^{90}Sr Transport through the INTEC Vadose Zone

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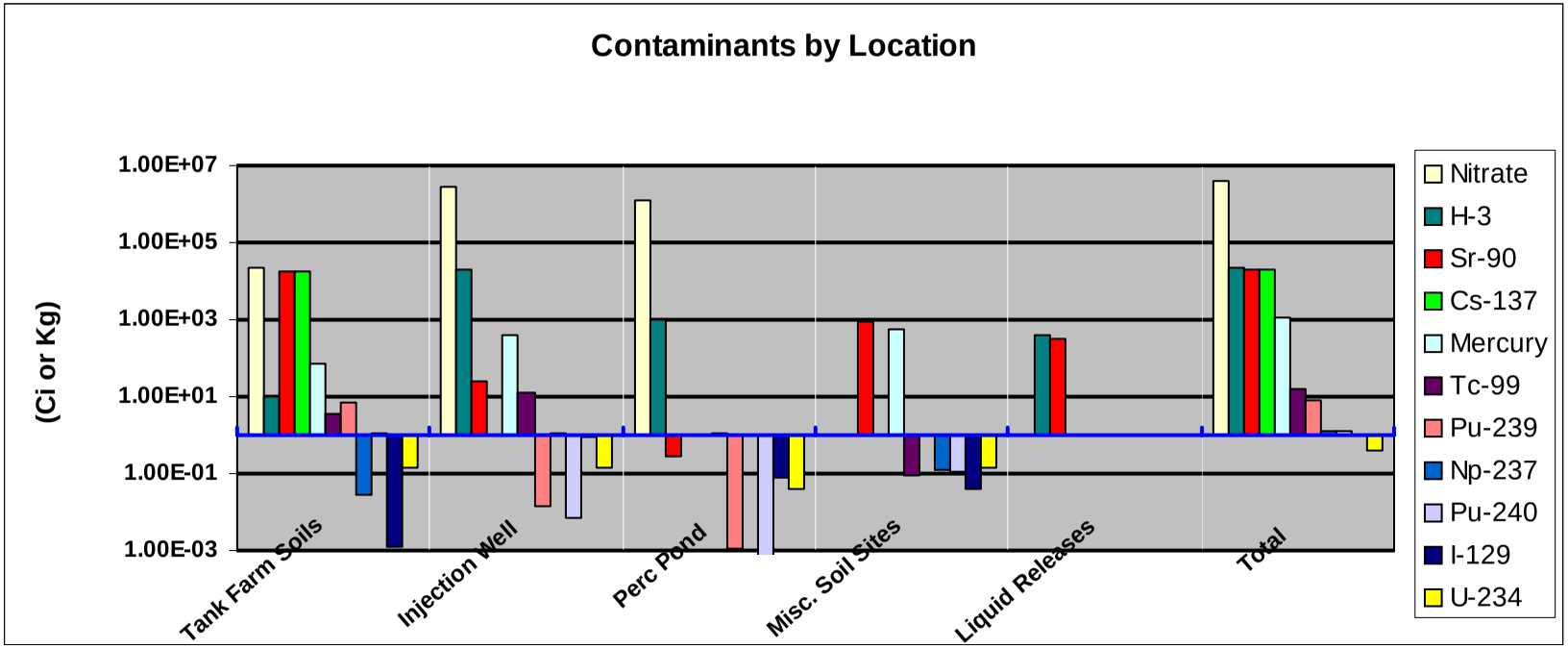
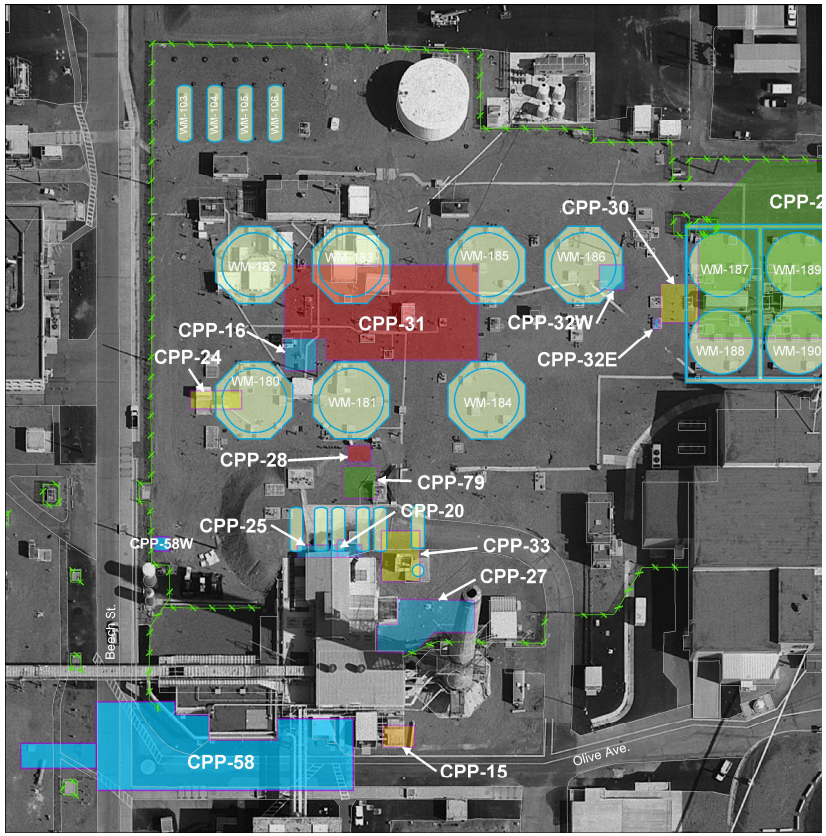
INTEC Contaminant Overview



Sr-90 Release Locations/Activities

Site	Activity (Ci)
Service Waste (~25)	
Former injection well	24.3 (total), 16 direct
Percolation ponds	0.295
OU 3-13 releases (<1300)	
liquid releases	308.8
soil sites	918
OU 3-14 releases (>18000)	
CPP-31	15,900
CPP-79 deep	874
CPP-27	720



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CPP-31 Release

- Occurred in 1972
- During transfer of 2nd/3rd Cycle Raffinate
- Lost 70,000 Liters (18,600 gallons) over 5 days
- Raffinate chemistry

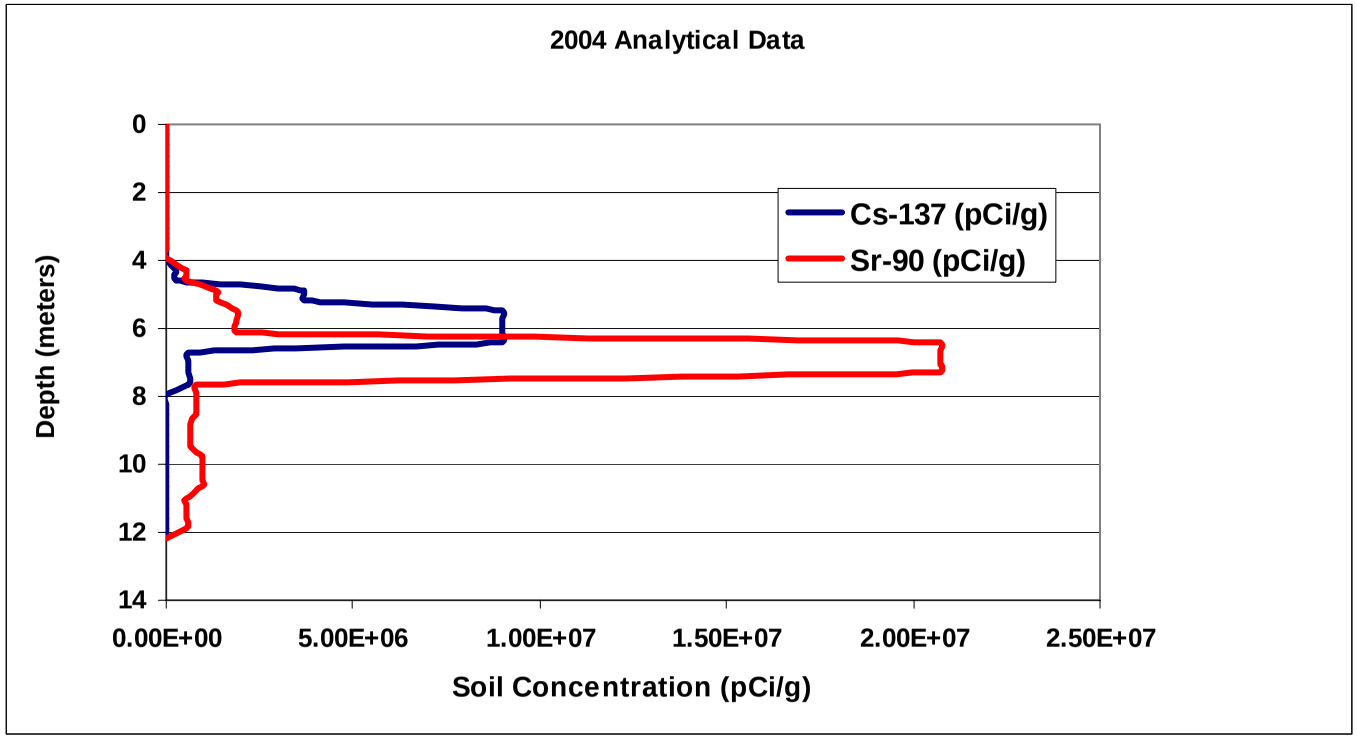
Nonradionuclides		Radionuclides	
Component	**Initial Concentration (mol/L)**	**Component**	**Initial Concentration (mol/L)**
H^+	1.5	^{134}Cs	5.83E-09
NO_3^-	4.5	^{137}Cs	2.02E-05
Na^+	1.5	Cs (total)	2.02E-05 (16,000 Ci)
Al^{+++}	0.5	^{90}Sr	1.74E-05 (15,900 Ci)
		^{99}Tc	2.67E-05

