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The Hanford Metal Ratio Method: How to Use It

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The Hanford Metal Ratio Method: How to Use It

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Plan for Today

Quick review of the Hanford Metal Ratio Study (MRS)

- Anthropogenic Beryllium (A-Be) is toxic, a major health concern
- Natural Be (N-Be) presumed not related to disease
- Would like to be able to evaluate A-Be vs N-Be in Total Be (T-Be) measurements in individual samples
- History and goals of study
  - Using ratios of N-Be with predictor metals in local soils to quantitate A-Be vs N-Be

    (A-Be estimate = T-Be measurement – N-Be prediction)
- Results and recommendations
- Current uses at Hanford

Plan for Today

Technology Transfer Activities proposed at BHSC Spring 2017

- **Careful write-ups of procedures developed during MRS**
- **Ideas about how another lab coming to Hanford Site might proceed**
- **Ideas about how to implement the Hanford MRM at another Site (DOE, DoD, or other)**
  - **Focus for today**
- **Submit article to peer-reviewed journal**
  - **(in progress)**
- **Prepare proposal for ASTM Guide**
  - **(in progress)**

Plan for Today

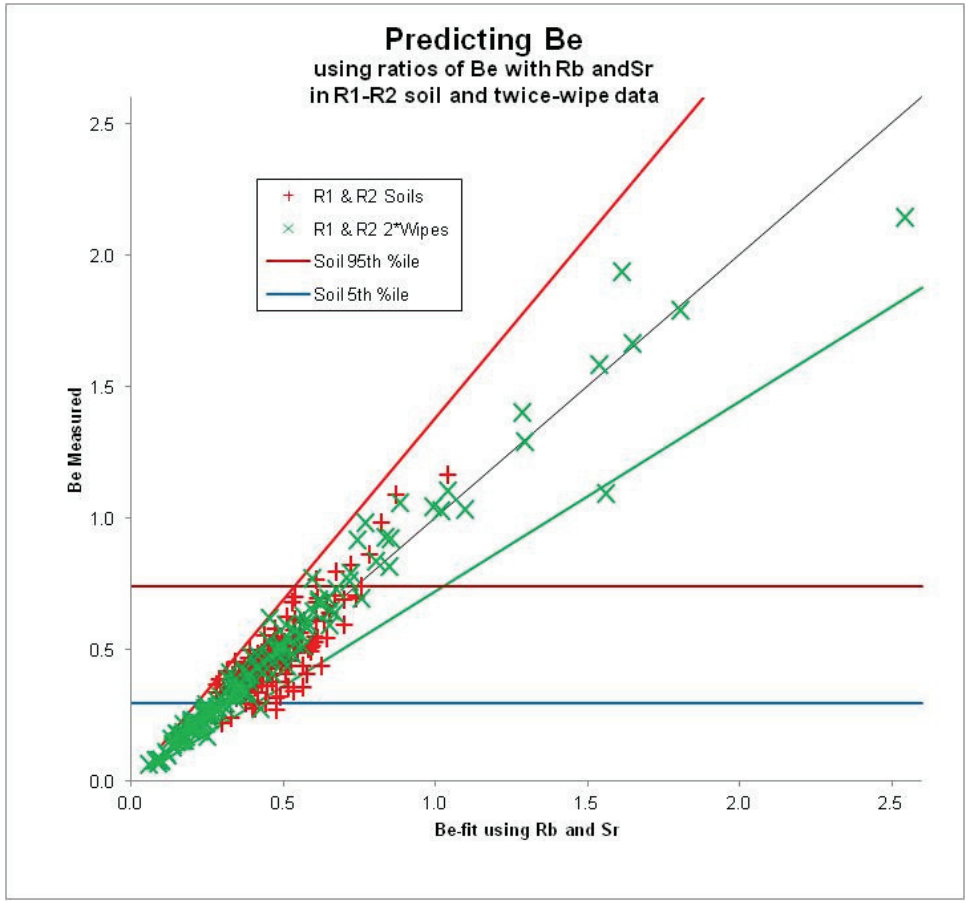
Thoughts on implementing a MRM at another Site

