The Hanford Metal Ratio Study
Part 2

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Structure

The Hanford Metal Ratio Study

- Objective: use other naturally occurring metals to predict N-Be
  - N-Be is naturally occurring in minerals
    - Hence not toxic, as shown in epi studies
  - Base predictions on ratios of Be with other metals
    - Prefer metals not otherwise present in facilities being evaluated
- History
  - Introduced during NV worker protection surveys and elsewhere
  - Proof-of-concept analyses and presentations at Hanford ~ 2011
  - Careful DQO and SAP development
    - Background soils scattered systematically around Hanford Site
      - Winds are notorious at Hanford; sieved to collect “blowable” fraction
  - Collected large quantities of soils from 65 locations

Structure

The Hanford Metal Ratio Study

- **Round 0**
  - **Soils from 7 locations**
  - **Purpose: allow lab to come up to speed on analytical requirements**
    - **Including ABF/HNO_3 digestion for BeO**
  - **Both ICP-AES and ICP-MS analyses, with multiple dilutions**
  - **38 candidate predictor metals**
- **Round 1**
  - **Soils from all 65 locations**
  - **Purposes: further refine methodology, slim down list of candidates**
  - **30 candidate predictors**
  - **Both ICP-AES and ICP-MS, but with single dilution**
    - **High intra-run correlations among metals make MR work**

Structure

The Hanford Metal Ratio Study

- Round 2
  - Soils from all 65 locations
  - Purpose: finalize list of predictors, develop predictive model
  - 15 candidate predictors, ICP-MS only, single dilution
- Issues
  - Is prediction adequately successful?
    - How many metals should one use?
    - Can one avoid certain metals possibly found in facilities?
    - Do any candidate predictors have non-detect issues?
  - Are there any issues regarding background location selection?
    - Under-representation of SW sector compared with SAP
    - Inclusion of a few non-background locations near 200 and 300 areas
  - Compare prediction success with bulks and wipes

Results

Predictor Metal Selection

- **Method: log-scale best subsets regression**
  - **Typical output**

Trial Best Subsets Prediction Analysis with R2 data																	
Using all 15 candidate predictors																	
Vars	R-Sq(adj)	S	Rb	Cr	Cs	Sn	Ce	Li	Y	Zr	Co	Ag	Nb	As	La	Sr	Th
1	72.4	0.141	X														
1	65.3	0.159		X													
1	54.0	0.183			X												
1	50.0	0.190				X											
2	77.1	0.129	X		X												
2	74.9	0.135					X	X									
2	74.5	0.136	X						X								
2	74.4	0.136	X							X							
3	81.0	0.118	X		X						X						
3	80.7	0.118	X		X					X							
3	80.6	0.119	X		X				X								
3	78.3	0.125		X				X		X							
4	**83.5**	**0.109**	**X**		**X**				**X**			**X**					
4	83.2	0.110	X		X			X		X							
4	83.1	0.111	X		X						X	X					
4	83.0	0.111	X		X			X			X						
. . .																	
15	88.1	0.093	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

Results

- **Details**
  - Log scale prediction allows easy transition to using ratios
  - R-Sq(adj) is squared multiple correlation adjusted for # predictors
  - S is log-scale StDev of errors, approximately log-scale PSE
  - PSE = prediction standard error
    - Includes estimated variability of Be measurement itself
    - Should also take uncertainty of coefficient estimates into account
      - Nearly the same as relative prediction error

        $\exp(\pm KS) \approx 1 \pm KS$
  - Note that S with best 4 predictors is close to S with 15 predictors
  - Note redundancy in predictor selection!

Results

- Performed intensive (and informative) data evaluation
- Issues
  - Batch-to-batch variation prominent
    - Within-batch duplicates agree better than between-batch duplicates for most analytes
  - Wipe results as function of amount of soil added unexpected
    - Non-zero intercept
  - Concerns with metals likely to be in facilities from non-natural sources
  - Comparing bulk and wipe results

Results

- **Metals omitted in final analyses**
  - **Cr (presence in wipes, possible presence in facilities)**
  - **Li (inconsistent recovery between analytical batches)**
  - **Ag (values low compared with instrument range, even for soils)**
- **Round 3 to be added**
  - **Further evaluate analytical issues and test prediction algorithms**

Results

- **Best subset log-scale regression repeated omitting Cr, Li, Ag**
  - **Results similar for Round 2 and Round 1 data, so combine them**

