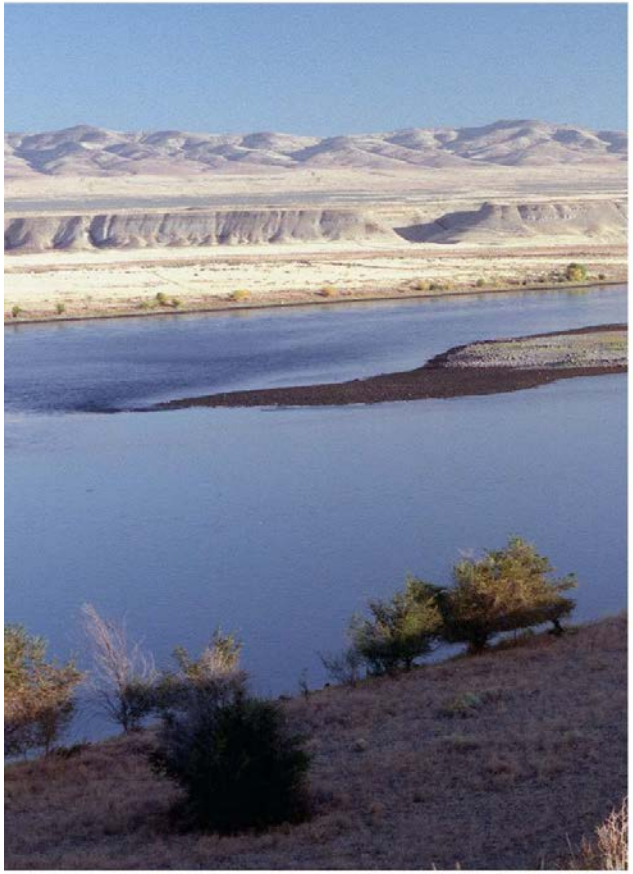
Hanford Metal Ratio Process Development

Presented to: Beryllium Health & Safety Committee

CHPRC-02757-VA Rev. 0



Hanford Metal Ratio Process Development

Scott Seydel, CIH
Senior Industrial Hygienist, CH2M, Inc.

Charles Davis, PhD
Principal Statistician, EnviroStat

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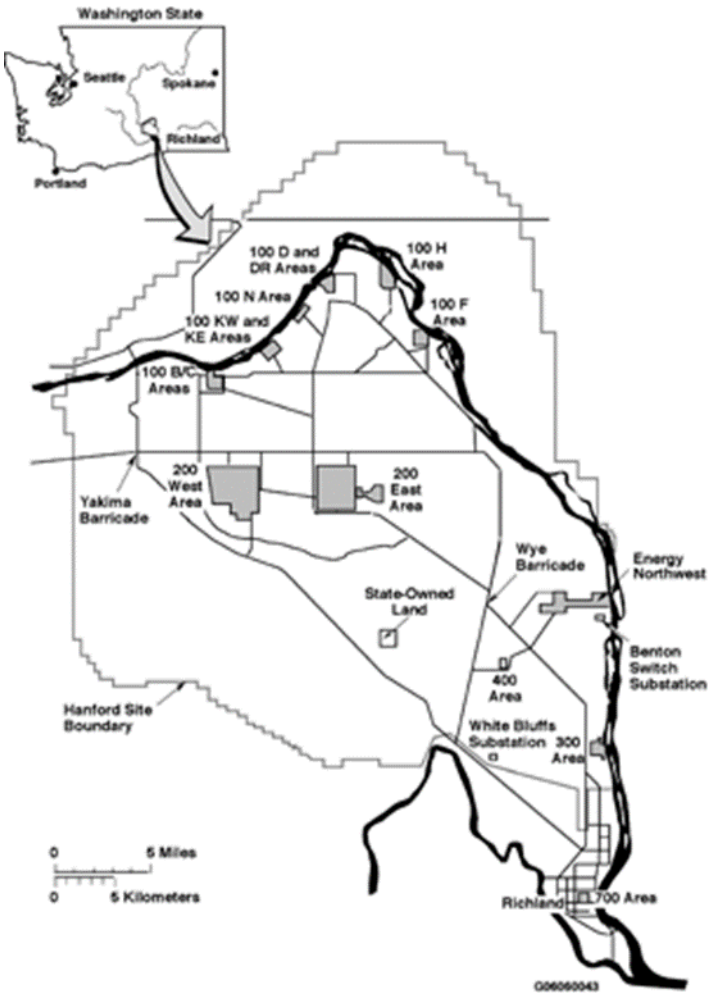
Beryllium at Hanford

