

Development of Analytical Methods for Anionic Fission Products and Application to Sediment and Groundwater Samples from Tank Farm Waste Management Areas

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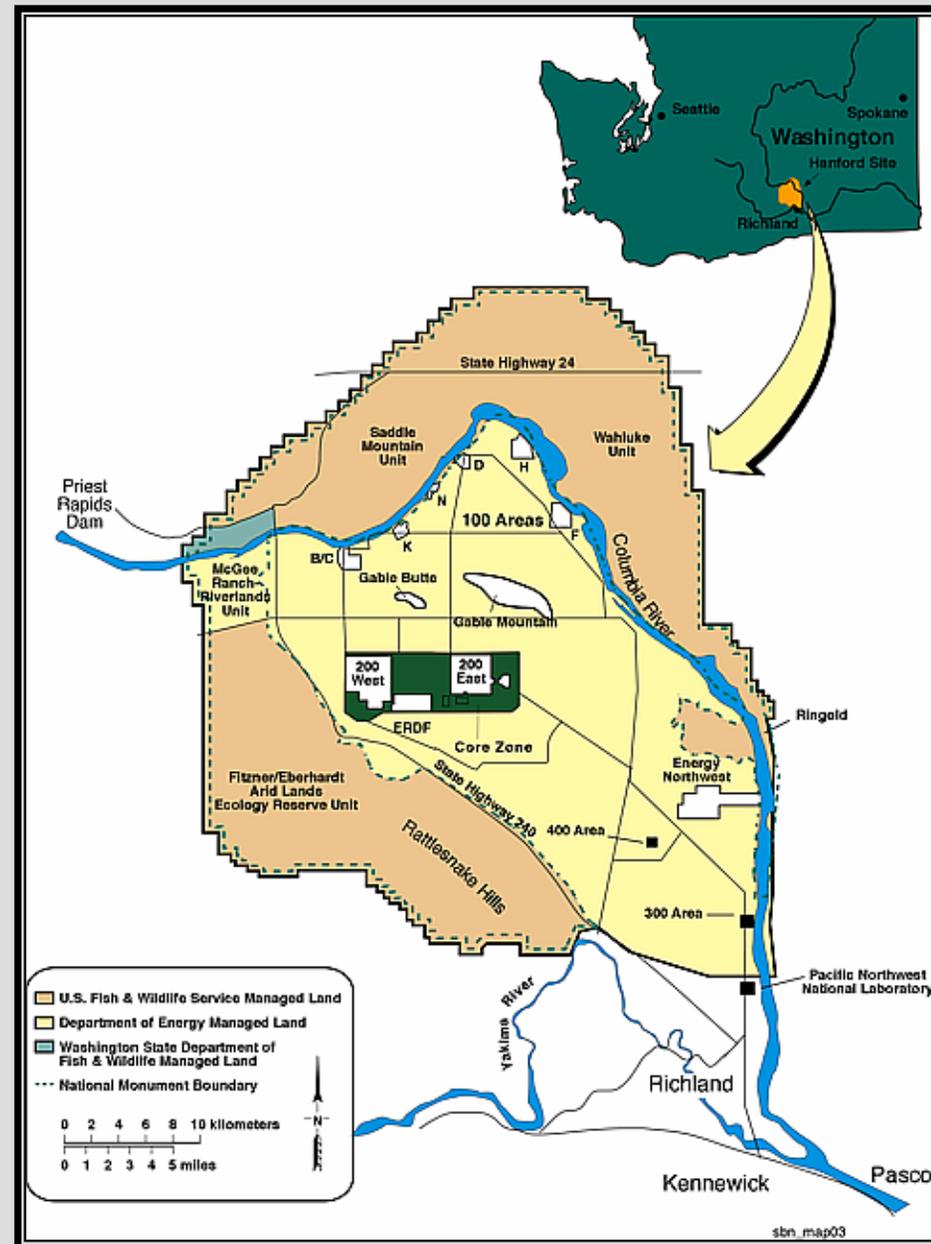
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Outline

- ▶ Provide a brief background on the Hanford Site
- ▶ Discuss the finding that prompted this study
- ▶ Sources of Tc-99 near the investigation site
- ▶ What has been done in the past to identify contaminant source terms
- ▶ Why ruthenium isotopes are a valuable tool
- ▶ Results from our method development
- ▶ Path forward

The Hanford Site

- ▶ Located in southeastern Washington (est. 1943)
- ▶ 562 square mile complex
- ▶ Created to produce weapons grade plutonium
- ▶ Consists of several “Areas”
 - 100 Area: 9 production reactors
 - 200 Area: waste treatment and storage
 - 300 Area: uranium fuel production
- ▶ Over 170 km² of contaminated groundwater



What is the source of the technetium-99 below the water table?

