Speciation and isotopic composition of plutonium in the groundwater at the DOE Hanford Site

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Talk Outline

- **Research Objectives**
  What do we know (or need to know) to understand Pu mobility in groundwater
- **Research Status**
  Techniques used to study Pu speciation, mobility and fate: lab & field work
- **Results from Hanford 100K area**
- **Linkage to the Hanford Site needs**
- **Longer term goals, R&D transition and relevance to DOE**

Research Objectives

1. Determination of the speciation of Plutonium in groundwater at the Hanford Site
   - ⇒ ***oxidation state determinations***
   - ⇒ ***particulate, colloidal & dissolved phase distributions***
   - ⇒ ***Pu isotopics- source information***

2. Characterization of groundwater colloids
   - ⇒ ***organic/inorganic properties***

3. Use field data to predict transport rate and fate of actinides in groundwater

Status: Objective #1 well underway, #2 & #3 to be completed in years 2 & 3 of proposal

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

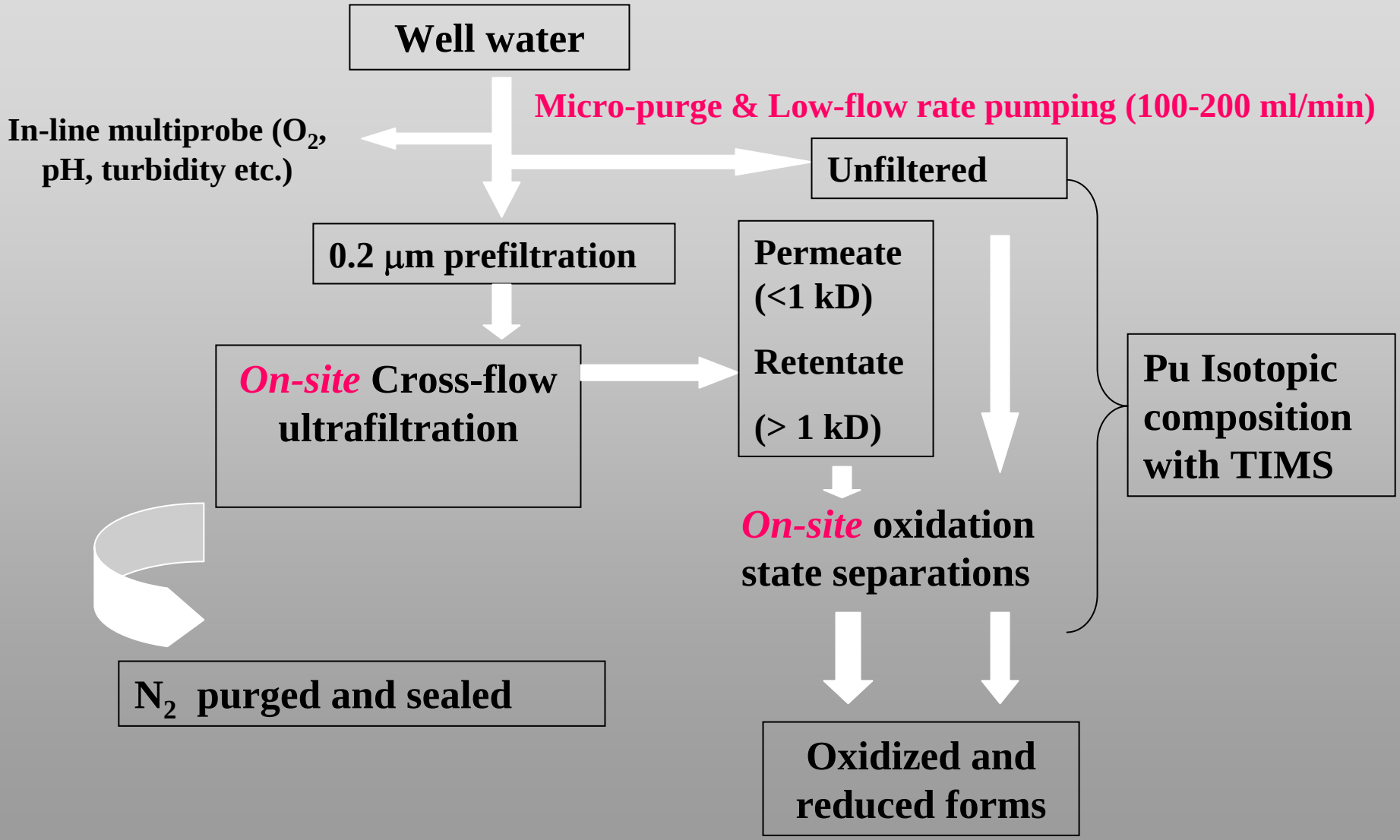
Evidence of high colloid abundances

Potential Problems:

