EMSP #DOE DE-FG07-96ER14733
Project #70132

Speciation, mobility and fate of actinide element isotopes in groundwater

Woods Hole Oceanographic Institution:

K.O. Buesseler

M.H. Dai

S. Pike

Pacific Northwest National Laboratory:

✓ J.M. Kelley

J.F. Wacker

U.S. Department of Energy
Pacific Northwest National Laboratory

TOPICS

- PURPOSE
- HISTORY
- METHODS
- RESULTS
- STATUS/FUTURE

PURPOSE

Provide a basis for accurate modeling and prediction of actinide element transport in groundwater through speciation studies stressing:

i) Maintenance of ambient geochemistry (e.g., redox states, size distribution) during sampling

ii) Prompt, onsite separation and collection of sample redox- and size fractions

iii) Measurements of isotopic abundances in addition to concentrations, at levels as low as 10^4 atoms

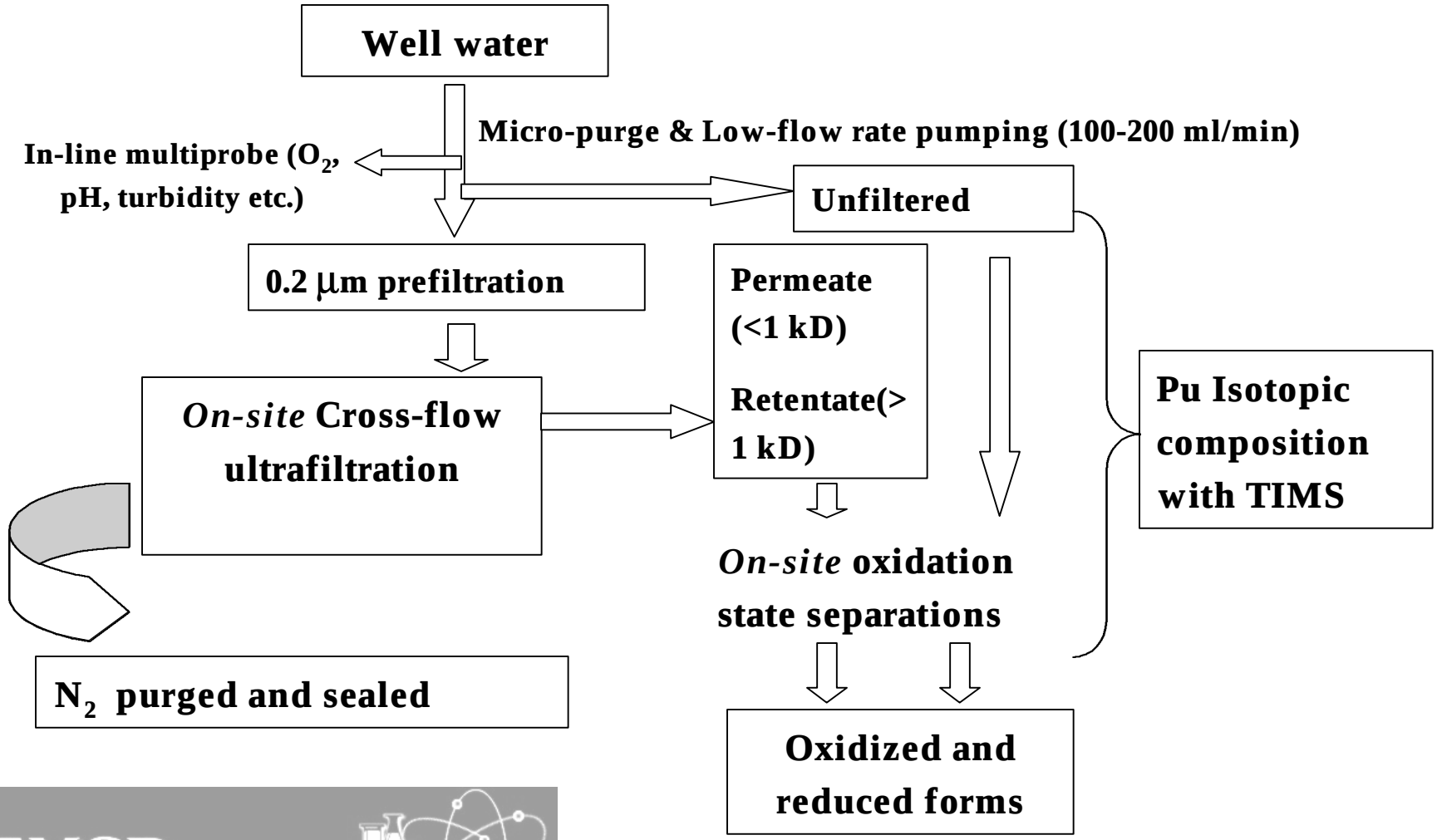
PROJECT HISTORY

- **Gulf of Maine**
  - Size-fractionated samples
  - Task completed
  - Publication: "Size-fractionated plutonium isotopes in a coastal environment" *J. Environ. Radioactivity* **53**, 9-25 (2001)
- **Savannah River Site**
  - Size- and redox-fractionated samples
  - Sampling (F-Area) and analyses completed
  - Publication: "Do colloids facilitate plutonium migration in groundwater?" (submitted to *Nature*, Nov. 2000)
  - Additional publications forthcoming
- ✓ **Hanford Site**
  - Size- and redox-fractionated samples
  - 100K-Area wells sampled April 1999
  - Analysis results undergoing review and additional sampling (100N & 200E Areas) planned