Downward Transport

- Release occurred 1.75 meters below land surface (bls)
- Alluvium is 13.5 meters thick
- Interbeds (and perched water) at INTEC exist at 30, 42, 85, and 116 meters
- Average precipitation infiltration rate 18 cm/yr average
- Additional 8 cm/yr (spatial average) anthropogenic water infiltration
- Porosity 32%
- Initial saturation in the alluvium ~30%

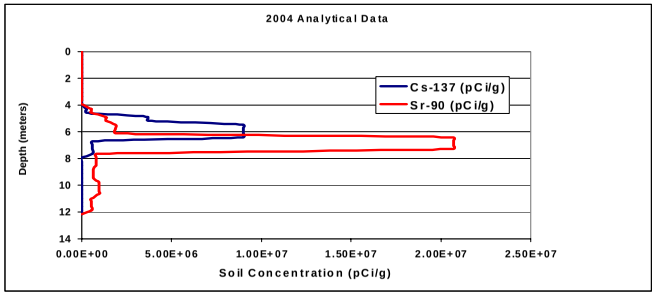
Soil Data Near CPP-31

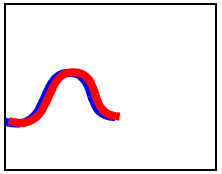
- 64 gamma logs taken in 2004 to depths of 12-14 meters
- One of the logged wells was cored and sent to the laboratory for ^{137}Cs

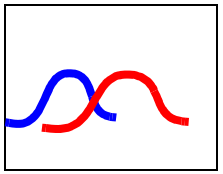


Soil Column Notes:

- Initial $^{137}Cs/^{90}Sr$ ratio = 1.16
  - Highest Cs at 5-6 m (8,990,000 pCi/g)
  - Highest Sr at 6.5-7.5 m (20,700,000 pCi/g)
- Distribution of ^{137}Cs and ^{90}Sr differ:
  - Gaussian ^{137}Cs
  - 700,000 pCi/g ^{90}Sr below the peak
  - 100 pCi/g ^{137}Cs below the peak
  - Lateral movement of $^{90}Sr >> ^{137}Cs$
  - Vertical offset does not support $V_{Sr} >> V_{Cs}$
- 90% of ^{137}Cs accounted for in alluvium
- Can't easily quantify the ^{90}Sr



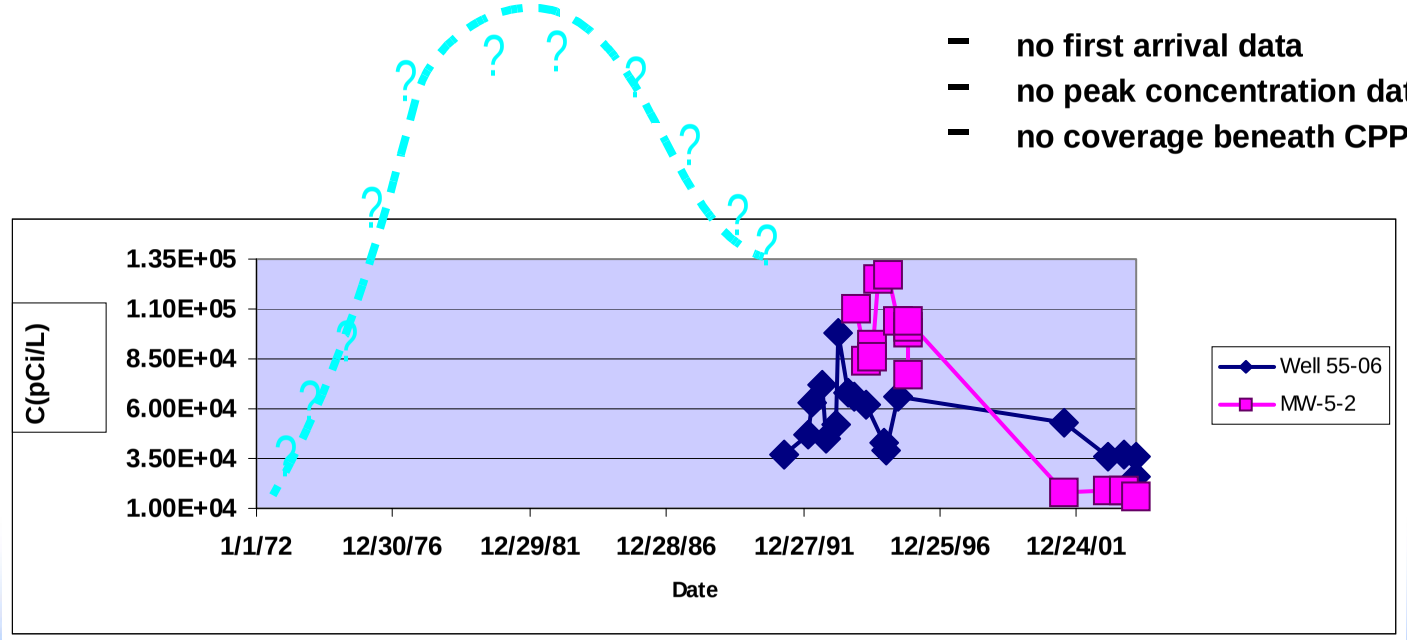




Perched Water Concentrations @ 30 m (bls)

- Data taken in the perched water at 30 m
- ^{90}Sr-90 as high as 480,000 pCi/L
- Matching ^{90}Sr concentrations requires constant K_d=0.2 mL/g
  - using K_d = 0.2 mL/g leaves no ^{90}Sr in the alluvium
  - measured K_d range is 13-145 mL/g (Liszewski et al, 1998)
  - using K_d = 100 mL/g allows no ^{90}Sr to leave the alluvium

- **no first arrival data**
- **no peak concentration data**
- **no coverage beneath CPP-31**



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Observations

- Traditional Kd approach is only valid for steady state systems
  - infiltration (leak) events are transitory
  - plume movements are transitory
  - chemical evolution is transitory
- Tank farm releases undergo extreme changes in pore water chemistry
- To evaluate the geochemical evolution we needed to consider
  - mineralogy, hydrology, and laboratory observations of Cs and Sr
  - geochemical processes
  - dynamic changes in geochemical evolution
  - highly transient flow

Mineralogy

- Excavated, homogenized, & backfilled mix of overbank and channel deposits

Mineral	Weight Percent by Source				
	Channel deposits[1]		Overbank deposits[1]		INTEC alluvium[2]
	(n=11)		(n=5)		(n=3)
	Range	Median	Range	Median	Range
Quartz	32 - 45	38	27 - 37	33	41 - 56
Plagioclase	16 - 30	23	11 - 19	16	18 - 21
K-feldspar	6 - 18	12	9 - 15	12	0 - 13
Calcite	0 - 6	3	3 - 12	7	3 - 12
Pyroxene	8 - 14	12	5 - 10	8	0 - 14
Dolomite	0 - 3	0	3 - 7	6	0 - 0
Clays	8 - 14	10	14 - 27	19	0 - 22
1. (Bartholomay, et al. 1989) 2. (Liszewski, et al. 1997)					

- **Raffinate Composition**

Non radionuclides		Radionuclides	
Component	**Initial Concentration (mol/L)**	**Component**	**Initial Concentration (mol/L)**
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Perched- and Infiltration-Water Composition

Component	Concentration (mole/L)
H^+ (pH)	5.369E-08 (7.30)
Ca^{+2}	1.64E-03
Na^+	2.2E-04
Cl^-	2.2E-04
HCO_3^-	3.64E-03

We Would Expect:

- Acid to rapidly react with calcite:

$$CaCO_3 + 2HNO_3 = Ca^{2+} + CO_2(g) + 2NO_3^- + H_2O$$

  - dissolves calcite
  - increases the pH of the influxing solution
  - supersaturates the influxing solution with respect to Aluminum -- forming gibbsite
  - releases gas-phase CO_2
  - decreases the pore-water pH
- Acid to slowly react with alumino-silicate minerals
  - alumino-silicate minerals may be inert if pH is buffered rapidly
  - reactions may be neglected
- Potential impact on hydrologic properties

Ion Exchange

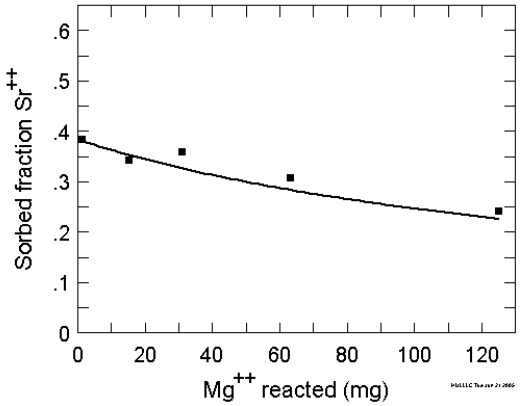
- Sr and Cs characterized by low ionic potential (valence/ionic radius)
- Exchange occurs rapidly for both species
- Sr exchanges primarily on planar sites on clays
- Cs exchanges on frayed edge and planar sites
  - edge sites are stronger bonding than planar sites
  - bonded stronger at low concentration, weaker at high concentration
  - not easily released from the edge sites

