Ultra-Trace Sample Analysis and Data Reduction

Robert Steiner, Stephen LaMont, Fred Roensch, Jeff Roach, Will Kinman, Rebecca Foley, Don Dry and Lee Riciputi

Nuclear and Chemistry Group

Los Alamos National Laboratory

Los Alamos, New Mexico 87545

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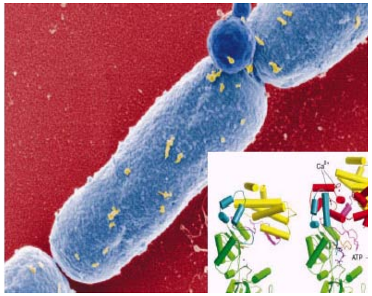
Outline

- What are we trying to do?
- Who we are doing it for
- Capabilities
- Sample Types
- Blanks and contamination control
- Data for environmental level swipes
- Enviromental sample analysis example
- Uncertainty analysis
- Summary

- Who, What, When, Where, How?
  (Why is someone else's problem)



- Bulk to ultra-trace quantities of material

✓ *Discrimination (matching)*

✓ *Classification (what are the groups, databases)*

✓ *Predictive – what causes characteristics, understanding through various "processing" stages*

- *Develop chemical/isotopic tools for potential forensics applications on a variety of materials (chemical, biological, nuclear)*
- *Improve analytical capabilities (sensitivity, precision, accuracy, throughput)*
- *Small sample capability in particular (material, radiological limits)*
- *Methodologies applicable to a wide variety of disciplines involving interactions among different pools of matter*

Programs Supported By the RC-45 Clean Facility

- LANL *in vitro* Pu, Am and H_3 Bioassay
- IAEA Safeguards
- National and International Security
- Basic Energy Sciences Geochemistry
- U.S. Dept. of Energy R&D Efforts
- LANL Environmental Monitoring

RC-45 Clean Chemistry and Mass Spectrometry Facility

RC-45

- New surface science facility (SIMS, SEM and prep labs)
- Proposed addition to RC-45 (office, general and clean chemistry laboratories, clean instrument laboratories)
- Institutional investment priority

Certification

- Annual certification under FED209E
- Class 10,000 hallways and laboratories
- Class 100 work areas and exhausted laminar flow work cabinets
- Test noise and light levels

Radiation Spectrometry

Alpha spectrometry
Sample screening and actinide quantification, especially ^{238}Pu and ^{241}Am

Ultra-Low Background Clover Gamma-Ray Spectrometer
Special radiochemical counting applications

Compton Suppressed Gamma-ray Spectrometry
Sample screening and quantification of activation and fission products

Clean Radiochemistry

Cleanroom compatible sample ashing
Class 100, low insulation ashing equipment for particle control

Radiochemistry processing
Class 10-100, glassware cleaning, sample dissolution and digestion, ion exchange chemistry, sample dry down

Sample loading areas
Class 10 -100, electroplating, carborizing

Bulk Analysis

Multi-collector ICP-MS
(MC-ICP-MS)
High precision, high accuracy
Isotope ratios (U, Sr, Pb, Fe, B…)
ng to <fg sample requirements

Sector Field ICP-MS
(SF-ICP-MS)
Ppq – ppm elemental concentrations

Multi-collector Thermal Ionization MS
(TIMS)
Pu, other actinide, Sr, Nd

In Situ Analysis w/Spatial Resolution

Laser ablation
193 nm ArF Excimer
In-situ analysis w/
ICP-MS systems
Few micron spatial resolution

