Understanding plutonium variability and mobility in groundwater at the Savannah River Site

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U.S. Department of Energy Office of Science
Environmental Remediation Sciences Program

Outline

- **Introduction**
  - Plutonium & DOE interests
- **Methods matter**
  - Innovative approaches for groundwater Pu studies
- **Savannah River F-area field data**
  - Pu concentrations
  - Pu colloid abundances
  - Pu redox state
  - Pu isotope ratios

Variability in Pu isotope ratios, redox state and colloid associations attributable to Pu source effects and groundwater chemistry

Plutonium & DOE Interests

Plutonium is predicted to be insoluble and highly sorbed in subsurface environment, however:

- early studies showed high groundwater colloidal % (Kaplan et al)
- evidence for far field transport (Kersten et al)
- but, new methods show low colloid association (Dai et al)

If Pu variability can be understood/parameterized:

For remediation

- this allows for design strategies to retard Pu, save time and money, develop improved models to predict remediation impacts

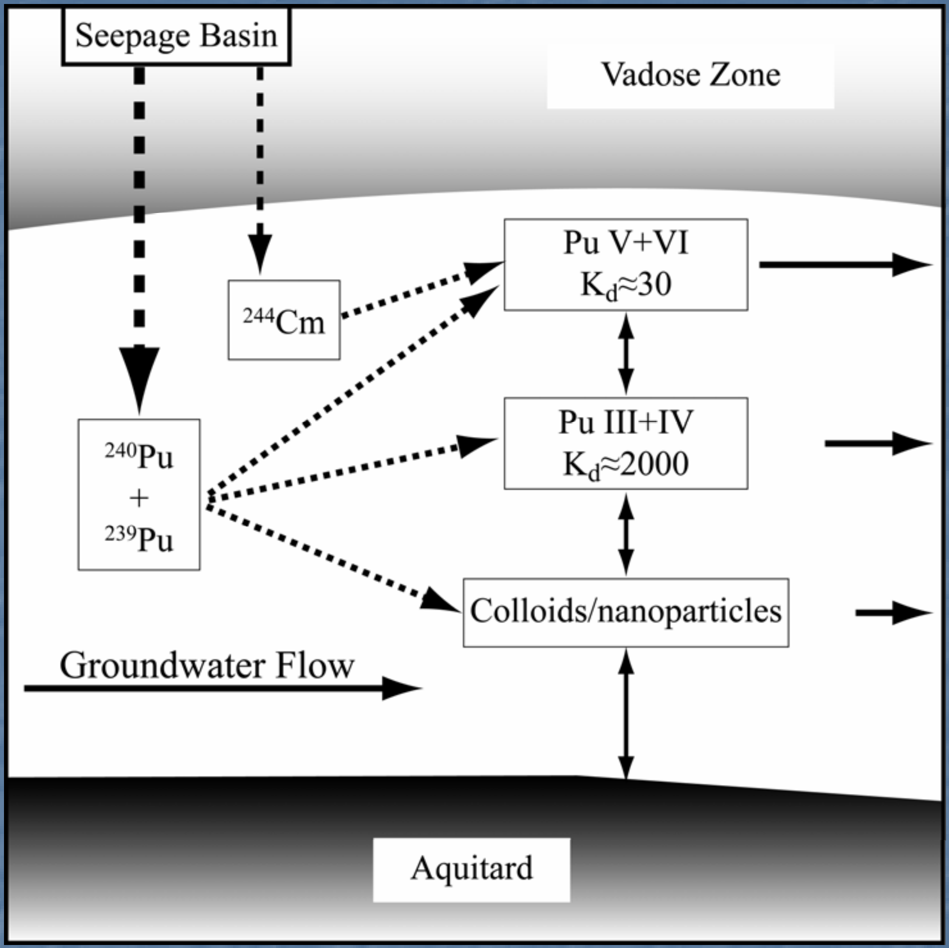
For stewardship

- this allows for better project management, prediction of off site migration & improved monitoring practices

Conceptual diagram of the fate of Pu released into the subsurface environment

Source dependent behavior
- Pu source controls

Source independent behavior
- Pu speciation controls via coupled biogeochemical processes

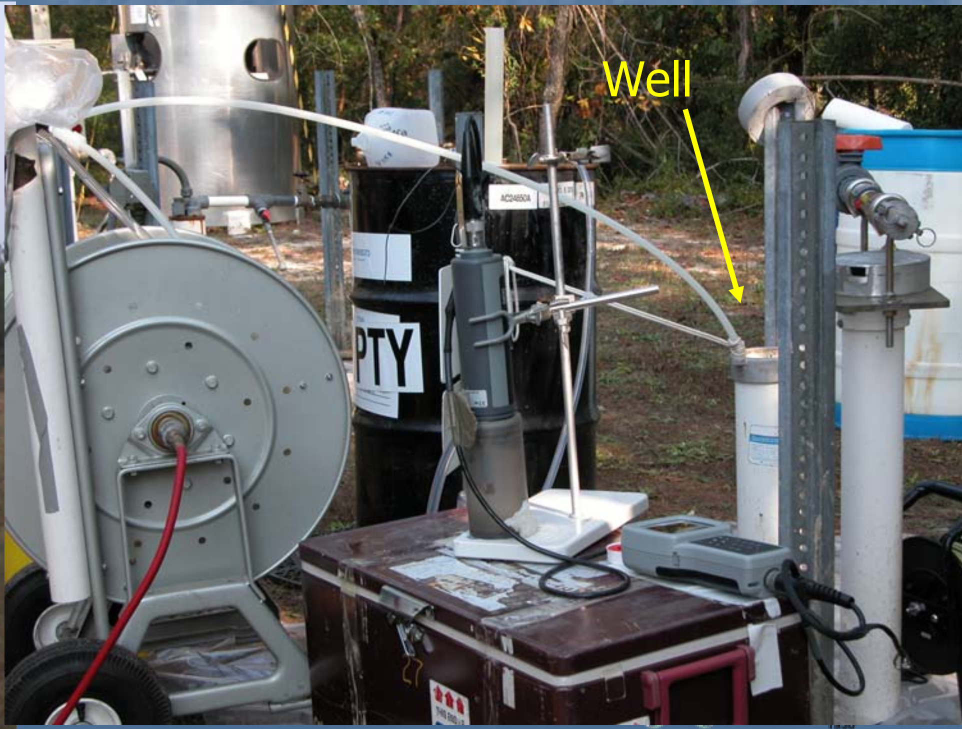


Fate of Pu is isotope specific and dependent upon temporal changes in groundwater conditions

Methods matter

In groundwater, Pu exists in multiple chemical forms/species
(Pu III, IV, V, VI; solution complexes, colloid associations)
and at concentrations $<10^6$ atoms per liter in different fractions
(= 0.0003 pCi/kg or 0.001 Bq/kg)

- **Well sampling**
  - "micro-purge" 150 ml/min & monitor groundwater geochemistry
  - Pu concentration increases >3x with standard well sampling (16L/min)



Methods matter

CFF system
>1kD to <0.2 µm = colloidal

- **Well sampling**
  'micro-purge' 100's ml/min & monitor gw geochemistry
- **Redox control**
  - N_2 controls during sampling & processing; immediate in field processing for colloids and redox state
- **Cross-flow filtration**
  - calibration; mass balance checks for loss and contamination

Mass balance (2004)
CFF ± 2-5%

N_2 glove bag

4L sample reservoir (>1kD)

Permeate out line (<1kD)