- Limited current beryllium mission activities
- Beryllium legacy contamination
  - Fuel production in 300 Area
  - Rocky Flats ash/oxide
  - Beryllium alloy components
- 1200 active buildings
- 290 inactive buildings
- 2050 structures and tanks



Metal Ratio Objectives

- Use other naturally occurring metals to predict N-Be
- N-Be is naturally occurring in minerals
  - Hence not toxic, as shown in epidemiological studies
- Base predictions on ratios of Be with other metals
  - Prefer metals not otherwise present in facilities being evaluated

Metal Ratio Development Process

- Data Quality Objectives (DQO)
- Sampling & Analysis Plan (SAP)
- Sample Collection
- Sample Analysis

DQO Summary

- Identify the Decision
- Identify Inputs to the Decision
- Define the Boundaries
- Develop the Analytical Approach
- Specify Limits on Decision Error
- Optimize the Design for Obtaining Data

Identify the Decision

Determine that a metals ratio approach can reliably distinguish anthropogenic beryllium from the natural beryllium (N-Be) in background soils and use this data to evaluate facility cleanup options.

OR

Determine that the metals ratio cannot reliably distinguish anthropogenic beryllium (A-Be) from natural beryllium in Hanford surface soils and pursue other options for minimizing cleanup costs while protecting workers.

Identify Inputs to the Decision

- Data describing the range of concentrations of beryllium and its relationship with the concentrations of other potential indicator metals in background surface soils at the Hanford Site
  - Data must be representative of background surface soils
  - Multiple analysis of samples required
  - Use of Conceptual Site Model (describes mineralogy and geochemistry of the soils)
  - Use of uncensored data
  - Analytical issues may exclude some metals from consideration

Define the Boundaries

- Target Analytes
  - Initial list of 38 candidate predictors
    - Used two different analytical methods and two dilutions in R0
  - Three rounds of analysis (R0, R1, R2)
  - Reduced to 16 analytes by Round 2
- Sampling Locations
  - Minimum of 60 locations recommended by DQO
  - 76 locations initially identified
  - 65 locations actually sampled
    - 11 locations eliminated due to ecological & cultural concerns

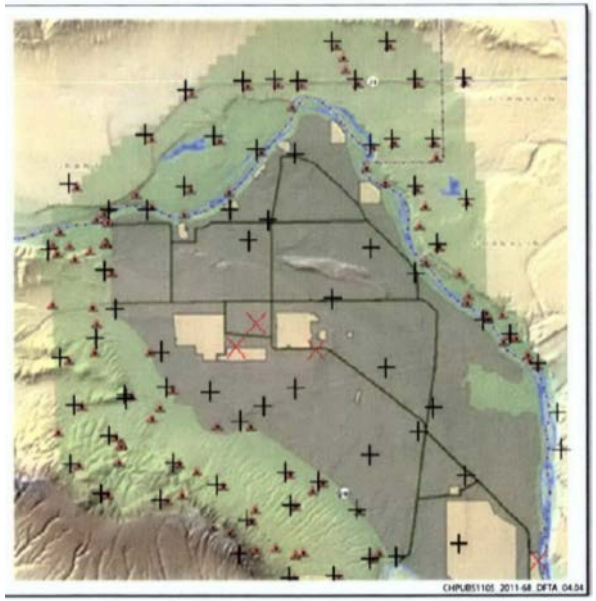


Figure 4-4. Location Overlay

Develop the Analytic Approach

- Sample data collected during this effort will be used to develop effective and reliable algorithms for predicting N-Be concentrations in future samples to be obtained inside facilities using a metal ratios approach.
  - Evaluated on its ability to predict N-Be
  - Ease of analysis
  - Reproducibility
  - Consideration of other sources of metal (e.g. Al, Cu, Fe, Li)
  - Potential for nuclear generation (e.g. Y, U, Cs, Zr)
    - Yttrium is acceptable so long as ICP-MS is used
    - Nuclear generation of cesium determined to be a non-issue

Specify Limits of Decision Error

- Log Scale Prediction Standard Error (PSE) describes how accurately one can predict the amount of N-Be that should be present in a bulk or wipe sample obtained inside of a facility
- Per the DQO:
  - PSE of 0.10 or lower is ideal
  - PSE of 0.15 or lower is acceptable
  - PSE of above 0.20 is too large