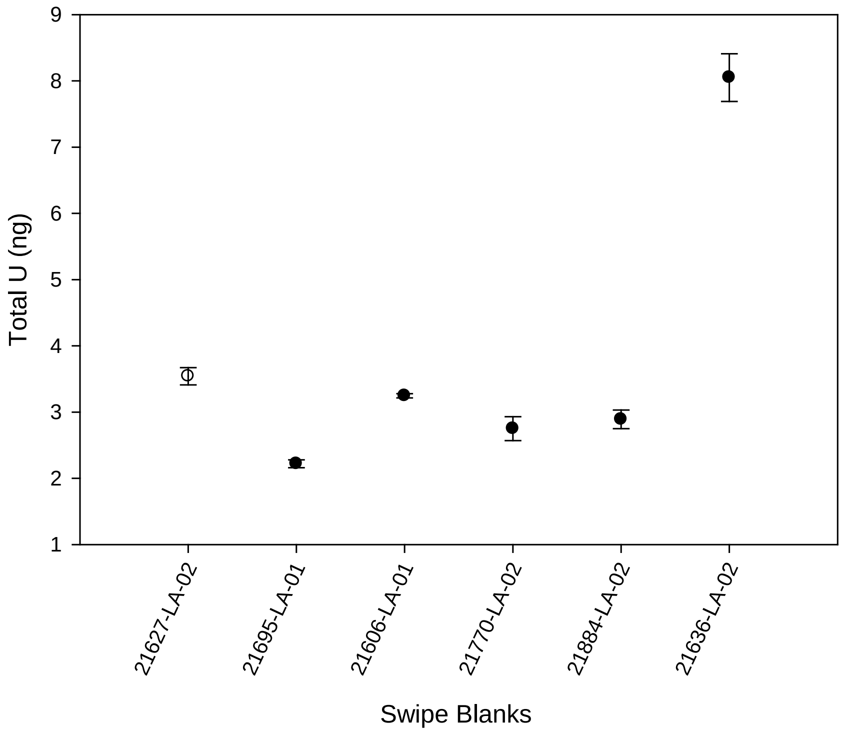
Field Emission Environmental SEM
(FE-ESEM))
Morphology
Major, minor elemental characterization w/
WDS, EDS systems

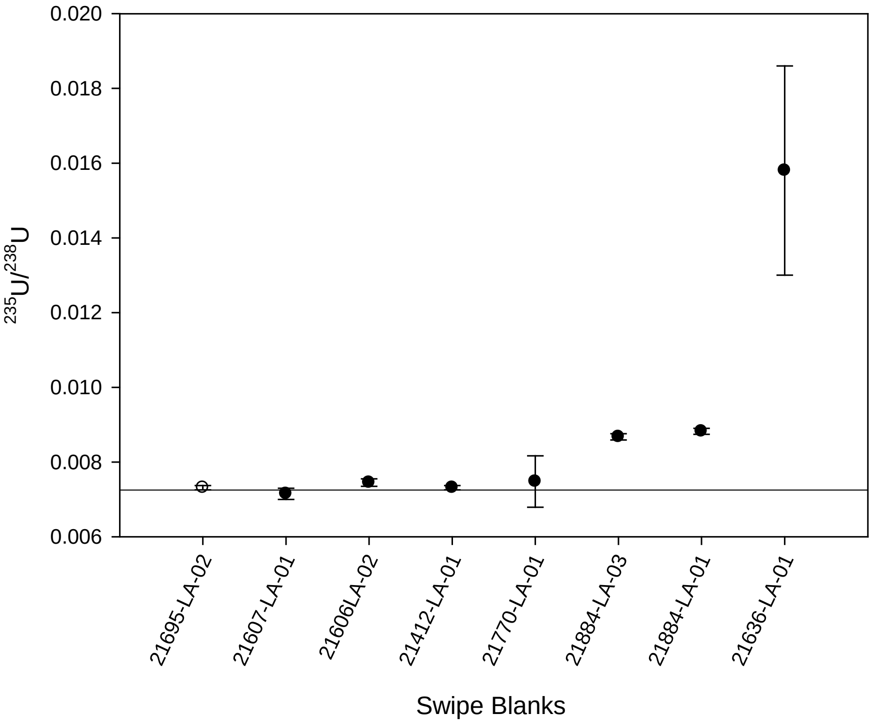
Cameca 1280
High transmission,
High sensitivity
Secondary Ionization MS
(SIMS)

