Speciation, mobility and fate of actinides in the groundwater at the Hanford Site

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Café Thorium

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Talk Outline

- What do we know (or need to know) to understand Pu mobility in groundwater
- Techniques used to study Pu speciation, mobility and fate
- Prior results from Savannah River Site
- Hanford sampling and preliminary results
- Longer term goals, scientific products, and relevance to DOE

Basis for Project & DOE/EMSP Relevance

- Pu mobility varies depending upon source and ambient geochemistry

⇒ hence, first step in safe remediation and contaminant management in the groundwater/vadose zone is to *measure in-situ actinide speciation and phase distributions and understand their relationship to the source(s)*

⇒ these speciation data needed to model and predict actinide behavior in environment

Bottom line: *studies of total actinide activity in groundwater are not sufficient for monitoring, assessment, and clean-up needs at DOE sites*

Pu migration hypothesis

Pu oxidation states control Pu solubility

Typical groundwater is reducing

Low valence states expected in groundwater hence higher K_d

Field results: Pu migrates farther than predicted
e.g. Kersten et al., 1999

Pu associate with colloids that move with water flow

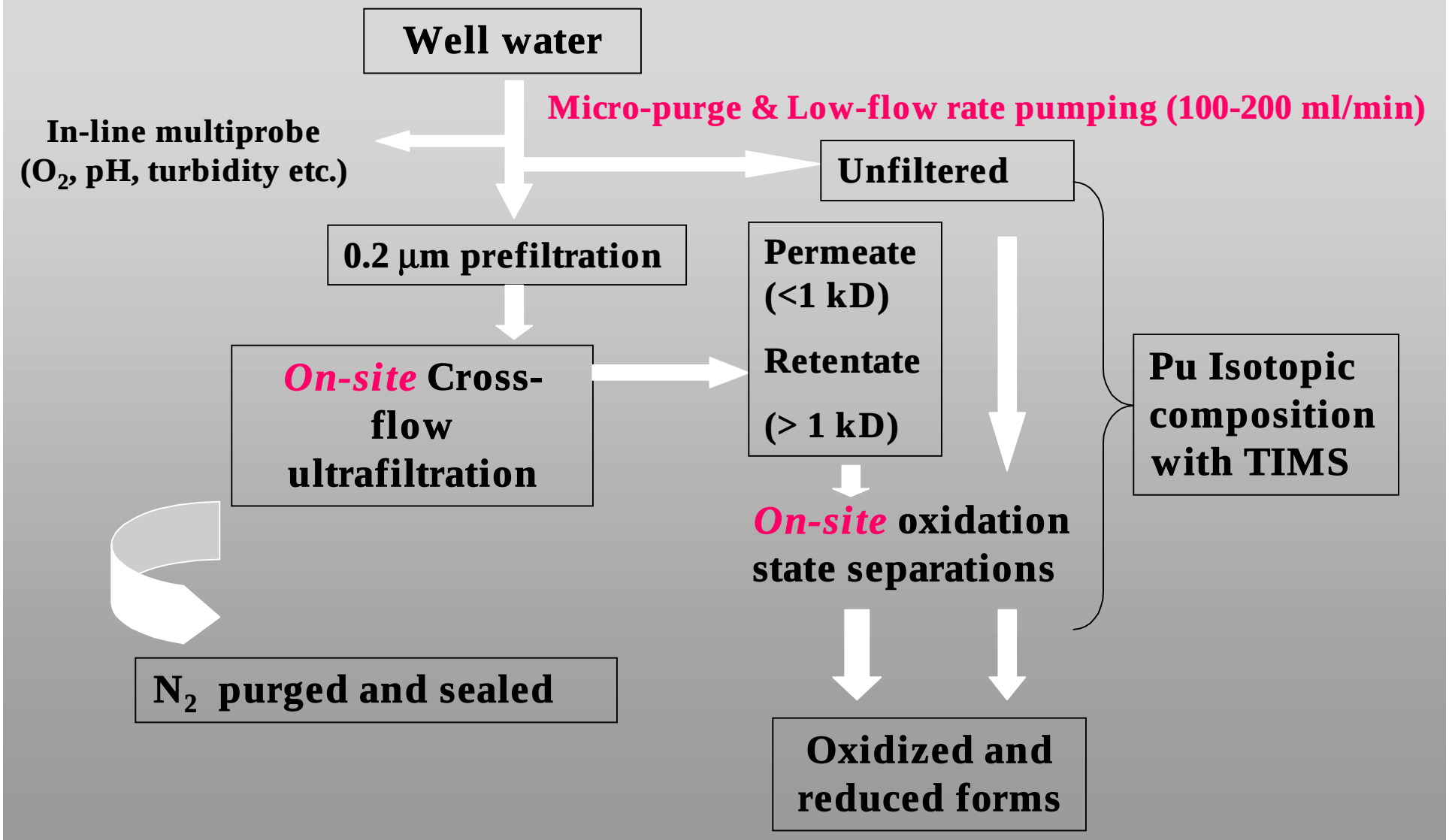
Evidence of high colloid abundances

Potential Problems:

1. Lack of in-situ oxidation states data- what is Pu speciation?

2. Colloid study may be biased by high rate pumping technique

Groundwater sampling and processing

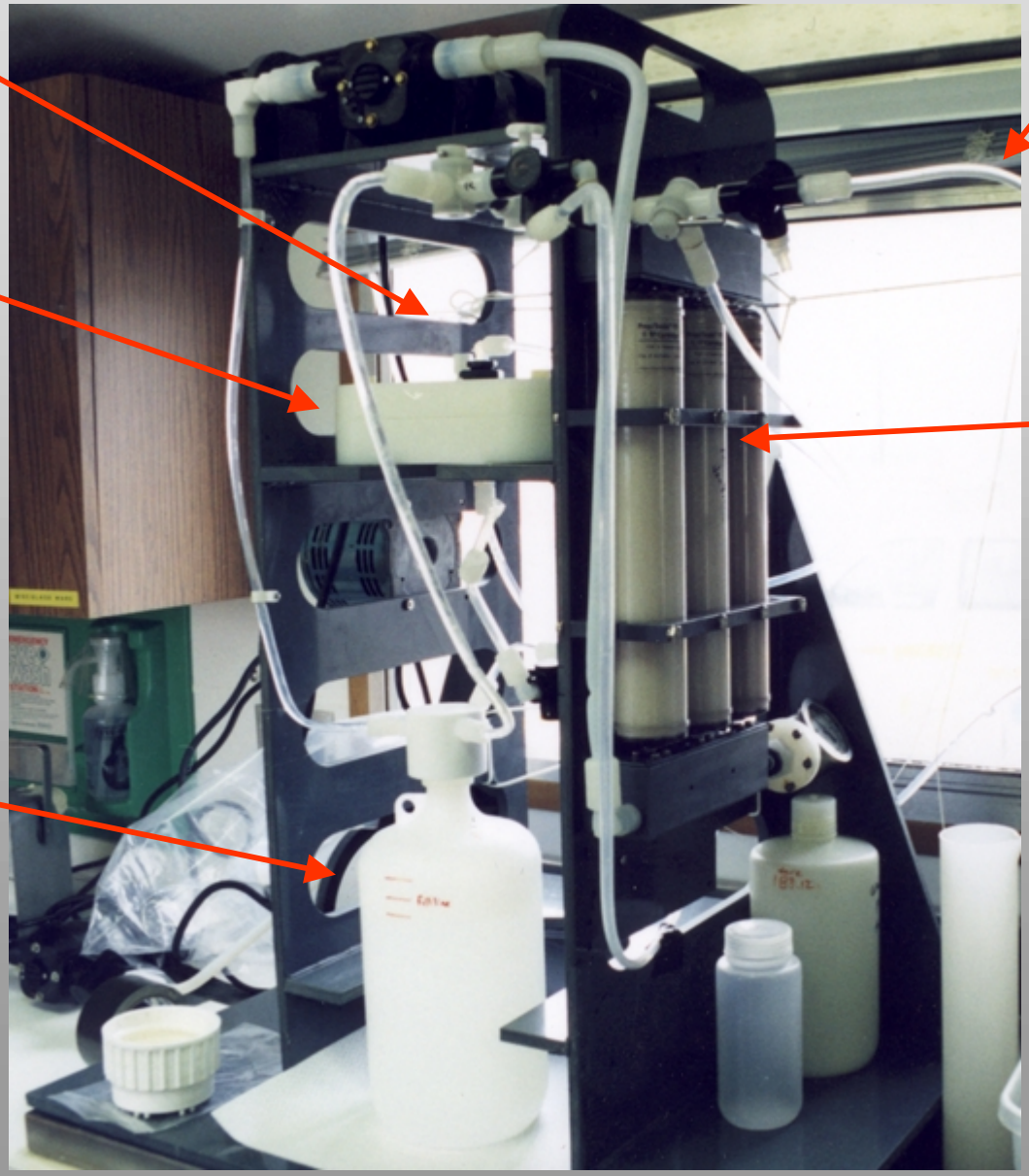


Cross Flow Filtration

Sample line

0.2 µm prefilter

Retentate reservoir (>1 kD)