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

2. Colloid abundances may be biased by high flow rate groundwater sampling techniques

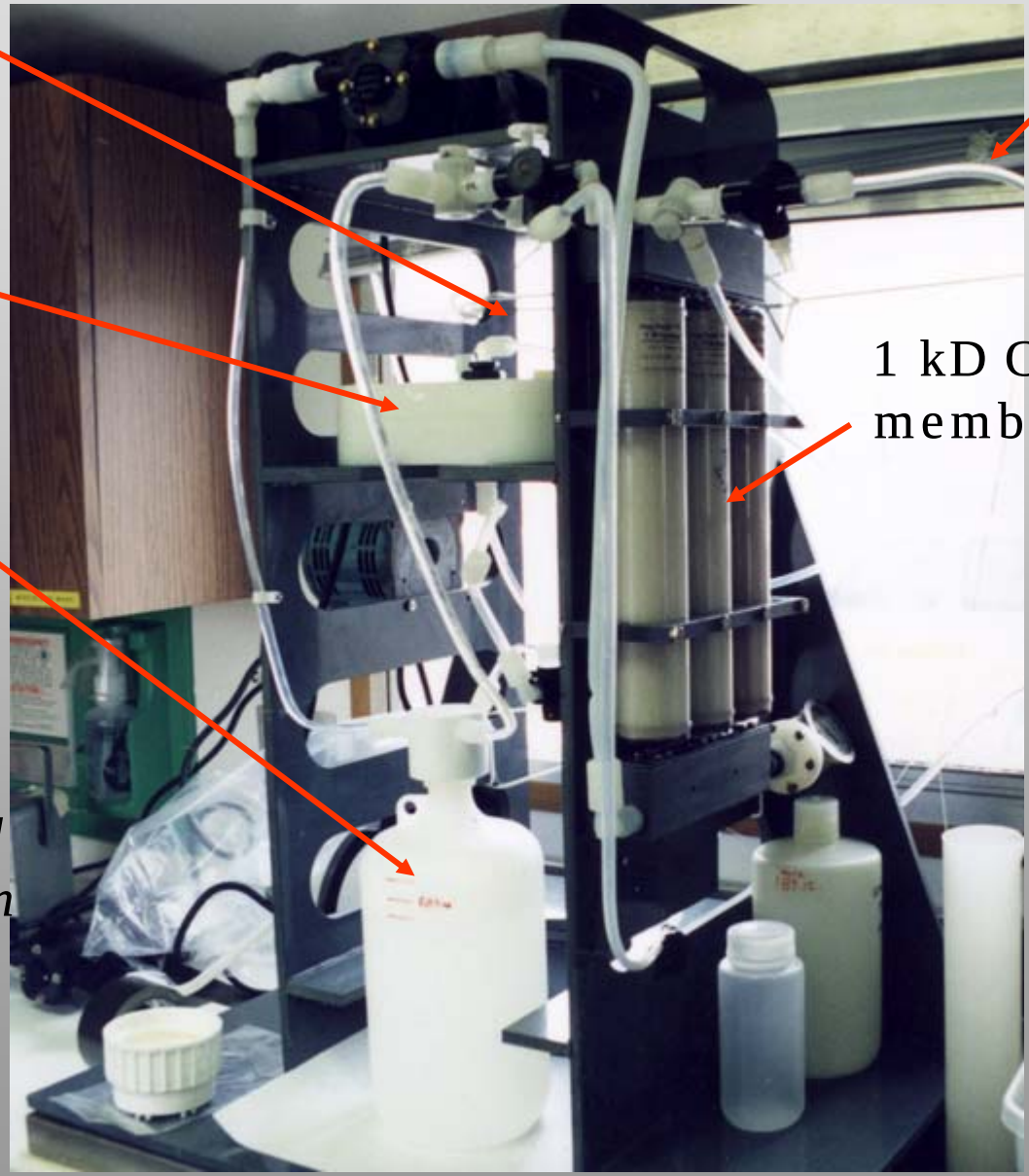
Groundwater sampling and processing



Field Sampling at Hanford Site

- *maintain and measure in-situ geochemistry*
- *use low flow sampling to reduce colloid formation*