- ▶ Well 299-W11-25B (2005)
 - 180,000 pCi/L Tc-99
 - Deeper peak activity
- ▶ Peak Tc-99 activity in wells screened near the water table was ~17,000 pCi/L
- ▶ Potential sources

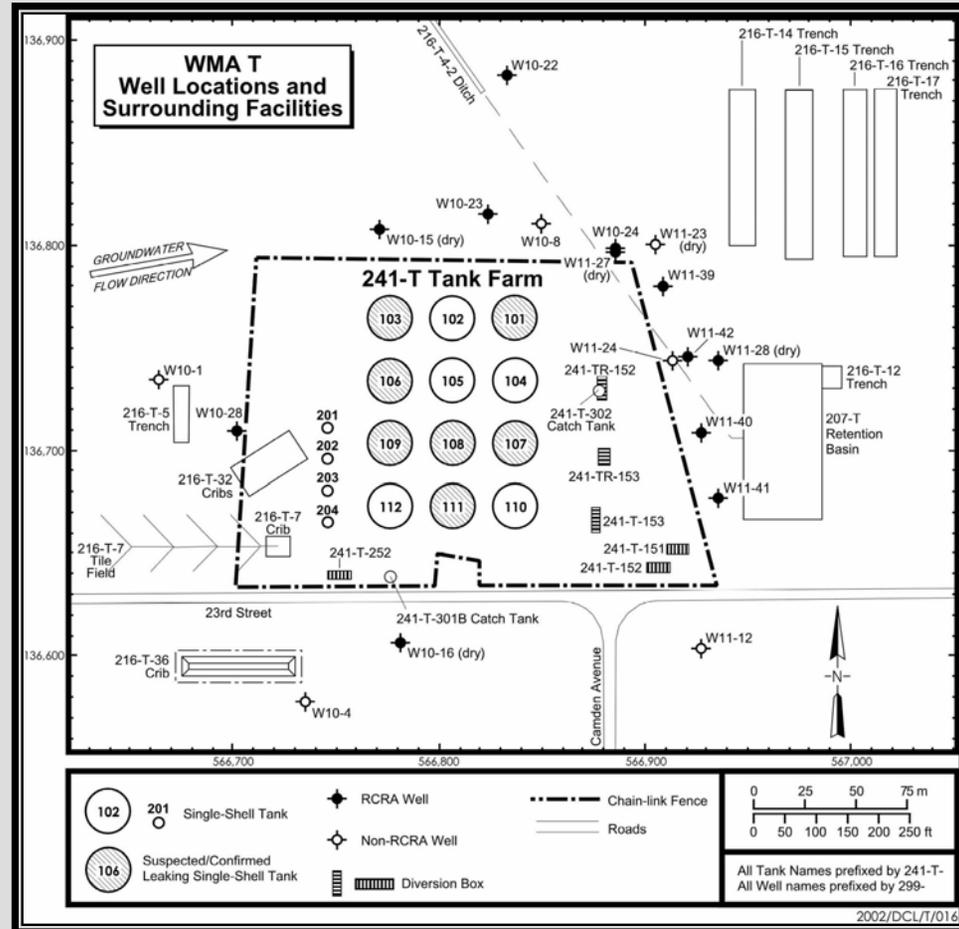
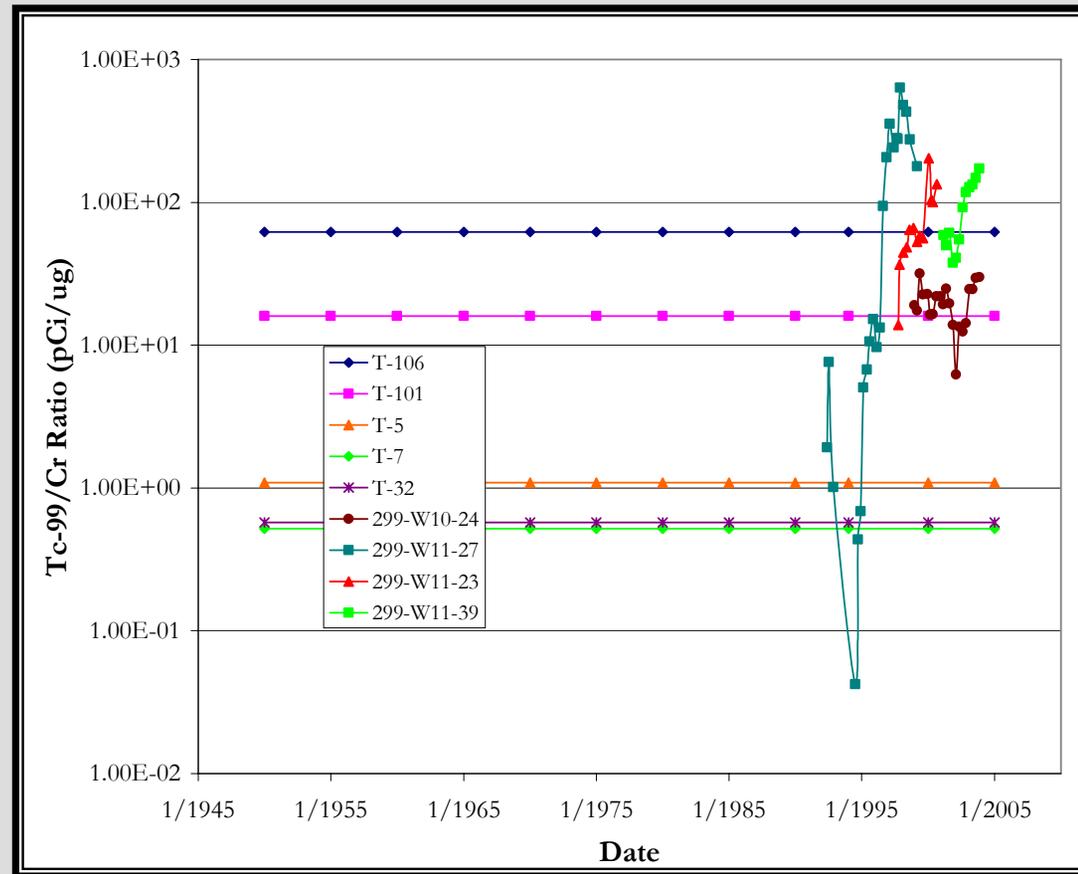