METHODS: Features

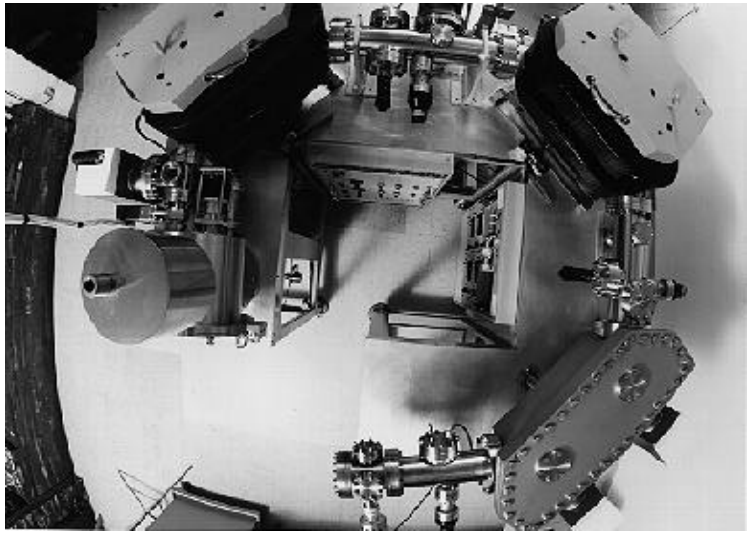
- Separation of Pu(III/IV) and Pu(V/VI) oxidation states
  - Coprecipitation as fluoride using La carrier and ^{244}Pu(III/IV) and ^{242}Pu(V/VI) tracers
  - Method adapted from Lovett and Nelson
- Separation of size fractions
  - Cross-flow ultrafiltration (CFF)
  - Low pumping rate (~0.15 L/min) to minimize collection-related colloid formation
- Isotopic measurements
  - Isotopic dilution, thermal ionization mass spectrometry (TIMS)
  - Such measurements are particularly sensitive and yield isotope ratios (e.g., ^{240}Pu/^{239}Pu, ^{241}Pu/^{239}Pu) that in favorable instances reveal provenance

METHODS: Sampling and processing



EMSP
Environmental Management Science Program

METHODS: TIMS measurements



Three-Stage Thermal Ionization Mass Spectrometer

APPLICATION

- Detect releases of actinide element isotopes in environmental type samples at levels as low as 10^4 atoms.
- Establish provenance and temporal information.

CONCERNS

- Ion emission processes
- Ion focusing
- Signal-quenching interferences
- Background interferences

