Welcome to the CLU-IN Internet Seminar

Incremental-Composite Sampling Designs for Surface Soil Analyses, Module 3 of 4

Delivered: February 24, 2012, 2:00 PM - 4:00 PM, EST (19:00-21:00 GMT)

Presenters:
Deana Crumbling, EPA Superfund (crumbling.deana@epa.gov)
Michael Stroh, MO Dept of Natural Resources (michael.stroh@dnr.mo.gov)
Robert Johnson, Argonne National Laboratory (rljohnson@anl.gov)
Moderator:
Jean Balent, U.S. EPA, Technology Innovation and Field Services Division (balent.jean@epa.gov)

Visit the Clean Up Information Network online at www.cluin.org

1

Although I'm sure that some of you have these rules memorized from previous CLU-IN events, let's run through them quickly for our new participants.

Please mute your phone lines during the seminar to minimize disruption and background noise. If you do not have a mute button, press *6 to mute #6 to unmute your lines at anytime. Also, please do NOT put this call on hold as this may bring delightful, but unwanted background music over the lines and interupt the seminar.

You should note that throughout the seminar, we will ask for your feedback. You do not need to wait for Q&A breaks to ask questions or provide comments. To submit comments/questions and report technical problems, please use the ? Icon at the top of your screen. You can move forward/backward in the slides by using the single arrow buttons (left moves back 1 slide, right moves advances 1 slide). The double arrowed buttons will take you to 1st and last slides respectively. You may also advance to any slide using the numbered links that appear on the left side of your screen. The button with a house icon will take you back to main seminar page which displays our agenda, speaker information, links to the slides and additional resources. Lastly, the button with a computer disc can be used to download and save today's presentation materials.

With that, please move to slide 3.

Module 3.1

Incremental-Composite Sampling Designs for Surface Soil Analyses

Introduction to 3rd Day

3

Instructors

- **Deana Crumbling,** crumbling.deana@epa.gov
  Office of Superfund Remediation &Technology Innovation
  U.S. Environmental Protection Agency
  Washington, D.C.
  (703) 603-0643

- **Michael Stroh,** Micheal.Stroh@dnr.mo.gov
  Hazardous Waste Program
  Missouri Department of Natural Resources
  (573) 522-9902

Today's Agenda

- Reiterate webinar purpose and goals
- ISM calculations and VSP
  - 10-min Q & A
- Case study for Cr(VI) in soil
- Case study for Pb in soil
  - 15-min Q & A

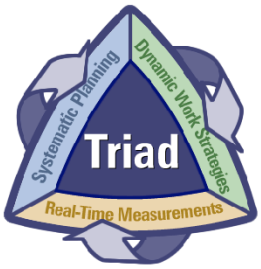
Software Resources and Disclaimer

- Disclaimer: “References to product or service providers are for information purposes only and do not constitute endorsement”
- ITRC Incremental Sampling Methodology (ISM) Web document: http://www.itrcweb.org/ism-1/
- 2 software programs referenced
- For more information on the software programs:
  - Visual Sample Plan (VSP) (http://vsp.pnl.gov/)
  - ProUCL (http://www.epa.gov/esd/tsc/software.htm)