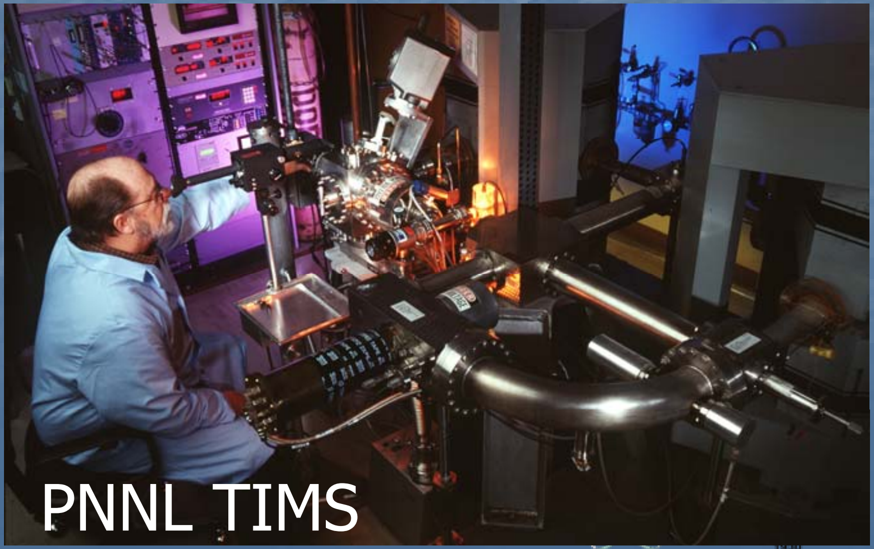
1kD Millipore CFF ($1m^2$)

Direct well feed

Methods matter

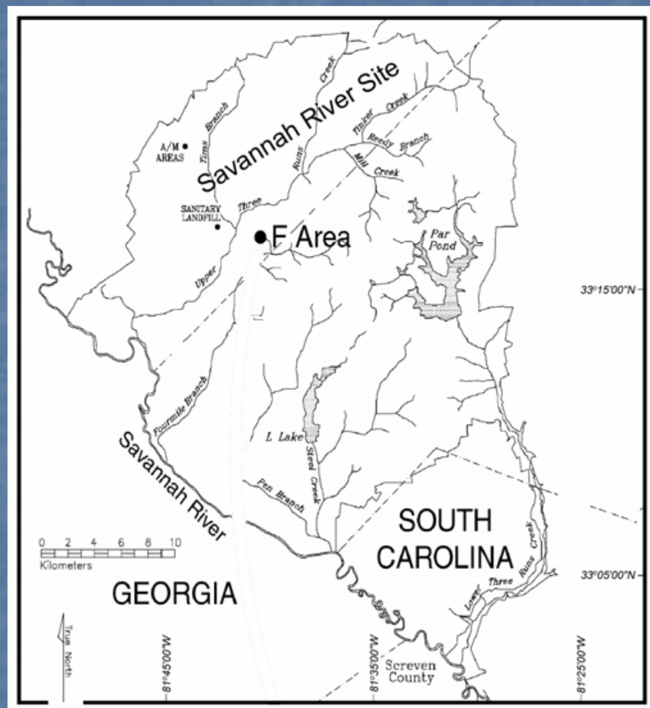
- **Well sampling**
  'micro-purge' 100's ml/min & monitor geochemistry
- **Redox control**
  - N_2 controls during sampling & processing; immediate in field processing for colloids and redox state
- **Cross-flow filtration**
  - calibration; mass balance checks for loss and contamination
- **Attention to blanks/TM clean methods**
  - blank levels of 10^4 atoms/sample
- **Thermal Ionization Mass Spectrometry**
  - identify separate Pu isotopes at environmental levels

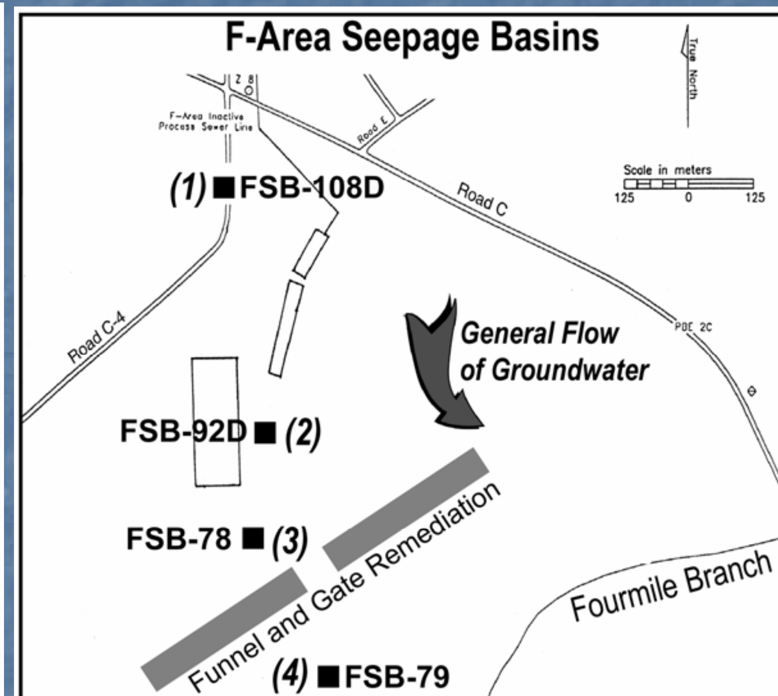
Portable clean field lab



SRS F-area Seepage basins

- waste from reactor separation facilities- nitric acid soln.



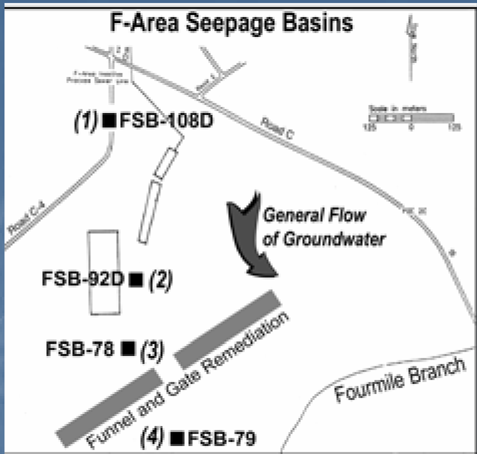


Project sampling in 1998 and 2004

Funnel and gate remediation since 2002/2003

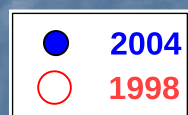
Millions liters of sodium hydroxide-sodium bicarbonate soln.

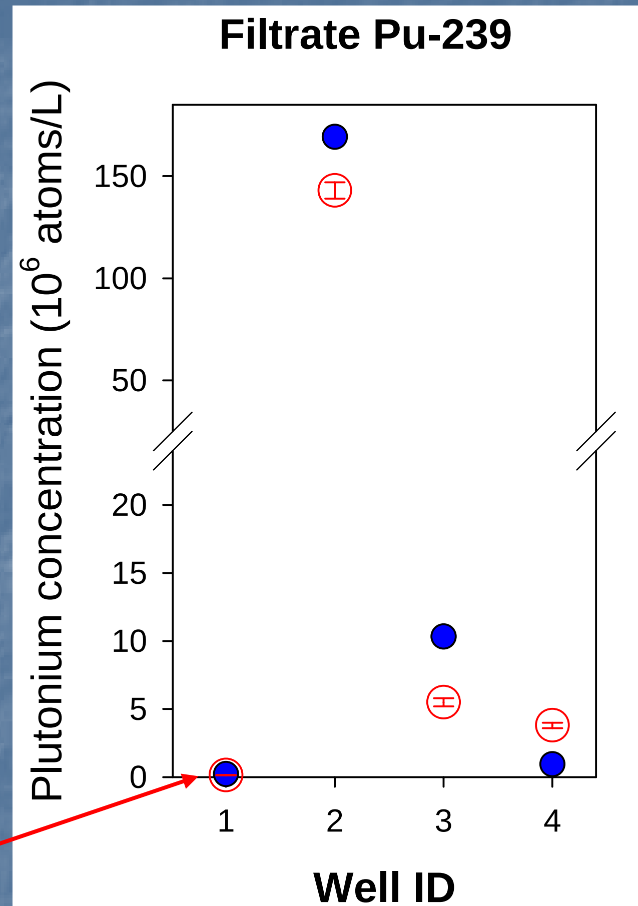
Increase pH from 4 to 6



Sharp decrease Pu-239 downstream from source

(Filtrate <0.2 µm)