Figure from Horton et al. 2003
(PNNL-13929)

What has been done in the past to identify contaminant source terms?

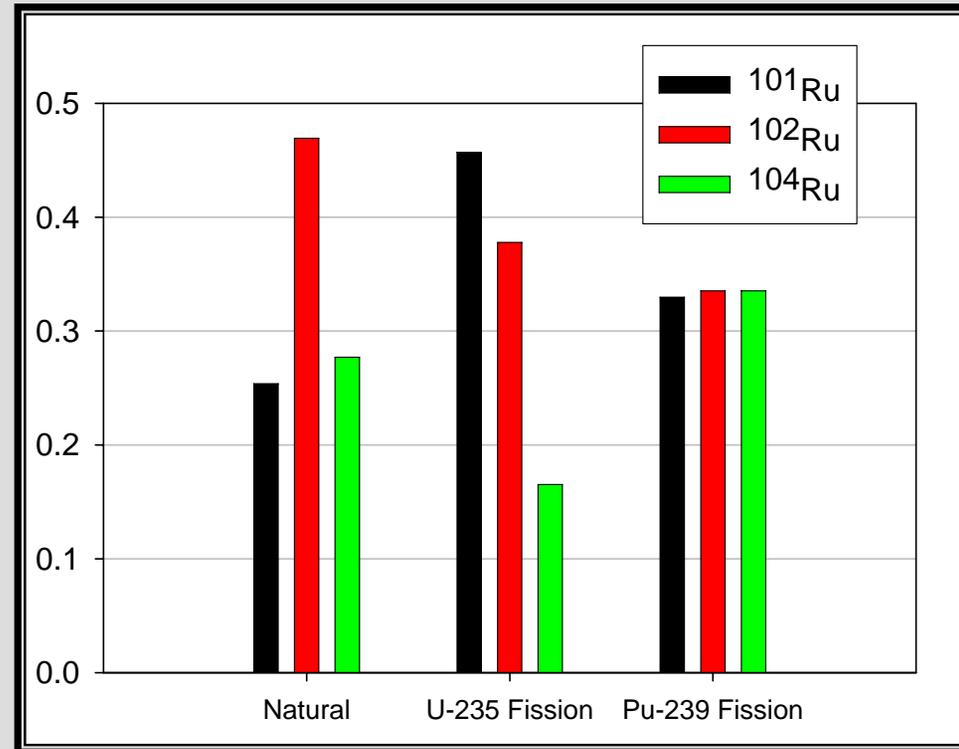
- ▶ Create ratio plots
 - 2 constituents
 - Compare ratios against historical data
- ▶ Problems
 - Incomplete inventories
 - Precise composition at time of leak or spill
 - Fractionation of contaminants
 - Little to no success