Cross Flow Filtration



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

- ***maintain redox state & keep trace metal clean***
- ***demonstrate low sorptive losses and negligible blanks***
- ***calibrate CFF***

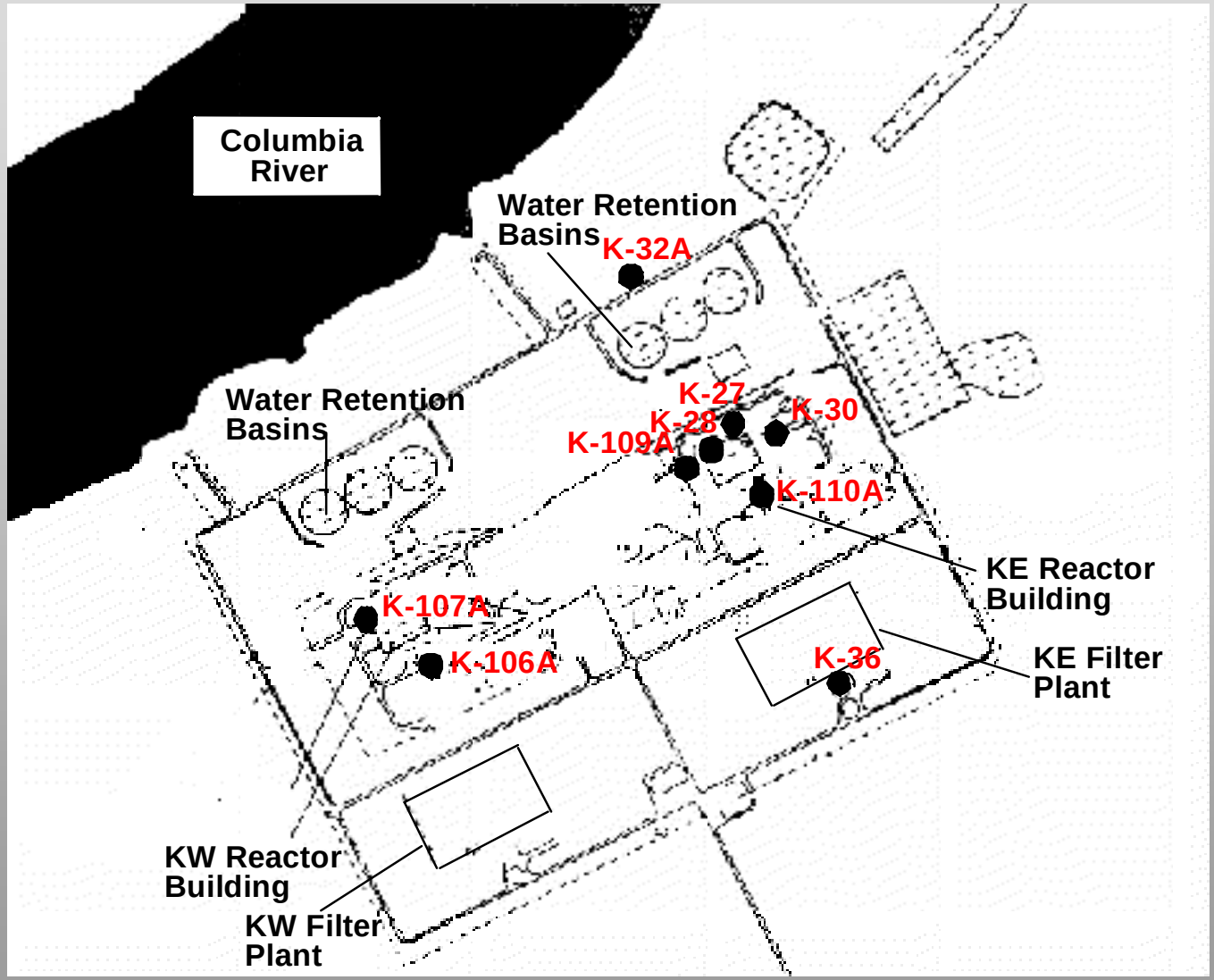
Issues important for accurate Pu speciation studies