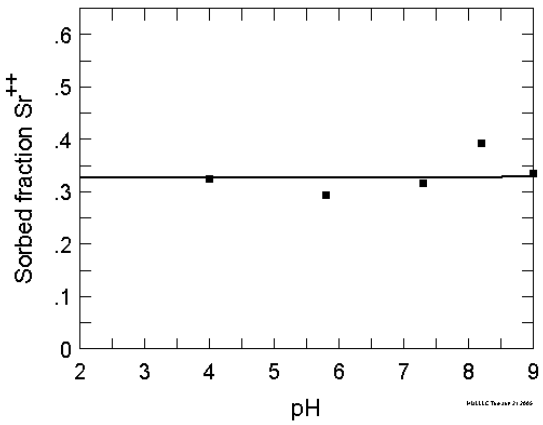
Ion exchange model parameters

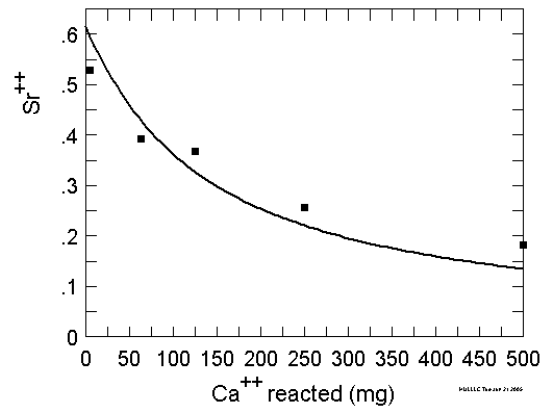
- Cation Exchange Capacity (CEC)
  - solid media property -- strong function of soil type
  - spatially variable (depositional environment)
  - INTEC specific values are not available
  - INL values are available from Liszewski, Bartholomay, Hawkins and Short, USGS
- Selectivity Coefficients
  - Ion specific
  - $Cs^{+} > Sr^{2+} > Ca^{2+} > Mg^{2+} > K^{+} > NH_4^{+} > Na^{+} > H^{+}$
  - literature is pretty consistent for order and relative magnitude

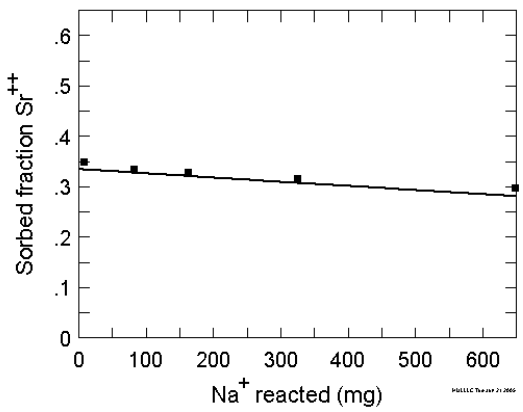
How Good are the Sr-90 Parameters for Ion Exchange?

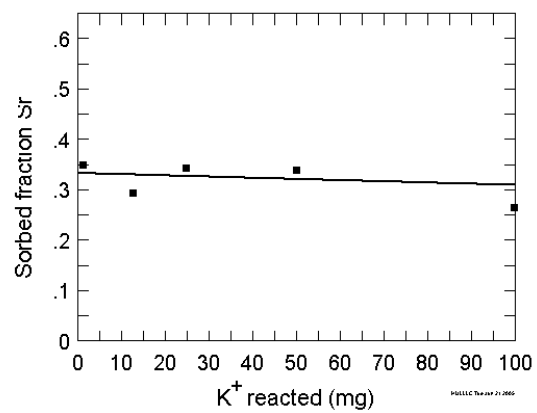
- Comparison of Batch Experiment to Hawkins & Short (1965) Data











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Comparison for ^{137}Cs Using 2 Exchange Sites

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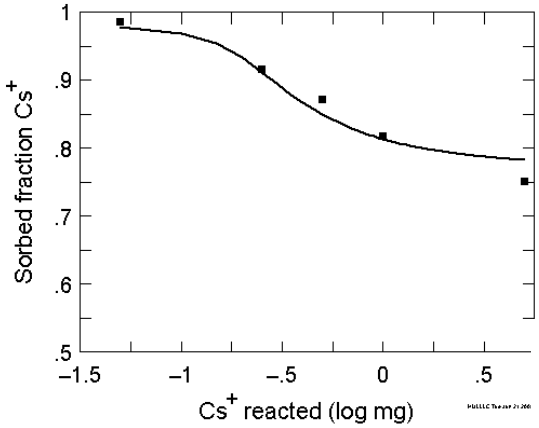

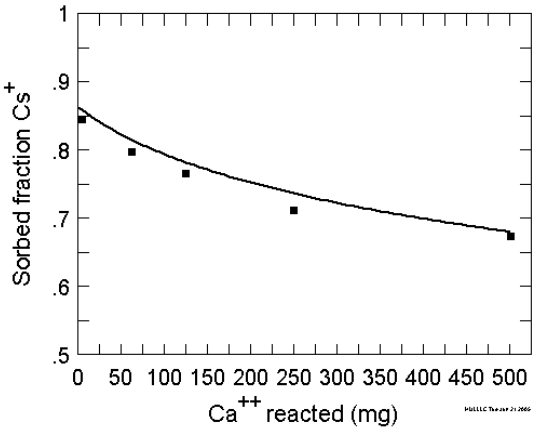

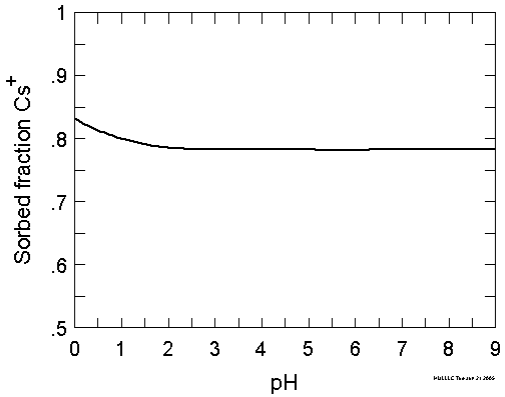

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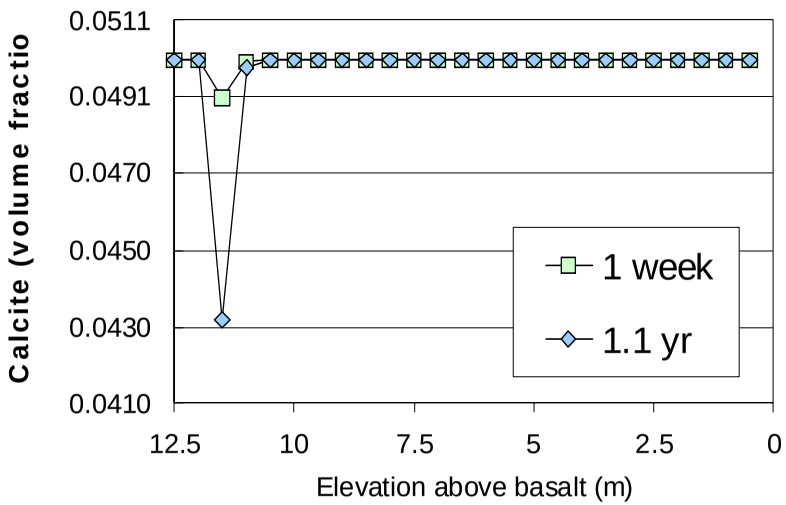
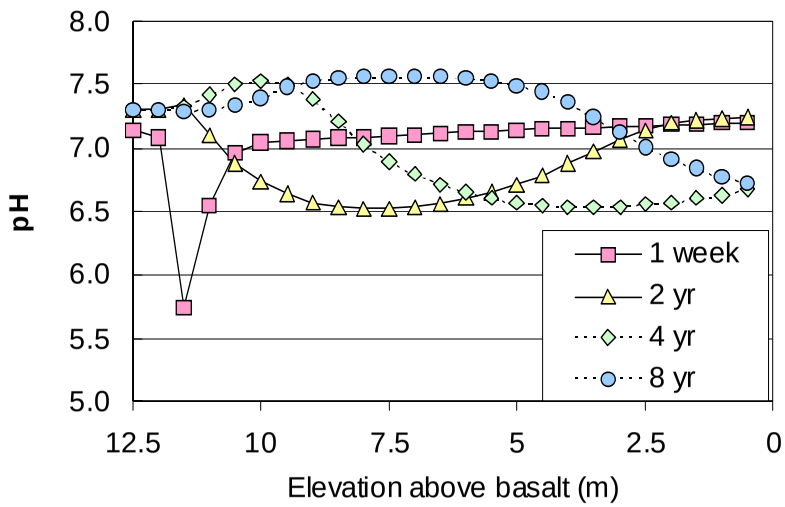
One-Dimensional Simulation Results

- Domain size: 60 m X 30 m x 18 m
  - roughly equal to gamma distribution from 1970s data
- Layered media
  - alluvium thickness 13 m
  - basalt underneath
  - hydraulic properties taken from the OU 3-14 RI/BRA/FS model
- Boundary conditions
  - 18 cm/yr infiltration at top
  - 18,600 gallons over 5 days during simulated release, released at 1.75 meters
  - saturated bottom boundary (perched water)
- Water flux and water content allowed to reach steady state (multiphase)
  - initial (pre-release) water saturation of ~30% (after equilibration)