Sample Types

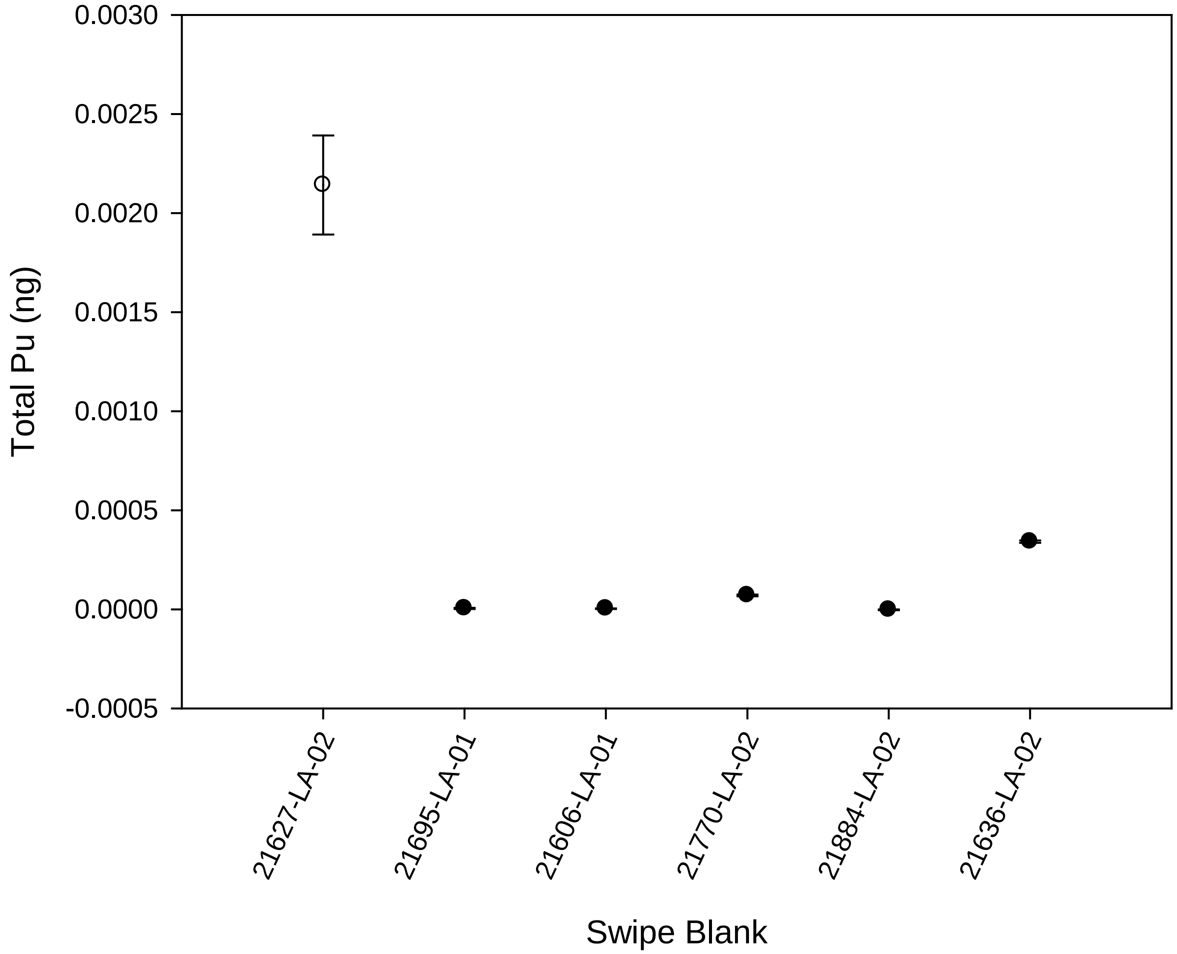
- Swipes
- Soil
- Water
- Vegetation
- Biological (urine, bone, tissue)
- Geological
- Sub-samples of bulk material for specialized analyses (e.g. age dating, morphology)