- Redox speciation studies
  - ***performed immediately in field under nitrogen gas***
  - ***lanthanium fluoride ppt w/^{244}Pu and ^{242}Pu spikes***

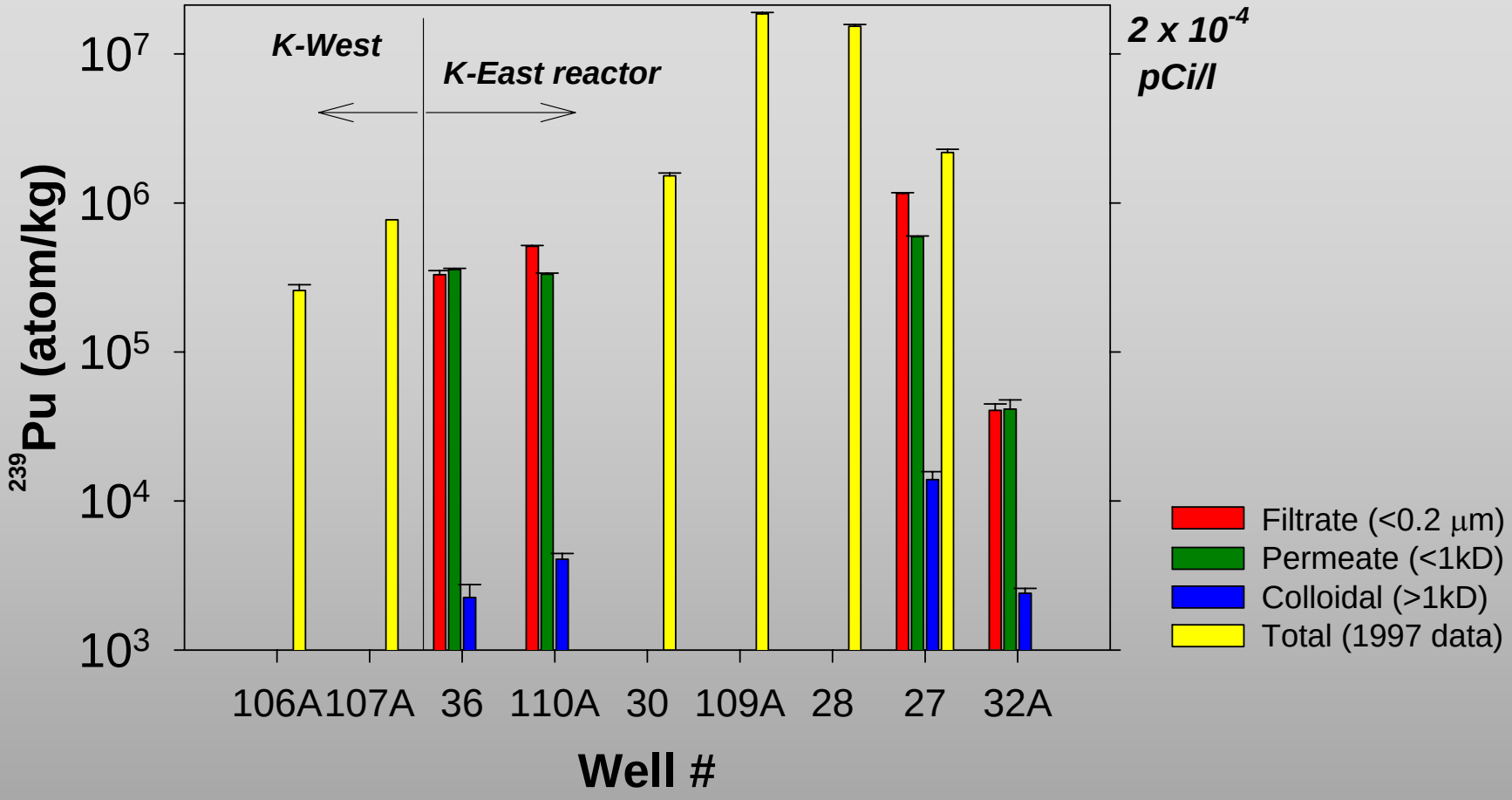
- Radiochemical purification (WHOI)
  - ***careful attention to blanks & yields prior to TIMS***

