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

K.O. Buesseler\textsuperscript{(1)}, M.H. Dai\textsuperscript{(1)} and J.M. Kelley\textsuperscript{(2)}, S. Pike\textsuperscript{(1)}, R. Nelson\textsuperscript{(1)}, S. Goodwin\textsuperscript{(2)} and J.F. Wacker\textsuperscript{(2)}

\textsuperscript{(1)} Woods Hole Oceanographic Institution, Woods Hole, MA 02543
\textsuperscript{(2)} Pacific Northwest National Lab, Richland, WA 99352

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

Well water

In-line multiprobe (O₂, pH, turbidity etc.)

Micro-purge & Low-flow rate pumping (100-200 ml/min)

Unfiltered

0.2 µm prefiltration

On-site Cross-flow ultrafiltration

Permeate (<1 kD)

Retentate (> 1 kD)

On-site oxidation state separations

Oxidized and reduced forms

Pu Isotopic composition with TIMS

N₂ purged and sealed
Field Sampling at Hanford Site

- maintain and measure in-situ geochemistry
- use low flow sampling to reduce colloid formation
Cross Flow Filtration

Sample line
- 0.2 µm prefiltre
- Retentate reservoir (>1 kD)
- N₂ flushed
- ultra clean
- 200 liter samples in 48 hours

Permeate stream (<1 kD)
- 1 kD CFF membranes

• 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 with 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
• The likely source of high $^{241}\text{Pu}/^{239}\text{Pu}$ 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.
Well 36 110A 27 32A

% oxidized 239Pu

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

Acknowledgements

\textbf{WHOI:} John Andrews
\textbf{Hanford Site:} Evan Dresel, Scott Conley, Teresa Wilson, Debi Morgan, Mike Thomson, Stuart Luttrell, Loni Peurrung, Dennis Brooks