TIMS Actinide Element Analysis: Major Tasks

Chemical Separation and Purification

↓

Mass Spectrometer Source Preparation

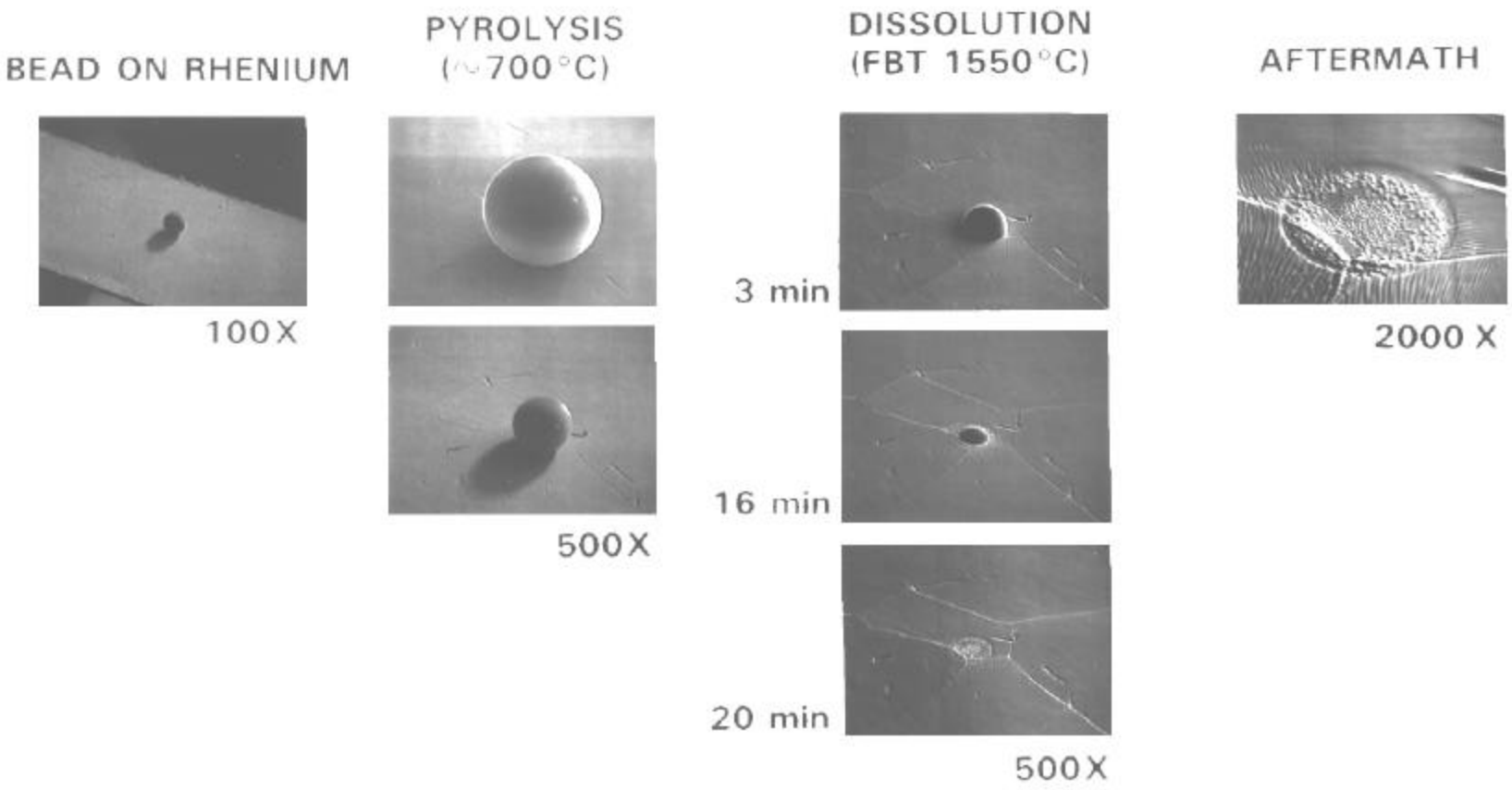
↓

Mass Spectrometer Measurements

↓

Report Results

Dissolution of a Quaternary Ammoniun–Type Anion Exchange Resin Bead into Rhenium



TIMS Analysis: Microchemistry and source preparation

Microvolume anion exchange
(100 µL column volume)

↓

Single bead anion exchange
(800 µm dia AG1x4 bead in 20 µL droplet)

↓

Incorporate analyte into a single bead (150 µm dia) and load onto a V-configured, Re mass spectrometer filament

↓

Pyrolyze the bead to produce an effective point source consisting of a 30-50 µm dia carbon sphere

↓

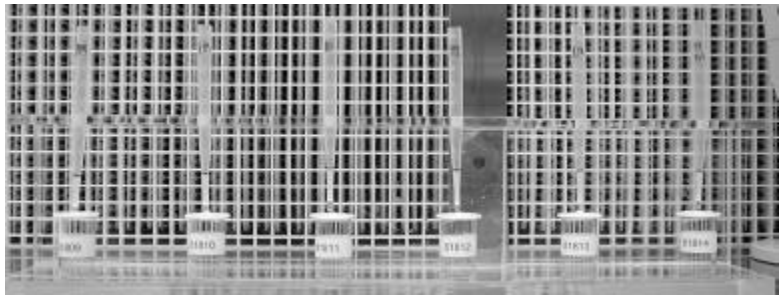
TIMS measurements

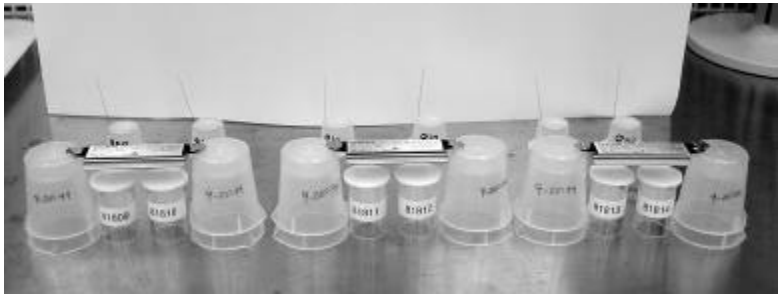
Typical microchemistry workstation

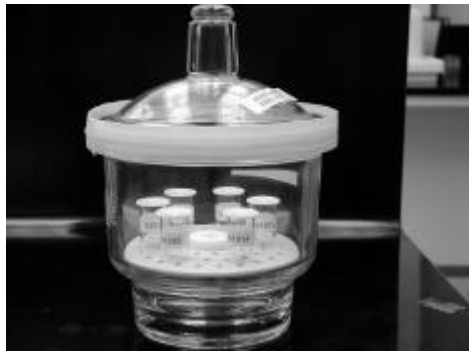
EMSP
Environmental Management Science Program

U.S. Department of Energy
Pacific Northwest National Laboratory

TIMS microchemistry paraphernalia





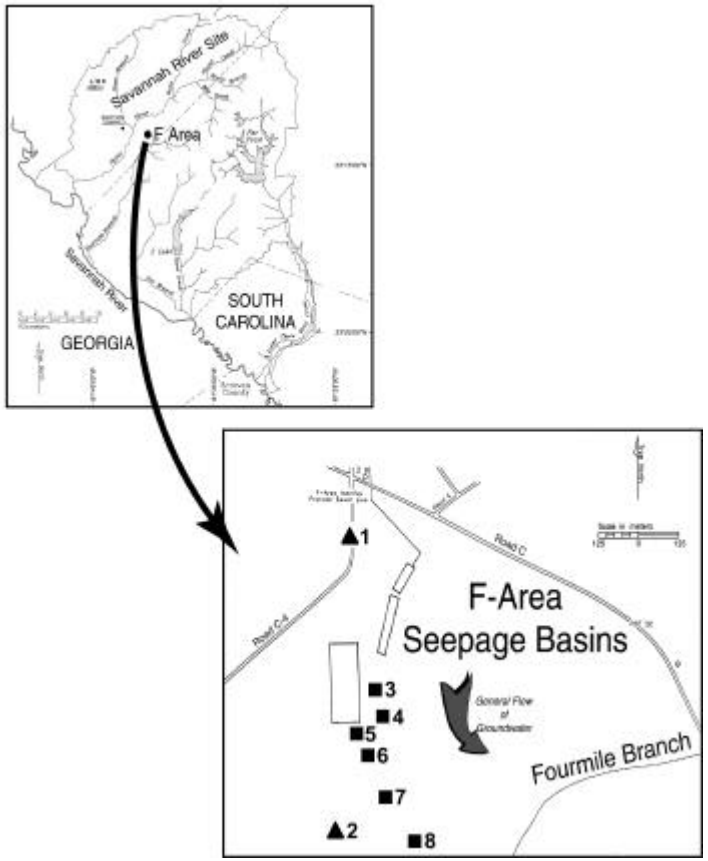


EMSP
Environmental Management Science Program

TOPICS

- PURPOSE
- HISTORY
- METHODS
- ✓ RESULTS
  - ➢ Savannah River Site (SRS)
  - ➢ Hanford Site (HS)
- STATUS/FUTURE