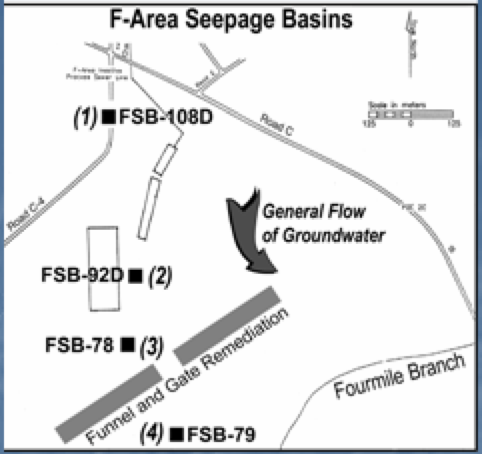


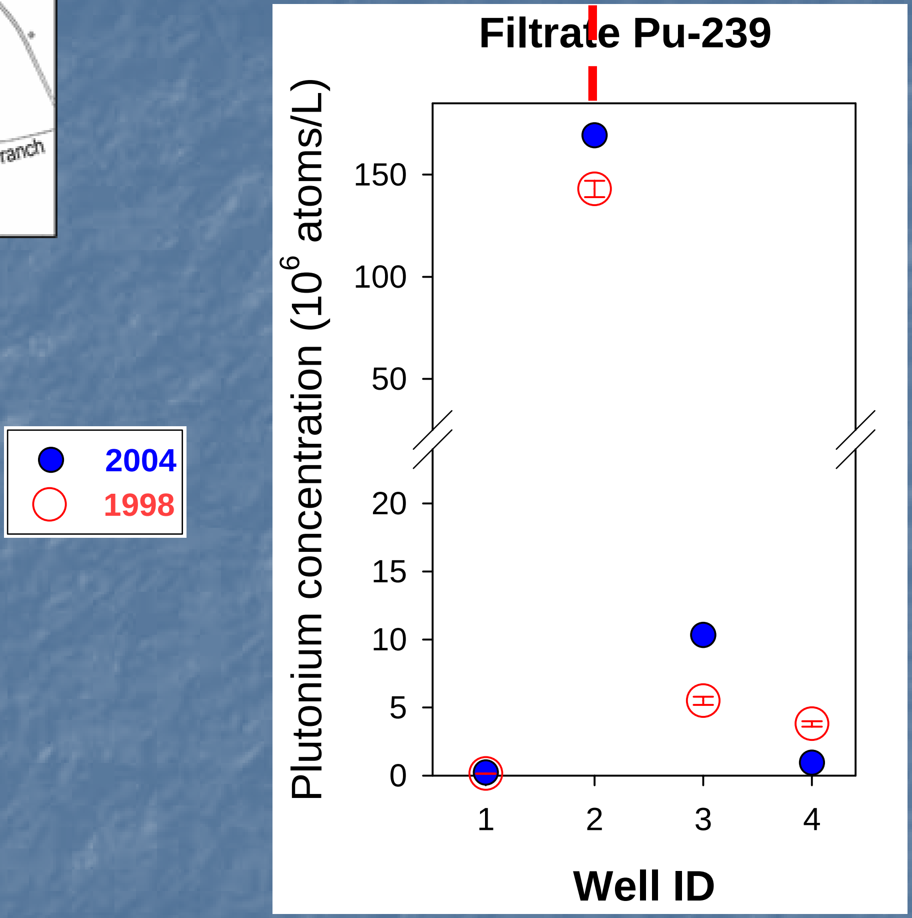


$^{239}Pu = 0.14\text{-}0.22 \times 10^6$

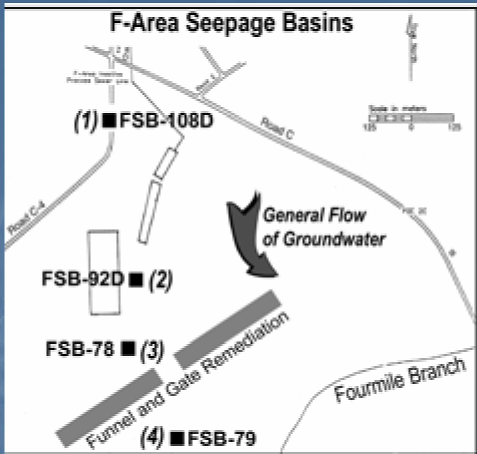
Reproducible data at $10^5 - 10^8$ atom/L levels
Pu highest in well #2 (near seepage basin)
Similar in 1998 and 2004 (but not identical)

^{239}Pu = 500 x 10^6 at 16L/min
Well pumping rate important

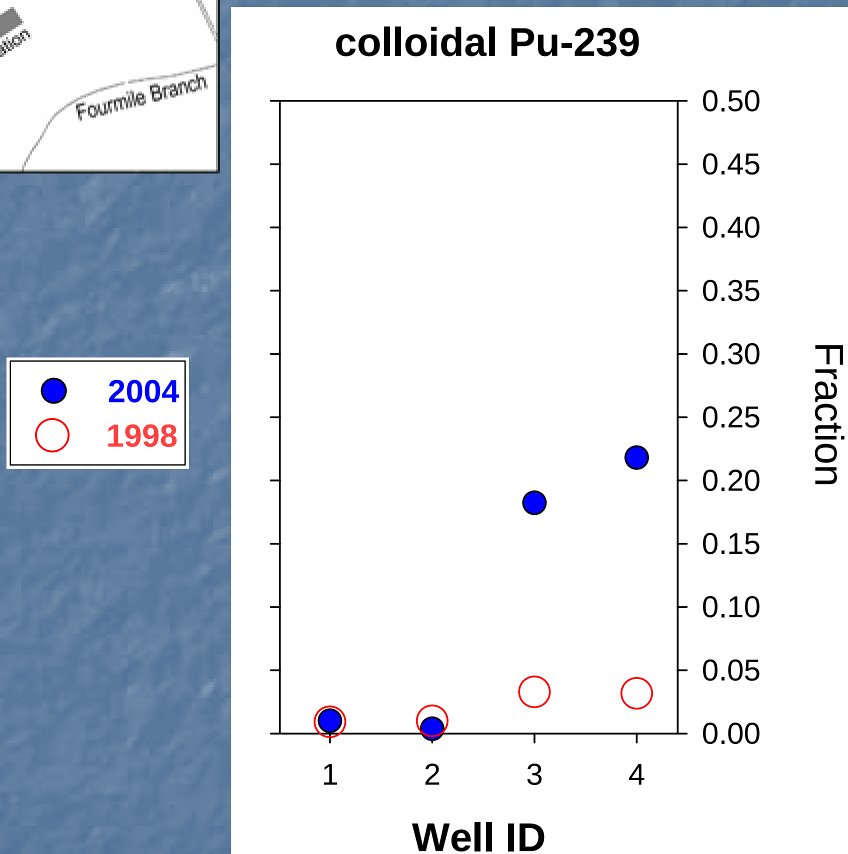




(Filtrate <0.2 μm)