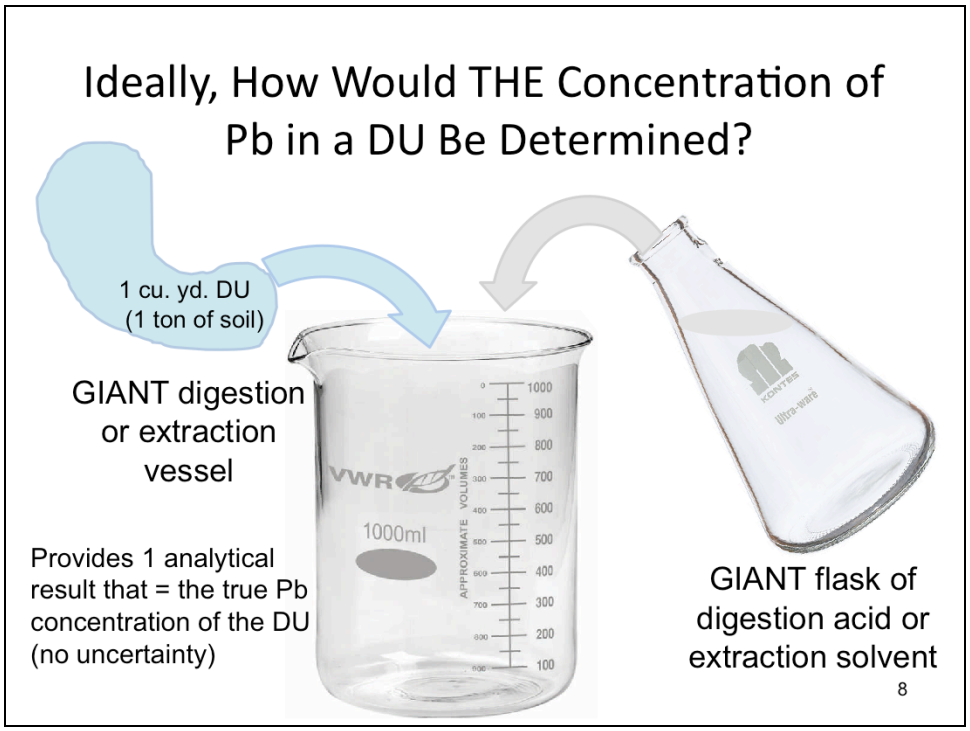
Module 3.2

Incremental-Composite Sampling Designs for Surface Soil Analyses

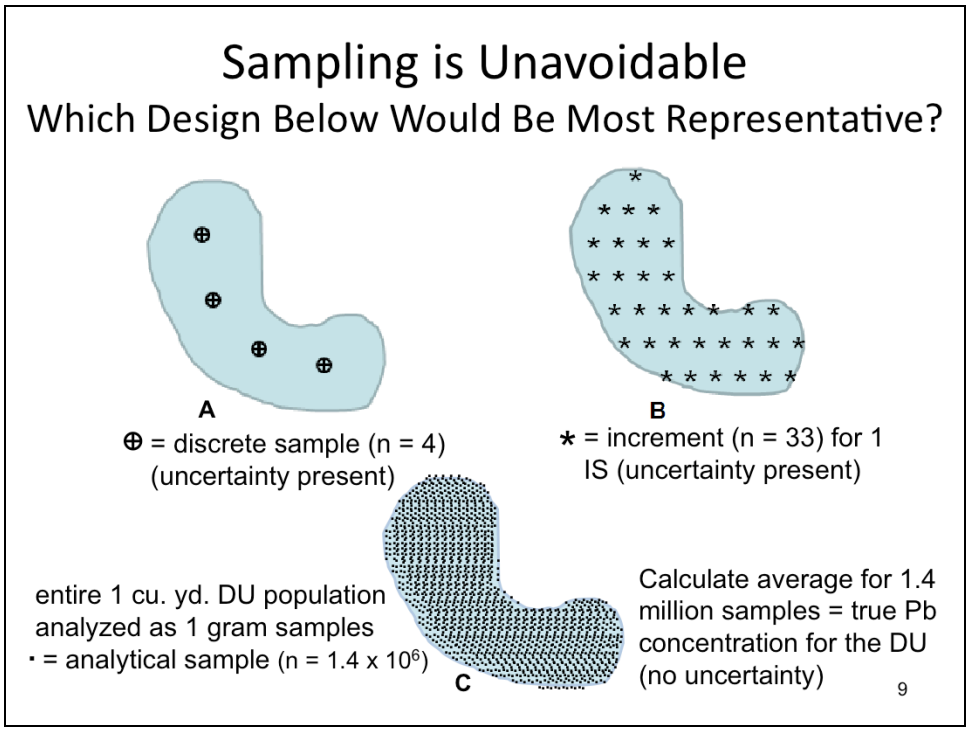
Calculations for Incremental Sampling



7



If the entire DU could be analyzed in a single giant analysis, there would be no uncertainty about the true Pb concentration. Note that this process would produce a result that represents a giant composite of all soil particles in the DU.



For this thought experiment, assume that there is no analytical error.

Since a single DU cannot be analyzed in a single analysis, we must take samples, analyze them, and then draw conclusions about the DU concentration from the concentration of the samples. In scenario A, we take 4 discrete (grab) samples. Because we want to use those samples to determine the actual concentration for the entire DU, we take the average of the 4 data points. Since we are using 4 small samples taken from a heterogeneous medium (soil), there is uncertainty in whether the average of the 4 data points accurately represents the concentration for the DU.

In scenario B, we take more samples (n = 33), but it is expensive to analyze them all. So we perform a physical averaging by combining all the samples (now called increments) together to form a single composite called an incremental sample, which is analyzed. This is equivalent to taking 33 samples and analyzing all individually, then mathematically averaging all 33 results. Again, because this is not a complete analysis, there is uncertainty about how close the sample average is to the true concentration.

In scenario C, we imagine splitting the entire DU into individual analytical samples. Each of those samples is analyzed individually so that the entire mass of the DU has been analyzed. If the mass of an analytical sample is 1 gram, and the mass of soil in the DU is 1 ton, then there are 1.4 million samples analyzed. The results from those samples are analyzed to determine the true concentration of the DU. Since the entire mass was analyzed, there is no uncertainty in the concentration calculated for the DU.

Obviously, scenario C is impossible, so we are left with designs that look like A or B. Which one looks like it would be more representative of the true concentration of the DU?

Real-World Data Involve Uncertainty

Anything less than total sampling of the DU will entail uncertainty because it is unknown whether the calculated mean is less than or greater than the true mean, and by how much.

The more samples collected, the more likely that the calculated mean will be close to the true mean.

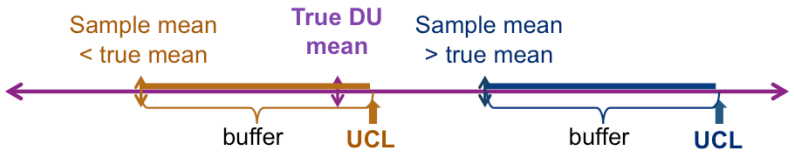
Because we cannot know the true concentration, we have to consider the possibility that our calculated mean is greater than the true concentration or less than the true. We also don't know by how much the over- or under-estimate occurs. To be protective, EPA is more concerned with the possibility of underestimating the true concentration.

*Calculating UCLs for Exposure Point Concentrations…*Dec 2002

page 1

Recall that…

EPA recommends using the average concentration to represent "a reasonable estimate of the concentration likely to be contacted over time" (EPA 1989). The guidance previously issued by EPA in 1992, *Supplemental Guidance to RAGS: Calculating the Concentration Term* (EPA 1992), states that, "because of the uncertainty associated with estimating the true average concentration at a site, the 95 percent upper confidence limit (UCL) of the arithmetic mean should be used for this variable."



2/24/2012 Clu-In Incremental-Composite Webinar Module 3.2 11

In the face of uncertainty, being protective means that underestimates of the mean must be minimized. So a "buffer" is added to the calculated mean to compensate for the uncertainty in the estimate, with the hope that the new value will equal or exceed the true mean a certain % of the time. This sum of the "buffer" and the calculated mean is called an upper confidence limit. A 95% upper confidence limit (or UCL) is expected to equal or exceed the true mean 95% of the time. The width of the "buffer" is determined by 4 things: see next slide.

Things that Influence UCL Values

Amount of uncertainty (width of the "buffer") influenced by 4 characteristics of the data set:

- number of samples (n)
- degree of variability [standard deviation (SD)]
- type of statistical distribution from which the data came
- degree of statistical confidence desired (90%, 95%, 99% etc.)

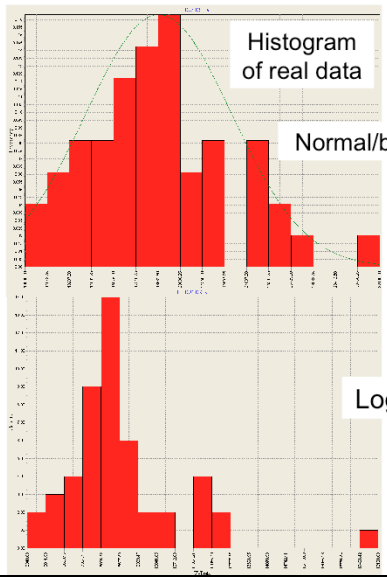
Example "buffer" calculation is t x SD/sqrt(n)

- this eqn only for normal or near-normal statistical distribution
- value of t depends on n and selected confidence: higher the confidence, the higher the t value and wider the buffer; the higher the n, the smaller the t value and narrower the buffer
- n in denominator => higher the n, narrower the buffer
- SD in numerator => higher the SD, wider the buffer

The width of the "buffer" is determined by 4 things: the type of statistical distribution the data come from, the number of samples in the data set used to estimate the mean, and the amount of variability in that data set, and the degree of confidence desired that the true concentration is not being underestimated.

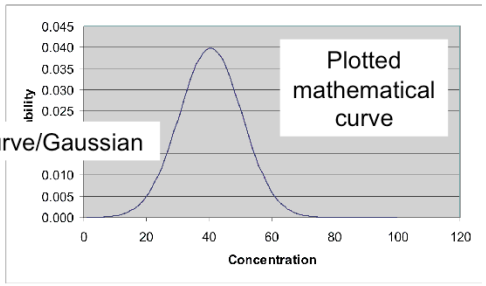
The type of statistical distribution from which the data came determine which UCL formula is used. To use the Student's t UCL equation, the data should come from a normal (bell-shaped) or near-normal distribution.