SRS, F-Area well locations

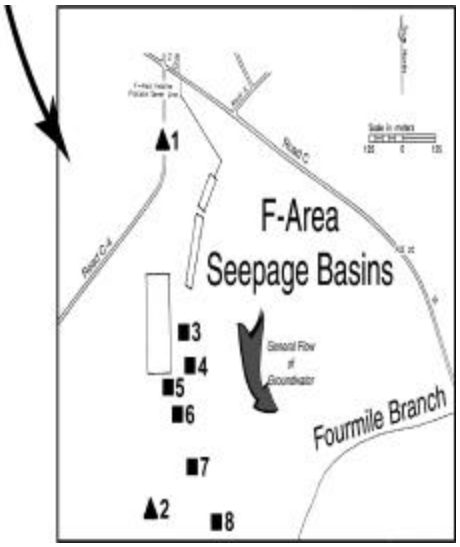


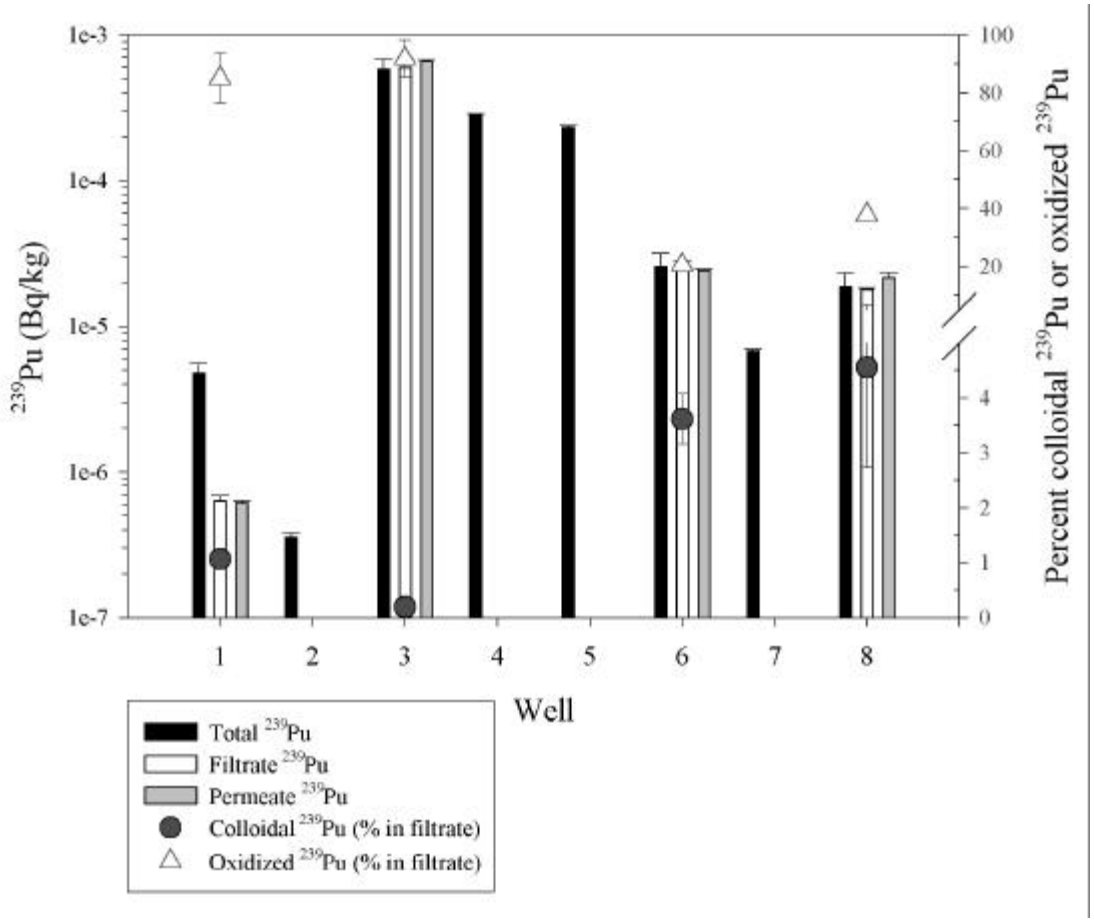
- The PUREX process was used at F-area to recover ^{239}Pu, ^{237}Np and ^{238}U from irradiated ^{238}U targets
- Waste was discharged to seepage basins and contained HNO_3, so the downstream groundwater is characteristically acidic (pH ~ 3-4)

Pu in SRS, F-area groundwater: Major findings

- < 5% of the groundwater Pu is colloid bound
- ^{239}Pu concentrations remain highest near the seepage basin source
- Abundances of ^{239}Pu in the oxidized, Pu(V/VI), forms are high, especially near the source (> 85% oxidized)
- Abundances of ^{240}Pu relative to ^{239}Pu are extraordinarily high, especially far downstream from the source (^{240}Pu/^{239}Pu ~ 17)
- ^{240}Pu in F-area groundwater stems from decay of waste ^{244}Cm ($t_{1/2}$ = 18.1 y) and tracks it's more mobile progenitor through the aquifer

