Module 10

XRF and Dynamic Work Strategies:

Case Study - Throop

Case Study Highlights

- Use of XRF
- Use of dynamic work strategies
- Use of stratified sampling strategies
- Incremental soil sampling
- Application of real-time analytical methods

Background

- Aerial deposition of Pb from a smelter over a town
- 10 yr ago - most properties cleaned
- Several properties had confusing data results & thought to be outside depositional area
- Data hinted that highest Pb was in front yards along street
- Street was the main road thru town & heavily traveled by facility trucks
- Residents suspicious that cast-off from trucks was cause & wanted facility to remediate
- Any potential remediation – under RCRA

Project Decision Goals

- **Resolve confusion** over past conflicting data about property status
- Estimate **mean** (95% UCL) for yards in question
  - Compare to 500 ppm risk-based AL
  - If over, cleanup high concentration areas
- Pb source? Suggested by spatial contaminant pattern
  - Is there evidence the facility is the source & so would be responsible for any cleanup
- Summary: want to compare yard average to AL, but also need spatial information to suggest attribution & guide any cleanup

Stratified Sampling

- Aim is to estimate mean concentration for an area that has been broken into subareas or stratums
- Higher sample density in stratums where there is expected to be more variability in results
- Mean and associated confidence limits for the area as a whole are estimated by weighting the mean and variances of subareas by their size
- Can be a much more efficient way of accurately estimating the overall mean.

Stratified Sampling Challenges

- To be effective we need to know how to break an area into subareas, and we need to know the variability to expect
- The first “need to know” can be based on a site conceptual model
- The use of a real-time technique (e.g., XRF) helps with the second “need to know”
  - Start be equally sampling all strata and measuring soils with XRF
  - Based on XRF data, can return to an individual stratum and collect more samples to better control variability

Stratified Data Collection Design

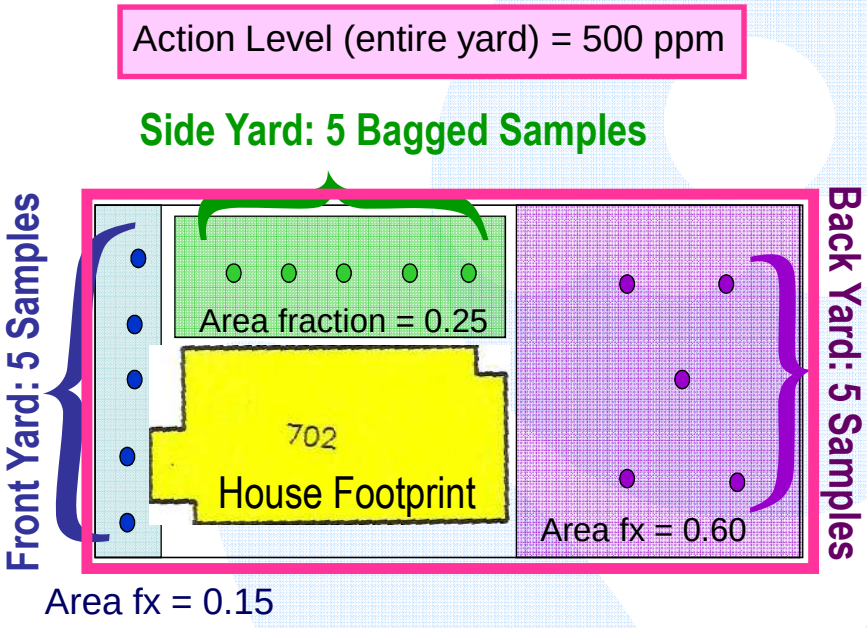
- Each yard divided into 3 physical sections (stratum 1, 2, and 3)
  - **S1: Front yard** (very small area)
  - **S2: Side yard** (medium, if present)
  - **S3: Back yard** (large area)
- Each stratum divided into 5 ~equal subsections
- Measure area of each yard stratum & subsections
- 1 grab soil sample (~300 g) per subsection into a plastic bag (i.e., 5 samples per yard section)