Combining R1 and R2 soil data														
Vars	R-Sq(adj)	S	Rb	Cs	Sn	Co	Y	Zr	Nb	La	As	Ce	Sr	Th
1	60.9	0.179	X											
1	40.9	0.220		X										
1	37.9	0.226			X									
1	33	0.234				X								
2	69.2	0.159	X	X										
2	67.1	0.164	X			X								
2	65.3	0.169	X				X							
2	65.3	0.169	X					X						
3	77.1	0.137	X	X		X								
3	74.9	0.143	X	X				X						
3	74.8	0.144	X	X			X							
3	71.5	0.153	X		X	X								
4	**80.6**	**0.126**	**X**	**X**		**X**			**X**					
4	79.9	0.128	X	X	X	X								
4	79.3	0.130	X	X		X				X				
4	78.2	0.134	X	X			X			X				
12	82.8	0.119	X	X	X	X	X	X	X	X	X	X	X	X

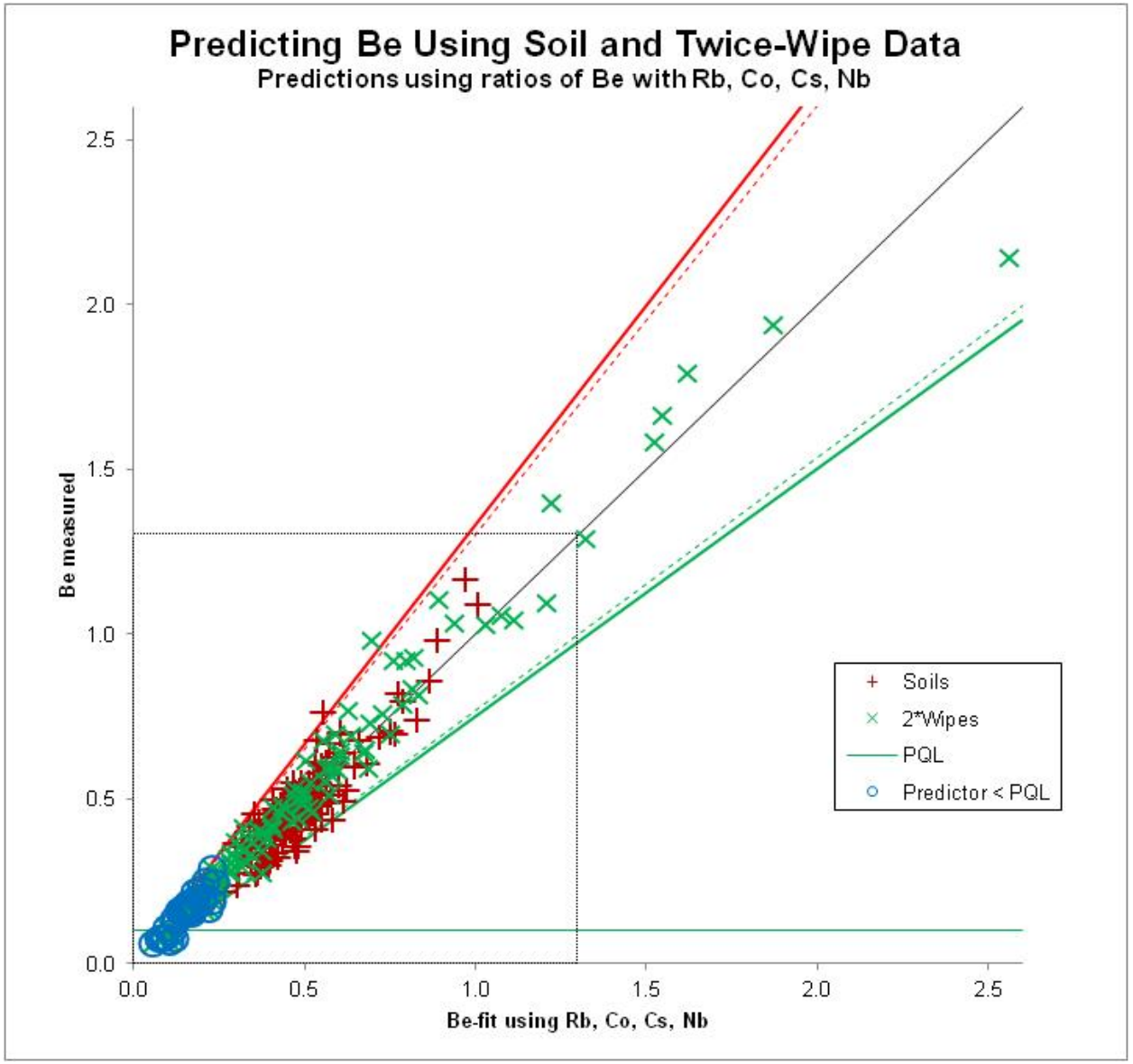
Results

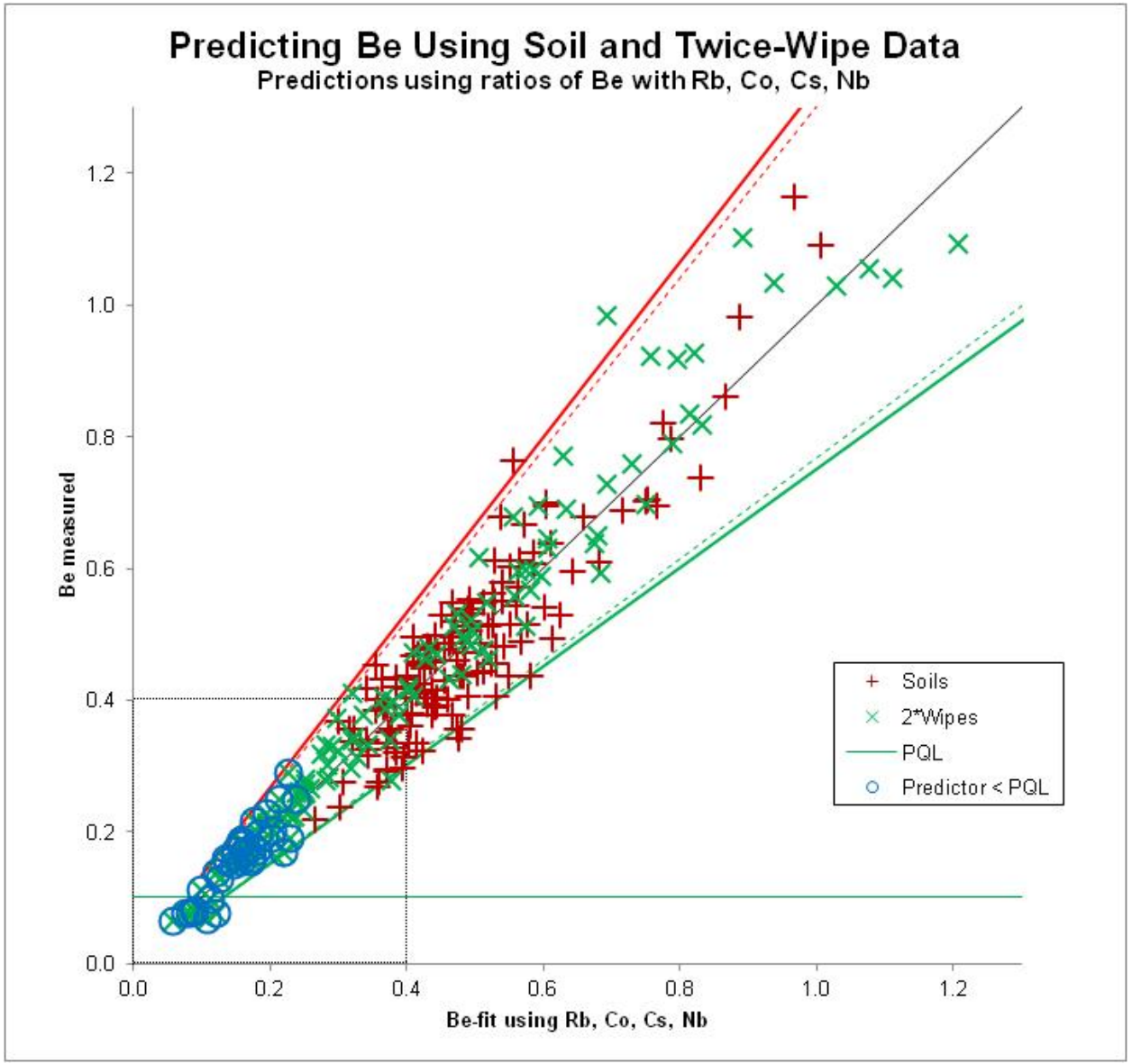
What about Wipes?