Types of Statistical Distributions: Each Has Its Own UCL Formulas



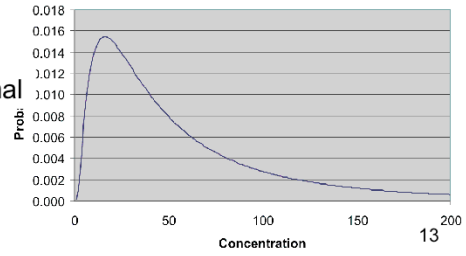
Histogram of real data

Normal/bell curve/Gaussian



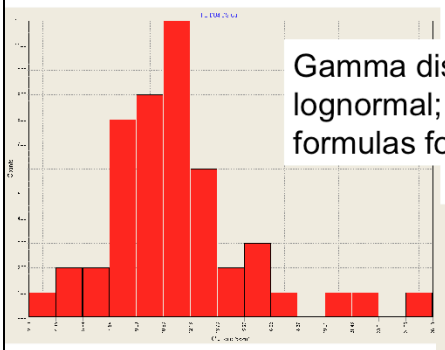
Plotted mathematical curve

Lognormal

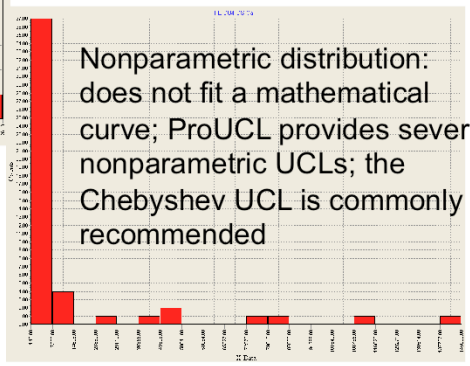


13

2 More Types of Distribution Used in ProUCL



Gamma distribution: similar to lognormal; has its own formulas for calculating a UCL



Nonparametric distribution: does not fit a mathematical curve; ProUCL provides several nonparametric UCLs; the Chebyshev UCL is commonly recommended

14

• Distributions that conform to a mathematically defined curve are called parametric distributions.

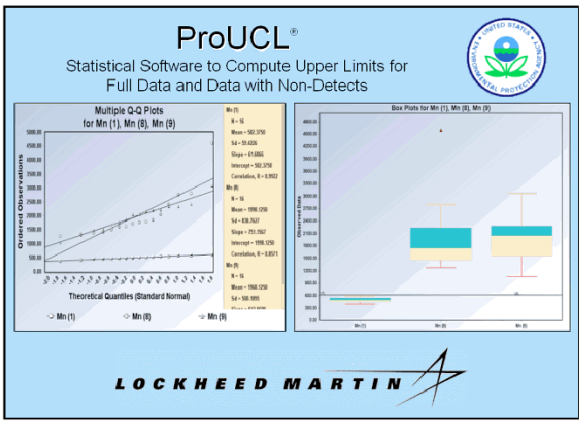
• Nonparametric UCLs are also termed “distribution free” since the equation can be used with any data set. But if the data set does fit a parametric distribution, it is better to use the UCL equation specific to that distribution, because nonparametric UCLs are almost always higher than parametric UCLs.

UCLs Are a Common Mechanism to Account for Data Uncertainty

- Often used for estimating a mean for decisions in addition to risk assessment
- Are required by some state regs
- **Can a UCL be calculated from incremental sampling data?**
  - Yes!
  - Requires at least 3 replicate ICS samples, or
  - Requires historical data, pilot data, a "sister DU" or other reliable and defensible information from which an estimate of the variability (SD) can be derived

Can ProUCL be Used to Calculate ICS UCLs?

Not usually because there are not enough replicate ICS data points. ProUCL requires at least 5 data points to run its algorithms; minimum of 8-10 recommended for reliable UCL output.



http://www.epa.gov/esd/tsc/software.htm

What Are UCL Options for ICS?

- Statistical theory (Central Limit Theorem) and simulations support using Student's *t*-UCL under certain circumstances.
  - Potentially valid because an IS sample result represents a mean (in contrast to a discrete sample)
- Under other circumstances a Chebyshev UCL should be used.
  - Chebyshev UCL always higher than corresponding t-UCL (given same n and SD)
- Both easily programmed into a spreadsheet; can download calculator from the webinar's Resources page (Excel file)
- Ref: ITRC ISM1 doc, Section 4.2.2

Which UCL to Use with Replicate Incremental Samples over a DU

- If have discrete data showing (or information justifying an assumption of) low variability across the DU, use Student's-*t* equation.
  - E.g., "uniform" deposition by air transport
- If have discrete data or information showing high variability, use the Chebyshev eqn.
  - E.g., Spill areas, disturbed areas
- If don't know how variable the concentrations are, use the Chebyshev.
- Reference: ITRC ISM1 doc, Section 4.2.2

Calculating a Mean & UCL for a DU Composed of Equal SUs

- Remember : SU results are not replicates, but represent concentration for small areas within a DU.
  - Therefore the SD for an SU data set will be higher than the SD for DU replicates; cannot assume normality
- If the SUs are all of the same area/volume, then the following recommendation can be used:
- Mean: calculated same as if data points were discrete samples
- UCL: If have <8 SUs/DU, select t-UCL or Chebyshev UCL per previous slide; if >8, can use ProUCL to calculate a DU UCL
  - Ref: ITRC ISM1, Table A.1

SU results DO NOT represent a mean over the DU, but rather the concentration of some smaller area within the DU.

Calculating a Mean & UCL for a DU Composed of Unequal SUs

- If the SUs are NOT all of the same area/volume, then weighting according to the relative area/volume must be done
- Cannot use ProUCL (doesn't do weighted calculations)
- Mean, SD and degrees of freedom all must be weighted to calculate the UCL
- Weighted mean & SD used to calculate the Chebyshev UCL
- More info in ITRC ISM1 doc, Section 4.4.1
- Weighted DU Calculator can be downloaded from webinar Resources list (Excel file)

Can Background and Site ICS data be Compared?

- Yes, but statistical tools are limited if site only has a few DUs.
- Must compare apples to apples: cannot directly compare DU-ICS data to background data from discrete samples.
- Must compare site DU-ICS data to comparable background DU-ICS data.
  - Until more statistical work done and experience gained, use same DU area and same number of increments for both.
- ProUCL will run 2-sample hypothesis testing of means to evaluate site vs. background even with few data points (e.g., <5 each), but reliability of those test results can be very low.
- Consult a statistician!!

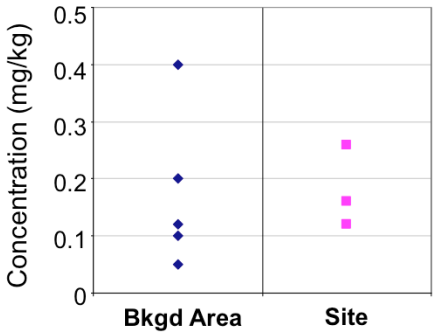
No associated notes.