Example Property & Preliminary CSM

Front yard:
- Smelter
- Leaded gas
- Lead Paint
- Expect relatively high

Side Yard:
- Smelter
- Lead Paint
- Expect unknown

Back Yard:
- Smelter
- Lead Paint
- Expect relatively low



On-Site XRF Used for Analysis

XRF Bag Analysis

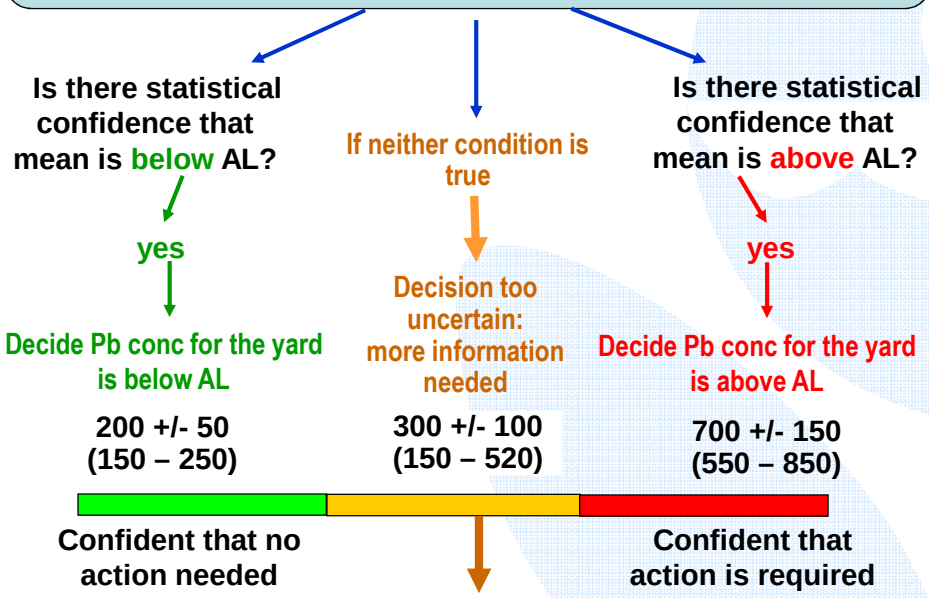
- 4 30-sec readings on bag
  - (2 on front/2 on back)
- Results entered into spreadsheet
- Spreadsheet immediately calculates:
  1. ave & SD for each bag
  2. ave & SD within each stratum
  3. ave & UCL for the decision unit (entire property).
  4. within-bag vs. between-bag variability & which is more significant
- **IF** statistical uncertainty interferes w/ desired decision confidence for DU:
  - Use #4 above & a series of decision trees to reduce statistical uncertainty until a confident decision is possible

Example Results

- **Front** yard individual average (at 95% statistical confidence) = 700 +/-150 (**550 – 850** ppm Pb)
- **Side** yard average = 500 +/-100 (**400 – 600** ppm)
- **Back** yard average = 300 +/-50 (**250 – 350** ppm)
- **Area-weighted total yard average determined statistically as 410 +/- 25 (385 – 435 ppm Pb)**

Decision Tree #1

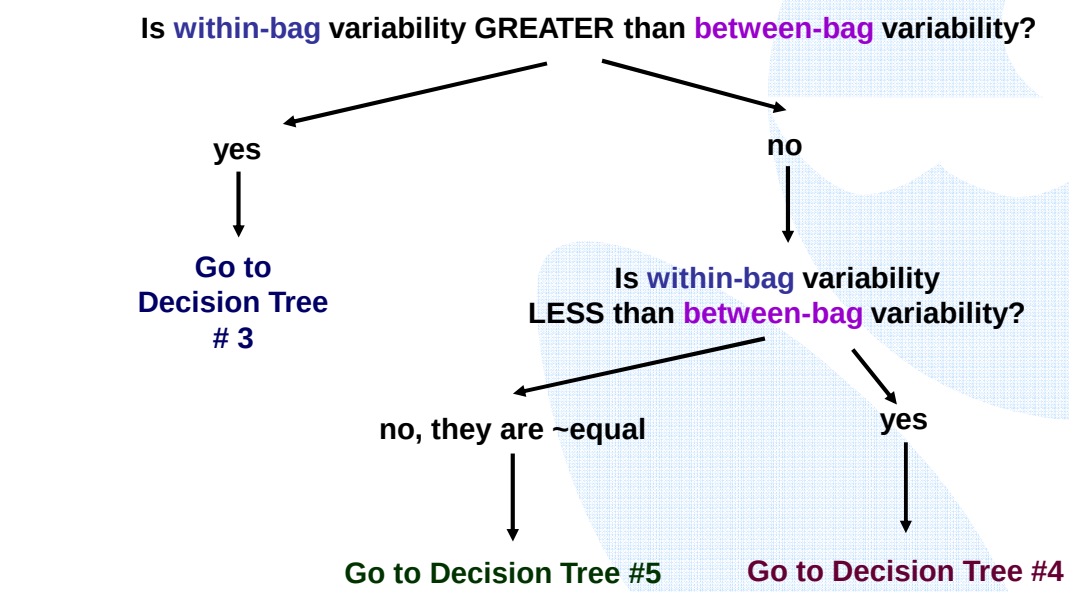
Evaluate statistical results for the ***yard*** & compare to the 500 ppm Action Level (AL)