- Tried predicting Be in wipes using Rb, Cs, Co, Nb
  - Overall S was 0.1322
- Can we combine wipe and soil data?
  - Idea: ratios come from minerals
  - Soils are minerals diluted with vegetable and animal matter
  - Bulk samples are soils diluted with “fluff”
    - Motivation for using ratios
  - Wipes are soils diluted with wipe matrix and “fluff”
  - With predictions are based on ratios, the “fluff” shouldn’t matter
  - BTW, chemists always think in terms of relative error
    - At least with data in working range
  - So try combining soil and twice-wipe data
    - Twice-wipes have same PQL as soils

Results

- **Pictures on next slides**
  - **Horizontal axis is predicted Be, vertical is measured Be**
  - **Horizontal line is Be PQL**
  - **Circled points have at least one predictor value < its PQL**
  - **Note that range of wipe Be values is larger than range in soils**
    - **Was controlled by how much soil was added**


Predicting Be Using Soil and Twice-Wipe Data
Predictions using ratios of Be with Rb, Co, Cs, Nb
Be measured
Be-fit using Rb, Co, Cs, Nb
0.0
0.5
1.0
1.5
2.0
2.5
Soils
2*Wipes
PQL
Predictor < PQL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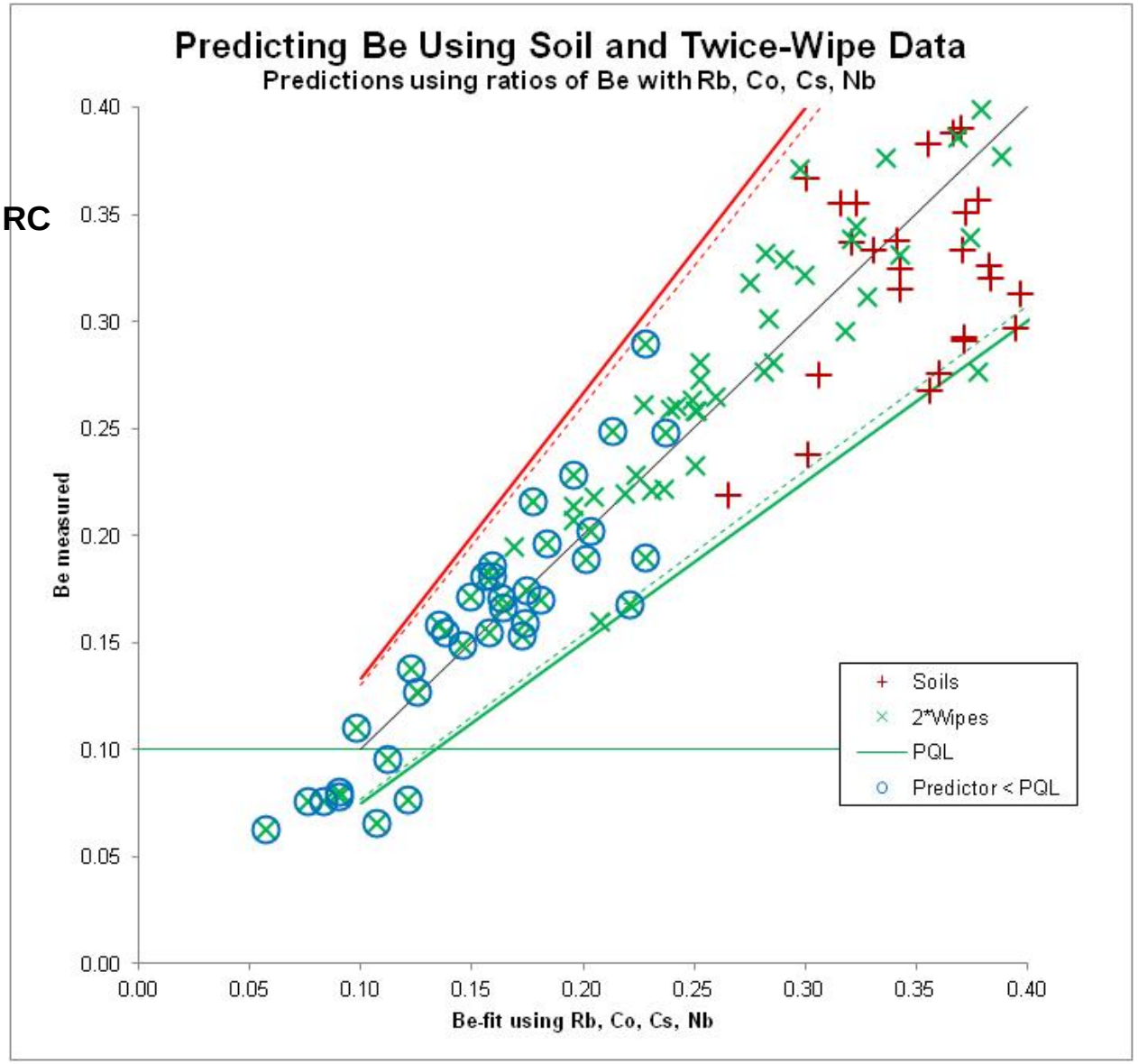
Be-fit using Rb, Co, Cs, Nb
0.0
0.2
0.4
0.6
0.8
1.0
1.2
Soils
2*Wipes
PQL
Predictor < PQL