^{239}Pu concentrations in May1998 in wells near the SRS, F-Area seepage basins





Total …….. Unfiltered groundwater

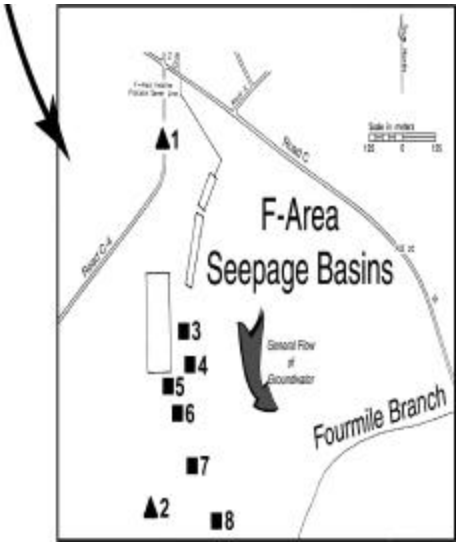
Filtrate …... < 0.2 µm

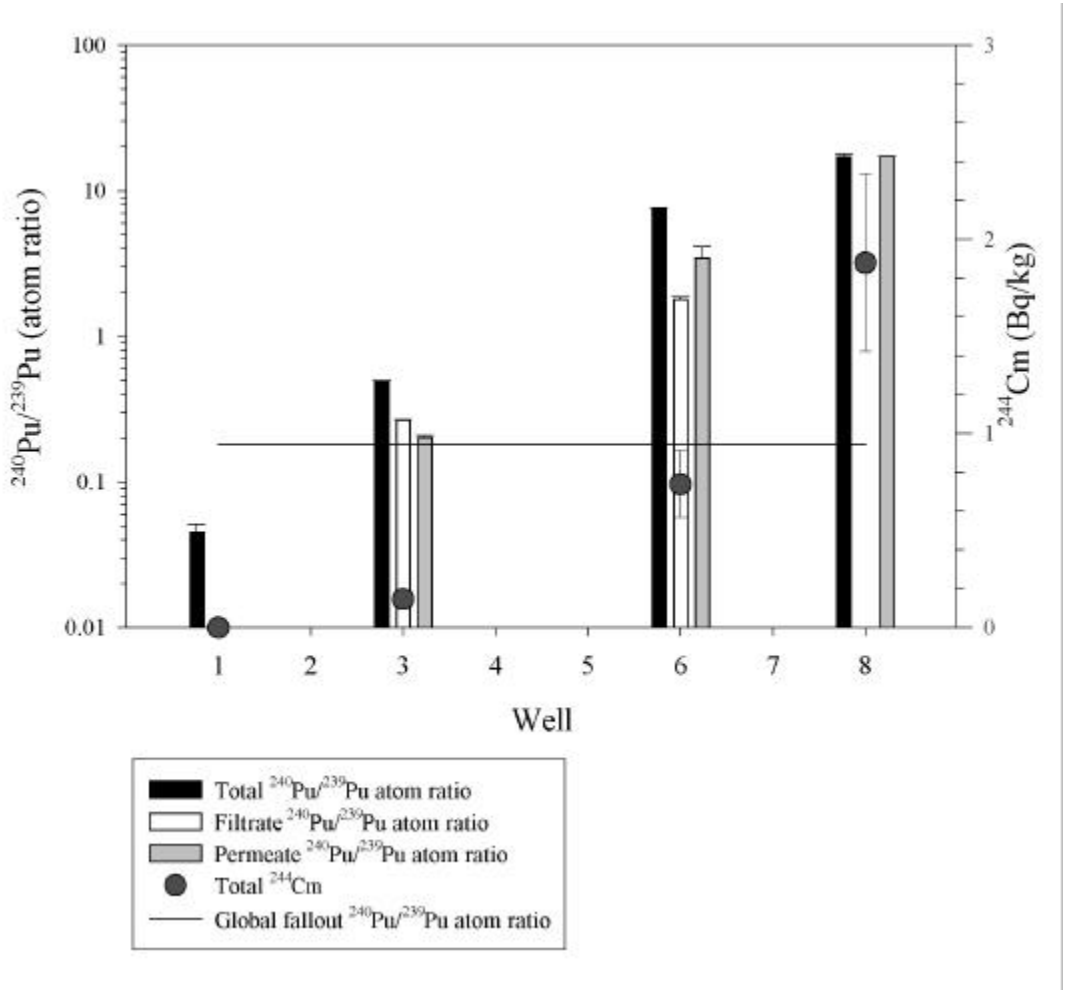
Permeate .. < 1 kD

Colloidal … 1 kD – 0.2 µm

EMSP
Environmental Management Science Program

$^{240}Pu/^{239}Pu$ atom ratios and ^{244}Cm concentrations, decay corrected to May 1998 sampling date, in SRS F-Area wells