1-D Simulation Results

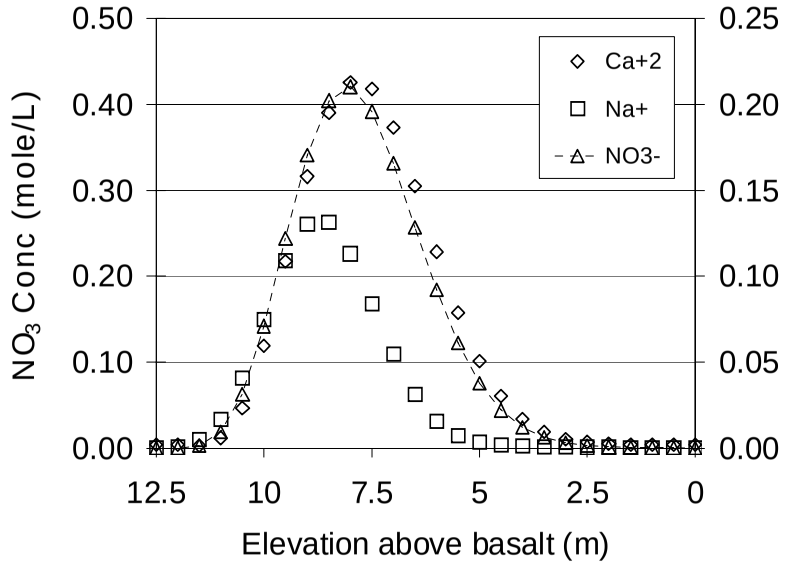
- Calcite and pH distributions
  - Calcite buffers pH rapidly
  - Transient drop in pH from dissolution
  - Returns to neutral once dissolution dissipates
  - Alumino-silicate dissolution is minor

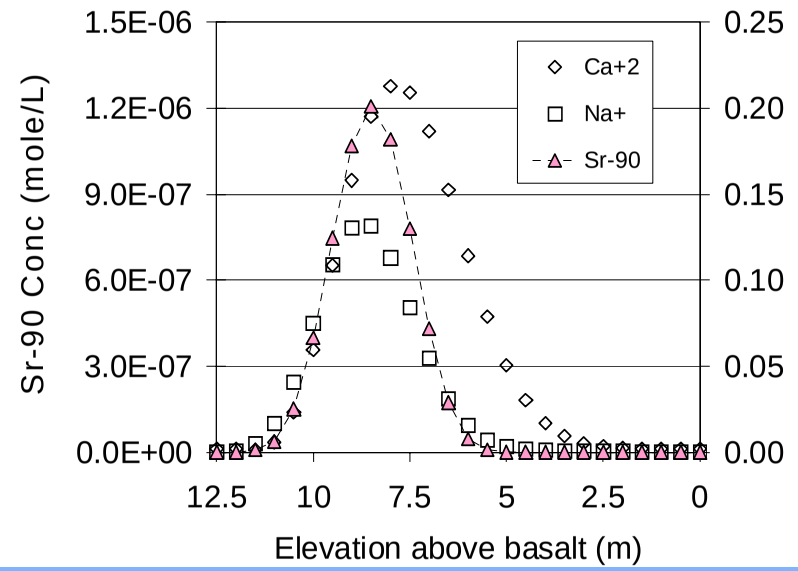




SOLUTION SPECIES AT 2.03 YRS

- Na^+ retarded relative to NO_3^- and Ca^{+2}
  - drives exchange reactions where sodium knocks calcium off clays
- calcium is kept in solution
  - moves faster than nitrate and Sr-90
- strontium
  - at 1 yr is about 4% in solution
  - moving slightly slower than nitrate





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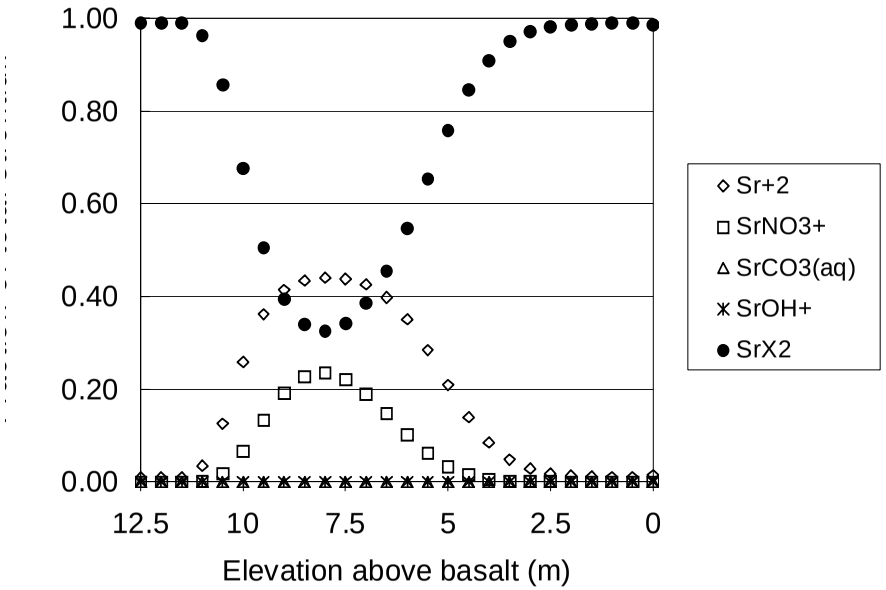
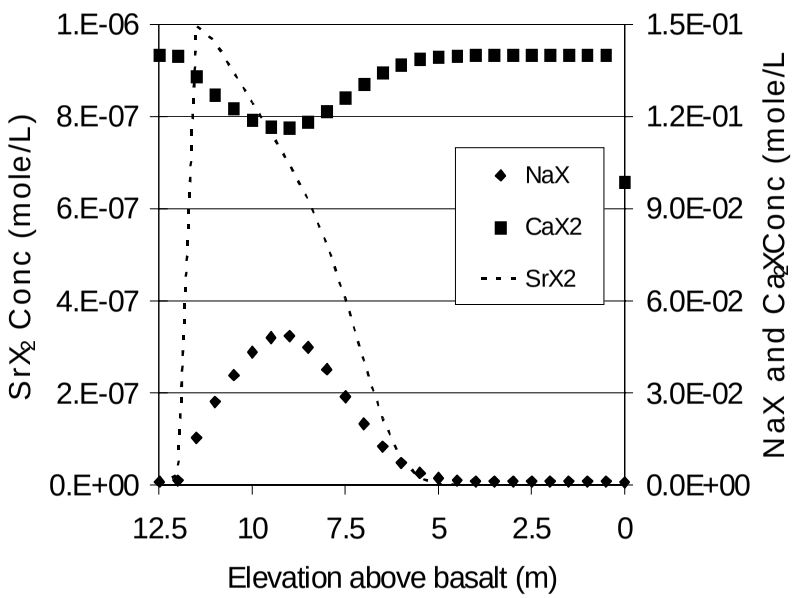
Distribution of Sr species at 2.03 yrs

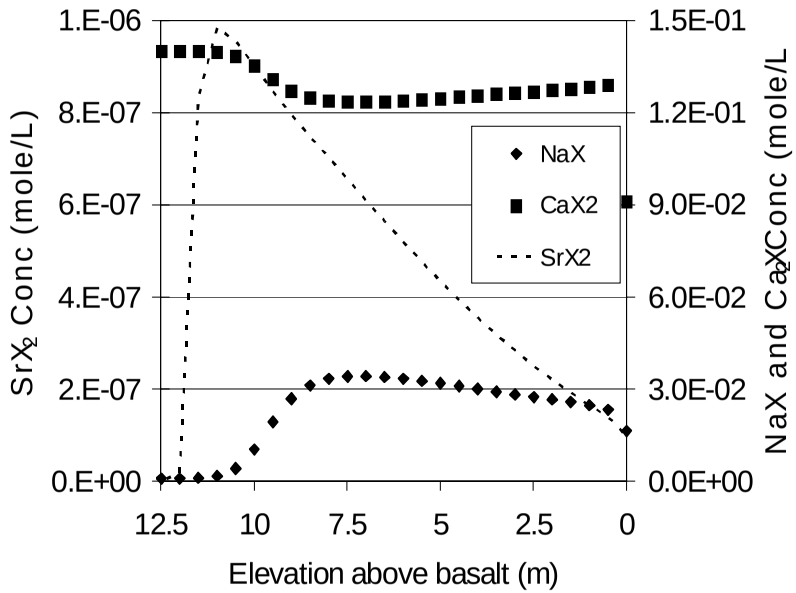
- Sr^{+2} and $SrNO^{3+}$ are the primary aqueous species
- Sr transport is multimodal
- High aqueous concentrations correspond to low exchange concentration