Uranium Swipe Blanks

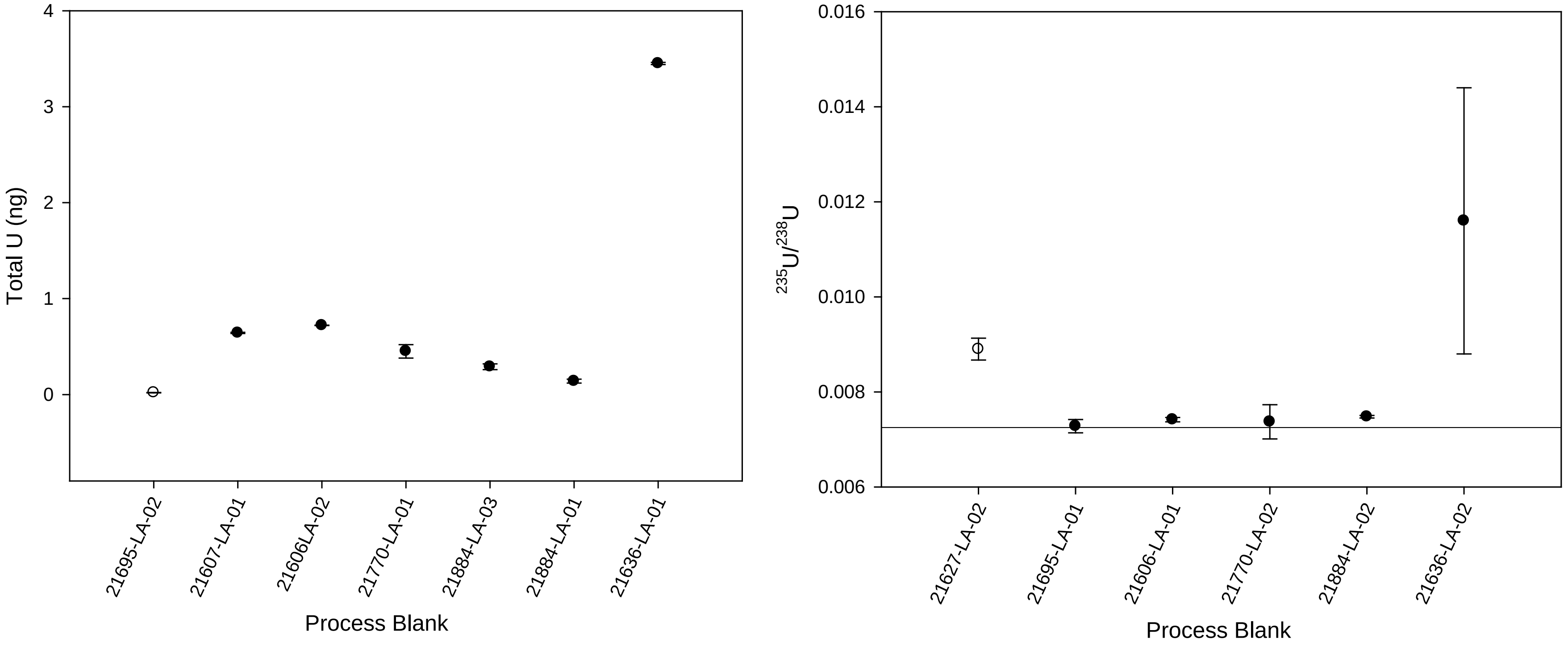




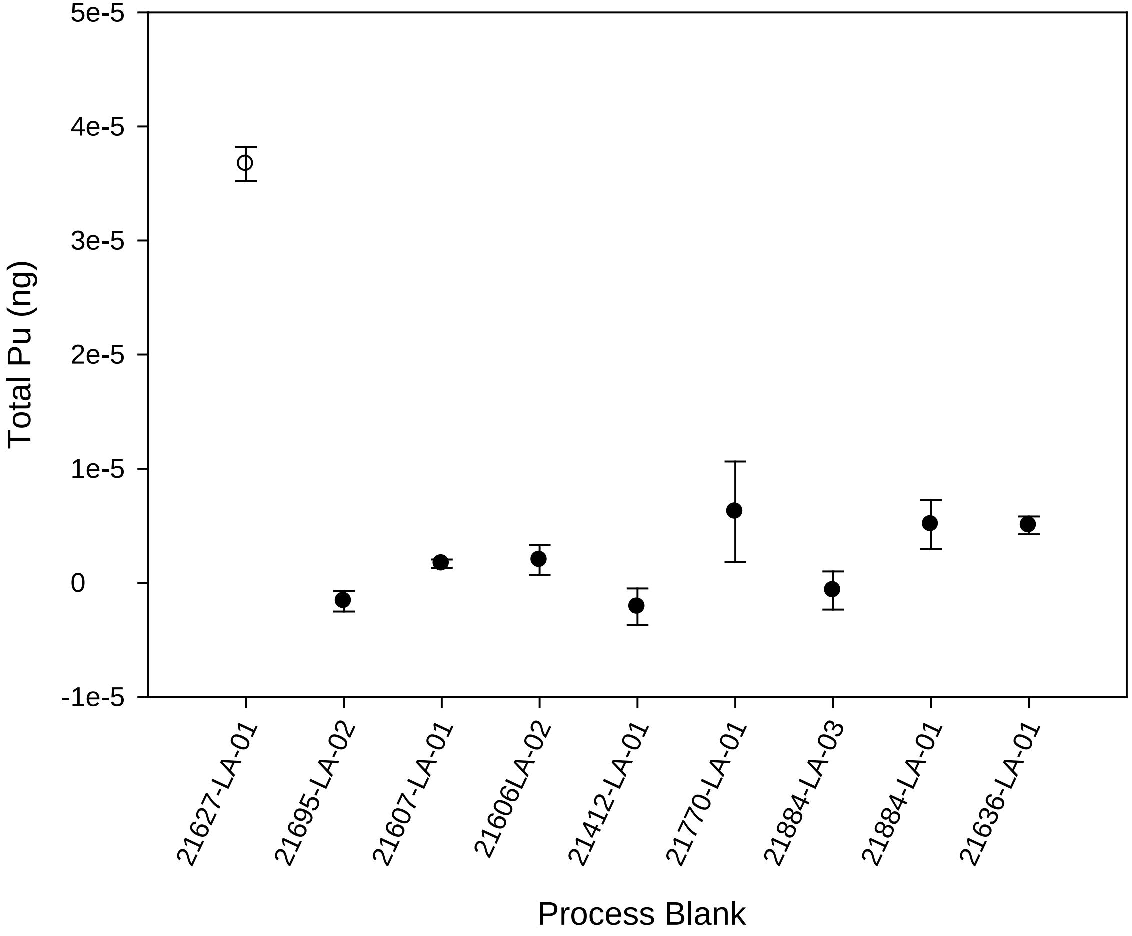
Pu Swipe Blank



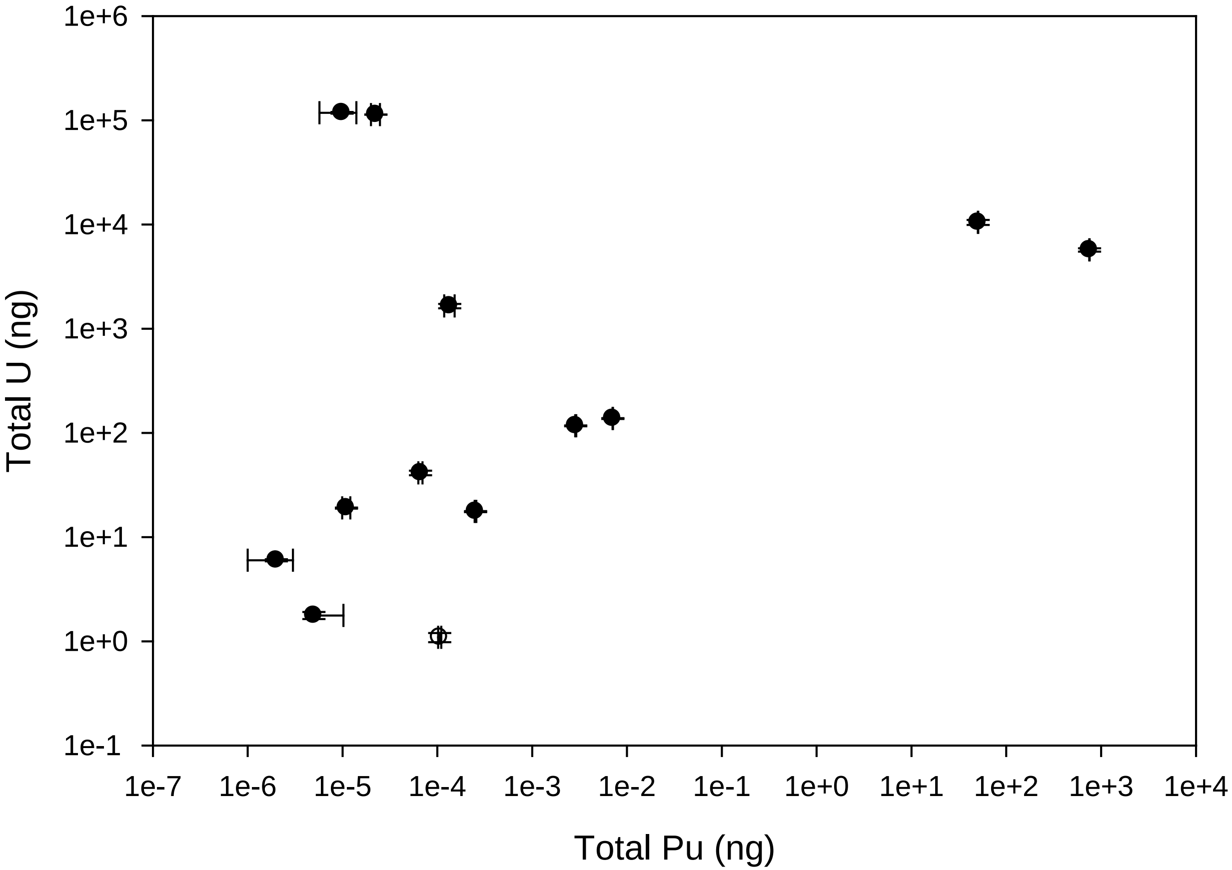
Uranium Process Blanks



Pu Process Blanks



Total U and Pu



Pu Cross-Contamination Control

Sample	Total Pu (ng)	$^{239}Pu/^{240}Pu$	Cross-Contamination Factor
21627-02-02	50.3±0.217	0.49	
21627-LA-01 (process)	0.0000367± 0.00000154	0.41	≈$1x10^{6}$
21627-LA-02 (swipe)	0.00214± 0.0000246	0.53	≈$2x10^{4}$
21636-05-02	755±3.78	0.30	
21636-LA-01 (process)	0.00000503± 0.000000783	0.10	≈$1x10^{8}$
21636-LA-02 (swipe)	0.000342± 0.00000593	0.31	≈$2x10^{6}$