From Serne et al. 2004 (PNNL-14849)

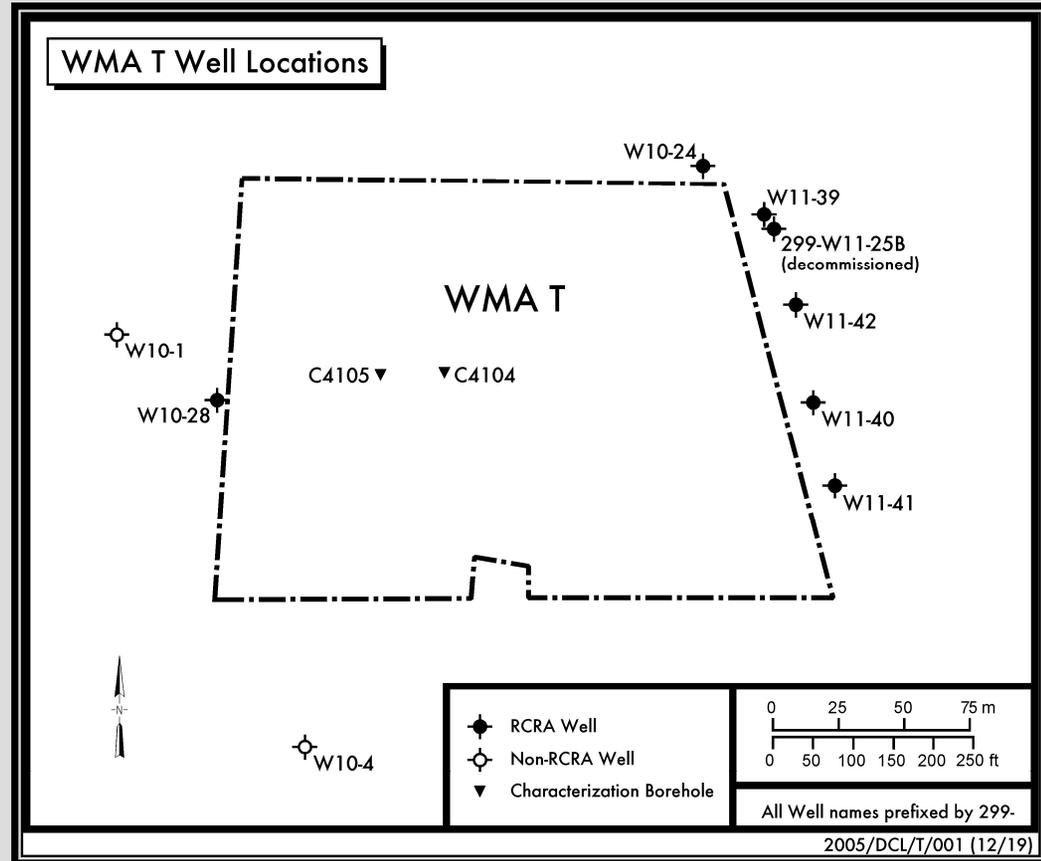
How can ruthenium isotopes help?