- Thermal Ionization Mass Spectrometry (PNNL)
  - ***subfemtogram detection limits (<10^{-15} gm or 10^{6} atoms)***
  - ***use ^{240}Pu/^{239}Pu and ^{241}Pu/^{239}Pu to determine Pu***

Hanford 100-K area sampling sites

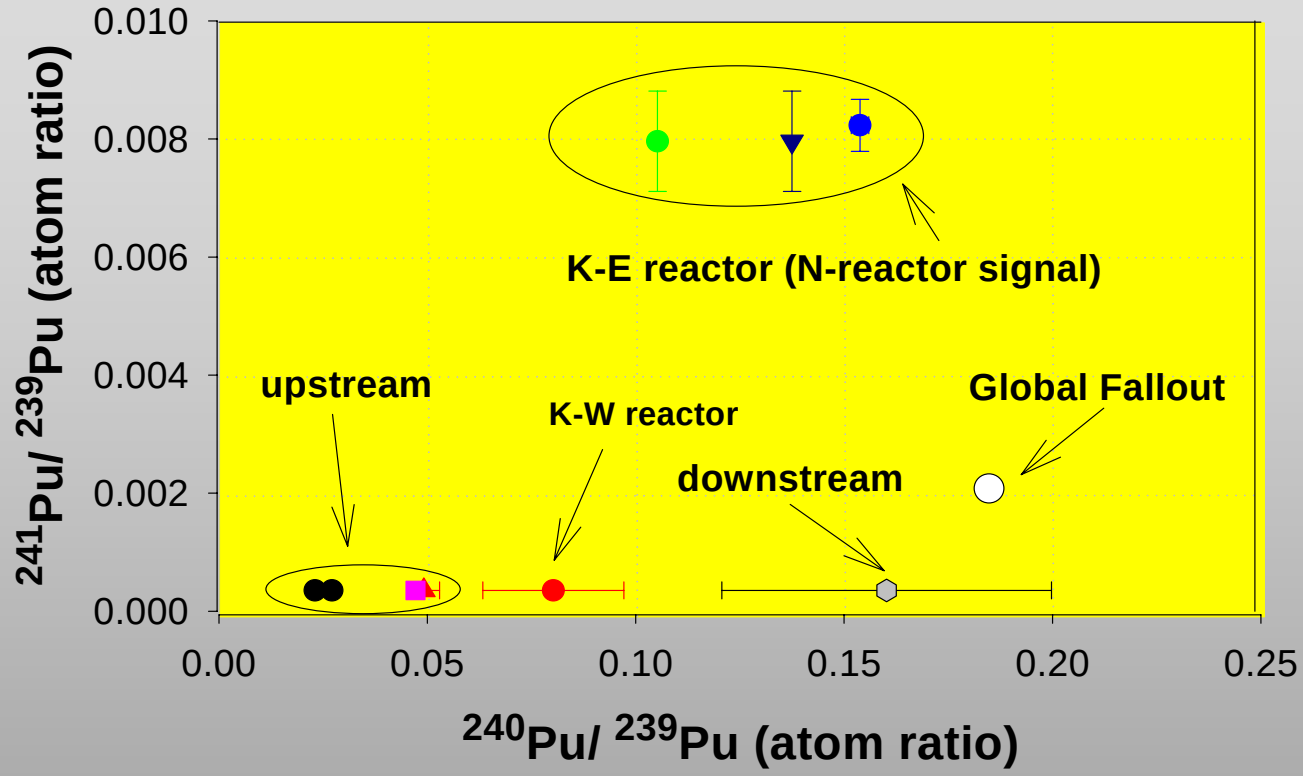


- Oct. 1997 site survey at 6 wells
- April 1999 8 wells sampled w/ speciation studies at 4