- Why do it?
  - Benefits
  - Costs
  - *Caveats*
- Scenarios
  - Where does N-Be come from and how does it get into facilities?
  - What kinds of in-facility samples will be compared?
  - What decision criteria will be used?
- Steps
  - Identify and sample background sources
  - Identify candidate predictor metals, get lab analyses
  - Select predictor metals to use
  - Fit and validate predictive model

Quick Background

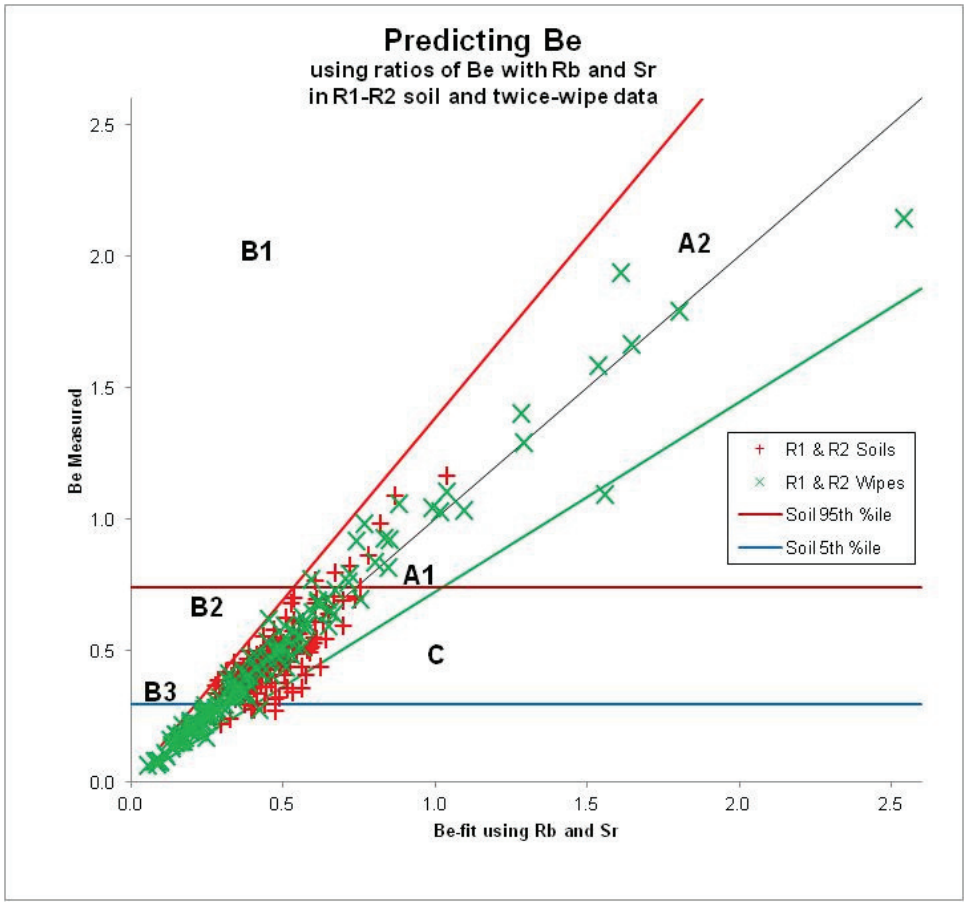
Began MRS in 2010, completed in 2017

- Why do this?
- How does it work?
- Quick example
  - Uses final fits
- Where's the cut-off using soil alone?
  - 95th %ile of soil?
  - 5th %ile of soil?
- Expanded on next slide