- ▶ Chemically similar
- ▶ Mobile in the environment
- ▶ Multiple stable isotopes
- ▶ Low natural background
- ▶ Large spread in isotopic abundances
- ▶ Isotopic fractionation should be negligible



Samples collected for analysis

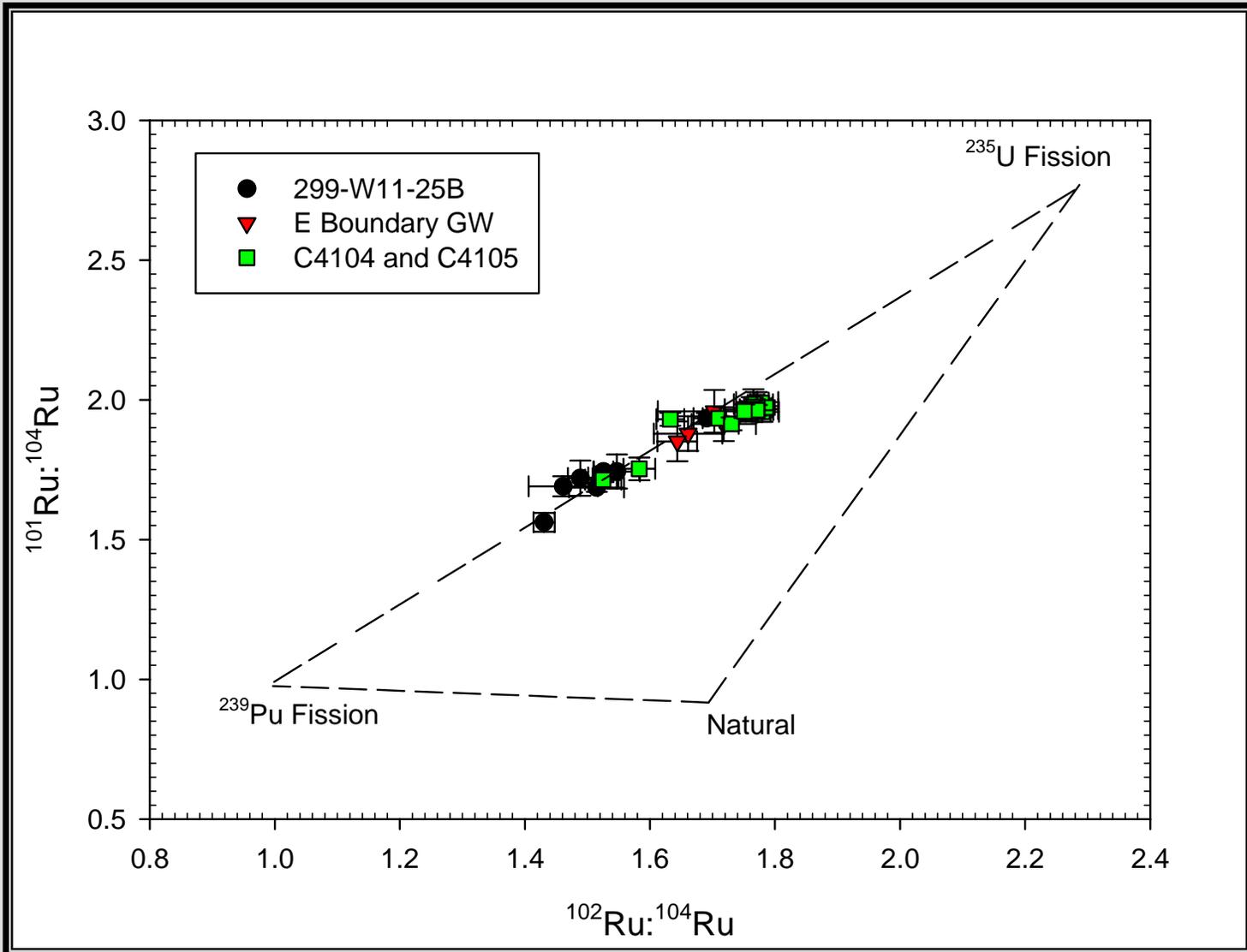
- ▶ 8 groundwater samples from the top of the water table
- ▶ 9 vertical profile groundwater samples from well 299-W11-25B
- ▶ 22 sediment samples from 2 vadose zone boreholes emplaced near tank T-106



Methods utilized

- ▶ Soil extractions
 - 1:1 sediment:water extracts
 - Centrifugation to separate pore fluids
- ▶ Soil extract sample pretreatment
 - Dowex AG 50W-X8 cation exchange resin
 - Used sufficient sample to supply 10 ng of total Ru
- ▶ Analysis of the samples using inductively coupled plasma mass spectrometry (ICP-MS)
 - Scan data used for evaluating interferences
 - peak hopping data used for ratio analysis