Optimize Design for Obtaining Data

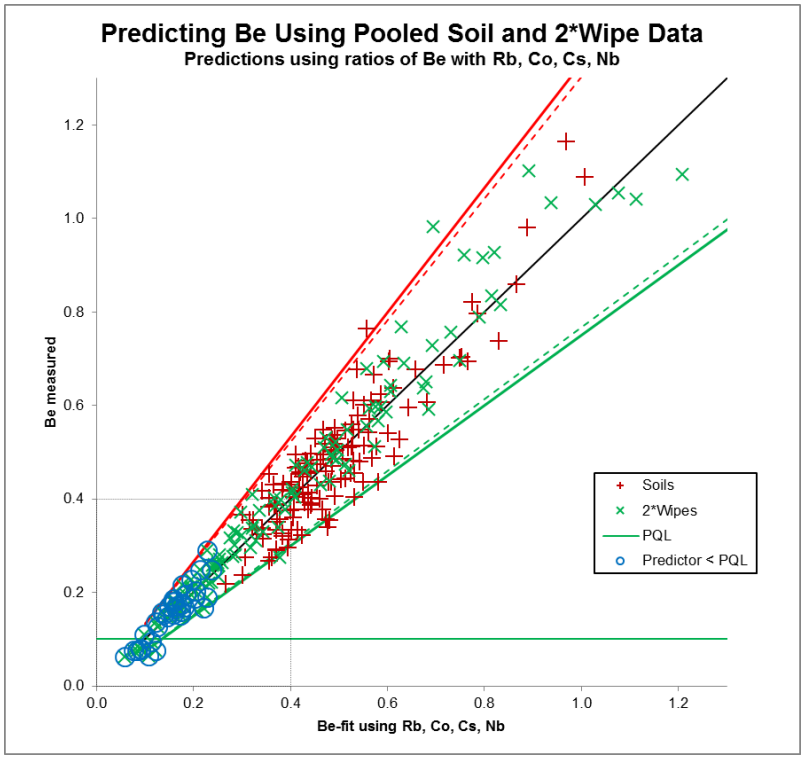
- Sample site selection process described in Chapter 4
- Screening of samples with a 1,000 µm sieve
- Analysis of both bulk and wipes
- Field and analytical duplicates during sample analysis
- Testing of multiple analytical methods
- Use of uncensored data
- Repeated rounds of analysis

Summary of Results

- Metal ratio process consistent with DQO requirements is feasible
- Metal ratio using four metals optimum
  - Additional metals provided minimal additional value
- A two metal ratio also met DQO requirements
- Data curiosities were noted
  - Inter-batch variations and non-zero intercepts
  - Worth additional investigation but not enough to prevent recommendation to proceed
- Analytical QC acceptance criteria met

Four Metal Ratio

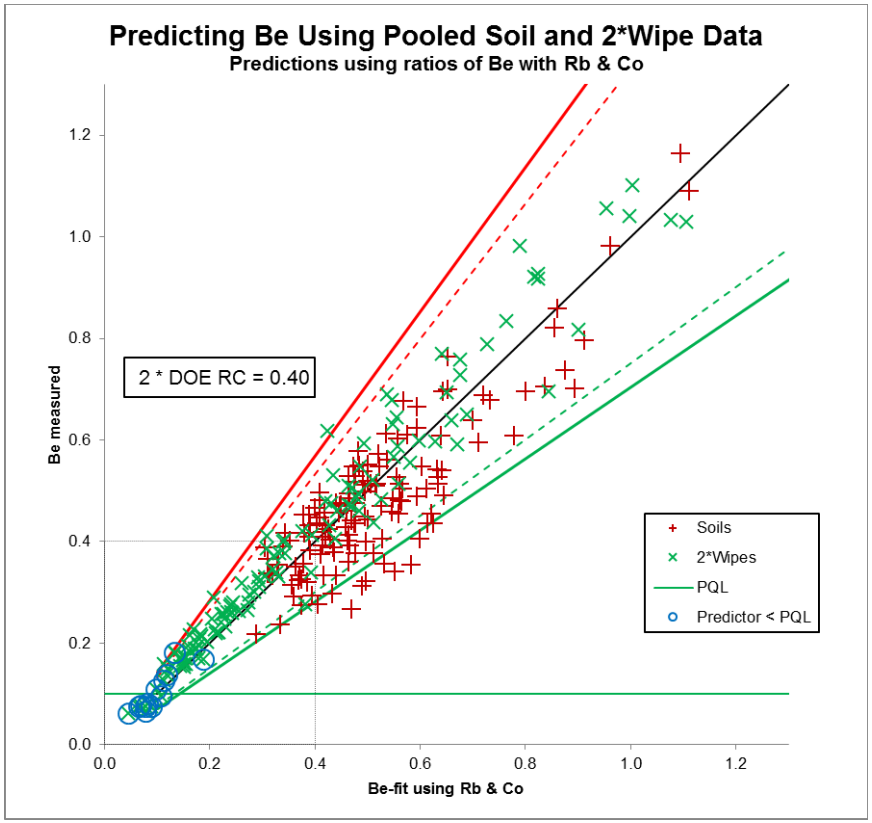
- Metals recommended
  - Cobalt (Co)
  - Cesium (Cs)
  - Niobium (Nb)
  - Rubidium (Rb)
- PSE = 0.1433
- Ratio works for both soils and wipes