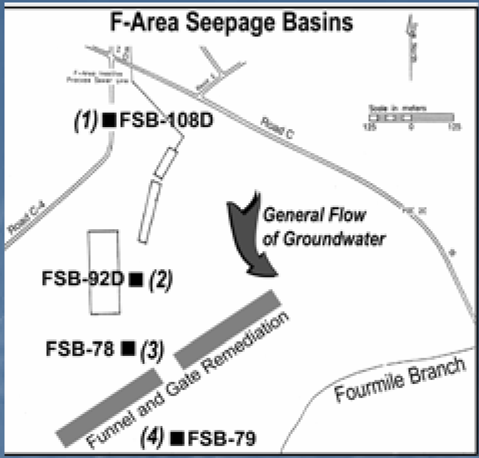
Pu-239 largely <1kD, non-colloidal



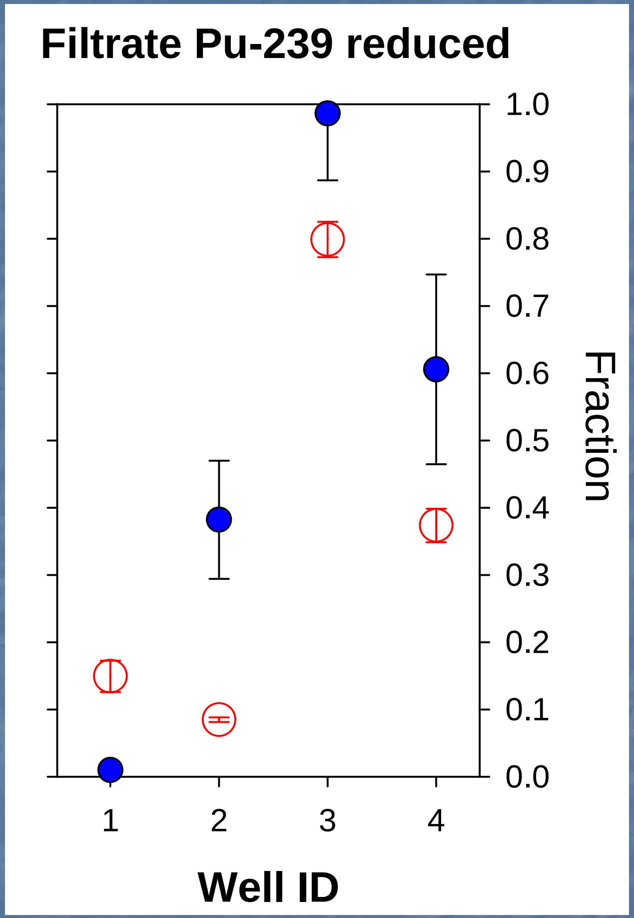
% ^{239}Pu colloidal	1998	2004
Well 1&2	<1%	<1%
Well 3&4	3%	20%

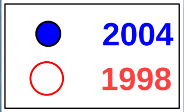
Other sites/same methods
Hanford K-area 10-30%
SRS Pond B 40-75%

Significant difference 1998 vs. 2004



Pu-239 fraction reduced higher downstream



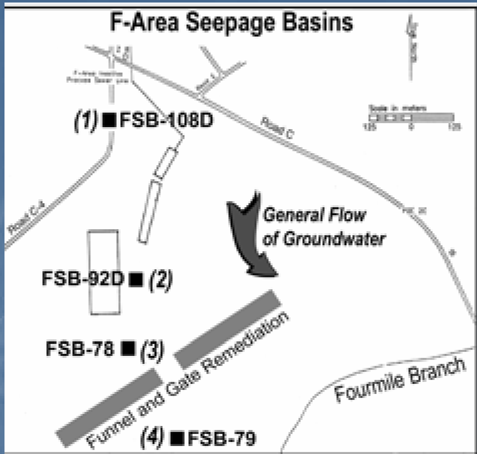


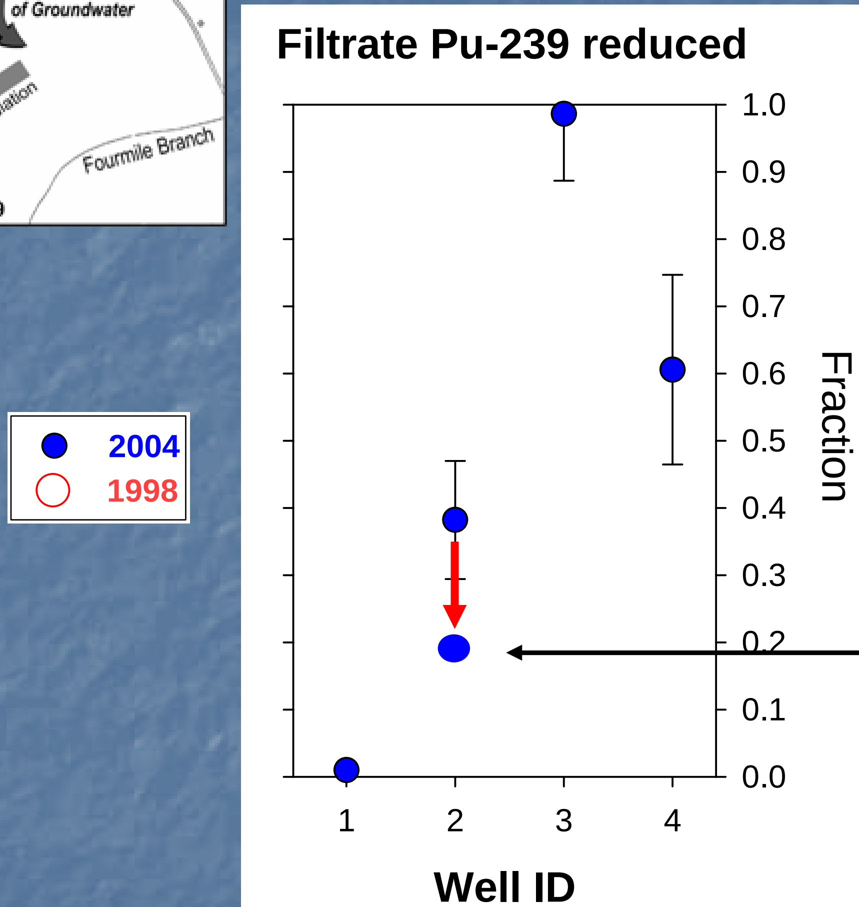
% ^{239}Pu reduced	1998	2004
Well 1&2	10-15%	1-40%
Well 3&4	35-80%	60-100%

Other sites/same methods
Hanford K-area 65%
SRS Pond B 70-100%

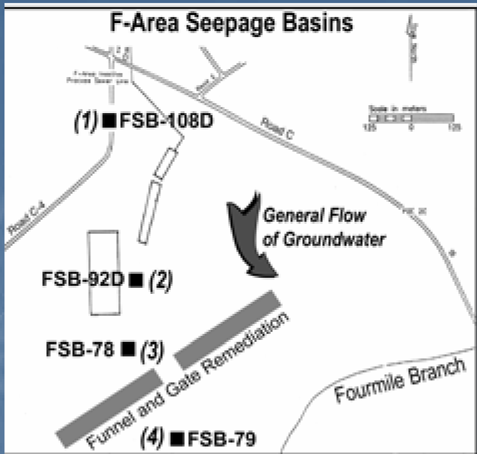
Fraction reduced higher in wells with higher colloidal %
Variable, but some differences 1998 vs. 2004