Distribution of exchangeable cations at 2.03 and 8.05 yrs

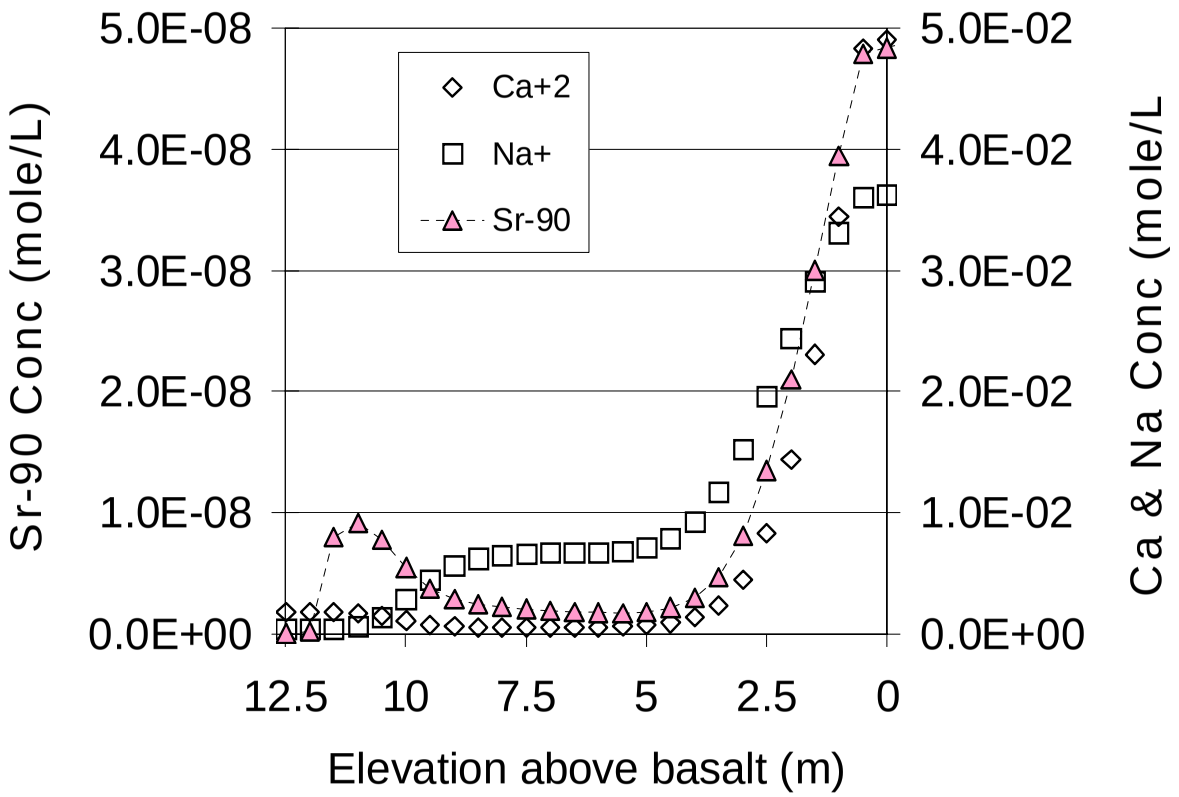
- Calcium is replaced by sodium (high sodium, low calcium)
- Sr exchange is preferred to Ca --> leaves more Sr on exchange sites
- High exchange species == low aqueous species
- Elevated leading edge cation concentrations enhance Sr migration





Concentration of cations in solution at 8.05 yrs

- Elevated aqueous concentrations at 30-40 ft
- Corresponds to elevated concentration on the cation exchange sites
- Bulk of the ^{90}Sr is deep in the column



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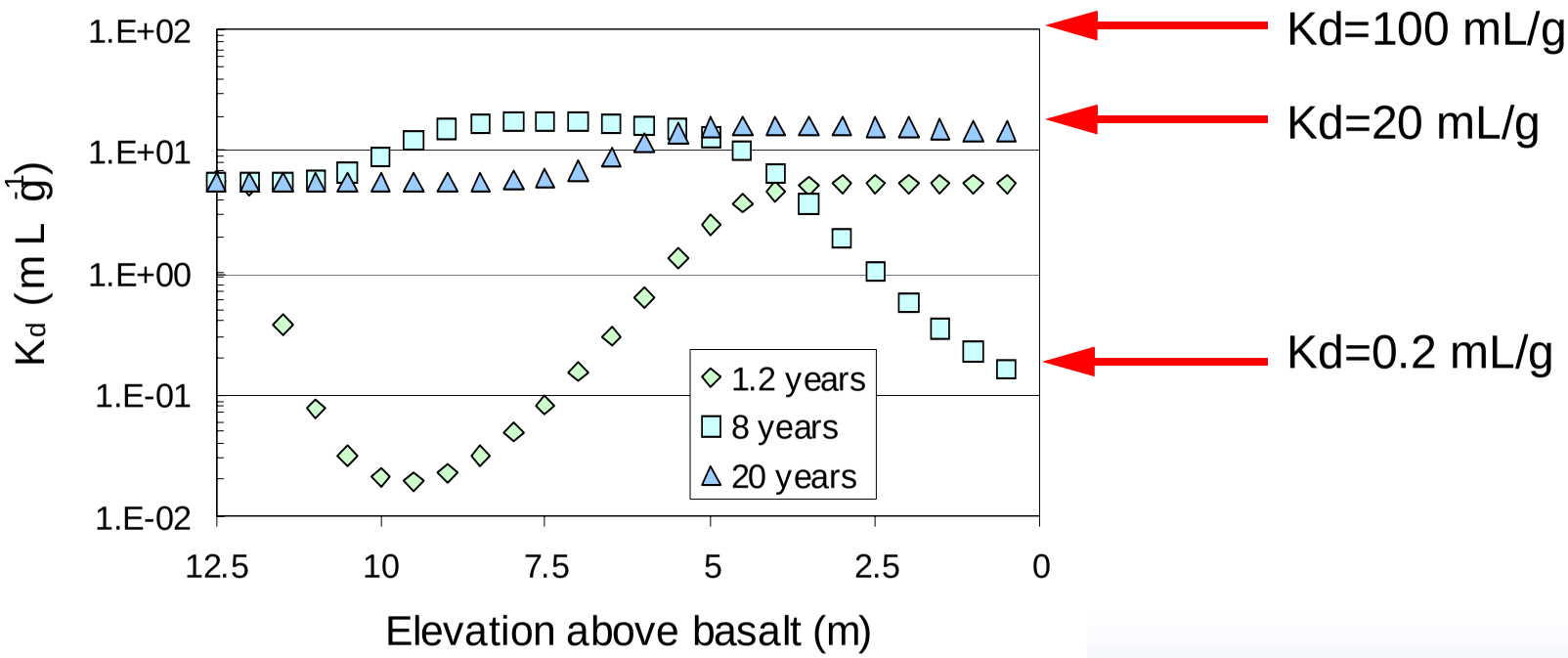
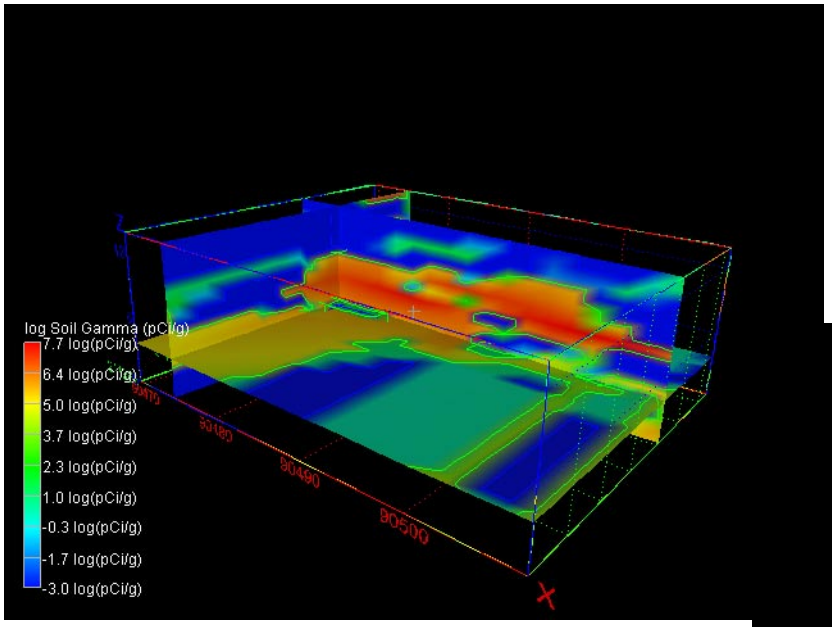
Predicted Sr K_d

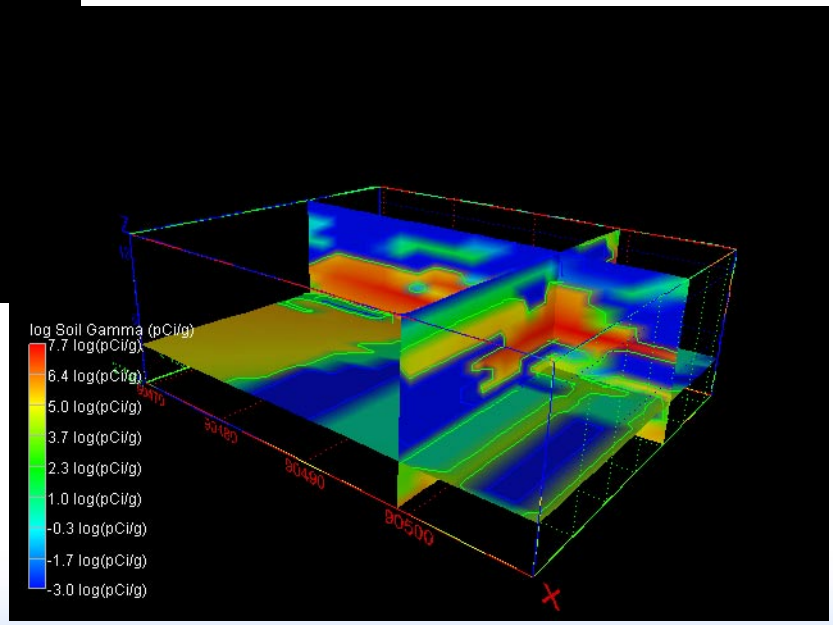
- Partitioning coefficient defined as: $K_d = \frac{C_{ads}}{C_{sol}}\left(S_l \frac{\phi}{\rho_{bulk}}\right)$
- Ion exchange results in a spatially and temporally variable partitioning