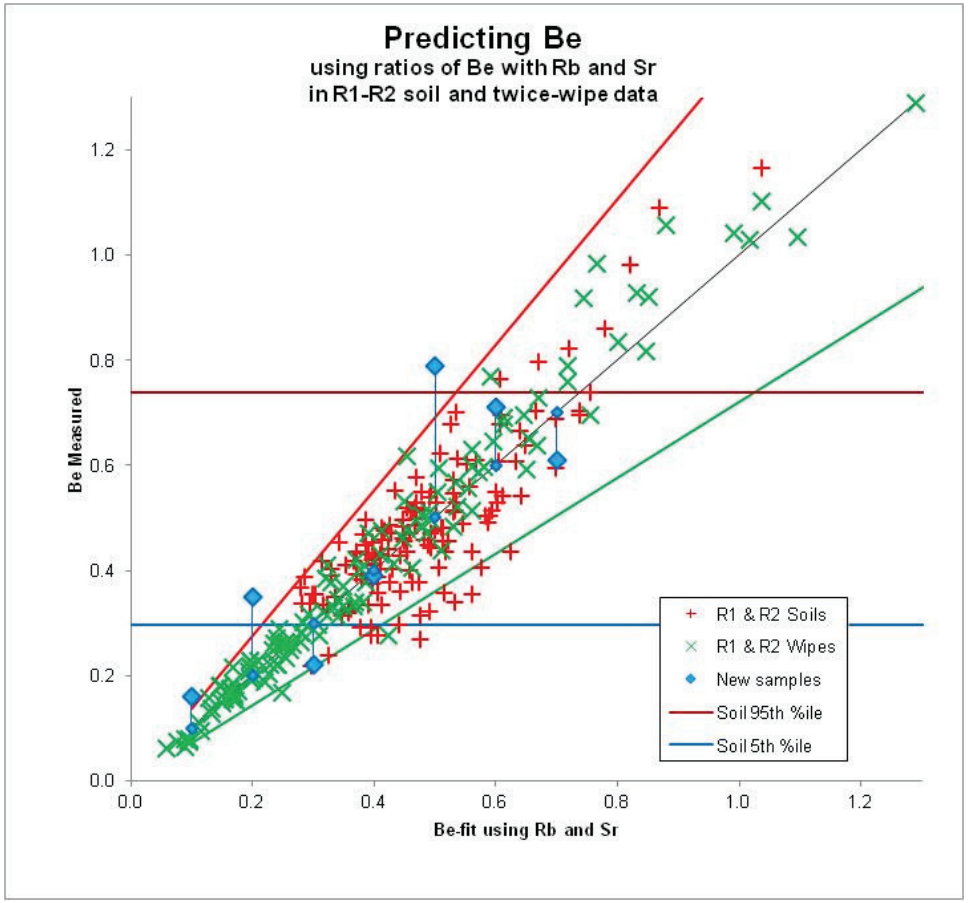
Quick Background

- New sample plots in
  - A1 – fine
  - A2 – OK but > typical soil
  - B1 – clearly A-Be
  - B2 – likely some A-Be but not so high
  - B3 – likely a little A-Be but pretty low
  - C – check the analysis
- This is for interpreting individual values
  - 95% prediction bounds
  - Don't forget <u>multiple comparisons issue</u>