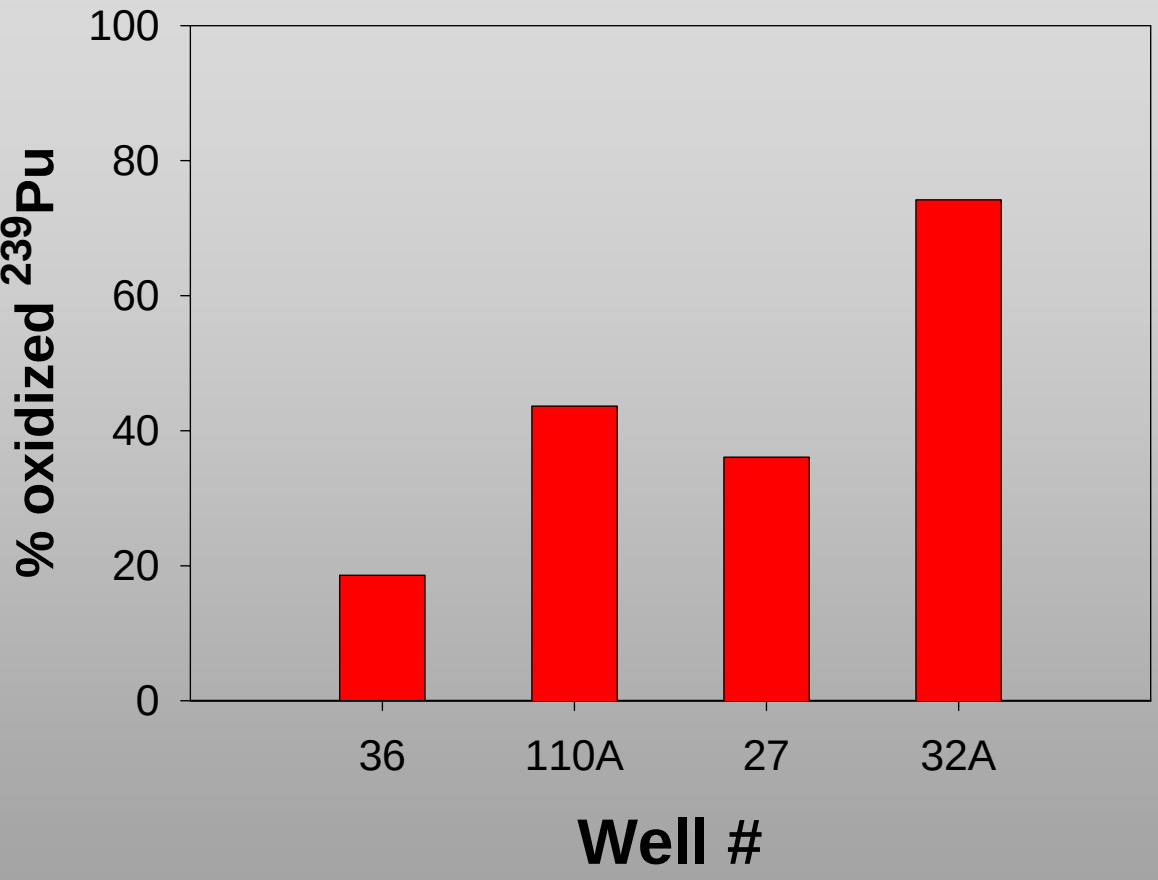
- ***Pu found in all groundwater samples from 100K area-*** ***low levels (fg/l, 10^{-4} to 10^{-6} pCi/l)***
- ***Colloidal Pu is minor fraction of total Pu in groundwater-*** ***<5-15% colloidal***

Pu-isotopic composition



- ***The likely source of high $^{241}Pu/^{239}Pu$ in wells K-109A and K-27 is N-reactor waste (the K-East reactor basin is currently being used to store irradiated fuel from the N-reactor).***
- ***The isotopic ratio in the other wells reflects the K-reactor signal, possibly mixed with fallout***

Oxidation state results: filtrate (<0.2 μm)



- ***Pu is primarily in reduced form with a trend towards more oxidized forms downstream***

Linkage to Hanford Site Needs

- This study provides actinide speciation data for accurate modeling, assessment and prediction of the fate of Pu released into groundwater at Hanford

- We can identify Pu sources & groundwater migration patterns at Hanford:

100K- K & N reactor sources

Total levels quite low

More than an order-of-magnitude reduction in concentration between reactor and Columbia river

EMSP relevance and R&D strategies

- Accurate in-situ speciation data needed for validation, verification and long-term monitoring of containment and treatment

- In-situ manipulation of groundwater redox states possible in order to reduce mobility or enhance extraction possibilities

- Current models are severely data limited wrt actinide speciation & considerable in-situ variability is possible
  - ⇒ ***No evidence of enhanced transport due to colloids***
  - ⇒ ***Oxidized forms of Pu in groundwater must be considered***

Future Work

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

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