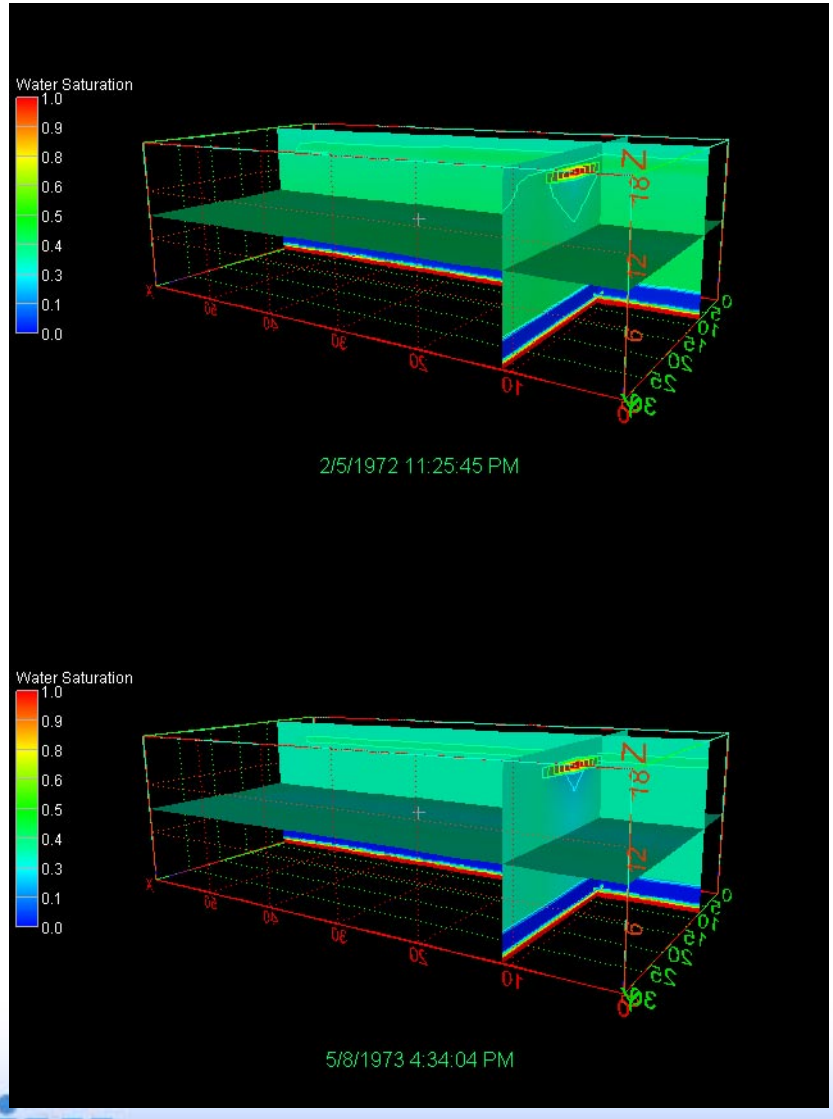
3-D SIMULATION RESULTS FOR CPP-31

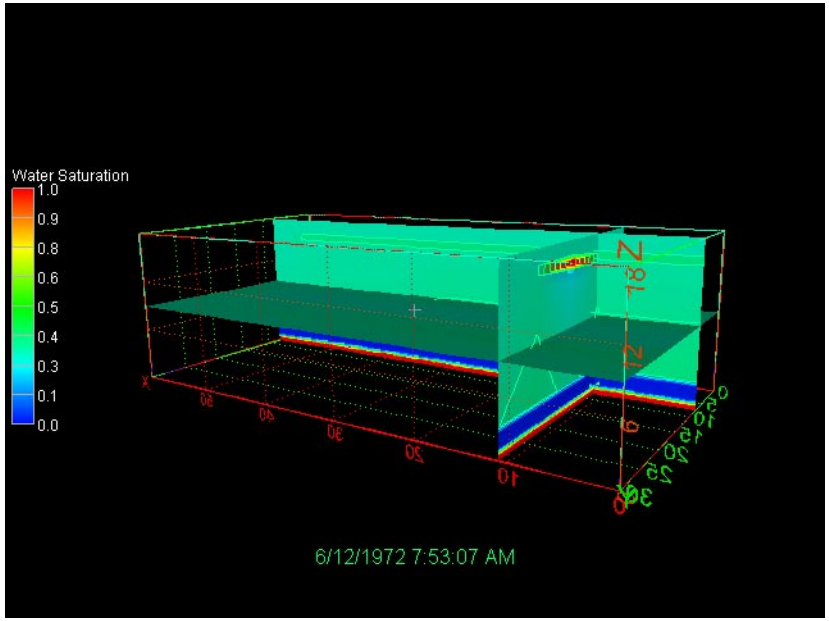
- Krigged log-10 (Cs-137) soil concentrations (corrected to 1972) pCi/g



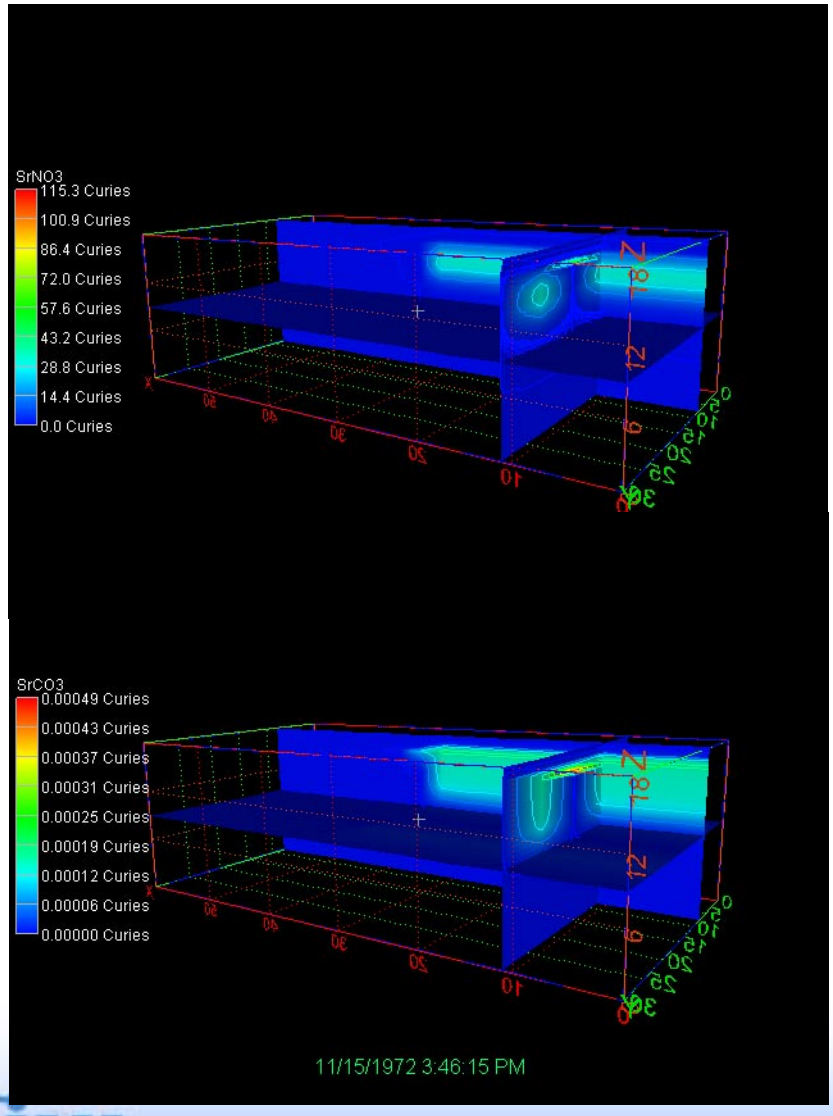


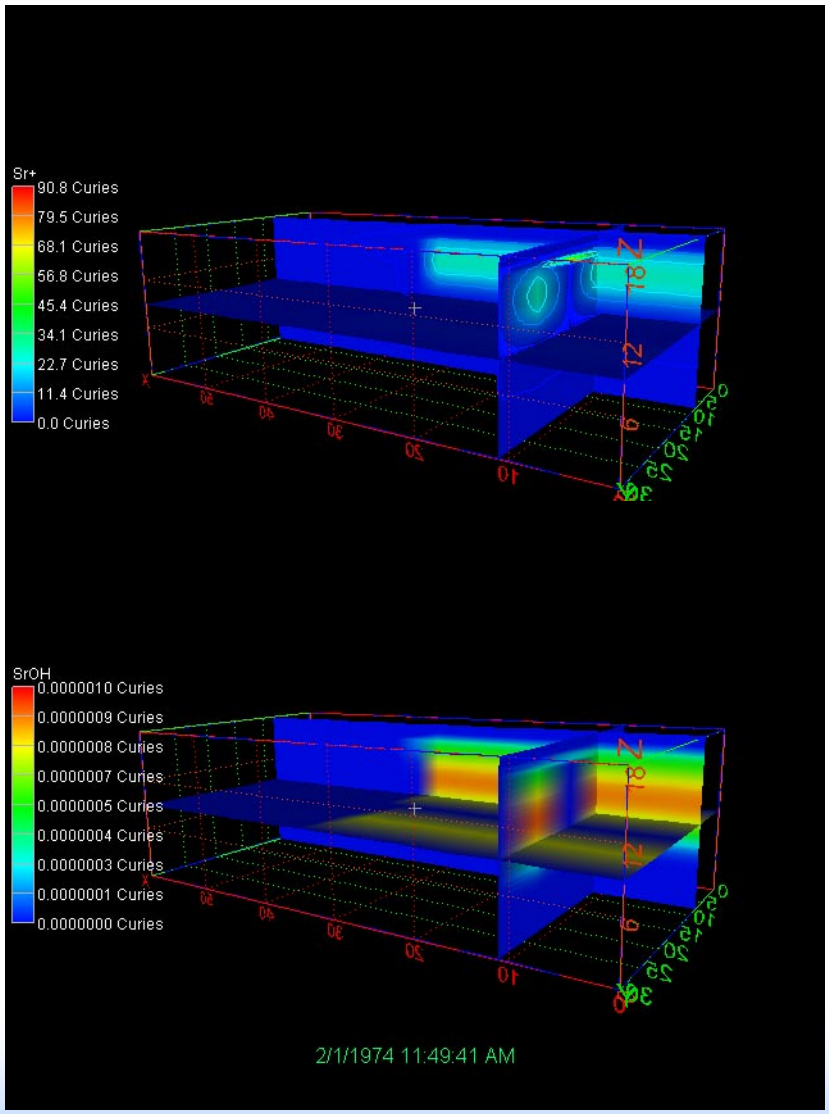
- Water Saturation 1, 5, and 17 months post CPP-31 release



