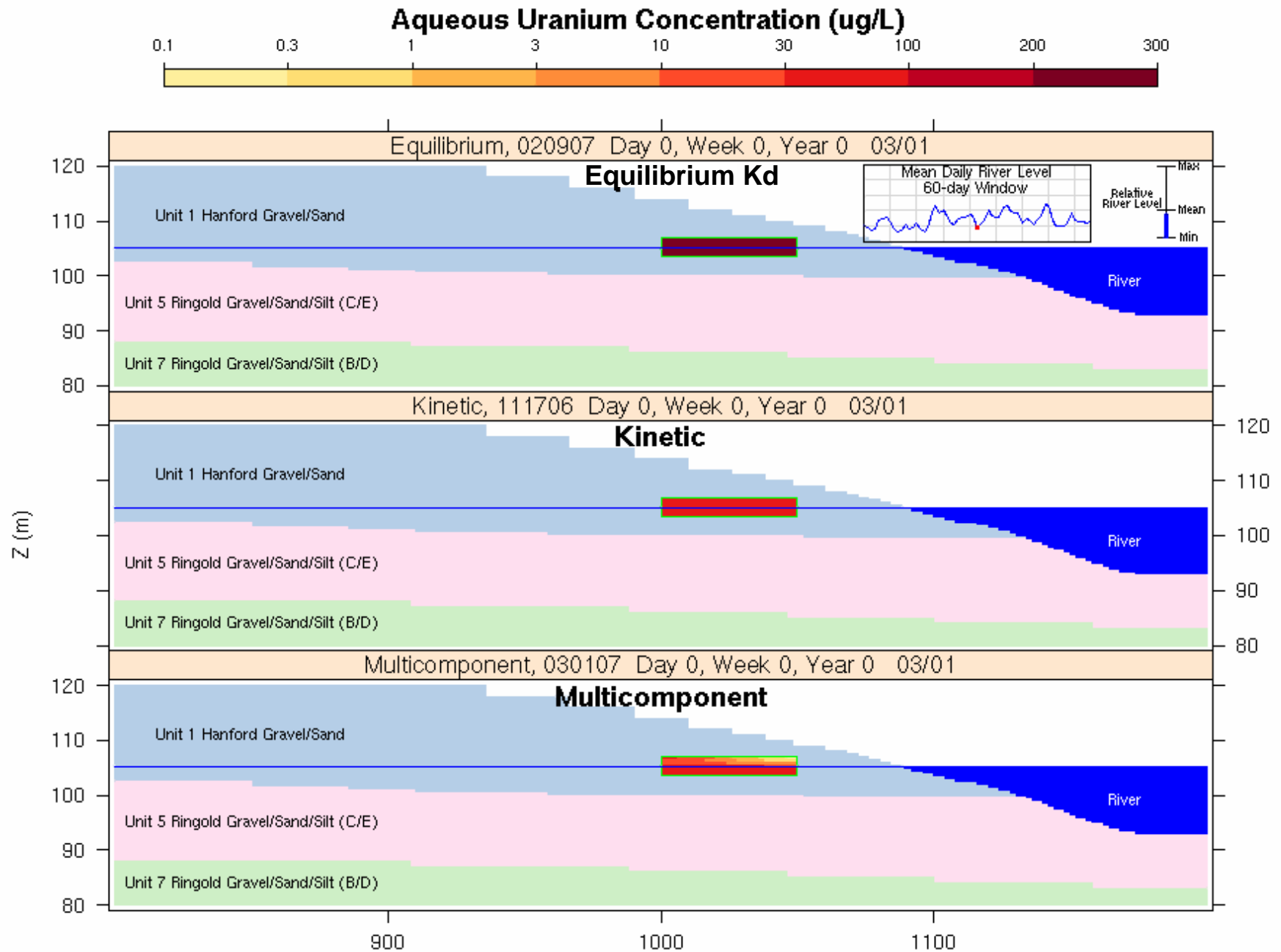# Large Grid Simulations
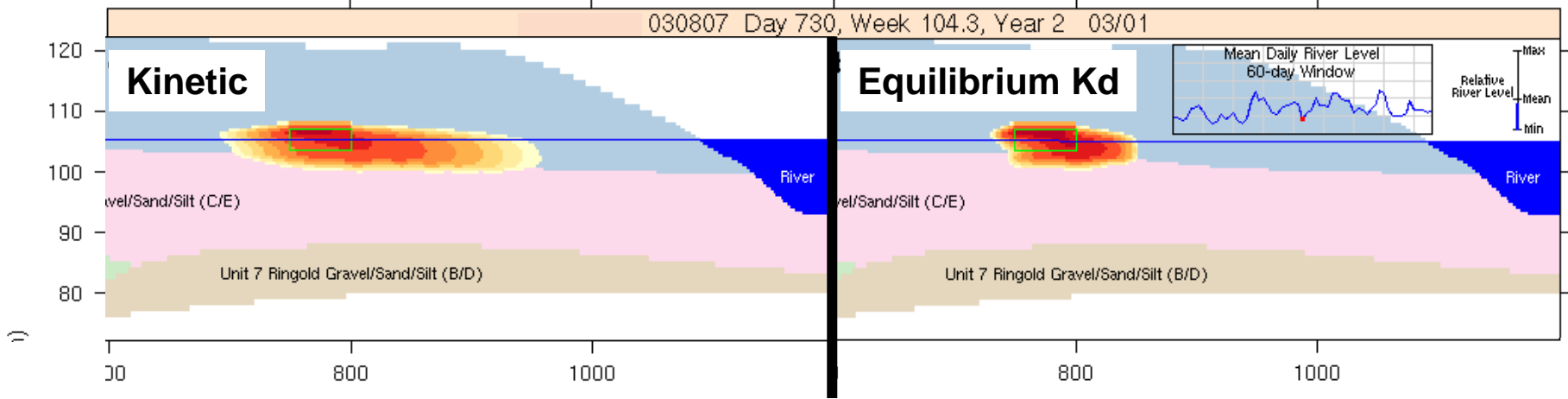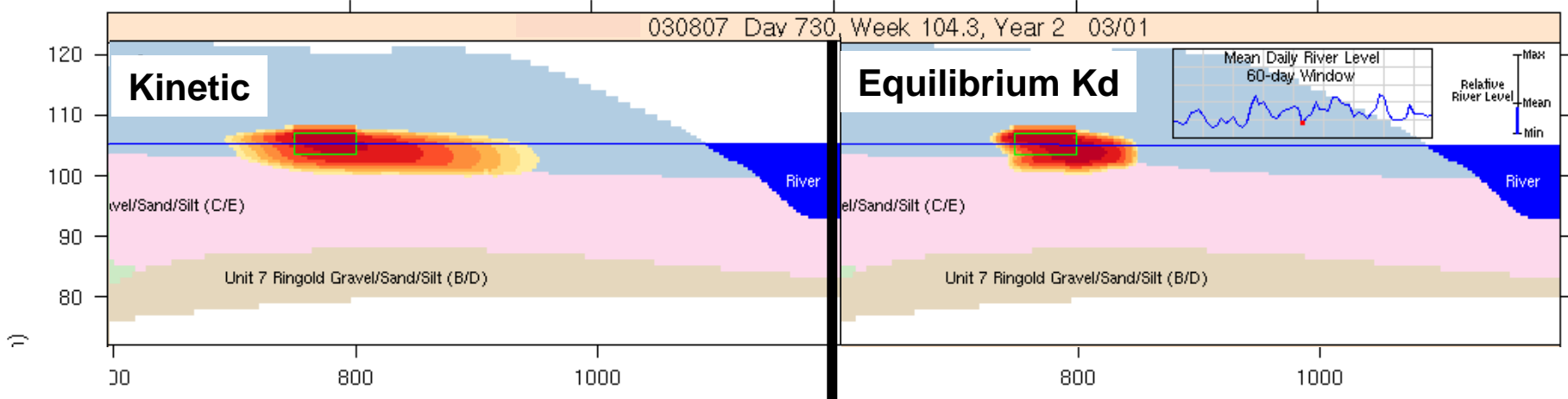
Tracer Transport Near River