Permeate stream (<1 kD)

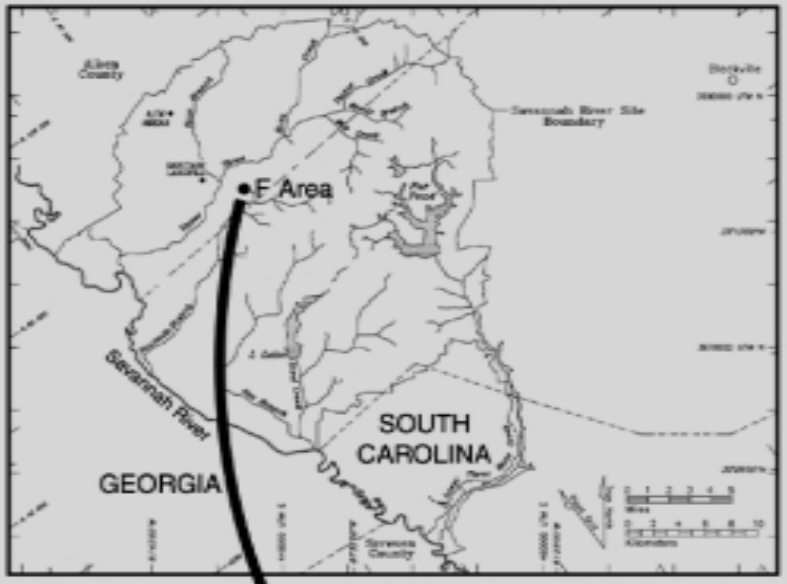
1 kD CFF membranes

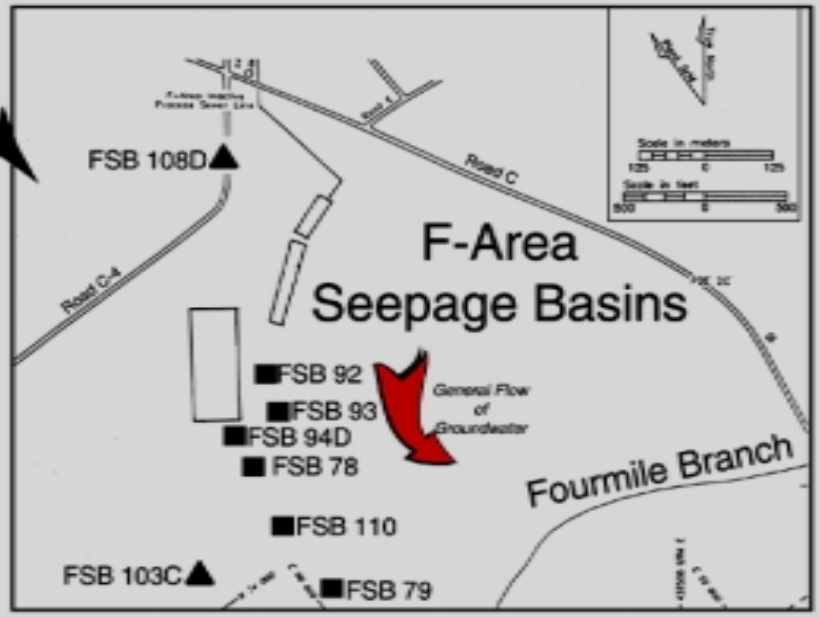
- *N_2 flushed*
- *ultra clean*
- *200 liter samples in 48 hours*

Issues related to accurate sampling & speciation studies

- Groundwater sampling
  - *maintain and measure in-situ geochemistry*
  - *use low flow sampling to reduce colloid formation*
- Cross-flow filtration for separation of colloids
  - *maintain redox state & keep trace metal clean*
  - *demonstrate low sorptive losses and negligible blanks*
  - *calibrate CFF with colloid standards*
- Redox speciation studies
  - *performed immediately in field under nitrogen gas*
  - *lanthanium fluoride ppt w/^{244}Pu and ^{242}Pu spikes*
- Radiochemical purification (WHOI)
  - *careful attention to blanks & yields prior to TIMS*
- Thermal Ionization Mass Spectrometry (PNNL)
  - *subfemtogram detection limits (10^{-15} gm or 10^{6} atoms)*
  - *use ^{240}Pu/^{239}Pu to determine Pu sources*