Recent Environmental Study

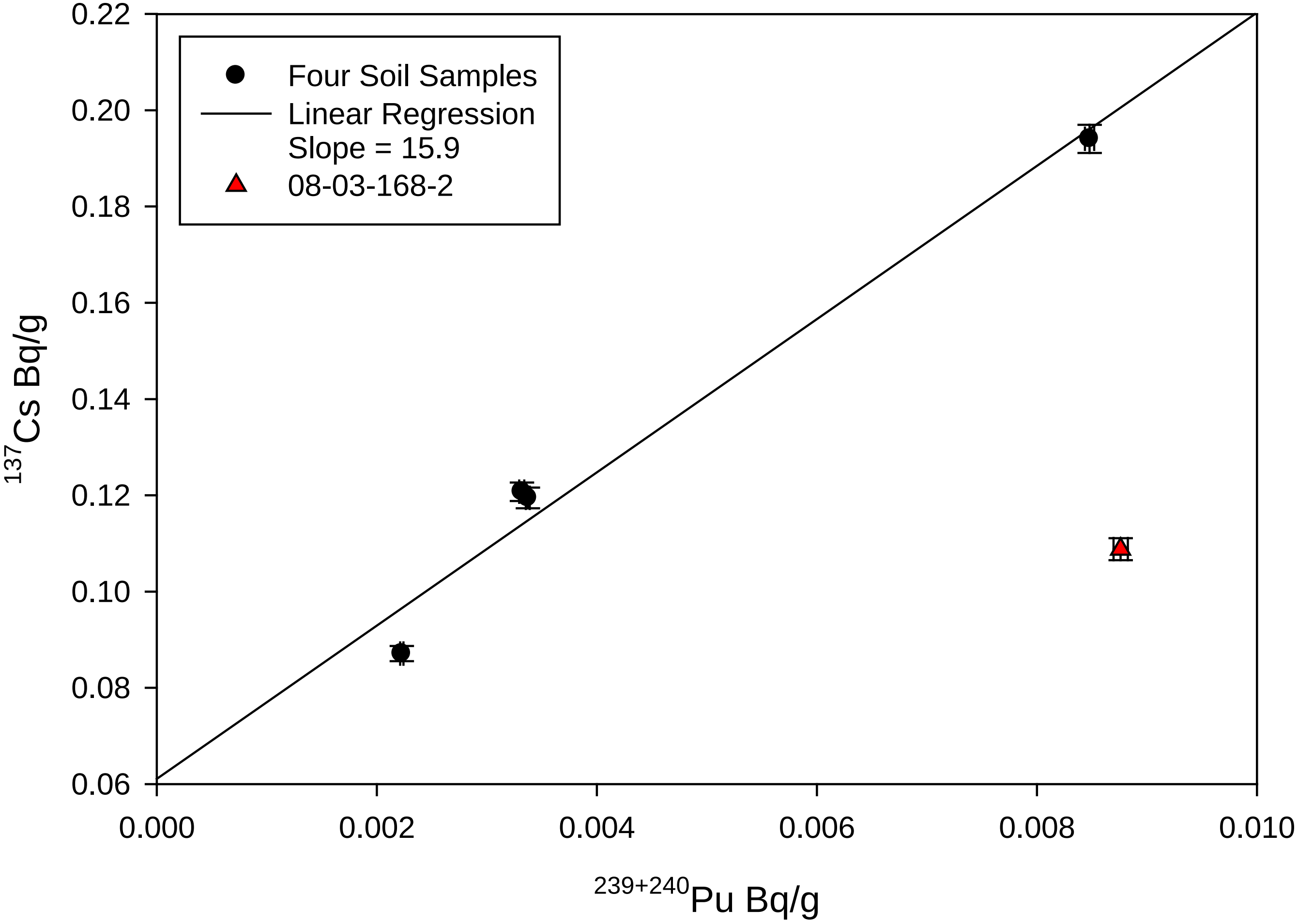
Background

- Five soil samples from local area showing elevated radiological activity
- Measure ^{137}Cs
- Measure ^{239}Pu, ^{240}Pu, ^{241}Pu
- Goal: Determine origin of material (i.e. global fallout, regional fallout, localized contamination)