Other Statistical Options

- Possibly a background threshold value (BTV) can be eatimated from a background DU data set
- When using a BTV, each site DU result is compared individually to the BTV
- Development of a BTV depends on the characteristics of the background data set
- Consult a statistician!!

When The Site is Composed of Very Few DUs

- If have few background or site ICS samples, one option is to use a graphical display of the data

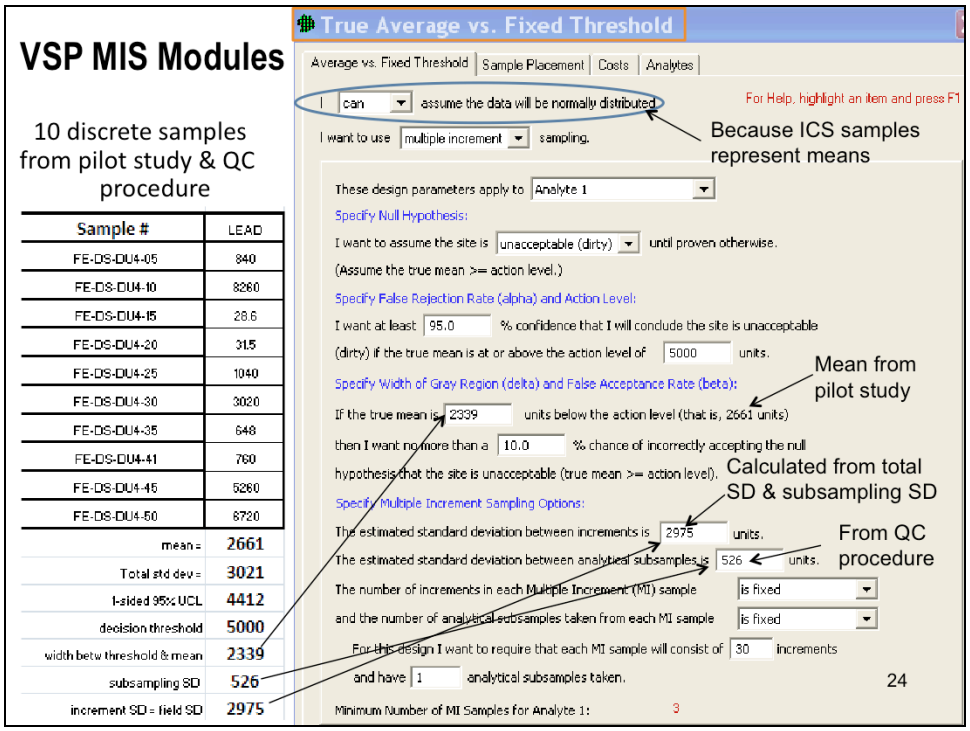


Replicate ICS mean = 0.17 = 0.18

Example of having 1 bkgd DU (with 5 replicate ICSs) and 1 site DU (with 3 replicate ICSs)

Desirable to have enough background data to capture the full range of background conditions.

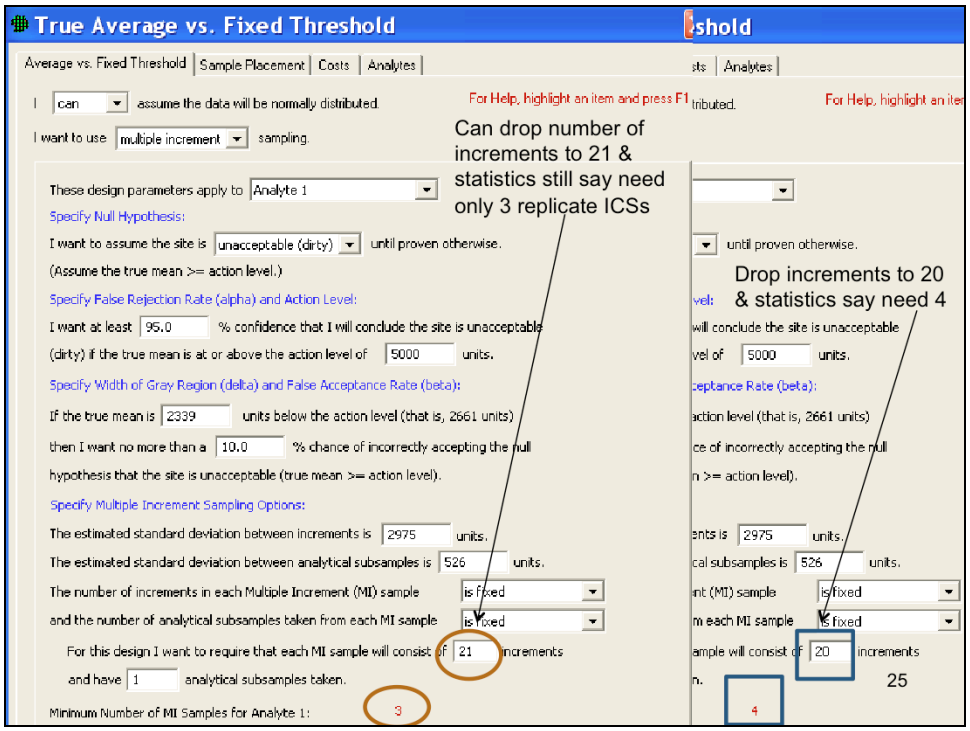
Ref: ITRC ISM1, Section 7.2.4



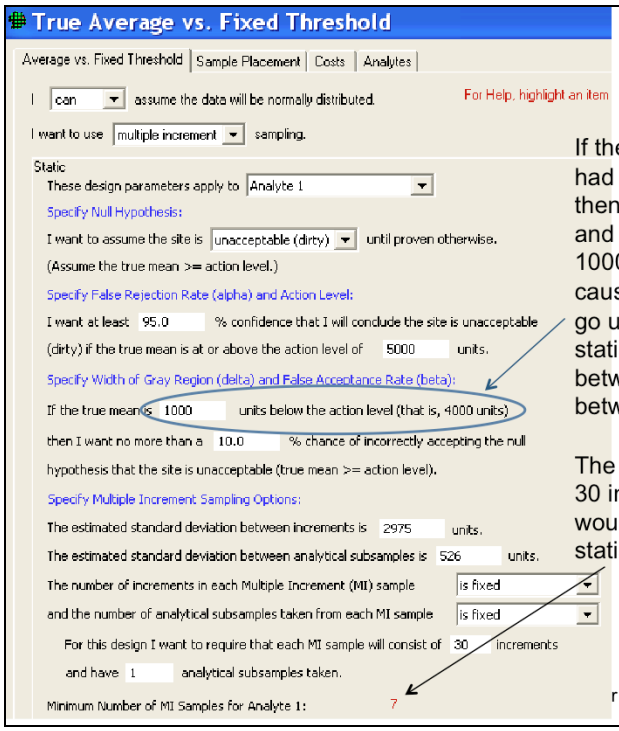
The goal is to figure out how many incremental samples to take, how many increments to take per incremental sample, and how many subsampling replicates should be analyzed per incremental sample.