Pu-239 fraction reduced higher downstream





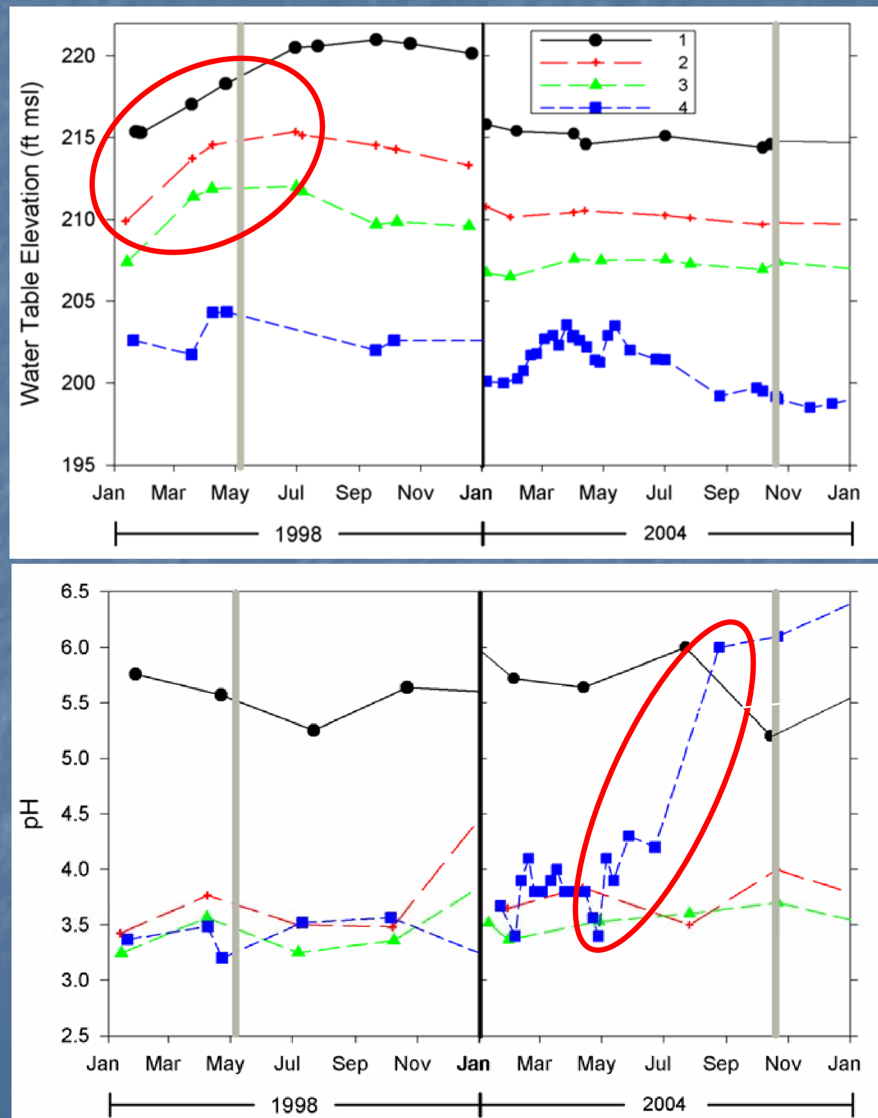
Fraction reduced drops from 38% to 18% after 3 days air exposure



Source independent controls

- did groundwater geochemistry impact ^{239}Pu speciation?

1998 sampling | 2004 sampling

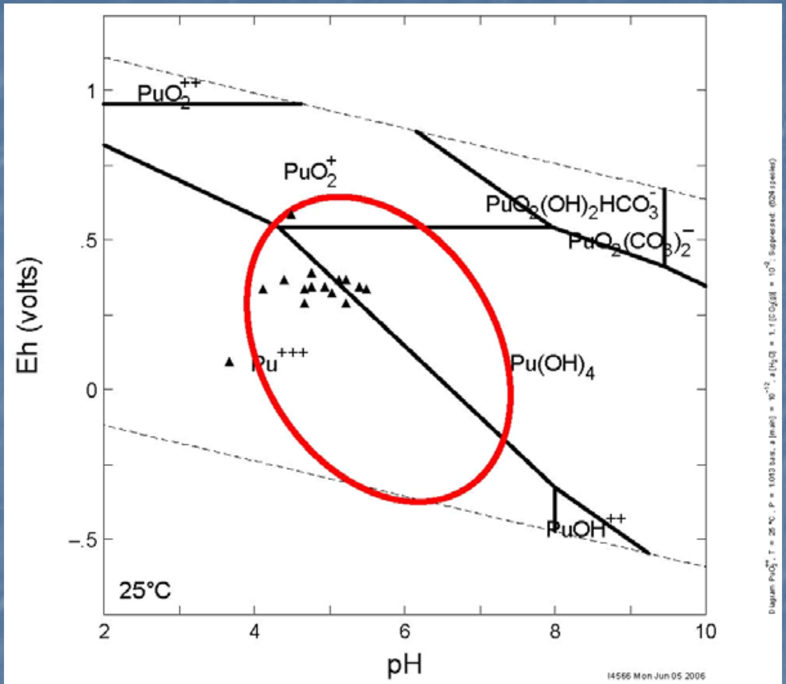


1998
"freshening"
event
(largest in 6 yrs)

1998
more oxidized,
lower % colloidal

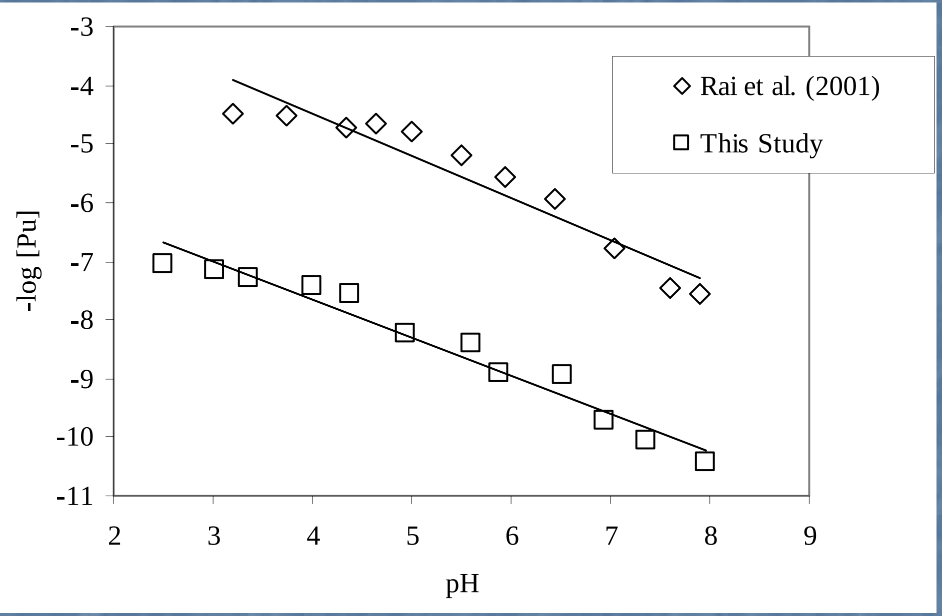
Note remediation
impacts pH well #4
-lower Pu and
esp. ^{244}Cm in 2004

Small changes to groundwater chemistry greatly impact Pu speciation



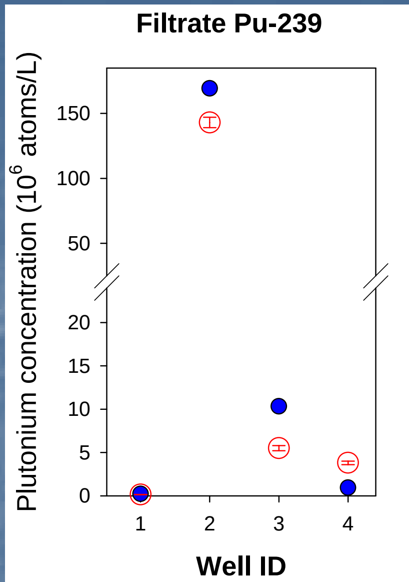
pH/Eh of F-area plume is Pu(III/IV/V)