0.40 = twice DOE RC



Results

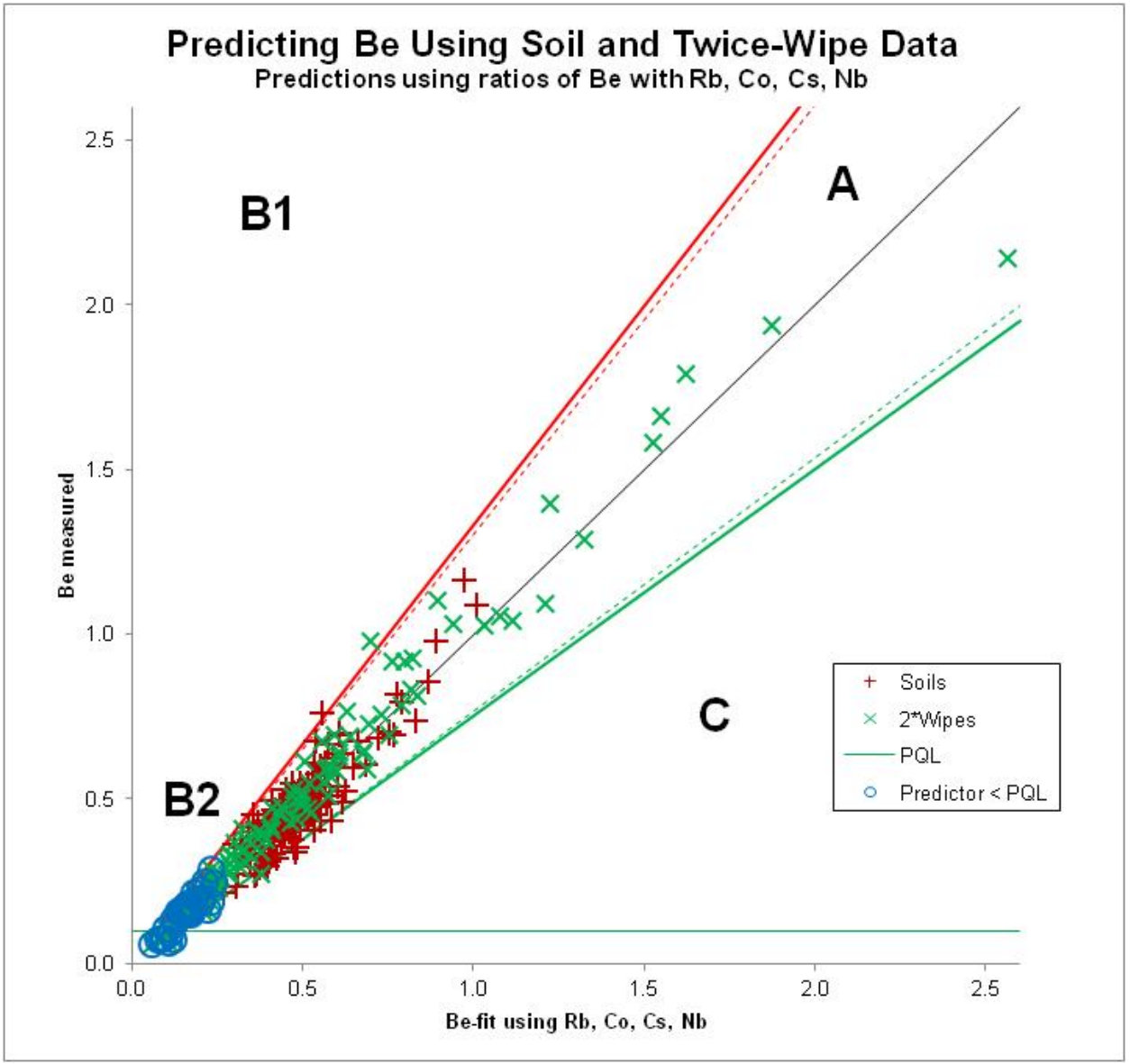
- **Technical issue – batch-to-batch variation**
  - **Original plan: develop short list and predictions using R1 data, test (cross-validate) with R2**
  - **Revised approach: use all 17 batches of soil and twice-wipe data to develop prediction equations**
  - **To estimate PSE, omit one batch at a time, develop prediction equations, apply to omitted batch, average PSEs**
  - **Result: average "leave-one-out" PSE is 0.1433**