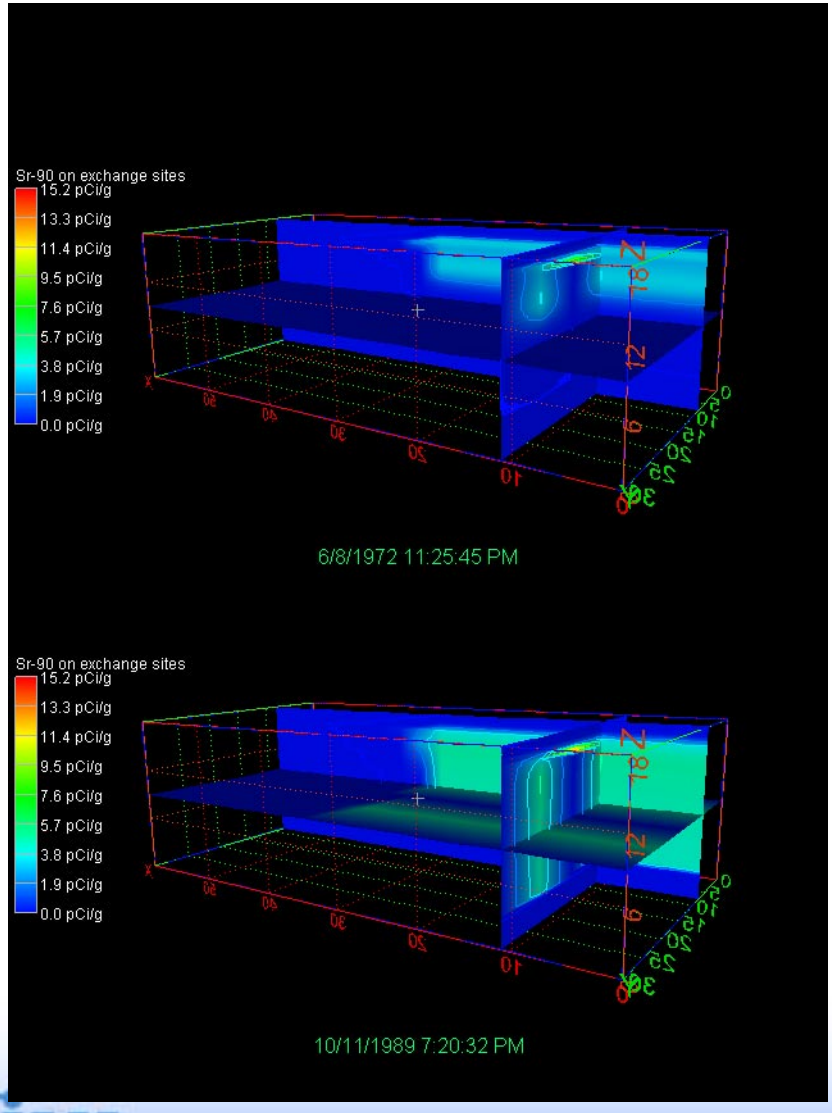


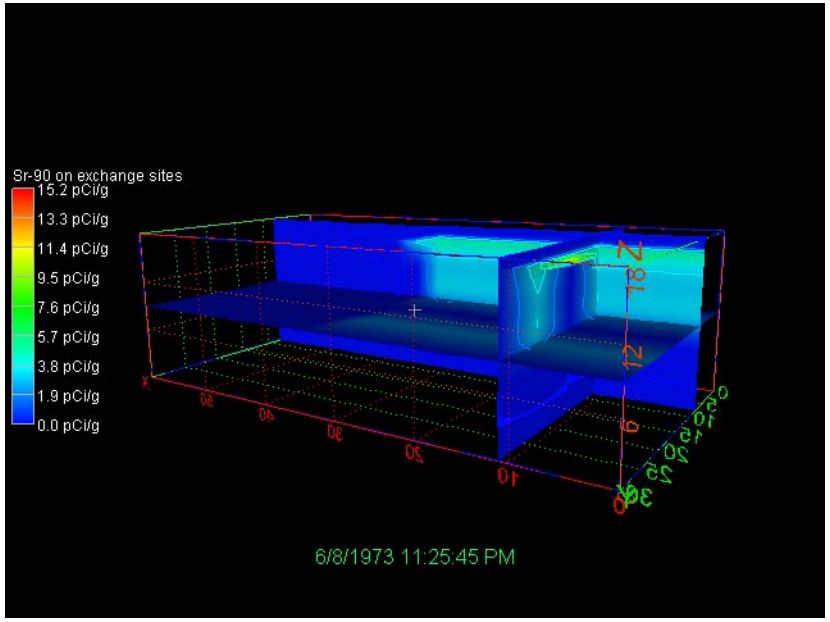
- Aqueous Species 12 Months Post CPP-31 Release



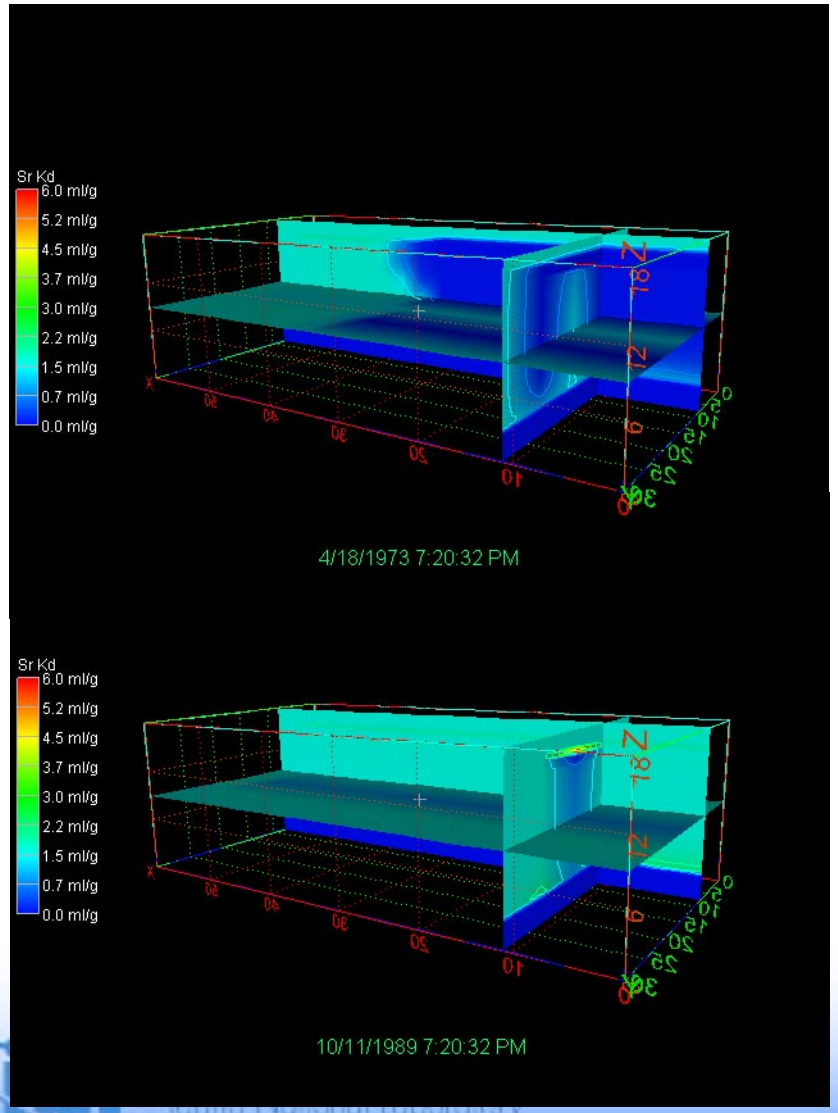


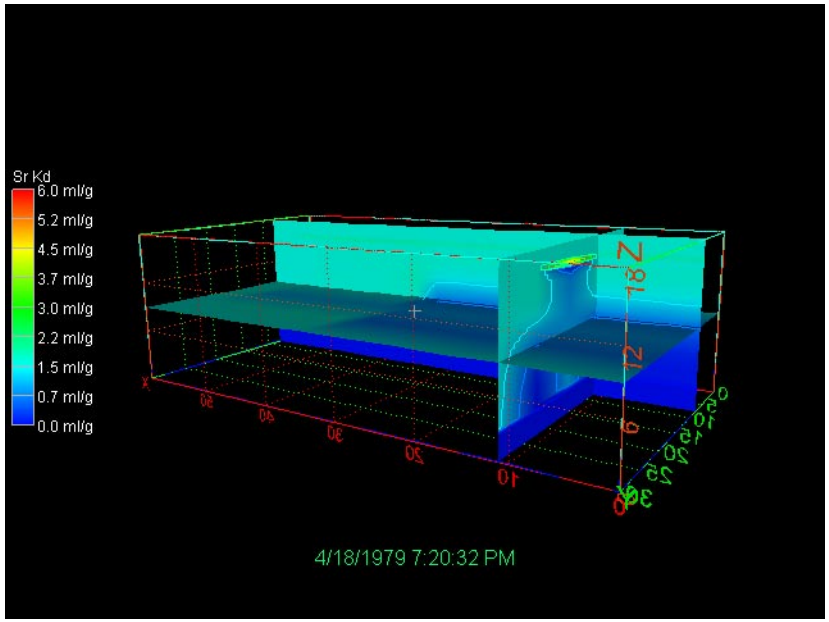
- Sr-90 on exchange sites 1, 2, and 3 years post CPP-31 release