Ruthenium isotopic ratio results

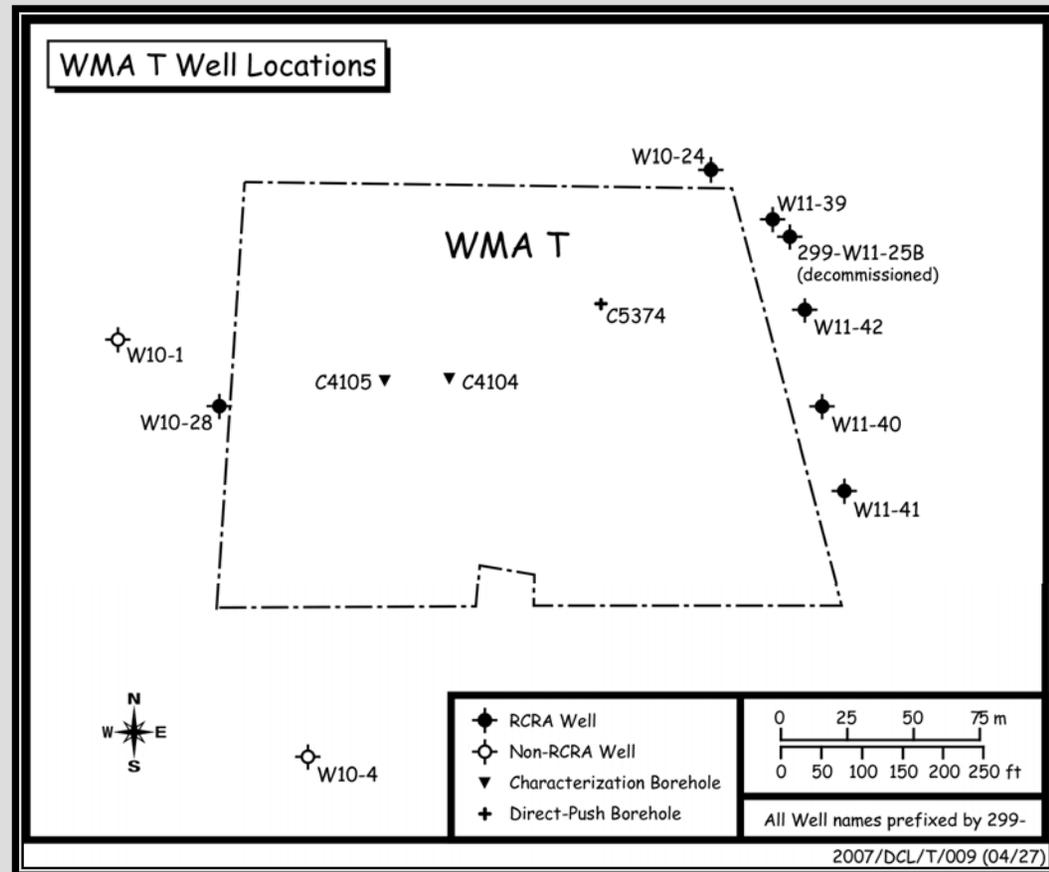


What were our concerns with the data?

- ▶ Poor recovery of ruthenium through the separation process
- ▶ Potential interference at mass 104
 - $^{88}\text{Sr} + ^{16}\text{O} = ^{104}\text{SrO}$
- ▶ Needed to identify a procedure for sample preconcentration