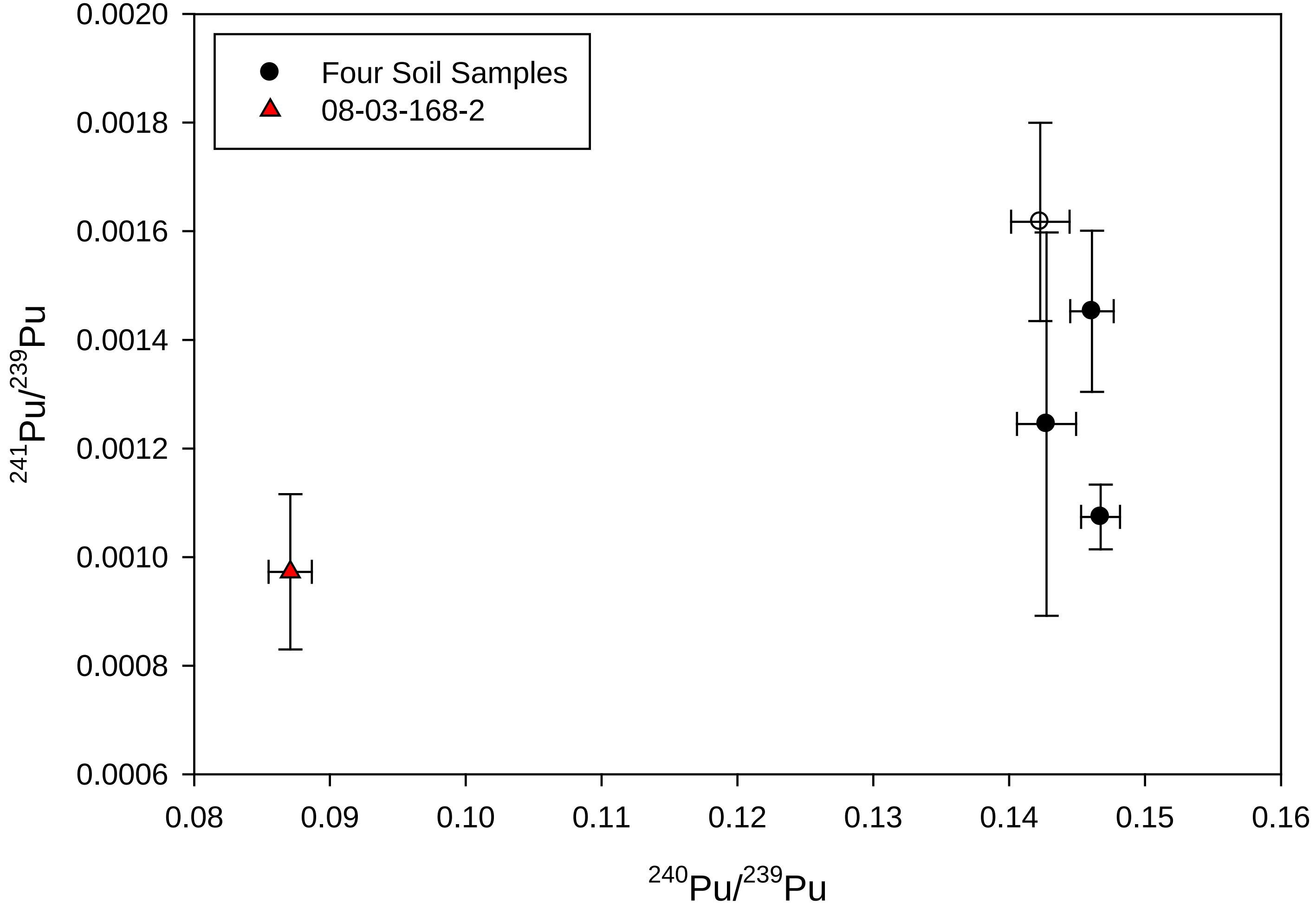
Experimental

- Samples and an appropriate SRM were analyzed by gamma-ray spectrometry to determine ^{137}Cs content.
- Samples and appropriate SRM were radiochemically processed.
- Samples and appropriate SRM were analyzed by alpha spectrometry to determine ^{238}Pu, $^{239+240}Pu$ and ^{241}Am content
- Samples and appropriate SRM were analyzed by thermal ionization mass spectrometry to determine ^{239}Pu, ^{240}Pu and ^{241}Pu content

^{137}Cs vs $^{239+240}$Pu Activity in Five Soil Samples



$^{241}Pu/^{239}Pu$ vs $^{240}Pu/^{239}Pu$ in Five Soil Samples



Conclusion

- One sample was significantly different than the other four.
- The unique sample has unambiguous characteristics of fallout from low yield atmospheric tests conducted at the Nevada Test Site.
- The data from the other four samples show characteristics of radionuclides distributed globally from large, high yield atmospheric tests by the US and the former Soviet Union.
- In all cases data is indicative of nuclear testing fallout and is not characteristic of localized contamination.