    DQO criterion for success was 15%: success!

Discussion

How to <u>Interpret</u> MR Prediction Results (see next slide)

- A: T-Be consistent with N-Be
  - Prediction bounds have 95% confidence
    - Prediction confidence level is a policy matter
    - Technical issue: “how many samples from this facility this time?”
- B1 and B2: T-Be apparently includes some A-Be
  - Does our reaction depend on how high T-Be itself is?
    - What if T-Be is below some reasonable reporting limit?
    - What if T-Be is below some traditional control or trigger level?
- C: T-Be lower than it should be
  - Is there some predictor metal in facility?
    - Forensic analysis warranted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Soils
2*Wipes
PQL
Predictor < PQL

Discussion

How to Use MR Prediction Results

- **Wipe suggestion**
  - **Have DOE RC, very often used as an OEL for facility surveys**
  - **So, for each sample let (A-Be estimate) = (T-Be – N-Be prediction)**
  - **Compare A-Be estimates with DOE RC as usual**
  - **Drawback: need other metal analyses for every wipe; $$$$**

    Insert plug for QNP UTL – uses only maximum value in dataset
- **Bulk suggestion**
  - **Have NO OEL such as the DOE RC**
  - **Still, for each sample let (A-Be estimate) = (T-Be – N-Be prediction)**
  - **Evaluate A-Be estimates somehow – TBD**

    If T-Be less than reasonable reporting limit, no issue

    Can we develop acceptable reporting limit for A-Be estimates?
  - **Drawback: need other metal analysis for every sample; $$$$**

Discussion

How to Use MR Prediction Results

- **Both wipes and bulks**
  - **May need to bring additional lab(s) up to speed, depending on throughput**