Samples selected for phase II of method development

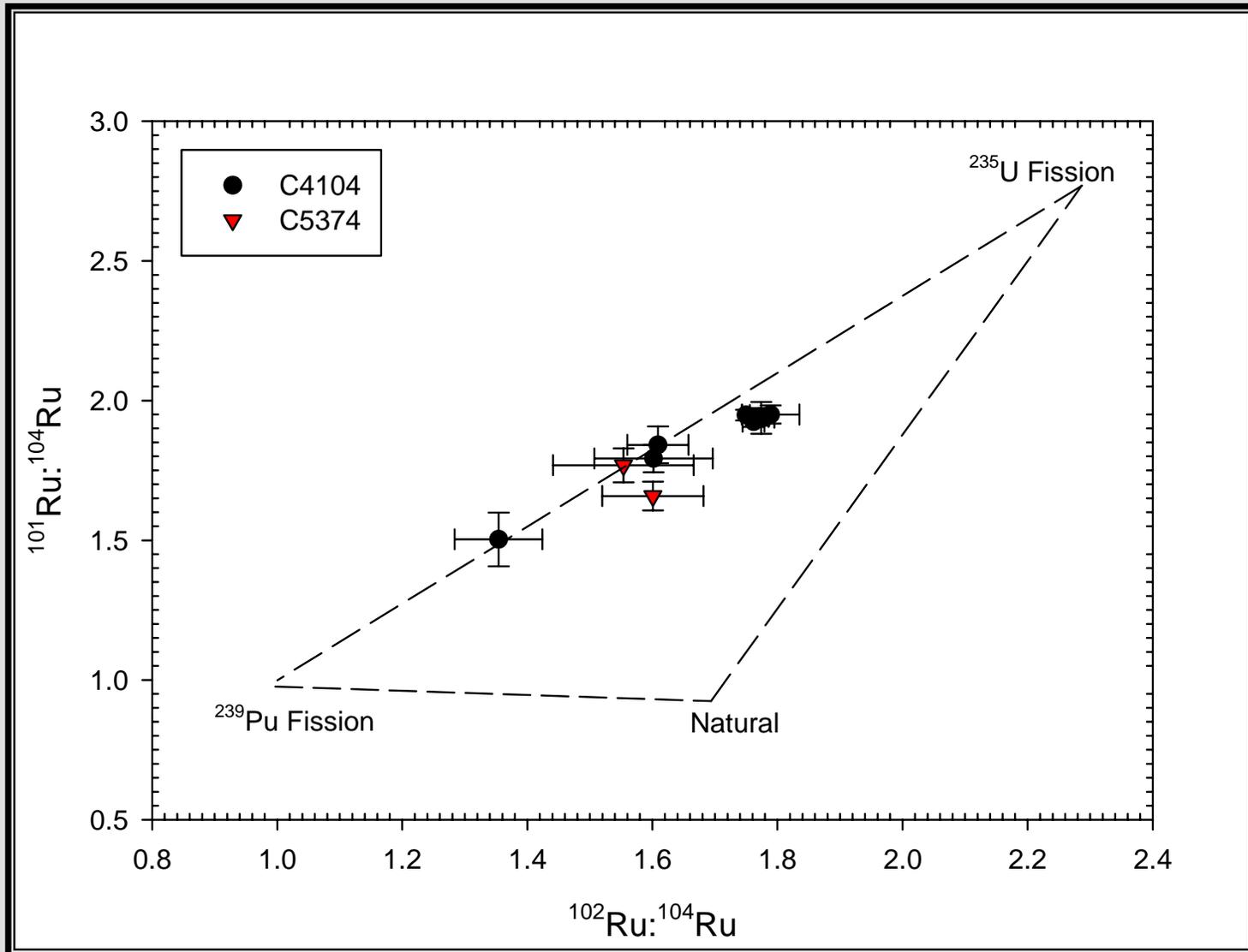
- ▶ 10 sediment samples from borehole C4104
- ▶ Sediment samples collected from a direct push hole near tanks 241-T-101/241-T-104
- ▶ Depth-discrete groundwater samples from 299-W11-25B
- ▶ RCRA groundwater monitoring wells