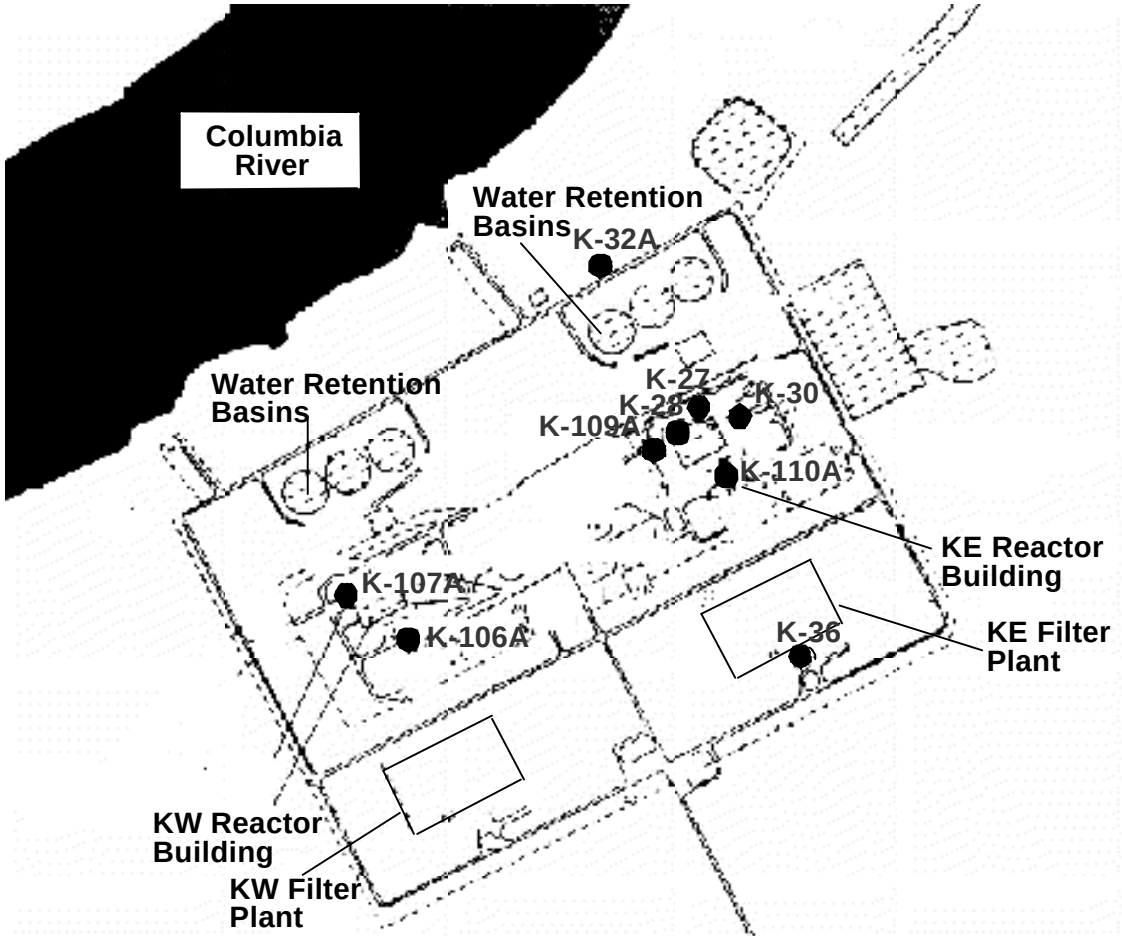
EMSP
Environmental Management Science Program

U.S. Department of Energy
Pacific Northwest National Laboratory

TOPICS

- PURPOSE
- HISTORY
- METHODS
- RESULTS
  - ➢Savannah River Site (SRS)
  - ✓Hanford Site (HS)
- STATUS/FUTURE

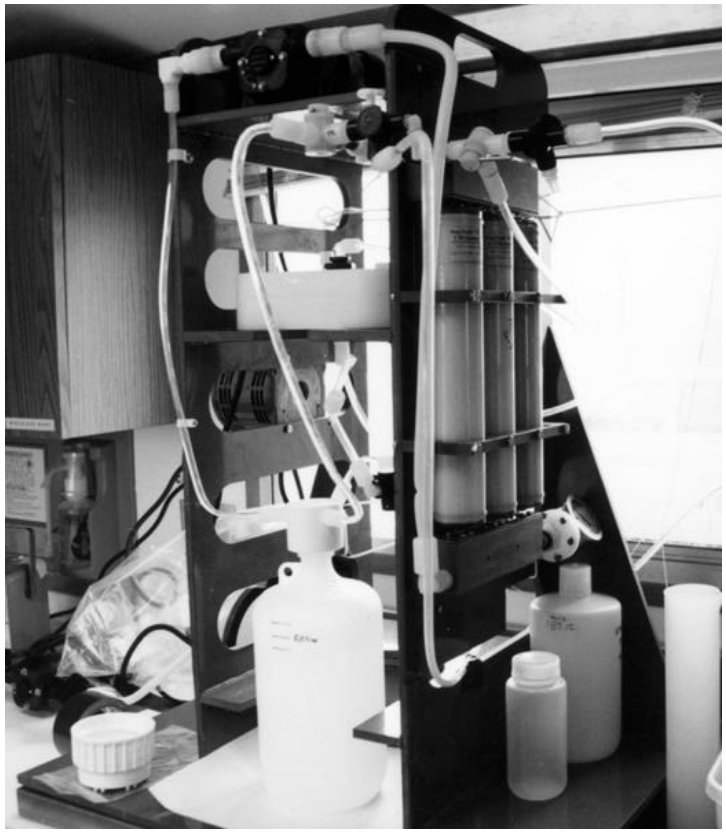
HS, 100K-Area well locations



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

April 1999 HS sampling, *acknowledgements*:

Shannon Goodwin, Evan Dresel, Scott Conley, Teresa Wilson, Debi Morgan, Mike Thompson, Stuart Luttrel, Loni Peurrung, Dennis Brooks