Go to Decision Tree #2

Decision Tree #2

Pick stratum with highest area-weighted variability. Determine the greater source of data variability (decision uncertainty).



Data Feeds for Decision Tree #2

- Look at the ***average within-bag*** "error" (std dev, SD) for each of the 5 bags from a yard stratum
- Look at the ***between-bag*** "error" SD for all bags from a yard stratum
- **Compare** the two: which is larger?
- See example data set

Example Data Set

Bag #1		Bag #2		Bag #3		Bag #4		Bag #5	
Shot #1	700	#1	550	#1	534	#1	769	#1	450
#2	670	#2	534	#2	440	#2	710	#2	400
#3	740	#3	654	#3	430	#3	960	#3	500
#4	650	#4	590	#4	420	#4	800	#4	550
Bag Mean	690		582		456		810		475
W/in-Bag SD	39		54		53		107		65

Mean of within-bag SDs = (39+54+53+107+65)/5 = *63*

To get between-bag variability

Between-bag "error" (SD) for 5 bag means = *150*

Within-Bag vs Between-Bag Variability

- **What causes within-bag variability?**
  - And what does that tell us?
  - What can we do about it?
- **What causes between-bag variability?**
  - And what does that tell us?
  - What can we do about it?

Decision Tree #3

Within-bag variability (SD) of Pb replicate results is GREATER than between-bag variability (SD). **[Major source of data error is from heterogeneity within samples] To control this source of variability:**

Re-shoot each bag another 4 times & add results to spreadsheet & recalculate statistics for bags, for yard sections & for whole yard. Examine results.

Can we confidently conclude the yard is either above or below the 500 pm AL?

no → **Go to Decision Tree #6**

yes → **Done**

Decision Tree #4

Within-bag variability (SD) of Pb replicate results is LESS than between-bag variability (SD). **(Major source of data error is from concentration variations across the yard section area)** **To control this source of variability:**

Collect another 5 bag samples from section area. Analyze 4 times/bag. Add results to spreadsheet & recalculate statistics for yard section & for whole yard.

Can we confidently conclude the yard is either above or below the 500 pm AL?

no → **Go to Decision Tree #6**

yes → **Done**

Decision Tree #5

1st Round sampling shows within-bag SD not significantly from between-bag SD. **(Concentration variability across the yard section & within sample bags about the same.) To control these sources simultaneously:**

Analyze original bags an add'l 4 times each. Collect another 5 bag samples from the section & analyze 8 times each. Add results to spreadsheet & recalculate statistics for yard section & for whole yard.

Is decision uncertainty now resolved?

no → **Go to Decision Tree #6**

yes → **Done**

Decision Tree #6

Real-time efforts to reduce data variability have been insufficient to reduce statistical decision uncertainty at the degree of confidence desired.

Options for path forward

1) If consequences of "assuming the worst" < cost of add'l sampling & analysis, default to the most protective decision without additional investigation.