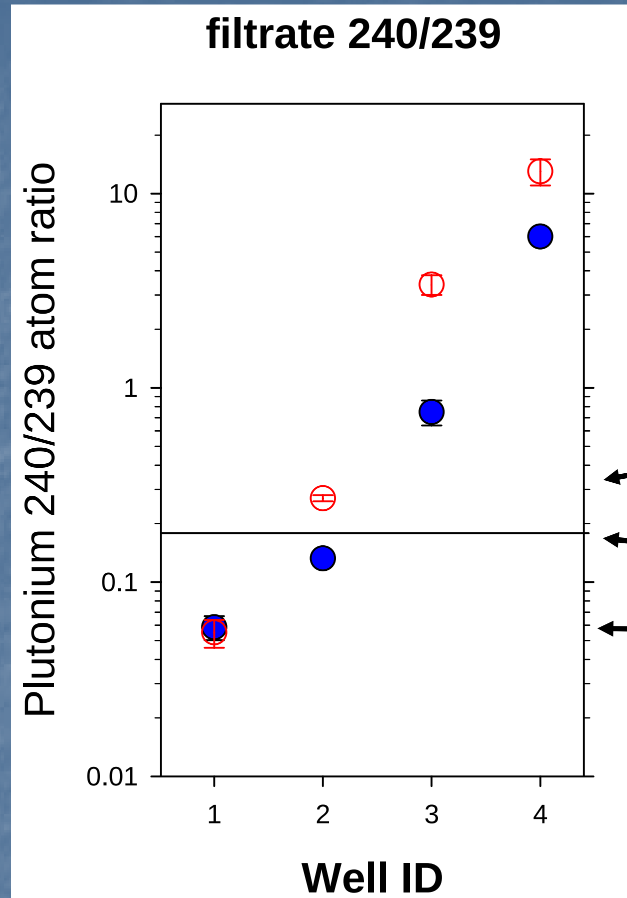
Pu(V) Kd = 30 mL/g
Pu(IV) Kd = 2000 mL/g



pH decrease from 6 to 5 results in a decrease solubility by 1 order of magnitude

Unusual increases in $^{240}Pu/^{239}Pu$ ratio downstream





2004
1998

$^{240}Pu/^{239}Pu$ >10

High yield tests & other reactor products = 0.3-0.4

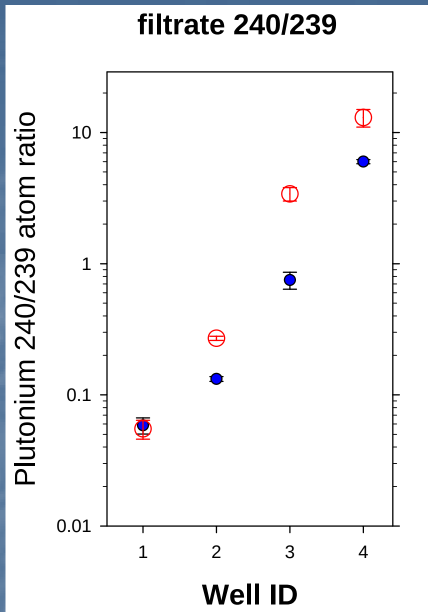
Global fallout = 0.18

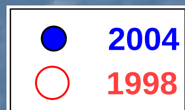
Local SRS = 0.06

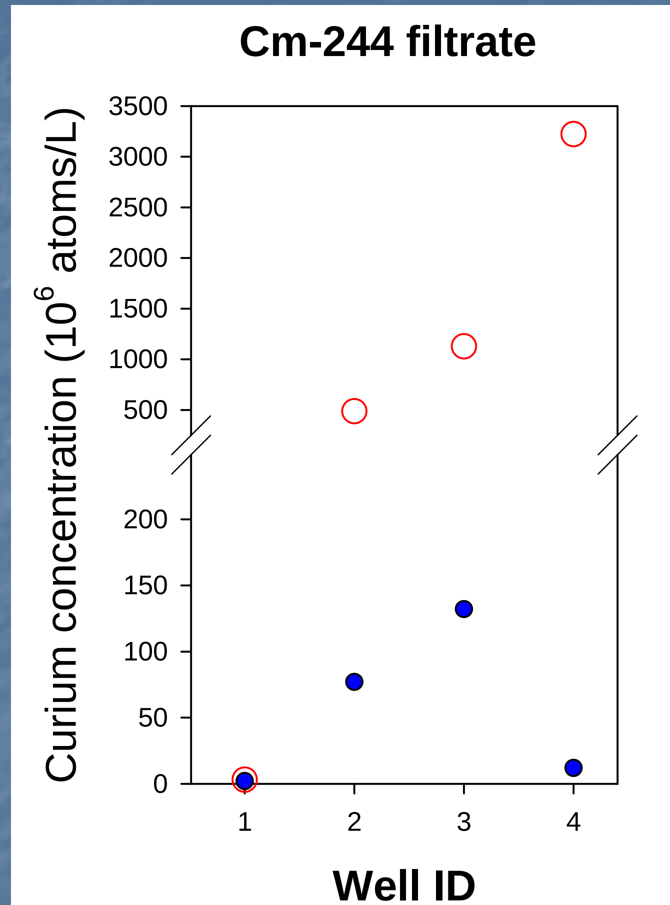
^{239}Pu t ½ = 24,100 yr
^{240}Pu t ½= 6,560 yr

Local SRS Pu source in background well #1
What is local source of ^{240}Pu?
Preferential transport ^{240}Pu in groundwater?

^{244}Curium- produced at SRS in 1960's







^{244}Cm-

$t_{1/2}$ = 18.1 yr

- Alpha decay to ^{240}Pu

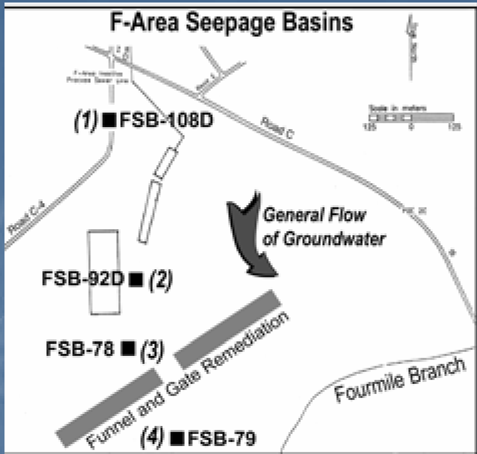
-Less particle reactive than Pu

^{244}Cm concentrations 1-2 orders of magnitude higher than ^{239}Pu

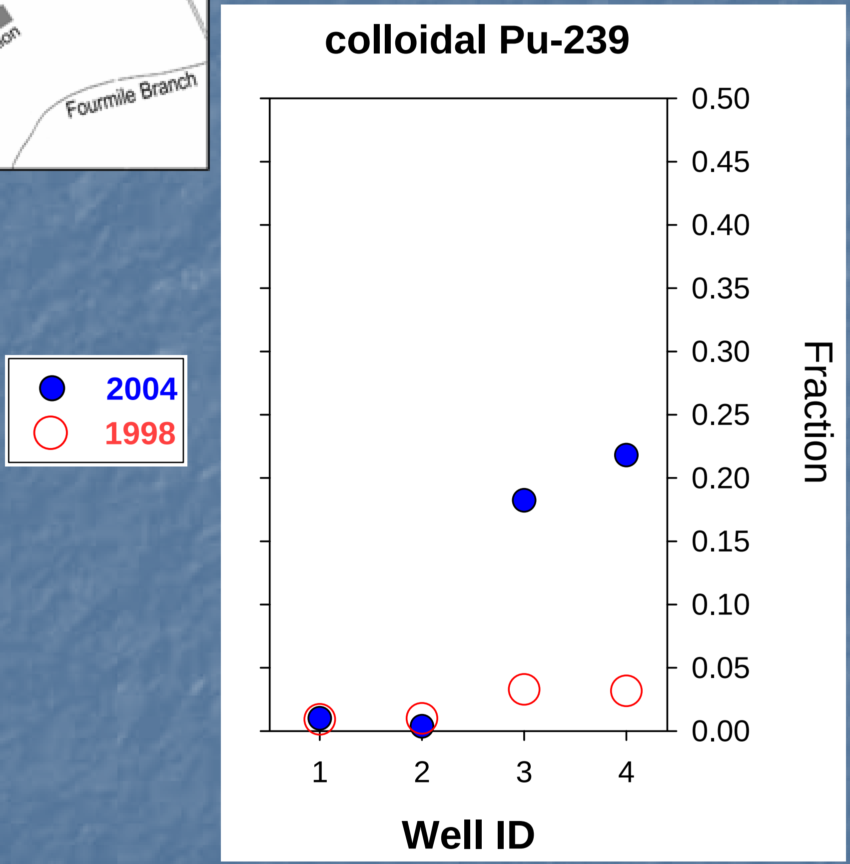
Increasing 240/239 ratio due to ^{240}Pu production from ^{244}Cm decay