▶ Net flux above water table is directed inland

▶ Net flux below water table is toward river

Tracer Aqueous Concentration (1/L)

Day 365, Week 52.1, Year 1   03/01

Small Grid: Near-River Simulations

Modeling Summary

► Interaction between hourly river stage dynamics, highly transmissive and heterogeneous sediments, and spatially variable uranium create field situation more complex than 1993 conceptual model

- Lower vadose zone uranium accessed by high river stage
- Diurnal cycling of high pore velocities
- Mixing zone of aquifer and river water chemistries
  - dictated by river forcing and hydraulic conductivity
  - sensitive to temporal resolution
- Equilibrium constant Kd is not consistent with lab results

► Uranium distribution and mobility can be significantly impacted by

- rate-limited mass transfer
- near-river mixing of groundwater and river water

► Work in progress

- Ongoing limited field investigation (LFI): sediment cores for detailed analysis, geophysical logging to map uranium distribution
- Laboratory studies provide framework for understanding uranium mobility
  - Solution chemistry
  - Kinetics
- Field-scale studies identify large-scale transport context for understanding uranium fate

Model Description

► Variably-saturated flow with hourly river-stage boundary condition

► Dynamic seepage face boundary condition for bank storage effects

► Recharge 60 mm/yr at surface, 0.9 mm/yr upward leakage from basalt

► Variable grid spacing

- 2.0 to 100 m in the horizontal
- 0.5 to 2.0 m in the vertical
- large grid: 26,268 (20,997 active) grid cells
- small grid: 8,512 (6,112 active) grid cells

► 30 minute time steps

Uranium Reactions

Reaction	log K (I = 0)
$UO_2^{2+} + H_2O = UO_2OH^+ + H^+$	-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
$Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = CaUO_2(CO_3)_3^{2-}$	25.4
$2Ca^{2+} + UO_2^{2+} + 3CO_3^{2-} = Ca_2UO_2(CO_3)_3 \ (aq)$	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
$SOH + UO_2^{2+} + H_2O = SOUO_2OH + 2H^+$	-4.548
$SOH + UO_2^{2+} + 2H_2CO_3 = SOUO_2(HCO_3)_2^- + 3H^+$	-4.047

Other Reactions

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
$Ca^{2+} + HCO_3^- = Calcite(s) + H^+$	-1.8542