GUM Compliance

- Data reduction and uncertainty calculation performed using GUM principles
- Uncertainty calculations validated using GUM workbench
- Currently assessing twoapproaches for uncertainty determination based on GUM approach (pooled uncertainty model vs. classical uncertainty determination)

U Isotopic Analysis Model Equation for $^{235}U/^{238}U$

{Mass fractionation corrected atom ratios}

$R_{sample1,235/238}=R_{sample1,235/238,meas}/CF_{235/238};$

{Atom percent abundance}

$AtP_{235}=100*R_{sample1,235/238}/(R_{sample1,234/238}+R_{sample1,235/238}+R_{sample1,236/238}+1);$

$AtP_{238}=100/(R_{sample1,234/238}+R_{sample1,235/238}+R_{sample1,236/238}+1);$

{Atomic weight}

$AtW=(AtP_{234}*AtM_{234}+AtP_{235}*AtM_{235}+AtP_{236}*AtM_{236}+AtP_{238}*AtM_{238})/100;$

{Weight percent abundance}

$WtP_{235}=AtP_{235}*AtM_{235}/AtW;$

$WtP_{238}=AtP_{238}*AtM_{238}/AtW;$

{Mass fractionation factor}

$CF_{235/238}=(R_{C,235/238meas}/R_{C,235/238cert});$

Uncertainty Budget

$R_{sample1,235/238}$: measurand; mass fractionation corrected U-235/U-238 of the sample

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$R_{sample1,235/238,meas}$	$6.91200 \cdot 10^{-3}$ atom / atom	$7.60 \cdot 10^{-6}$ atom / atom	normal	1.0	$7.6 \cdot 10^{-6}$ atom / atom	28.4 %
$R_{C,235/238meas}$	0.0101340 atom/atom	$17.0 \cdot 10^{-6}$ atom/atom	normal	-0.68	$-12 \cdot 10^{-6}$ atom / atom	65.9 %
$R_{C,235/238cert}$	0.01014900 atom/atom	$5.00 \cdot 10^{-6}$ atom/atom	normal	0.68	$3.4 \cdot 10^{-6}$ atom / atom	5.7 %
$R_{sample1,235/238}$	$6.9222 \cdot 10^{-3}$ atom / atom	$14.3 \cdot 10^{-6}$ atom / atom				

Uncertainty Budget (Cont.)

$CF_{235/238}$: interim quantity: calculated mass fractionation correction factor for the U-235/U-238 ratio

Quantity	Value	Standard Uncertainty	Distribution	Sensitivity Coefficient	Uncertainty Contribution	Index
$R_{C,235/238meas}$	0.0101340 atom/atom	$17.0 \cdot 10^{-6}$ atom/atom	normal	99	$1.7 \cdot 10^{-3}$	92.0 %
$R_{C,235/238cert}$	0.01014900 atom/atom	$5.00 \cdot 10^{-6}$ atom/atom	normal	-98	$-490 \cdot 10^{-6}$	8.0 %
$CF_{235/238}$	0.99852	$1.74 \cdot 10^{-3}$				

Results for $^{235}U/^{238}U$ Isotopic Analysis

Results:

Quantity	Value	Expanded Uncertainty	Coverage factor	Coverage
$R_{sample1,235/238}$	$6.922 \cdot 10^{-3}$ atom / atom	$33 \cdot 10^{-6}$ atom / atom	2.32	95% (t-table 95.45%)
$CF_{235/238}$	0.999	0.018	2.32	95% (t-table 95.45%)
AtP_{235}	0.6874 %	$3.3 \cdot 10^{-3}$ %	2.32	95% (t-table 95.45%)
AtP_{238}	99.3075 %	$3.3 \cdot 10^{-3}$ %	2.32	95% (t-table 95.45%)
WtP_{235}	0.6788 %	$3.2 \cdot 10^{-3}$ %	2.32	95% (t-table 95.45%)
WtP_{238}	99.3162 %	$3.2 \cdot 10^{-3}$ %	2.32	95% (t-table 95.45%)

Lessons Learned

- Application of GUM workbench is straight forward for samples that can be analyzed multiple times
- Application of GUM methodology is more difficult for samples of very limited amount
- Development of a pooled uncertainty approach is labor intensive and requires matrix matched QCs

Summary

- LANL has many years of experience supporting environmental-level programs
- A diverse set of capabilities exist with new capabilities coming on-line
- LANL continues to strive for the highest and most defensible data quality
- There are many areas for future collaboration