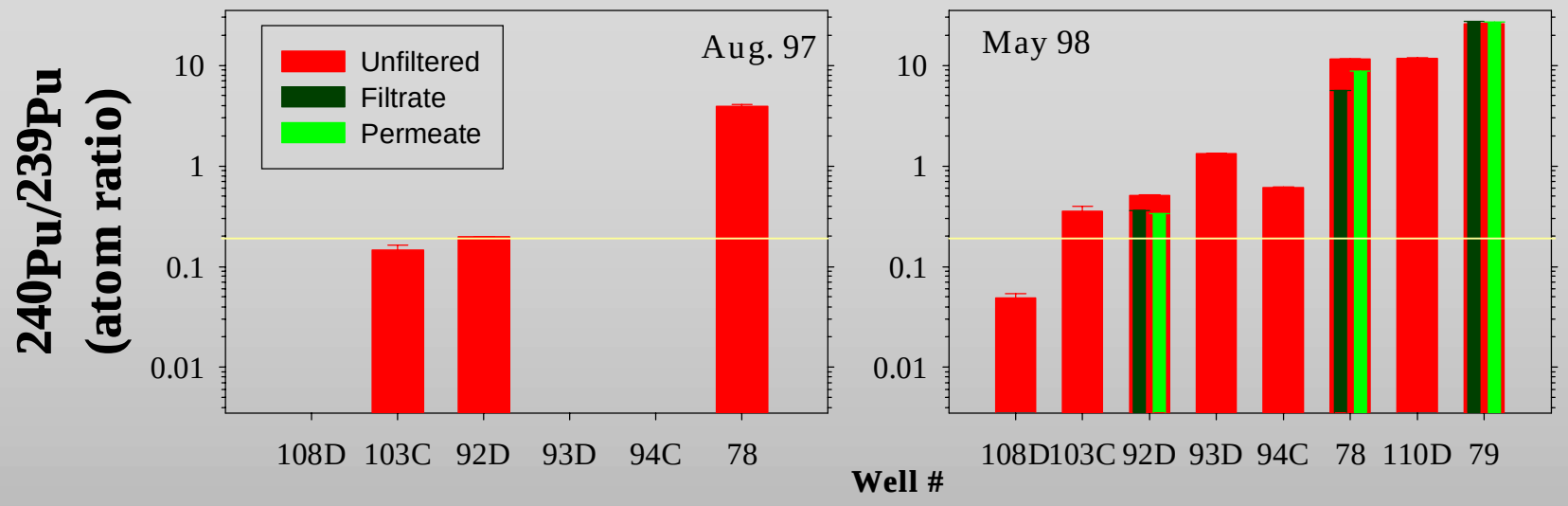
Savannah River Site
F-area seepage basins