The pilot study mean is assumed to reasonably estimate the true mean.

The subsampling SD and between-increment SD come from the Variability QC Procedure discussed on Day 2.

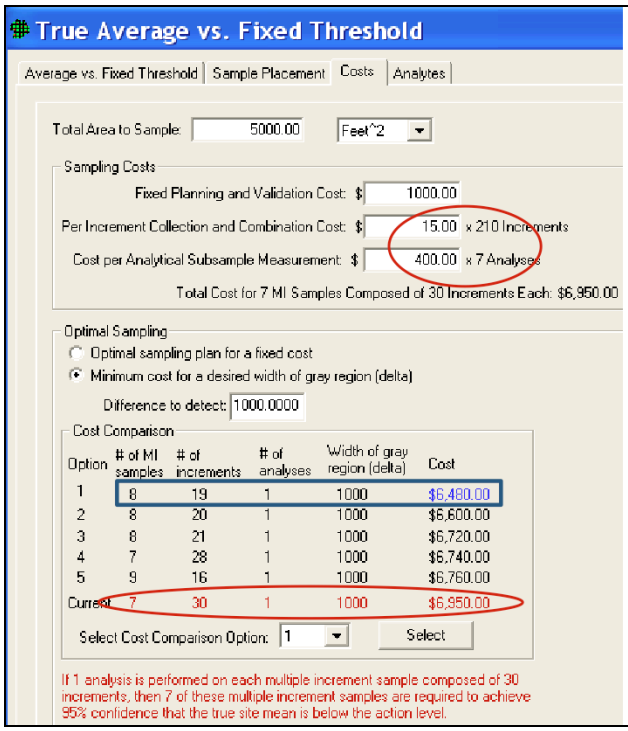


VSP module: If you want to stay with 3 ISM replicates, but want a statistically indicated number of increments, sequentially enter values for the number of increments (1st brown circle) until number of incremental samples ("MI samples") goes to 4 (blue boxes).



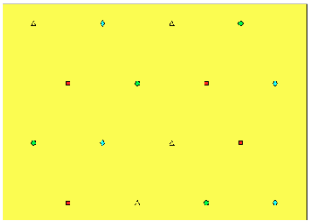
If the mean from the pilot study had been 4000, instead of 2660, then the width between the mean and action level would only be 1000. This narrower width causes the number of samples to go up, because it is harder statistically to tell the difference between 4000 and 5000 than it is between 2660 and 5000.

The statistics predict that if using 30 increments per ICS, you would need 7 ICSs to meet statistical goals.



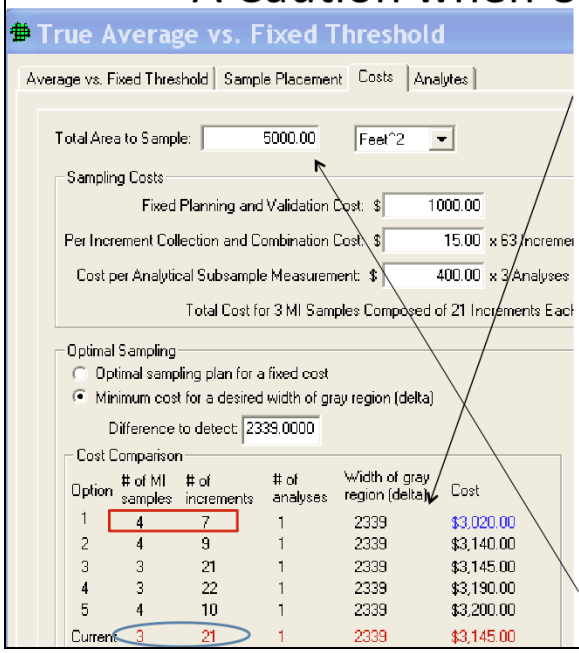
Can enter costs & the module will optimize the number of increments & ICSs based on price of increment collection vs. price of analysis

VSP will also plot out sampling designs with coordinates



27

A Caution when Using VSP



VSP may give options that greatly reduce the number of increments below 30.

This is a potential issue because the assumption of normality was based on having increment numbers of about 30, and the validity of VSP's statistics is based on normality. Low numbers of increments jeopardize the assumption of normality.

Remember also that the size/ area of the DU is not a factor in the VSP calculations (even tho area is an entry).

28

What about Hot Spots *within* a DU?

- Density of ICS increments more likely to incorporate a *representative number* of small hot spots into exposure area concentrations
  - –Ensure hotspot inclusion by defining hot spot size & adjusting increment density within DU (VSP can be used)
- Investigate suspected release areas or sensitive areas separately
  - –As smaller, separate DUs with 30 increments (if an accurate estimate of the hot spot mean concentration is needed)
  - –As SUs within a DU (if areas are so small that 30 increments doesn't make sense, or if only a rough concentration estimate is needed)

Focus on identification and investigation of known or suspected spill areas as separate DUs.

This is the best you can do.

Collecting a grid of discrete samples and removing individual sample locations as "hot spots"

is erroneous and gives a false sense of understanding about the site.

In addition isn't our fundamental question, "What is the average concentration for a given exposure area = volume of soil?"

What volume does a discrete sample represent? – nothing more than the sample size you collected.

For a ISM sample, the volume represents the decision unit, therefore the analytical result represents the DU/SU.

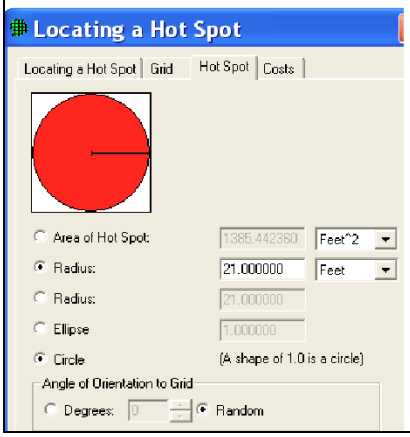
It's not about dilution, it is about the volume over which you wish to know the average value of a parameter.

Photograph from Ryan et al, 2004, Reducing Children's Risk From Lead in Soil: Environmental Sciences & Technology, January 1, 2004.

An example of incremental versus discrete data for the same property is coming up.

Are You Finding Hot Spots Now?

- Case where risk assessor would not approve ISM because "wanted to find hot spots"
- Risk assessor signed off on 175-ft grid spacing using discretes



To be detected 95% of the time, a circular hot spot needs to be at least ¾ acre to be detected in 175-ft grid

ISM with 36 increments in 175-ft grid cell will incorporate hot spots as little as 1/30 acre 95% of the time

This is just geometry (use VSP's Hot Spot module)

30

With a 175 ft grid spacing, a circular hotspot needs at least a 100-ft radius (200 ft diameter or ¾ acre) to be detected 95% of the time.

ISM with 36 increments within the 175-ft grid cell would "hit" a 21-ft radius (42 ft diameter or 1/30th of an acre) 95% of the time.