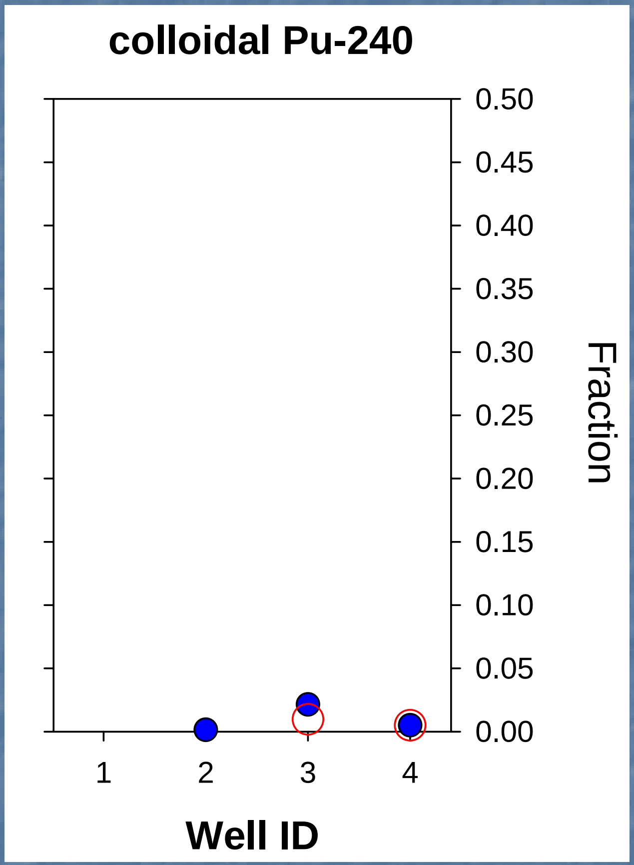
Less ^{244}Cm in 2004 than 1998-

K_D= 40 mL/g @ pH=4; K_D = 15,000 mL/g @ pH=6.7



Source dependent controls
on ^{240}Pu speciation

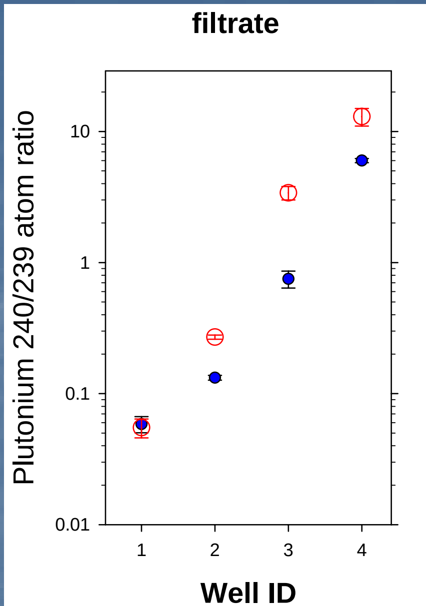


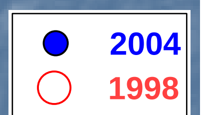


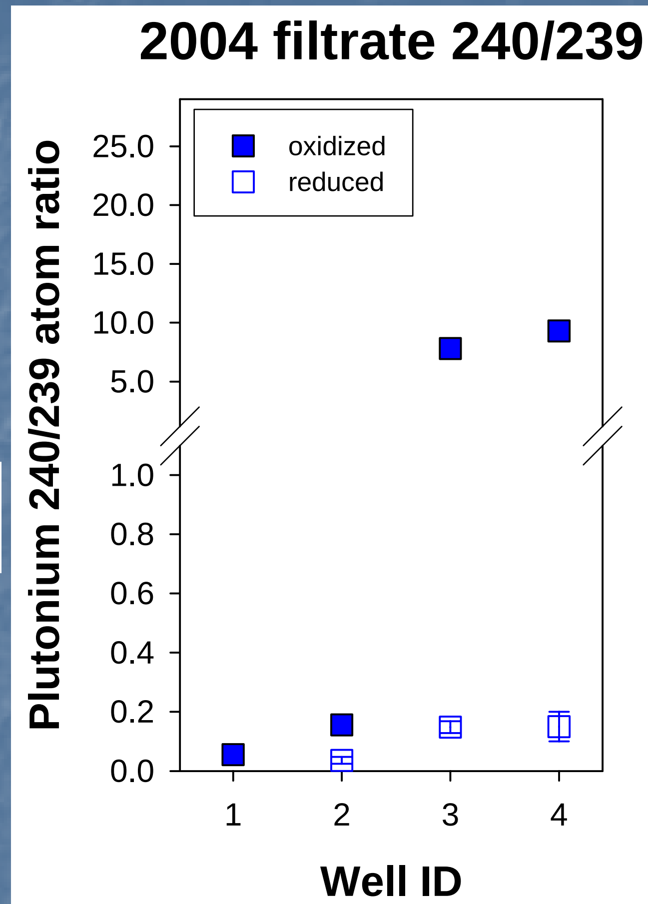
Less colloidal ^{240}Pu

Less reduced- 1-25% in 1998; 5-55% in 2004

Source dependent controls
on ^{240}Pu speciation







- ^{240}Pu produced from ^{244}Cm decay results in more oxidized forms
- Isotope specific differences in apparent Pu mobility
- Prior work w/ ^{239,240}Pu? Other sites- Oak Ridge?

Summary

Variability in Pu isotope ratios, redox state and colloid associations attributable to Pu source effects and groundwater chemistry

- **Methods matter**

  - Considerable effort devoted to improving gw Pu speciation methods
- **Are colloids important in F-area groundwater for Pu?**

  - low ^{239}Pu colloidal abundances (1-20%)

  - rapid decrease in ^{239}Pu concentration downstream from source (<1km)
- **Impacts of natural groundwater variability and remediation are seen in Pu concentrations and speciation**

  - 1998 "Freshening Event" - more oxidized/lower colloidal ^{239}Pu

  - remediation changes to pH result in lower ^{244}Cm, ^{239}Pu
- **^{240}Pu differs from ^{239}Pu**

  - ^{240}Pu found further downstream from source than ^{239}Pu

  - ^{244}Cm source results in more oxidized/mobile forms of ^{240}Pu

Future Needs

Field studies provide important insights into processes that impact Pu speciation and transport in the subsurface environment

- Continued use/development of reliable field methods for in-situ speciation
- Need time-series sampling to capture seasonal and episodic variability
- Consider groundwater methods intercomparison, multi-lab "Colloid cookout"?
- Improve parameterization for colloid reactive transport models

Recent references (used for this presentation)

Methods

Dai et al., 2001 (J. Envir. Rad. v53)
Buesseler et al., 2003 (ES&T v37)
Hassellov et al., 2006 (Sci. Total Envir., sub.)