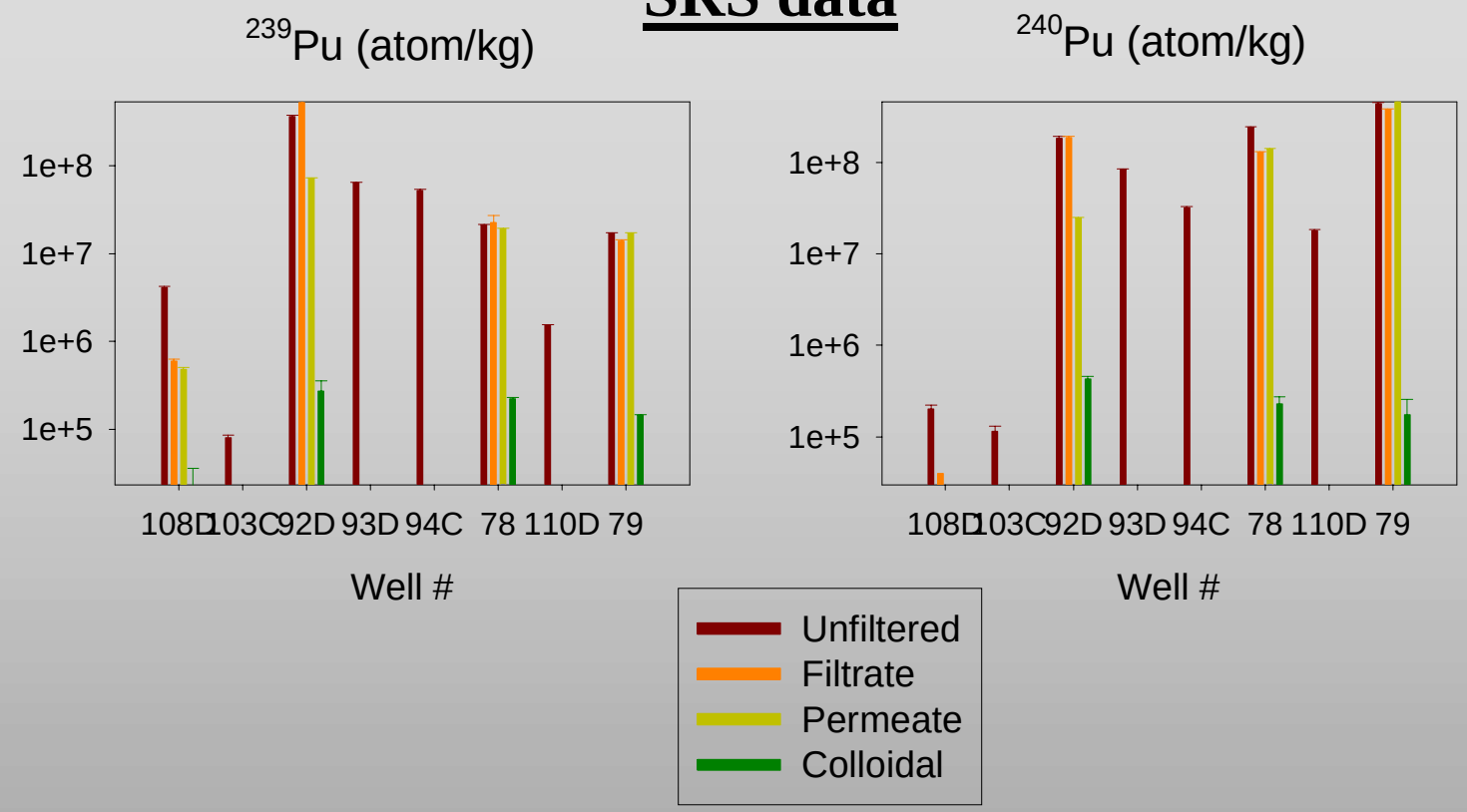
- Mixed waste effluents
- nitric acid- pH =3-4
- ^{3}H; ^{239}Pu, ^{244}Cm, ^{238}U
- Prior studies indicate actindes in groundwater *(e.g. Kaplan et al.)*

SRS data



- Variable $^{240}Pu/^{239}Pu$ atom ratios (v.s. the global fallout average being 0.18), elevated values downstream
- We attribute the highest $^{240}Pu/^{239}Pu$ ratios to samples that have been impacted by the decay of ^{244}Cm (t½ = 18.1 yrs.) to ^{240}Pu in the seepage basin wastes.
- A low $^{240}Pu/^{239}Pu$ ratio signifies a source other than global fallout and is most likely due to weapons grade Pu waste of some local origin.

SRS data



- < 5% colloidal Pu - consistent with the higher oxidation states, and with overall low natural colloidal organic carbon levels at this site.
- Contrasts with Kaplan et al. (1994) at well 79 who found 100% ^{239,240}Pu in their 0.5 – 3 kD colloidal fraction
- Note that Kaplan et al. sampled in early 1990's using different CFF membranes and sampling techniques, and we processed and separated CFF samples immediately in the field using an on-line sampling mode