VSP Hot Spot Example

- Stakeholder concerns desire that circular hot spots of 21-ft radius and larger not be missed.
- What increment density will ensure that such hot spots are included in the estimate of the mean?
- 1 DU = 1 acre
- VSP output:

> In order to have a 95% probability of locating a circular hot spot with a radius of 21.00 feet using point samples arranged in a square grid pattern, you need a maximum spacing of 35.06 feet between samples (see diagram on grid page). This would require approximately 36 samples

- So can set up increment spacing at 35 ft.

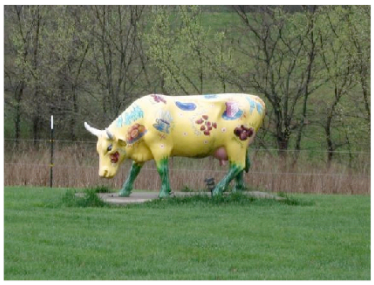
1 acre = 43,560 sq ft

Any Questions?

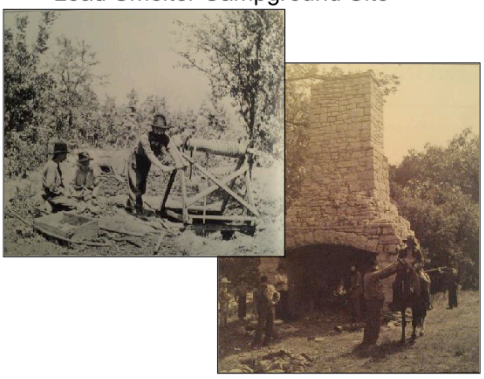
Missouri Department of Natural Resources

TWO CASE STUDIES

Tannery Waste Farm Field Site



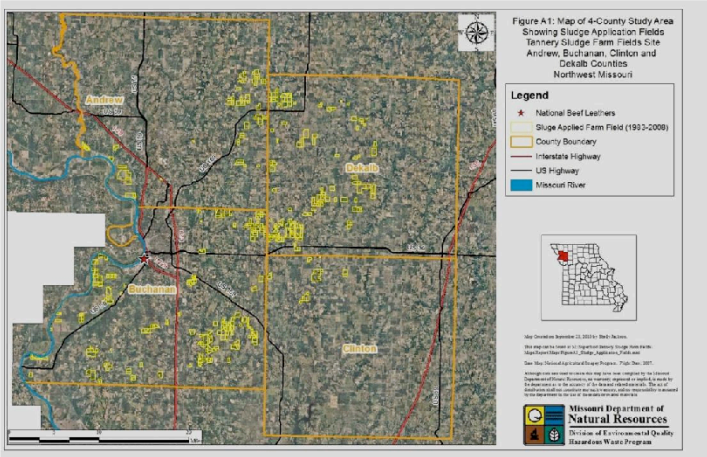
Lead Smelter Campground Site



- I'm going to cover two case studies in MO that used an ICS sampling design.
- Hopefully you will recognize some of the concepts Bob and Deana introduced in the first two modules.
- One is multi-county site in NW MO where tannery waste was used as a farm field fertilizer, and the other is a small historic lead smelter in south-central MO.

Missouri Department of
Natural Resources

CASE STUDY #1
TANNERY WASTE AS FARM FIELD FERTILIZER



- The red star on this map shows the location of the tannery in St. Joseph, MO along the MO River.
- The yellow polygons are locations of WWTP sludge application between 1983-2009
- 100+ farm fields, >10,000 acres affected
- Concern is about residual levels of hex Cr in sludge and whether they pose a health threat.

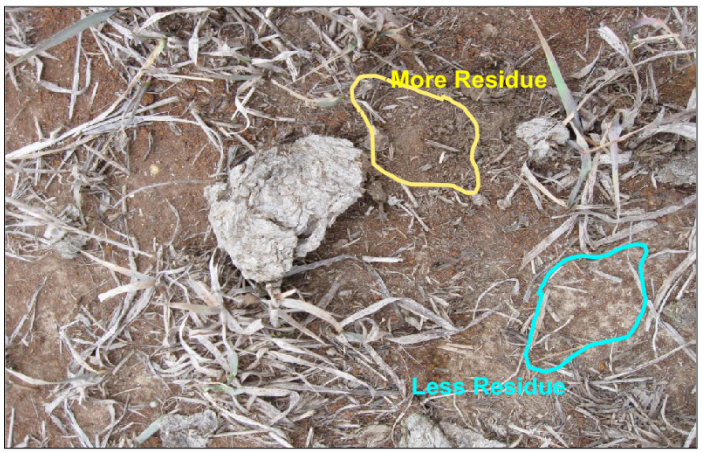
Missouri Department of Natural Resources

SLUDGE STOCKPILE & MECHANICAL SPREADER

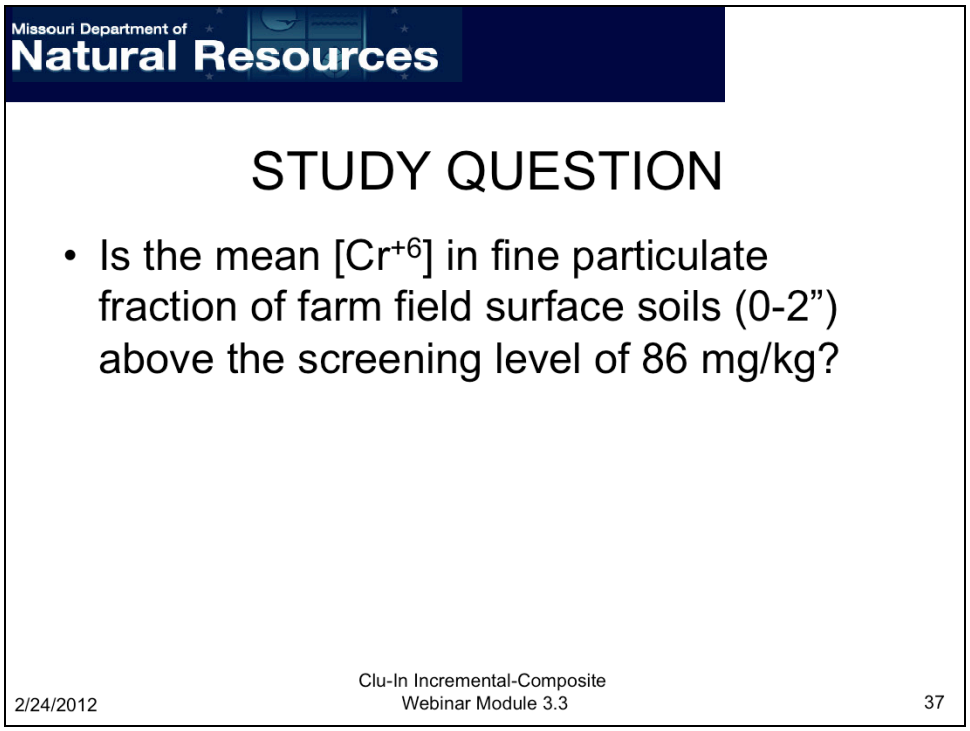
- Sludge from facility WWTP was stored in bays prior to loading on trucks
- Transported to farms and spread at no cost to farmers

Missouri Department of Natural Resources

SLUDGE RESIDUE IN FIELDS



- In pastures and no-till row crop fields, you can actually see the sludge residue
- This photo shows the visual fingerprint of sludge in a pasture



- Here is our study question.
- EPA Region 7 developed a site-specific screening level for us of 86ppm
- Interested in the fine particulates since those most available via direct contact and most likely to be transported in dust.