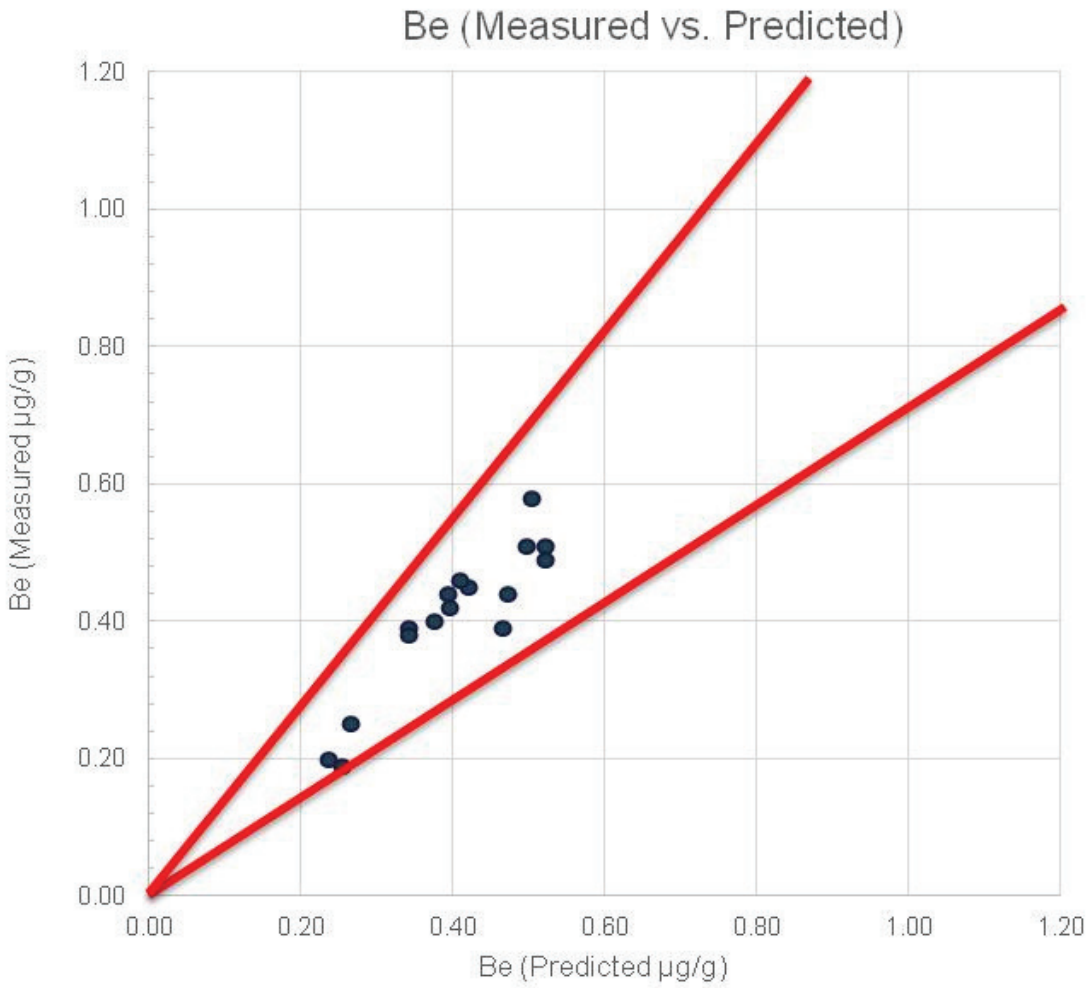
Quick Background

- For datasets
  - A-Be estimate = T-Be measured – N-Be predicted
  - Use dataset of A-Be estimates
  - Many A-Be estimates will be negative



Quick Background

- Recent example
- Samples were from CONEX boxes not expected to have any A-Be
  - Almost too pretty!



On Using the Hanford MRM at Another Site

Why do it?

- **Benefits**
  - **Evaluate A-Be components of individual samples**
    - **Useful in evaluating samples taken in windy, arid forward areas**
    - **Useful in evaluating samples taken in D&D facilities in such areas**
    - **Useful in focusing worker protection budgets on areas of greater concern**
- **Costs**
  - **Need to develop prediction methods for your site**
    - **BG study involved, though not a big science project like Hanford MRS**
    - **After that, need to analyze each sample for 2-5 metals**
      - **Adding a metal usually not that costly**
- ***Caveats***
  - **Use existing data, such as USGS, as suggestions, but verify!**
    - **Check soil strata, analytical methods, etc.**
    - **Existing data likely not obtained using aggressive digestion for BeO**

On Using the Hanford MRM at Another Site

Scenarios

- Developed for ASTM Standard Guide proposal
- WF – windblown soil source, facility bulk/wipe samples
  - Similar to Hanford or NNSS or . . .
- WA – windblown soil source, air samples
  - May occur occasionally
- WD – windblown soil source, soils to be evaluated
  - Soils of interest may be near source facilities
  - Or may involve checks on remediation
- IF – don't have accessible soil source, but have A-Be-free comparable facilities
  - Comparable in terms of nature of activities, likelihood of N-Be presence

On Using the Hanford MRM at Another Site

Steps

- Identify and sample background sources of N-Be
  - If soils, sample not too close but not too far
    - Want soils without A-Be from facilities of concern
    - But still want geochemistry similar to what would be in those facilities if no operations involving A-Be had taken place
  - Sample appropriate soil strata, usually surface – how do minerals containing N-Be get into facilities or areas of concern?
  - For IF scenario, identify comparable facilities
  - Recommend randomized grid sampling
    - See Practitioners Guide Chapter 6 for discussion
  - How many locations? Depends on perceived complexity of geochemistry – used 65 in Hanford MRS, likely less (15-20 or so at your Site)
  - Obtain enough background material at each location to allow for multiple (at least 4) BG analytical batches!