SRS results & conclusions

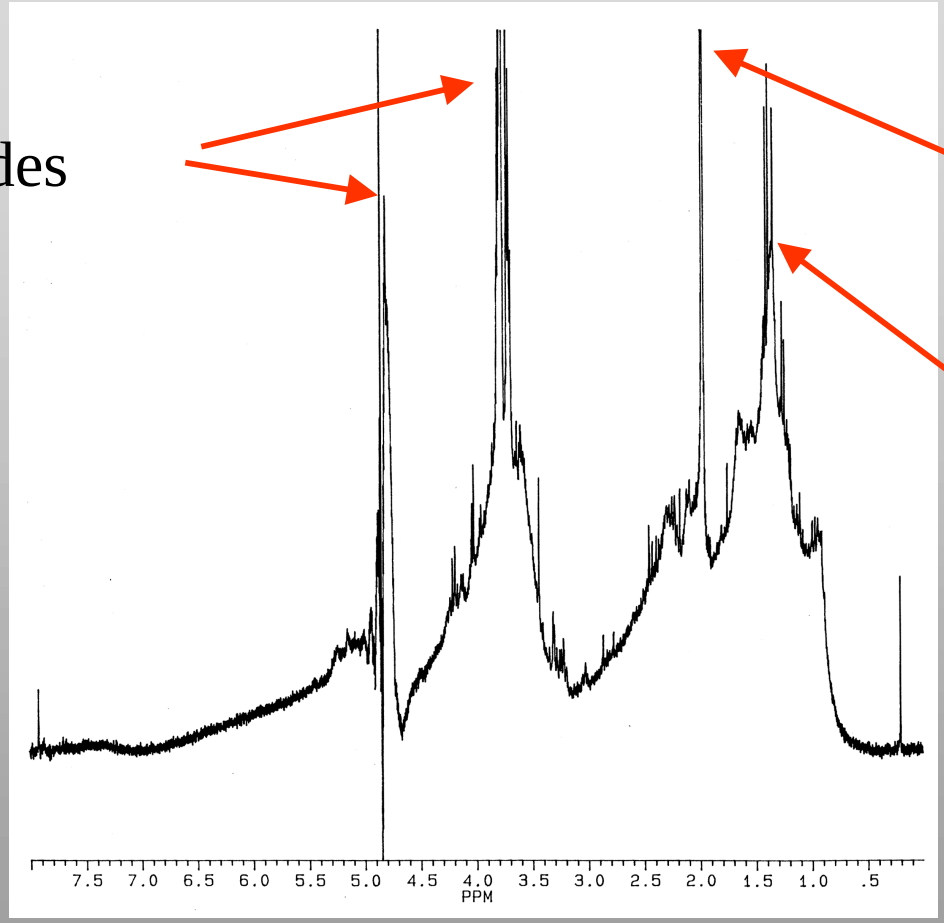
- **For ^{240}Pu, >75-95% of the Pu is in oxidized form**
- **Colloidal Pu is a minor fraction of total Pu at SRS**
- **Unique ^{240}Pu source from more mobile ^{244}Cm leads to enhanced mobility in the oxidized form → increased ^{240}Pu/^{239}Pu ratio downstream.**

Implications:

a) The oxidized <1kD forms of Pu found at the SRS would be significantly more mobile than standard models predict