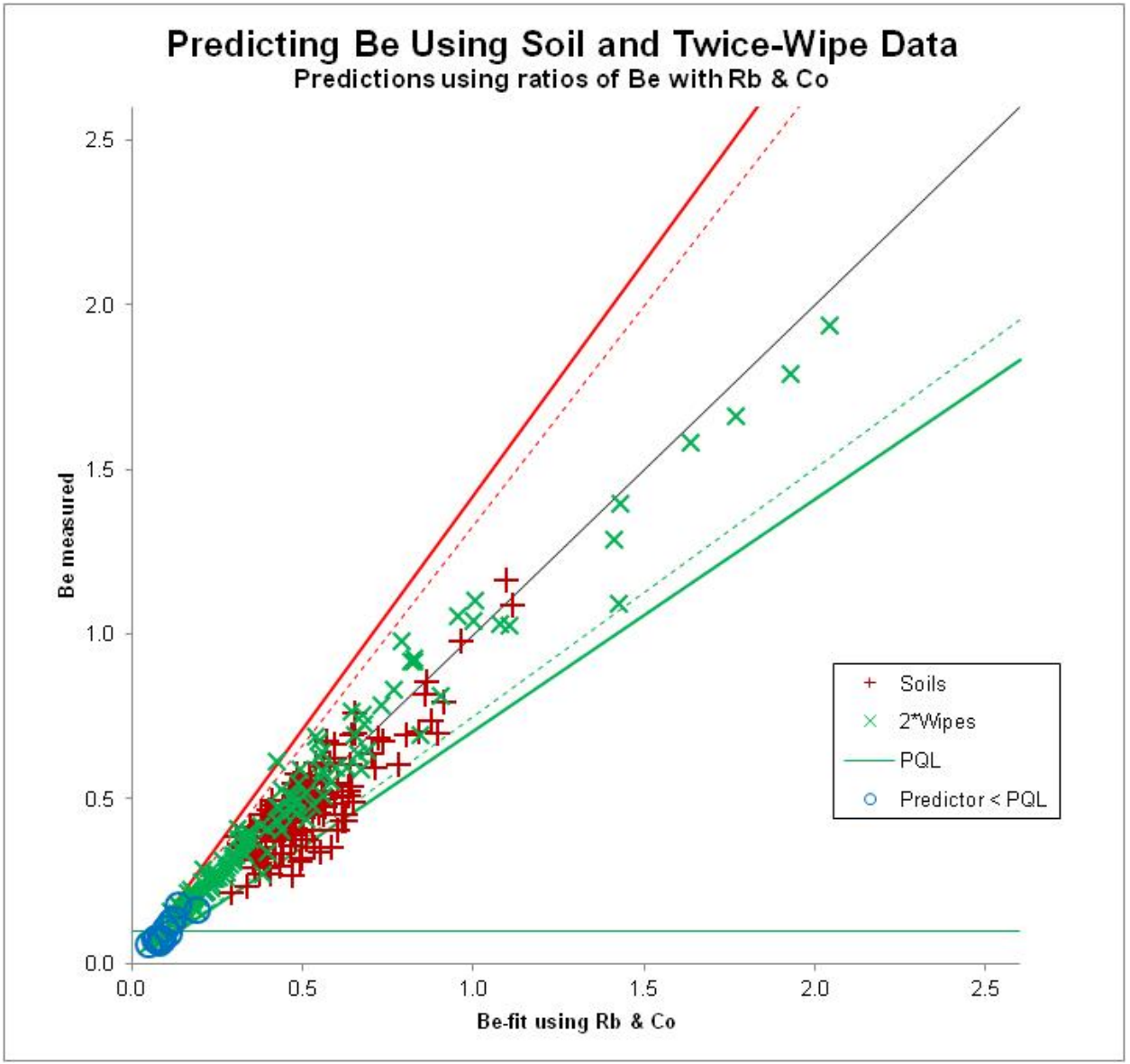
Discussion

How to save $$$$

- Went to 4 predictors based on comparing S with 4 predictors to S with all predictors
- While the final per-sample cost is not yet determined, it may be cheaper to use 2 predictors than 4
- How much prediction power do we lose with only 2 predictors?
  - Try with just Rb and Co (recall the best-subsets regression tables)
  - "Leave-one-out" PSE is now 0.1756, a bit higher than desired
  - DQO upper bound for acceptability is 0.20; we're still OK
  - Compare prediction power graphically

    Dotted lines are 4-predictor prediction limits, solid are 2-predictor

    Wipe predictions appear a bit tighter than soil predictions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And Finally

Predictions really are based on ratios of Be with other metals!

- **4-Predictor equation is**

$$\log(Be) = a_0 + a_1 \log(Co) + a_2 \log(Cs) + a_3 \log(Nb) + a_4 \log(Rb) + \text{error}$$

  - **With the constraint $a_1 + a_2 + a_3 + a_4 = 1$, this is equivalent to**

$$(Be/Co)^{a1} * (Be/Cs)^{a2} * (Be/Nb)^{a3} * (Be/Rb)^{a4} = e^{a0} * \text{Error}$$

$$(Be/Co)^{0.342} * (Be/Cs)^{-0.541} * (Be/Nb)^{-0.073} * (Be/Rb)^{1.272} = 0.00692 * \text{Error}$$

  - **With 2 predictors we have $(Be/Co)^{0.186} * (Be/Rb)^{0.814} = 0.03126 * \text{Error}$**

And Finally

What about redundancy?