EMSP
Environmental Management Science Program

Pu in HS, 100K-area groundwater: Some preliminary findings

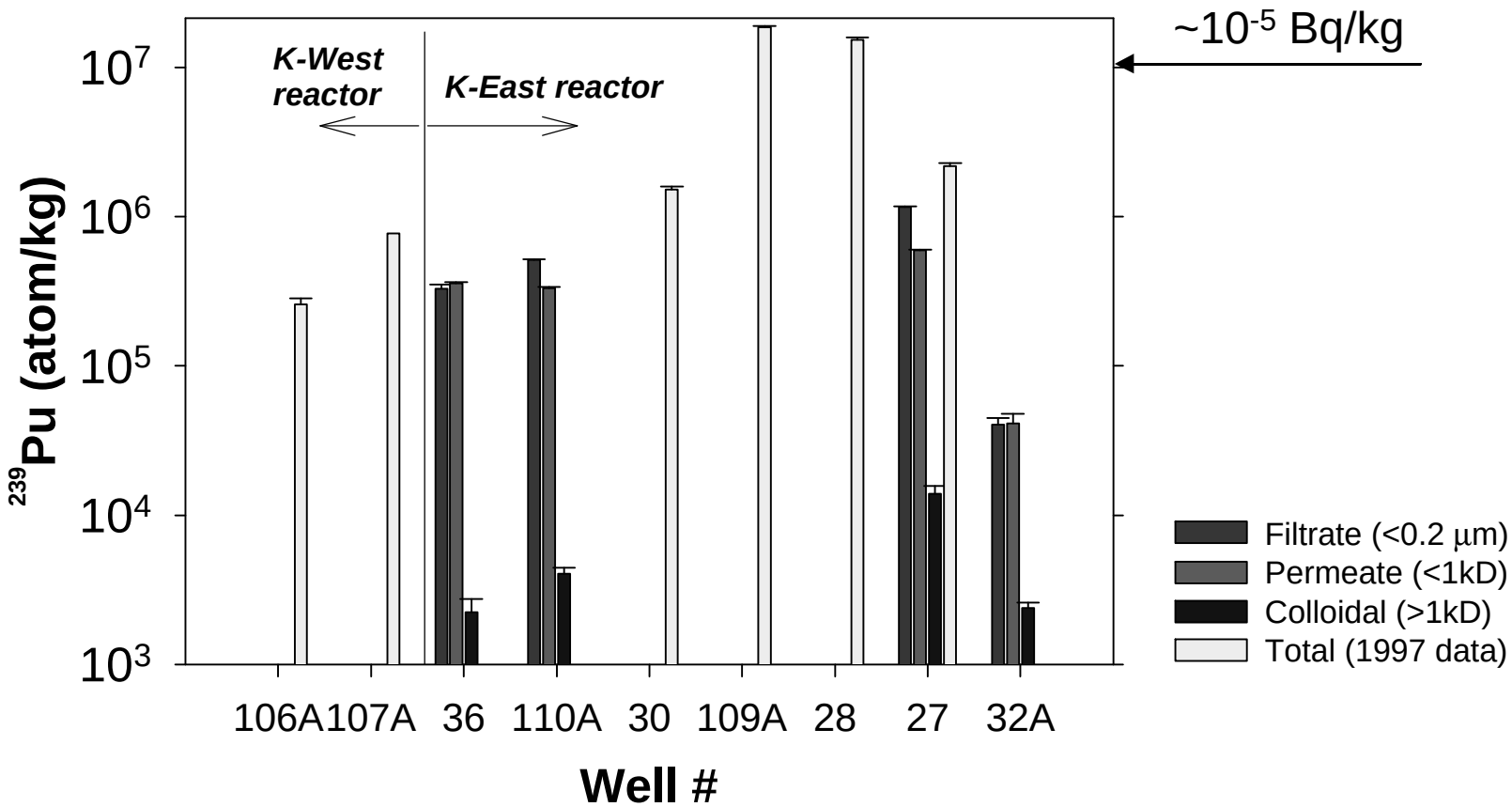
- ^{239}Pu concentrations are very low, but are highest (~ 2×10^{-5} Bq/kg) near the K-East reactor

- Little of the groundwater Pu is colloid bound

- Abundances of ^{239}Pu in the oxidized, Pu(V/VI), forms are lowest (~ 20% oxidized) upstream from the K-East reactor (Well 199-K-36), generally increasing in the downstream direction (to ~ 75% oxidized, Well 199-K-32A)

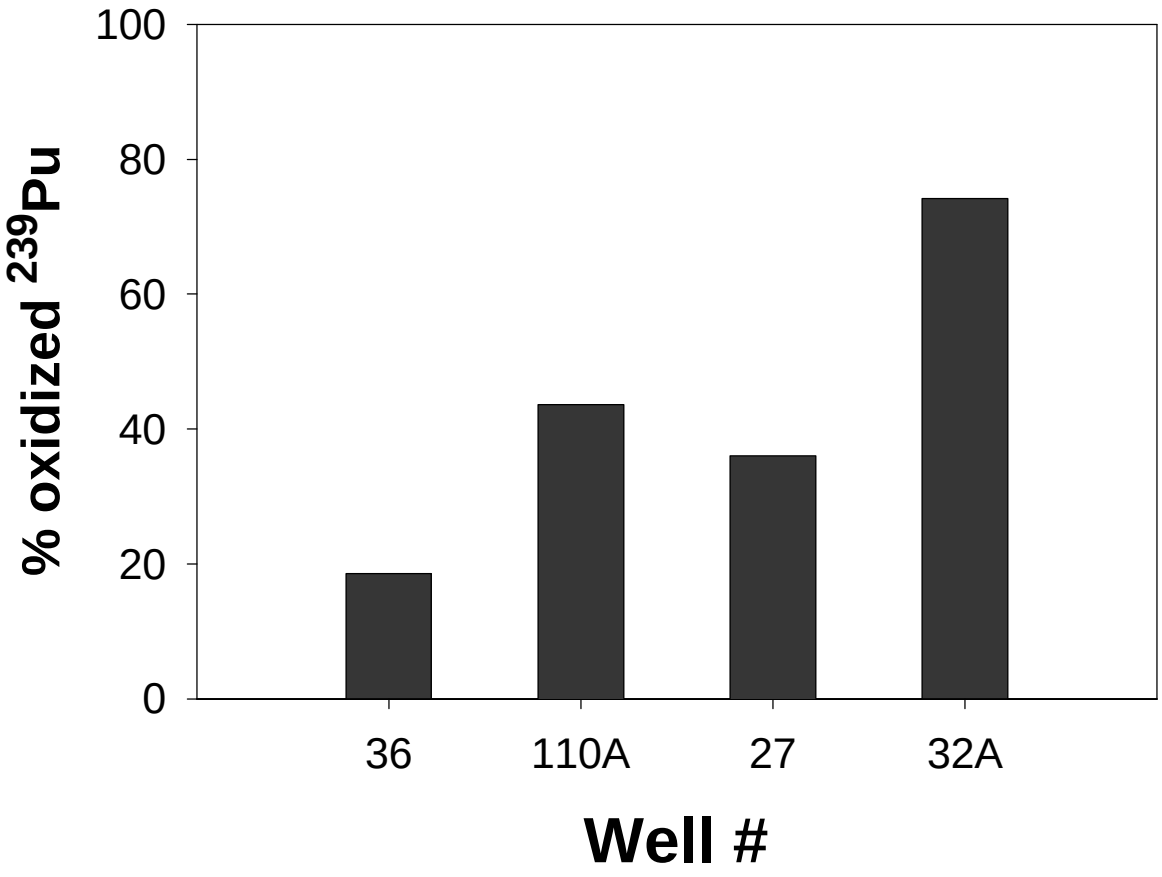
- The isotopic signature of N-reactor operations is evident in Wells 199-K-27 and –109A. Other wells reflect K-type reactor operations.