Field

Dai et al., 2002 (ES&T, v36)
Dai et al., 2005 (J. Cont. Hydro., v76)

Lab

Kaplan et al. 2004, 2006a,b (ES&T, v38, v40)
Powell et al. 2004, 2005, 2006 (ES&T, v28, v39, v40)

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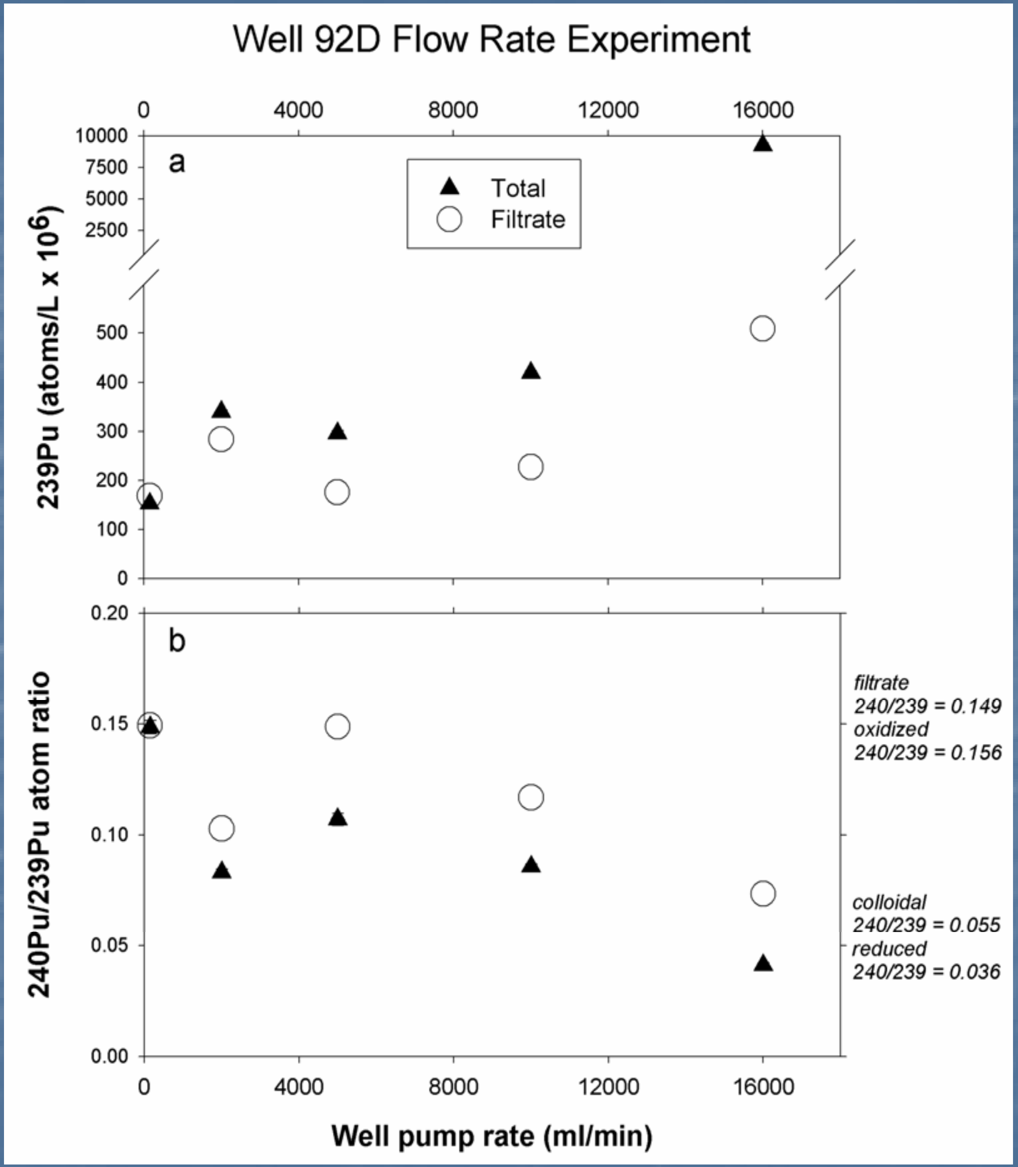
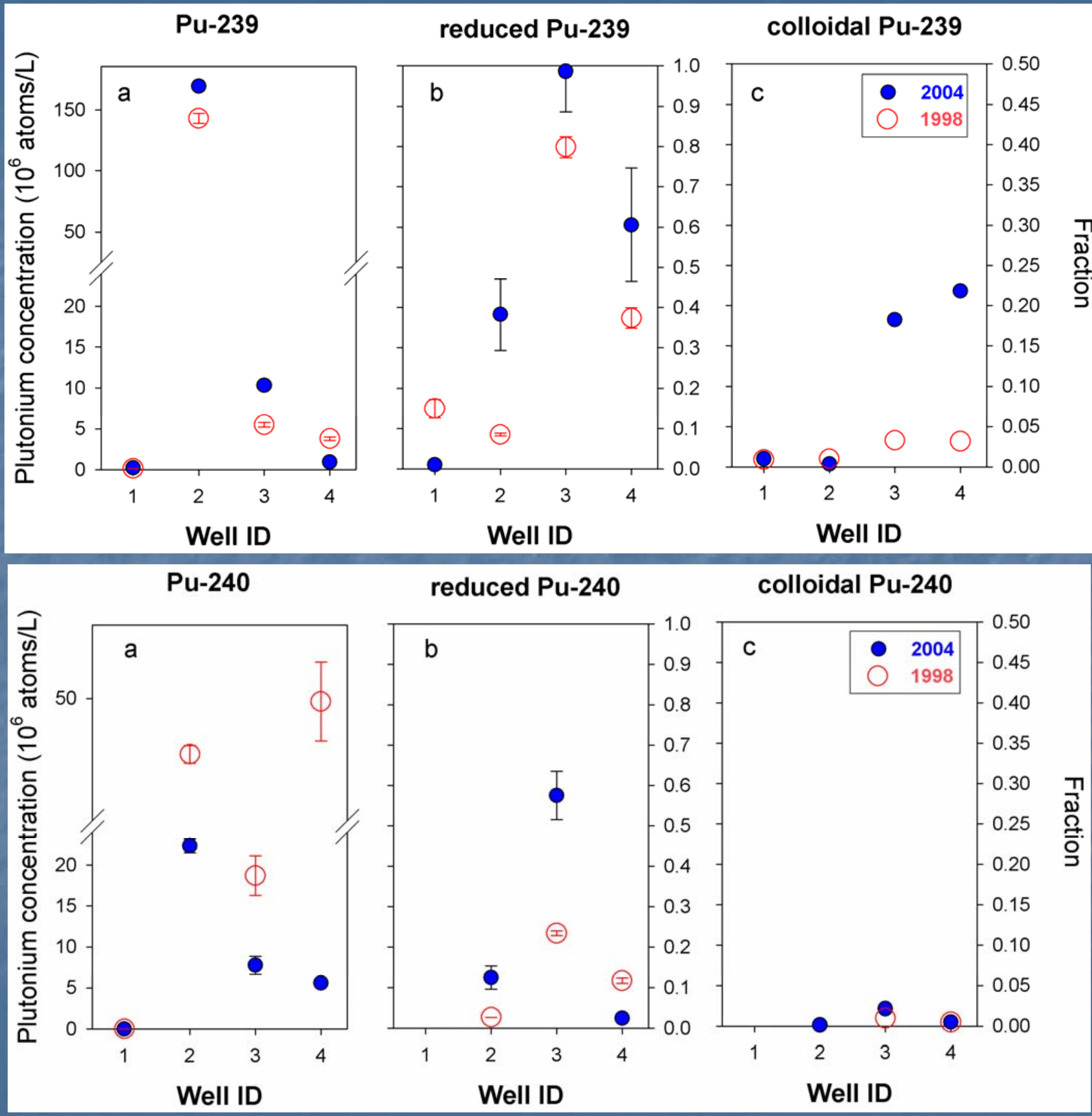


Well 92D Flow Rate Experiment
a
Total
Filtrate
239Pu (atoms/L x 10^6)
b
240Pu/239Pu atom ratio
filtrate
240/239 = 0.149
oxidized
240/239 = 0.156
colloidal
240/239 = 0.055
reduced
240/239 = 0.036
Well pump rate (ml/min)


Pu-239
reduced Pu-239
colloidal Pu-239
a
b
c
2004
1998
Plutonium concentration (10^6 atoms/L)
Fraction
Well ID
Well ID
Well ID
Pu-240
reduced Pu-240
colloidal Pu-240
a
b
c
2004
1998
Plutonium concentration (10^6 atoms/L)
Fraction
Well ID
Well ID
Well ID

Groundwater sampling and processing diagram