- **Correlations of metals in Rounds 1 and 2 (log soil data):**

	Be	Ag	As	Ce	Co	Cr	Cs	La	Li	Nb	Rb	Sn	Sr	Th	Y	Zr
Be	1	0.40	0.57	0.58	0.58	0.81	0.64	0.52	0.78	0.50	0.78	0.62	0.40	0.47	0.41	0.39
Ag	0.40	1	0.20	0.75	0.68	0.44	0.33	0.65	0.27	0.55	0.37	0.59	0.53	0.44	0.70	0.64
As	0.57	0.20	1	0.43	0.29	0.70	0.67	0.49	0.49	0.45	0.69	0.66	0.36	0.55	0.15	0.02
Ce	0.58	0.75	0.43	1	0.71	0.69	0.62	0.96	0.38	0.79	0.65	0.83	0.62	0.81	0.71	0.62
Co	0.58	0.68	0.29	0.71	1	0.53	0.45	0.65	0.29	0.68	0.45	0.65	0.44	0.43	0.94	0.90
Cr	0.81	0.44	0.70	0.69	0.53	1	0.77	0.71	0.65	0.70	0.86	0.82	0.51	0.70	0.36	0.24
Cs	0.64	0.33	0.67	0.62	0.45	0.77	1	0.66	0.54	0.56	0.94	0.81	0.29	0.74	0.27	0.25
La	0.52	0.65	0.49	0.96	0.65	0.71	0.66	1	0.26	0.81	0.67	0.85	0.65	0.86	0.65	0.54
Li	0.78	0.27	0.49	0.38	0.29	0.65	0.54	0.26	1	0.28	0.67	0.47	0.17	0.37	0.13	0.09
Nb	0.50	0.55	0.45	0.79	0.68	0.70	0.56	0.81	0.28	1	0.62	0.81	0.64	0.64	0.63	0.52
Rb	0.78	0.37	0.69	0.65	0.45	0.86	0.94	0.67	0.67	0.62	1	0.82	0.39	0.71	0.26	0.24
Sn	0.62	0.59	0.66	0.83	0.65	0.82	0.81	0.85	0.47	0.81	0.82	1	0.59	0.78	0.55	0.46
Sr	0.40	0.53	0.36	0.62	0.44	0.51	0.29	0.65	0.17	0.64	0.39	0.59	1	0.48	0.46	0.36
Th	0.47	0.44	0.55	0.81	0.43	0.70	0.74	0.86	0.37	0.64	0.71	0.78	0.48	1	0.37	0.27
Y	0.41	0.70	0.15	0.71	0.94	0.36	0.27	0.65	0.13	0.63	0.26	0.55	0.46	0.37	1	0.93
Zr	0.39	0.64	0.02	0.62	0.90	0.24	0.25	0.54	0.09	0.52	0.24	0.46	0.36	0.27	0.93	1

And Finally

- **Principal Component Analysis of that correlation matrix**

PC	1	2	3	4	5	6	7	8
Eigenvalue	9.542	2.581	1.182	0.695	0.538	0.370	0.287	0.264
Proportion	0.596	0.161	0.074	0.043	0.034	0.023	0.018	0.016
Cumulative	0.596	0.758	0.832	0.875	0.909	0.932	0.95	0.966
PC	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**
Eigenvalue	0.189	0.120	0.090	0.055	0.035	0.025	0.018	0.009
Proportion	0.012	0.008	0.006	0.003	0.002	0.002	0.001	0.001
Cumulative	0.978	0.986	0.991	0.995	0.997	0.998	0.999	1

Variable	Be	Ag	As	Ce	Co	Cr	Cs	La
PC1	0.25	0.22	0.20	0.30	0.25	0.28	0.26	0.29
PC2	0.17	-0.27	0.32	-0.12	-0.30	0.22	0.26	-0.08
PC3	-0.44	-0.03	0.06	0.15	-0.28	-0.05	0.00	0.30
PC4	-0.21	-0.21	-0.07	0.04	0.13	-0.13	0.41	0.09
Variable	**Li**	**Nb**	**Rb**	**Sn**	**Sr**	**Th**	**Y**	**Zr**
PC1	0.18	0.27	0.27	0.30	0.21	0.26	0.22	0.19
PC2	0.31	-0.09	0.29	0.06	-0.11	0.11	-0.41	-0.43
PC3	-0.48	0.19	-0.07	0.13	0.31	0.35	-0.17	-0.27
PC4	-0.24	-0.06	0.15	0.07	-0.72	0.24	0.08	0.19

- **Interpretations????**

And Finally

Questions remaining

- How to implement procedure
  - On-going method checking
  - Training new lab at same site or in same area
  - Technology transfer to new site with different background soils
  - How to “validate” MR as a “method”

Discussion?