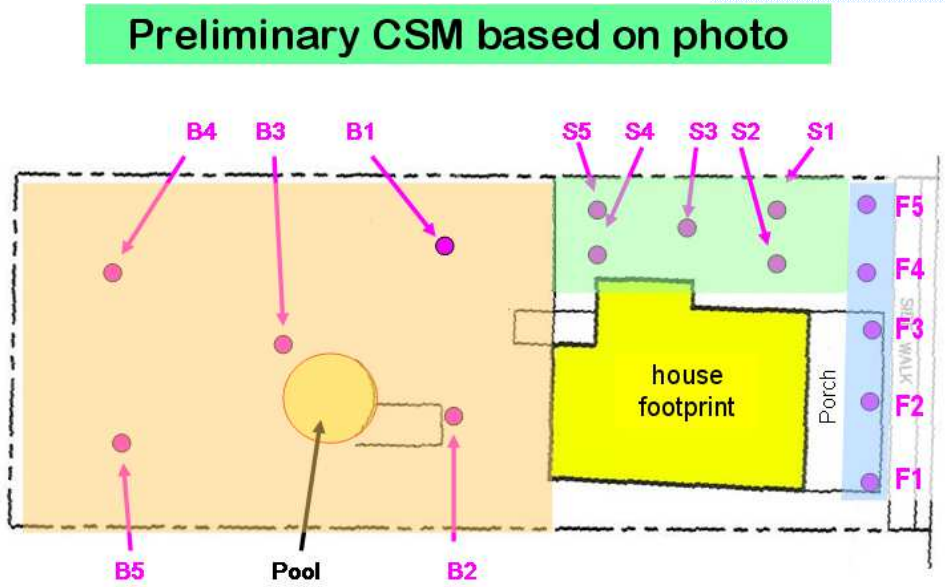
2) If add'l investigation preferable to "assuming the worst" & statistical confidence is desired, design a follow-on sampling & analytical program. Perhaps do soil composition analysis for Pb-bearing particles (degraded paint chips, smelting slag, or Pb-battery fragments)

3) Negotiate for accepting a lower statistical confidence

Logistics

- Field team
  - 1 XRF run from back of truck
  - 2 field samplers
  - 1 data analyst
  - 1 RCRA project manager
- XRF was the bottleneck
  - Samplers were fast; brought bags to XRF
- For the back yards, Pb consistently low (except near houses, garages, painted fence & bird bath)
  - But the 5 sampling units in the back yards were very large compared to front & side

An Example Yard



Sampling Results

F Section		
	Section Mean =	762
	Section SD =	190
	Section 95%LCL =	526
	Section 95%UCL =	998
	Average within-bag SD =	92
	Between-bag SD =	190
	Within-bag SD > 1.5 x between-bag SD?	no
	Within-bag SD < 0.5 x between-bag SD?	yes

S Section		
	Section Mean =	512
	Section SD =	265
	Section 95%LCL =	183
	Section 95%UCL =	841
	Average within-bag SD =	50
	Between-bag SD =	265
	Within-bag SD > 1.5 x between-bag SD?	no
	Within-bag SD < 0.5 x between-bag SD?	yes

B Section		
	Section Mean =	85
	Section SD =	51
	Section 95%LCL =	21
	Section 95%UCL =	149
	Average within-bag SD =	16.0
	Between-bag SD =	51.4
	Within-bag SD > 1.5 x between-bag SD?	no
	Within-bag SD < 0.5 x between-bag SD?	yes

Calculation of property Mean & UCL using stratified statistics & Preliminary CSM

Area weighted for the entire property

	mean	stdev	weight	# samples	total area = 5052 sq ft
Front (area = 400)	761	202	0.079	5	
Side (area = 675)	512	265	0.134	5	
Back (area = 3977)	85	51	0.787	5	
	check sum =		1.000	15	= sum
				(no extra sand fill sample)	

Property Mean, Standard Deviation, and LCL/UCLs

Wt'd section	mean	stderror	LCL	UCL	
	196	25	147	245	95% (as 2-sided)
				237	95% (as 1-sided)
				228	90% (as 1-sided)

Project Outcome

- After waiting 10 yrs, residents had their results that day
- High Pb nearest painted items
- In 2 yards, paint chips present from recent stripping of old paint
  - Toddlers present in worst yard
  - Project manager provided immediate advice to parents
  - Paint chips tested by XRF
    - 1 multi-layer chip = 18% Pb
    - SCREENING result: XRF calibrated for soil is not accurate for paint—WAY outside linear range
    - Still, the culprit was obvious

Not proof that trucks made some contribution

Any Questions?