Missouri Department of Natural Resources

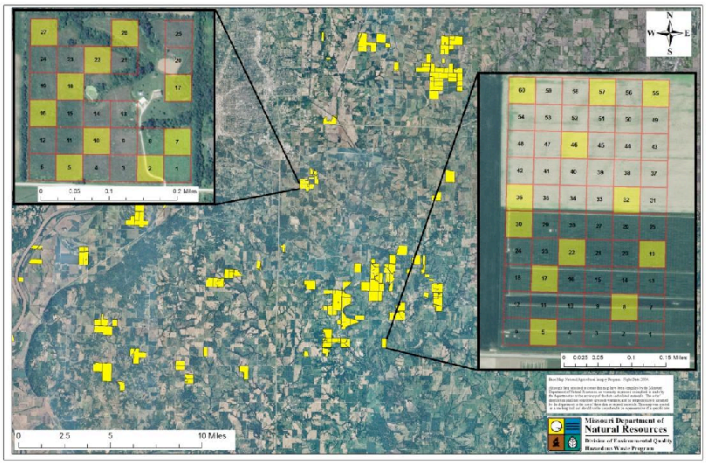
CONCEPTUAL SITE MODEL JACKPOT

Quarter	Section	Township	Range	Coord_N	Coord_W	County	Acres	Date Completed	Date Completed	Wet_Tons	Dry_Tons	Dry Tons Ac	Dry Tons Accum	Lbs Chr Acre	Crop Planted
NW	22	58N	32W	39 48.7	-94 37.4	Dekalb	175	2/25/2005	3/9/2005	1584	443	2.53	2.53	0.67	Milo
NW	22	58N	32W	39 36.7	-94 41.4	Dekalb	175	3/1/2005	3/9/2005	1120	313	1.79	1.79	0.49	Milo
SW	20	59N	31W	39 48.7	-94 36.7	Dekalb	20	8/2/1999	8/5/1999	363	143	7.22	7.22	12.8	Grass/Hay
NE	30	59N	31W	39 36.2	-94 39.8	Dekalb	70	5/15/1999	5/24/1999	911	367	5.26	5.26	6.31	Grass/Hay

- You are not intended to read this table.
- It is only to illustrate the extensive data available from the tannery regarding sludge applications.
- This data aided us in developing a CSM and selecting fields to screen based on worst case conditions

Missouri Department of Natural Resources

DECISION UNITS & SAMPLING UNITS



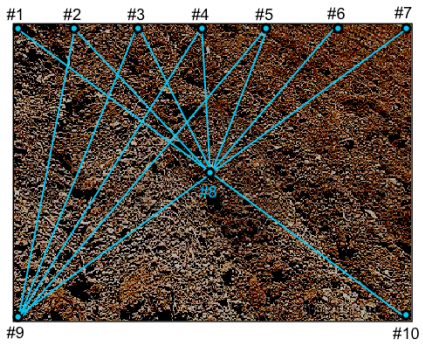
- We used the CSM to identify a subset of worst case farm fields to assess. If they came back clean, we would have high confidence that the others were OK as well.
- This is the same map as we saw before with yellow polygons being ffs that got sludge.
- The inset maps on this aerial photo show two individual farm fields. Each field was considered a DU
- Dus based on Eus ~ 80 acres
- Goal is to obtain estimate of mean for the DU
- To make the sampling more manageable, the Dus were divided into 1-acre SUs. This is the scale at which ICS will be collected.

Missouri Department of Natural Resources

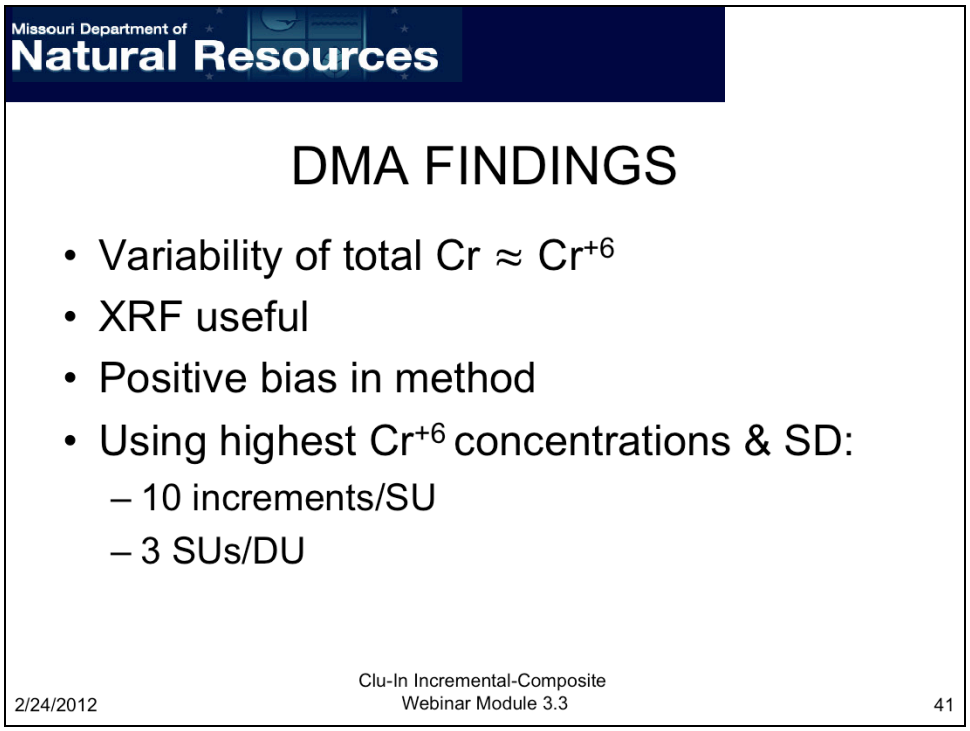
DEMONSTRATION OF METHOD APPLICABILITY (DMA)