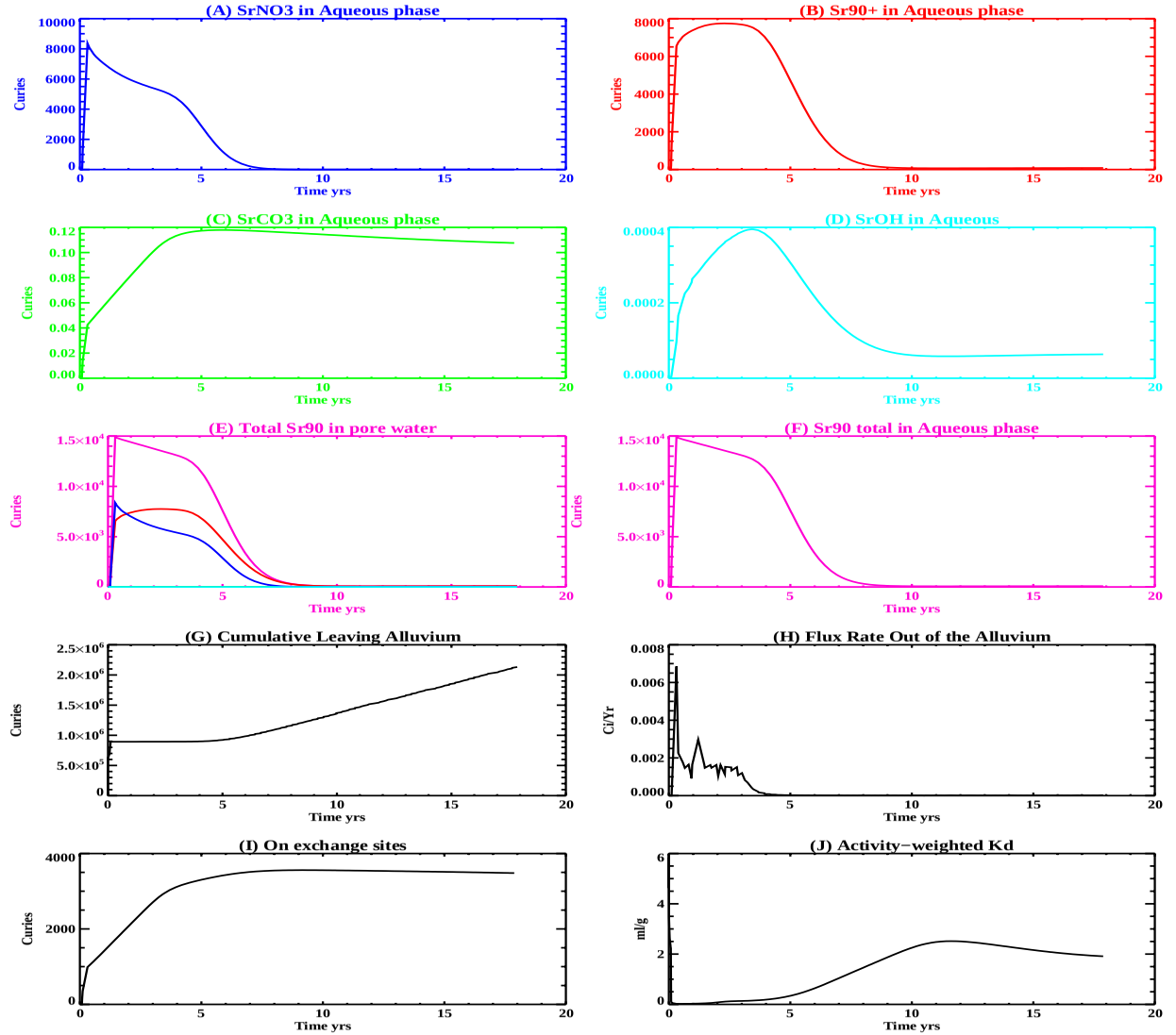


- Effective partitioning at 0.5, 1.5, and 17.5 years post CPP-31 release



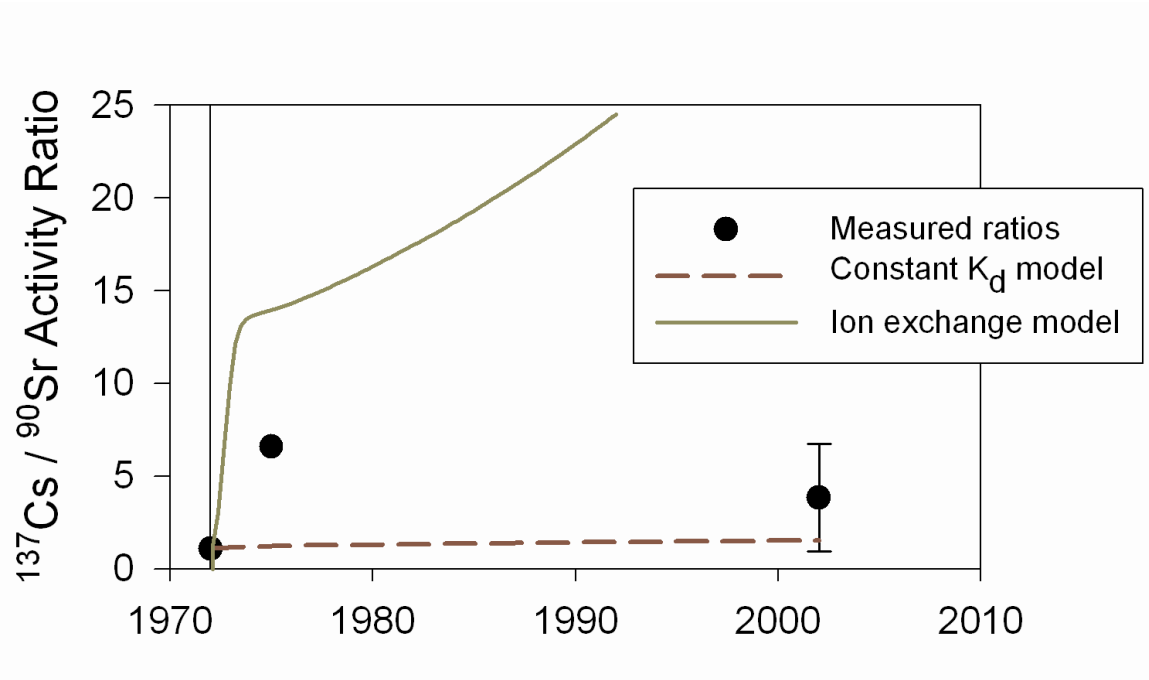


- Summary measures



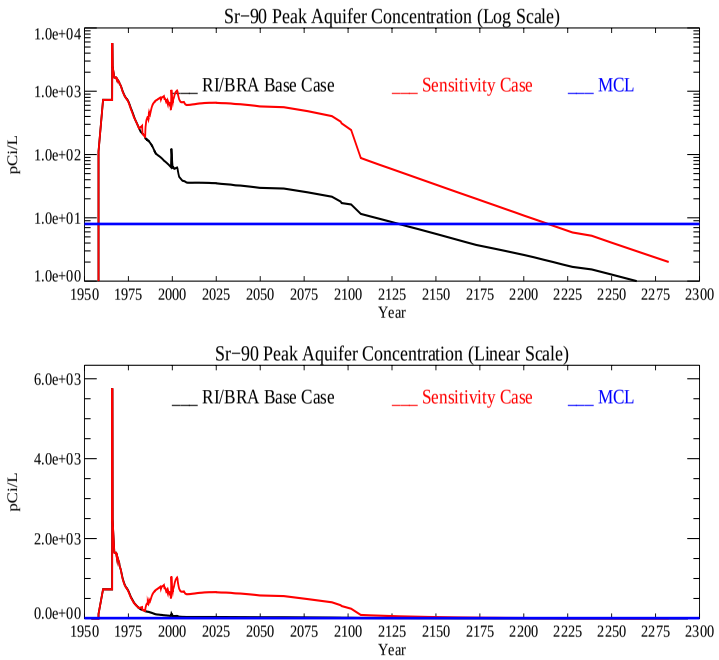
Where are we?

- This model explains early arrival in perched water and soil concentrations
- It does not correspond to observed 1977 ratios of $^{137}Cs/^{90}Sr$:
  - core taken near CPP-31 by Rhodes et al.
  - suggests multiple processes are still occurring
- Probably different in the perched water and alluvium:



Final Observations

- Direct injection of
  - 16 Ci of ^{90}Sr
  - over 20 years
  - SRPA ^{90}Sr ~900 pCi/L
  - the MCL is 8 pCi/L
- CPP-31 and CPP-79
  - catastrophic releases
  - >17,000 Ci total
  - 110-concentrations ~ 300,000 pCi/L
- Predicted aquifer concentrations:
  - evolution of the surface releases
  - geochemical processes in sediments
  - topology/distribution of interbeds
  - infiltration rates



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