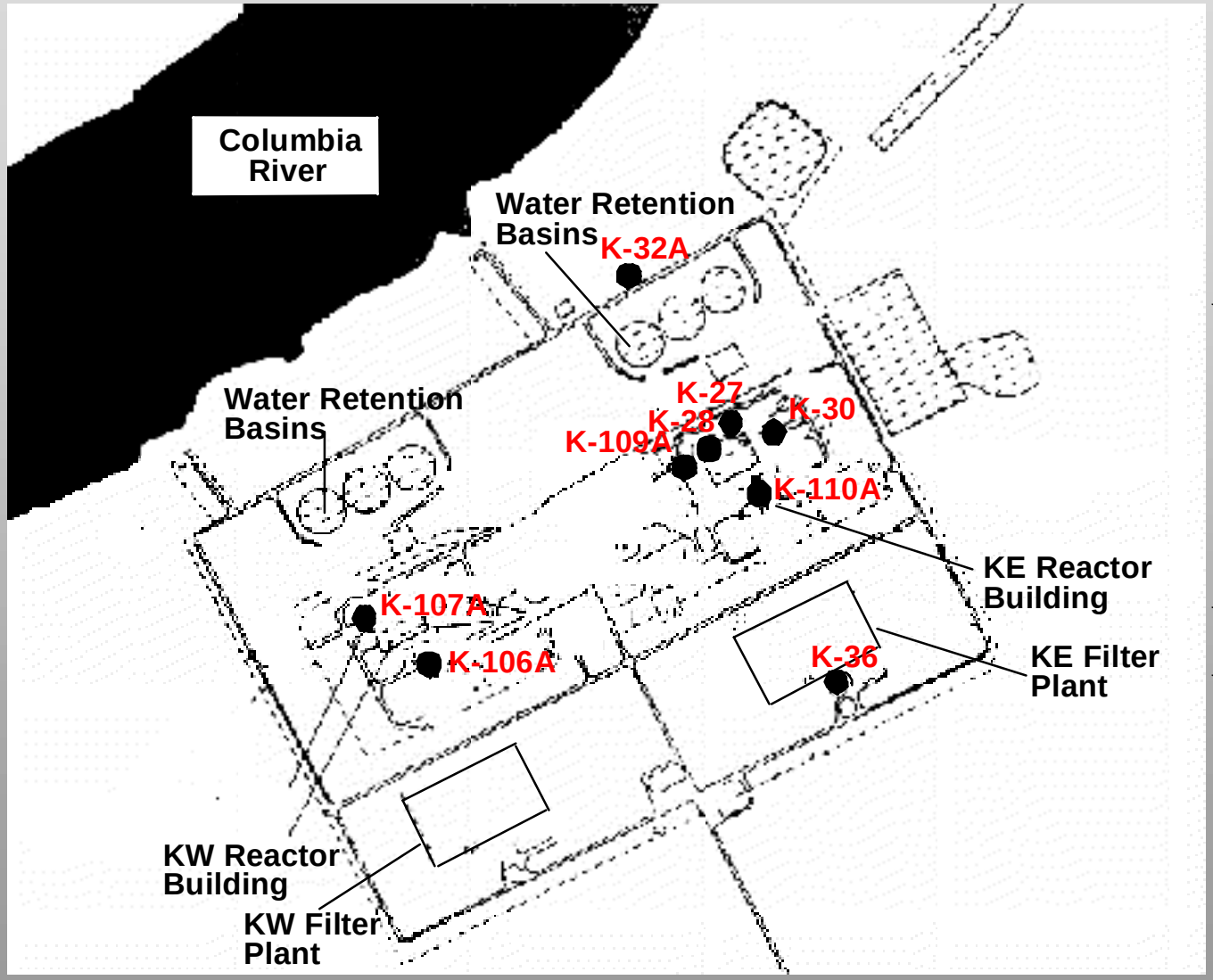
b) Colloids don't play a significant role in the Pu migration at SRS

Colloid characterization studies



Proton NMR spectrum of colloids from SRS "acylpolsaccharides" *Repeta et al.*

Hanford 100-K area sampling sites



- Oct. 1997 site survey at 6 wells
- April 1999 8 wells sampled w/ speciation studies at 4

Preliminary results on Pu isotopes in the groundwater of Hanford Site 100-K area in Oct. 1997

Well#	$^{240}Pu/^{239}Pu$ atom ratio	$^{241}Pu/^{239}Pu$ atom ratio	^{239}Pu fg/l	^{240}Pu fg/l
K-107A	0.081	N/A	0.150	0.012
K-30	N/A	N/A	0.155	0.006
K-106A	N/A	N/A	0.026	0.002
K-28	0.0498	N/A	1.567	0.078
K-27	N/A	N/A	0.222	0.041
K109A	0.1549	0.0082	1.870	0.291

- *Pu isotopes were detectable (10^{-4} to 10^{-6} pCi/l ≈ 10^{6} to 10^{8} atoms/l levels)*
- *The high $^{241}Pu/^{239}Pu$ in the well #K109A may signify material from N-reactor (the K-East reactor basin is currently being used to store irradiated fuel from the N-reactor).*
- *The isotopic ratio in the other wells reflect the K-reactor signal, possibly mixed with fallout*

Hanford 100-K sampling in March/April 1999

Sampling at 8 wells, with speciation work at n=4

- ~ 40 Pu isotopic composition samples
- ~ 50 Pu oxidation state samples

(processed *on-site*)

- 4 concentrated colloidal fractions for in/organic characterization
- 1 water sample from the Columbia river downstream of the 100-K area

Future Work

- Finish SRS study
- Process and analyze 1999 Hanford samples
  - *Pu isotopes plus some Np, U*
- New samples to be collected in 2000-2001
  - *Groundwater at 100K/100N & 200E*
  - *Comparison of two sites with contrasting sources and different vadose zone residence times*
- Colloid characterization
  - *Organic & inorganic properties*
- Groundwater speciation & transport models

Project Products and Relevance to DOE:

1) **Provide actinide speciation data for accurate modeling, assessment and prediction**
2) **Identify Pu sources & groundwater migration patterns**
3) **Possible to use data to design remediation strategies**

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