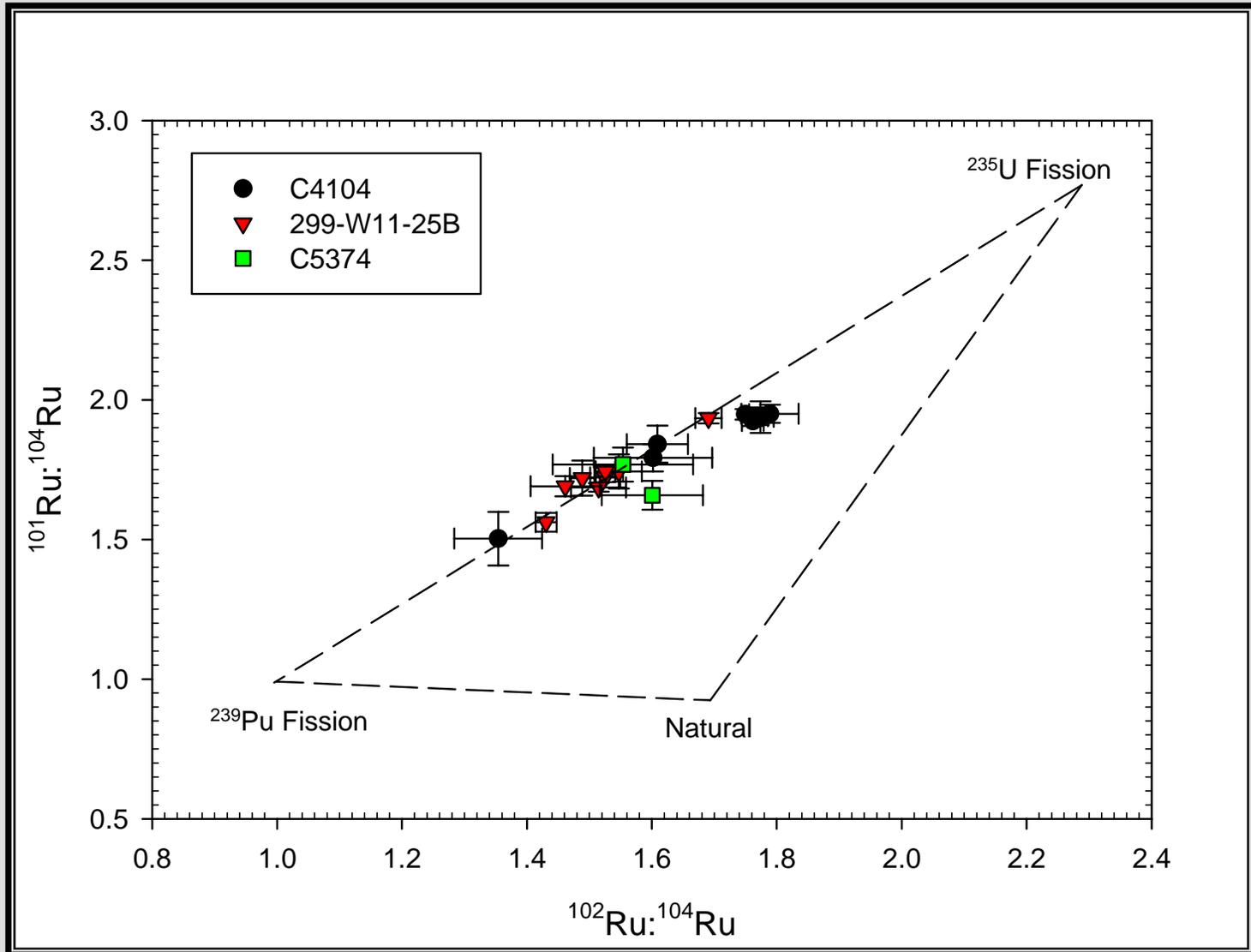
Revised methods

- ▶ Soil extractions
 - 1:1 sediment:water extracts
- ▶ Soil extracts and groundwater pretreatment
 - All sample processing performed in a HCl matrix
 - Samples and groundwaters passed through Dowex-1 anion exchange resin
 - Trapped ruthenium on the columns and subsequently eluted it for analysis
- ▶ Analysis of samples via ICP-MS
 - Peak hopping data used for ratio analysis

Phase II ruthenium isotopic ratio results



Phase II sediment data with phase I groundwater data



What can we say so far?

- ▶ Ruthenium and technetium do not behave identically
- ▶ Removal of stable strontium from samples is key
 - Anion exchange resin
- ▶ Sample pre-concentration is necessary
- ▶ Quadrupole-based ICP-MS can provide sufficient sensitivity and precision
- ▶ Ruthenium fission product isotopes can be used to constrain possible contaminant sources
 - Technetium-99 in the groundwater at Waste Management Area T appears to result from two distinct sources
 - Shallow groundwater contamination has a signature similar to contamination measured in the vadose zone near T-106
 - Deeper groundwater contamination appears to be from a different source

Where do we go from here?

- ▶ Need to refine the technique to permit quantitative analysis of upgradient groundwater samples
- ▶ Need to apply the technique to additional vadose zone samples
 - Two boreholes emplaced during 2006
 - Two boreholes emplaced during 2007
- ▶ Revisit the vadose zone samples from the direct push campaign around tanks T-101 and T-104
- ▶ Acquire and analyze depth-discrete groundwater samples that have not been preserved with nitric acid
- ▶ Extend the technique to other fission products