^{239}Pu concentrations in HS, 100K-Area wells



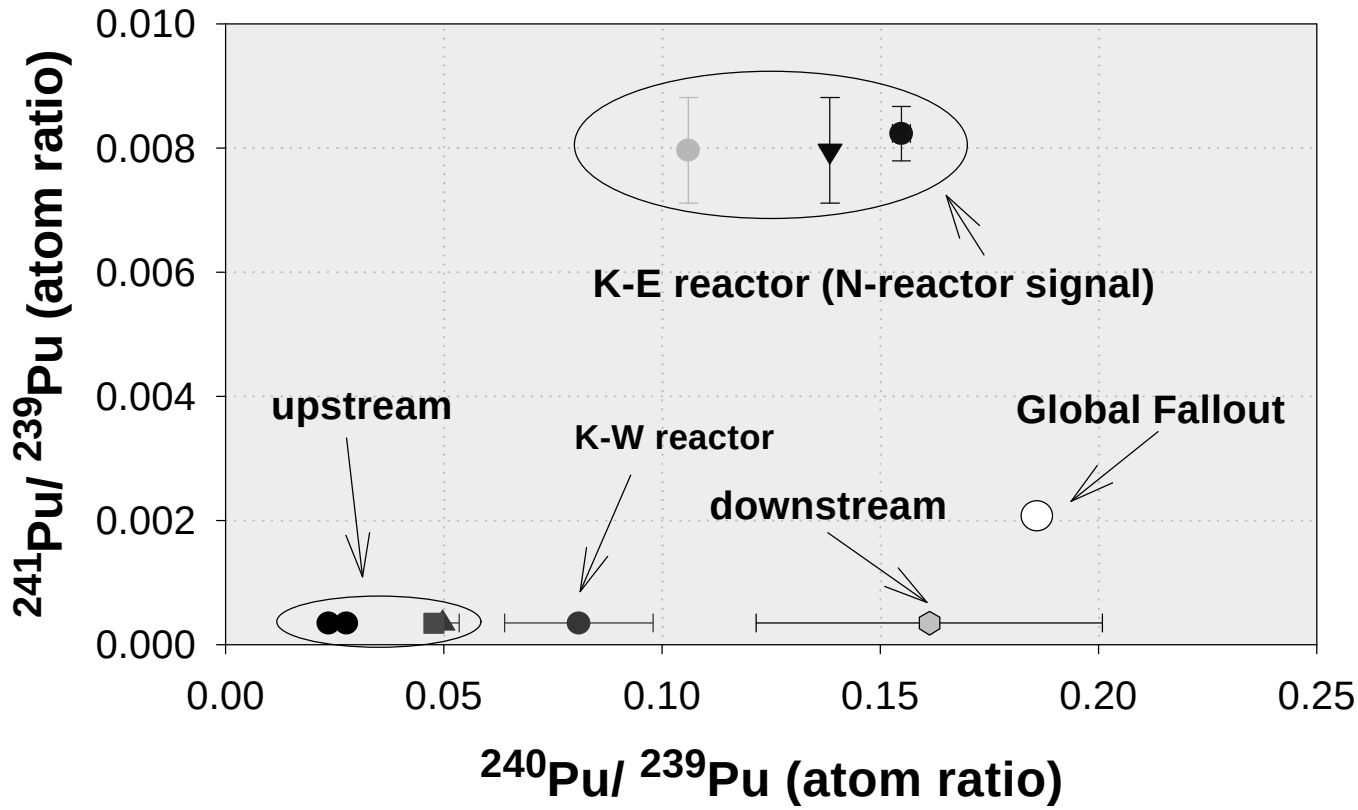
EMSP
Environmental Management Science Program

Oxidation state results (filtrate fraction, < 0.02 µm)



EMSP
Environmental Management Science Program

Signatures of provenance from Pu isotopics of HS 100K-Area groundwater samples



Status and future work

- TIMS measurements on 1999 HS 100K-area samples nearing completion
- Data analysis is underway and dissemination of results is forthcoming
- New groundwater samples to be collected in the spring of 2001, at 100N and 200E areas
- These will be processed as were the 100K area samples, after which speciation and transport phenomena will be ascertained and compared

Relevance to Hanford Site needs

This research provides actinide speciation data for accurate modeling, assessment and prediction of the fate of Pu and other actinide element isotopes released into Hanford groundwater. Moreover, in favorable instances, provenance is established. Such information is required to design strategies to reduce risks and plan effective clean-up and monitoring approaches.

Acknowledgements

WHOI: *John Andrews*

PNNL: *Lee Bond, Shannon Goodwin, Tapas Maiti, Steve Petersen*