On Using the Hanford MRM at Another Site

Steps

- **Identify candidate predictor metals**
  - **Can use available databases as suggestions**
    - **At Hanford, had geochemical database from analyses of archived soils from 2004-2005 and 2009**
  - **Suggest selecting metals typical of local mineralogy**
    - **Hanford experience: Rb has high correlation with Be, but Sr varies among minerals prominent in Hanford BG area, has low correlation with Be itself; the combination works well**
  - **Ensure that sample prep and analysis procedures are those to be used in the future; document and follow rigorously**
    - ***Caveat*: analytical methods discuss accuracy of analyses of individual analytes but not consistency of ratios!**
  - **Obtain background data from lab in multiple batches**
    - **Suggest tweaking bulk samples or amounts of soil added to wipes to cover range of Be expected in in-facility bulk or wipe samples**

On Using the Hanford MRM at Another Site

Steps

- **Select predictor metals**
  - **ALL ANALYSES USE LOG DATA!**
    - **(1) Good variance-stabilizing transformation for environmental data >>0**
    - **(2) Allows predicting based on ratios, which is necessary for scaling down to bulks with lots of "fluff" and wipes**
  - **Best subsets regression is useful; example from final iteration in Hanford MRS**
  - **But FIRST, verify consistency of Be/Metal ratios across analytical batches!**

This turned out to be interesting in the Hanford MRS

Best subset prediction results						
Vars	R-Sq	S	Rb	Ce	Nb	Sr
1	85.9	0.17	X			
1	76.5	0.22		X		
1	76.3	0.22			X	
1	61.9	0.28				X
2	87.7	0.16	X			X
2	87.4	0.16	X		X	
2	87.0	0.16	X	X		
2	78.3	0.21		X	X	
3	88.0	0.16	X		X	X
3	88.0	0.16	X	X		X
3	87.5	0.16	X	X	X	
3	79.0	0.21		X	X	X
4	88.0	0.16	X	X	X	X

On Using the Hanford MRM at Another Site

Steps

- Fit and validate predictive model
  - Log-scale least-squares model with *p* predictors
  - log(Be) = A + ß1 * log(M1) + …. + ß*p* * log(M*p*) + error

    With constraint ß1 + … + ß*p* = 1 to make predictions based on ratios
  - If *p* = 1, ß1 = 1, so we have just log(Be/M1) = A + error

    Estimate of A = average of log(Be/M1) – go to next slide
  - For *p* > 1, there's a trick to doing the constrained fit

    Subtract log(M*p*) from log(Be), log(M1), …

    Fit log(Be) – log(M*p*) = A + ß1 * [log(M1)-log(M*p*)] + …

    This gives estimates of A, ß1, … ß(*p*-1); let ß*p* = 1 – [ß1 + … + ß(*p*-1)]

    (Challenge to math types – verify that this gives same result as formal constrained least-squares computation)

On Using the Hanford MRM at Another Site

Steps

- Fit and validate predictive model
  - For validation, recommend "leave-one-out" approach
  - Have B analytical batches; leave each out in turn, fit predictive model to remaining (B – 1) batches, used that fitted model to predict Be in omitted batch, obtain log-scale standard error of prediction
  - Average (root-mean-square) those PSEs over the B batches
  - Average PSE is approximately the ± percent value once prediction equations are unwrapped back to original scale
- How good a fit would we like?
  - PSE ~ 0.10 is too good to be realistic; approximates accuracy requirements for Be analysis itself!
  - PSE ~ 0.15 is very nice (per our DQO discussions)
  - PSE > 0.20 is getting too loose for comfort
  - Final Hanford MRS PSE ~ 0.163 (slide 6)

On Using the Hanford MRM at Another Site

Conclusions

- A MRM like that developed for Hanford can work at your Site
- There is some cost and effort involved in
  - Identifying and sampling appropriate background materials
  - Getting BG lab analyses in multiple batches
- Benefits
  - Being able to see clearly how much N-Be is expected in each sample based on minerals in that sample

Discussion?