$$\log(\text{Be-fit}) = -4.9740 + 0.3423*\log(\text{Co}) - 0.5410*\log(\text{Cs}) - 0.0734*\log(\text{Nb}) + 1.2722*\log(\text{Rb})$$

Two Metal Ratio

- Metals recommended
  - Cobalt (Co)
  - Rubidium (Rb)
- PSE = 0.1756
- Ratio works for both soils and wipes
- log(Be-fit) = –3.4655 + 0.1858*log(Co) + 0.8142*log(Rb)



Metal Ratio Process Options

- Next step is to determine what the approach should be:
  - Take no action
  - Technical evaluation
  - All samples
  - All bulk samples and suspect wipes
  - Suspect bulk and wipe samples
  - Large Area Wipes
  - Some combination of the above approaches

Technical Evaluation Process

- Collect additional samples for metal analysis whenever a sample is at/above the control and/or trigger level
- Use data to develop a technical evaluation per the existing process in DOE-0342-002 and DOE-0342-004 (Hanford Site Assessment & Characterization Procedures)
  - Doesn't require any change to procedures
  - Not a significant cost increase to implement
  - Currently no way of analyzing original sample for metal ratio
    - Possibility of saving digestate and re-analyzing if necessary

All Samples

- Analyze all samples using metal ratio process
  - Would generate the most data regarding beryllium sources
  - Would greatly increase cost of program
  - Would require revisions to DOE-0342-002 and DOE-0342-004
  - Throughput issues until additional labs could be qualified
  - Vast majority of wipe samples report beryllium to below the MDL or reporting limit
  - What to do if sample is below the trigger/control level but metal ratio indicates at least some A-Be is present?
    - Focus on ensuring A-Be is below the trigger/control level?

All Bulk and Suspect Wipe Samples

- Analyze all bulk samples and “dirty” wipe samples using metal ratio process
  - Would generate more data than TE process
  - Addresses issues with most wipe Be results being <RL
  - Would greatly increase cost of program
  - Would require revisions to DOE-0342-002 and DOE-0342-004
  - Throughput issues until additional labs could be qualified
  - What to do if sample is below the trigger/control level but metal ratio indicates at least some A-Be is present?

Suspect Bulk and Wipe Samples

- Analyze all suspect bulk samples and “dirty” wipe samples using metal ratio process
  - Would generate more data than TE process
  - Addresses issues with most wipe Be results being <RL
  - Reduced cost than analyzing all samples
  - Would require revisions to DOE-0342-002 and DOE-0342-004
  - Throughput issues until additional labs could be qualified may still exist
  - What to do if sample is below the trigger/control level but metal ratio indicates at least some A-Be is present?

Metal Ratio – Large Area Wipes

- Wipe multiple surfaces until the wipe is loaded with material
  - May reduce overall program cost
  - Would require revisions to DOE-0342-002 and DOE-0342-004
  - Throughput issues until additional labs could be qualified
  - Samples can't be directly compared to the trigger/control level unless the total area wiped is measured
    - One 1000 cm^2 **wipe sample whose result is divided by 10 ≠ ten wipe** samples of 100 cm^2 each

More Questions Being Considered

- Should the prediction interval be expanded to address accommodate the number of samples involved in making decisions in a particular instance?
- Should the metal ratio apply to surface soils outdoors?
- Should a correlation study be conducted for sub-surface soils?
- How should routine validation of results be conducted?
- Who will develop the process for proficiency testing of other labs wanting to do metal ratio analysis?

Ongoing Work Outside of the Metal Ratio Process

- Analysis of Inter-Lab Comparison Data
  - Comparing sample beryllium data from ALS, Bureau Veritas, and Test America-Richland to the RJ Lee Metal Ratio beryllium data
  - Labs used their standard sample preparation methods, not beryllium study method
  - Data has been received and is currently being analyzed by Dr. Charles Davis
- Round 3 Sample Analysis
  - Limited number of analyses to look at the data curiosities
  - Development of lab Standard Operating Procedures