Purposes

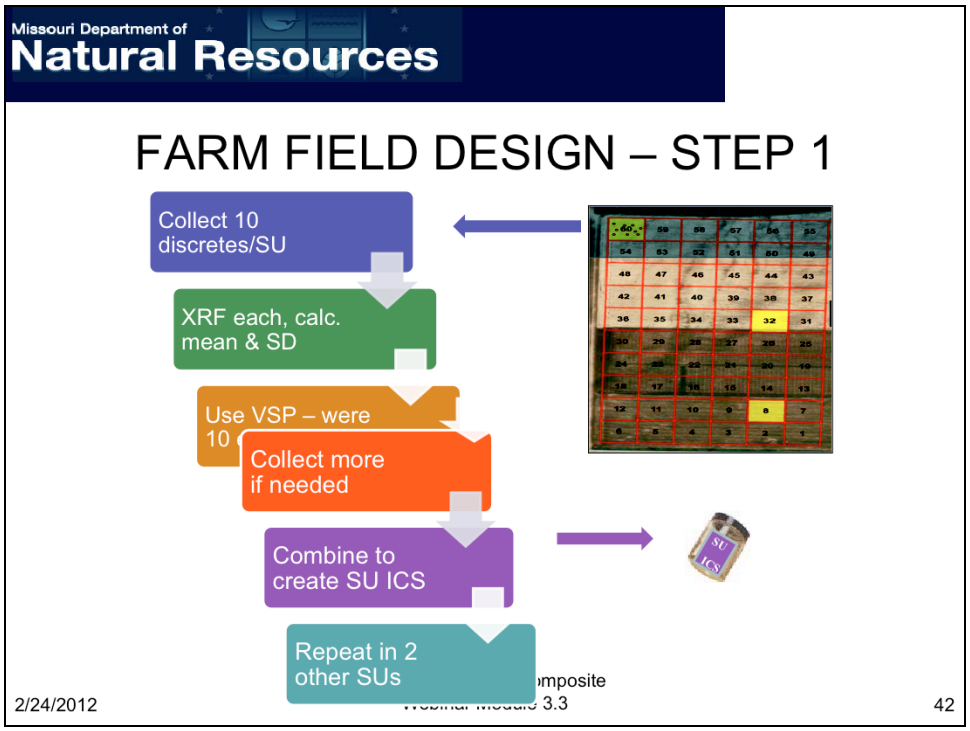
- Evaluate analytical method
- Test usefulness of XRF
- Test CSM assumptions
- Obtain initial estimates of Cr^{+6} levels & variability
- Input for ICS design



- We conducted a DMA (pilot study) This is not something that would always be warranted, but it was in this instance due to the scope and complexity of this investigation.
- List the purposes and refer to vario-plot in photo.



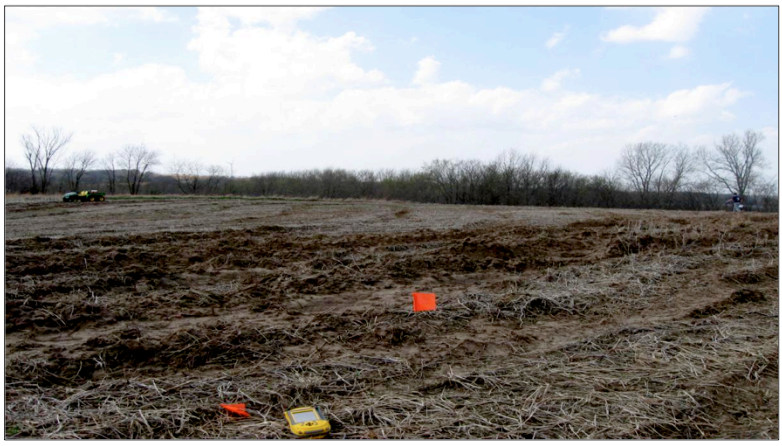
- The XRF would be useful – DL was low enough to see Cr in fields
- Our varioplots showed that total Cr and hex varied similarly across fields
- Problems with lab method identifed and corrected before full scale implementation
- We got some initial ideas about sampling density



- In the next few slides, I'm going to step you through the design
- Our ICS will be collected in the 1-acre SUs, so the first step is to determine how many increments in each ICS
- We did this by collecting the increments as discrete samples
- DMA told us 10 would be in the ballpark so we collected that #
- Then we analyzed incr. total Cr by XRF and used VSP to see if 10 were enough
- If not, collect more incr.
- When we had enough, we combined all the incr. together to form the SU ICS
- This was repeated in 2 other Sus, so that we ended up with 3 bags of soil
- This is a little diff than the examples of composite averaging Deana showed Tuesday on Module 2. Here, we are not sampling in all portions of the DU. Instead, we are only sampling in some and then using the mean and SD to see

Missouri Department of Natural Resources

FLAGGING AN SU FOR SAMPLING

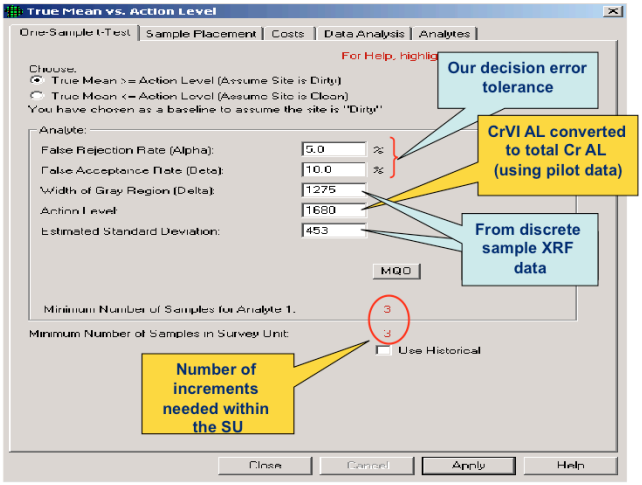


This photo shows us flagging out a 1 acre SU prior to increment collection

We used GIS tools in the office to lay 1 acre sampling grids across the Dus, loaded that onto GPS units and used those in the field to find and flag SU corners

Missouri Department of Natural Resources

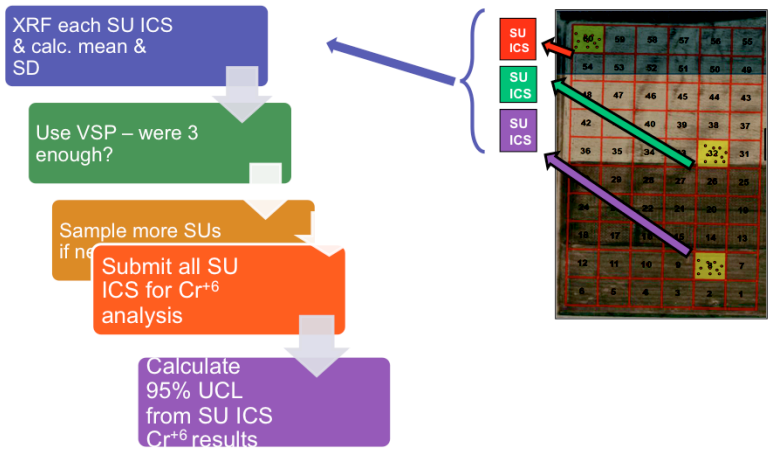
VISUAL SAMPLE PLAN ANALYSIS



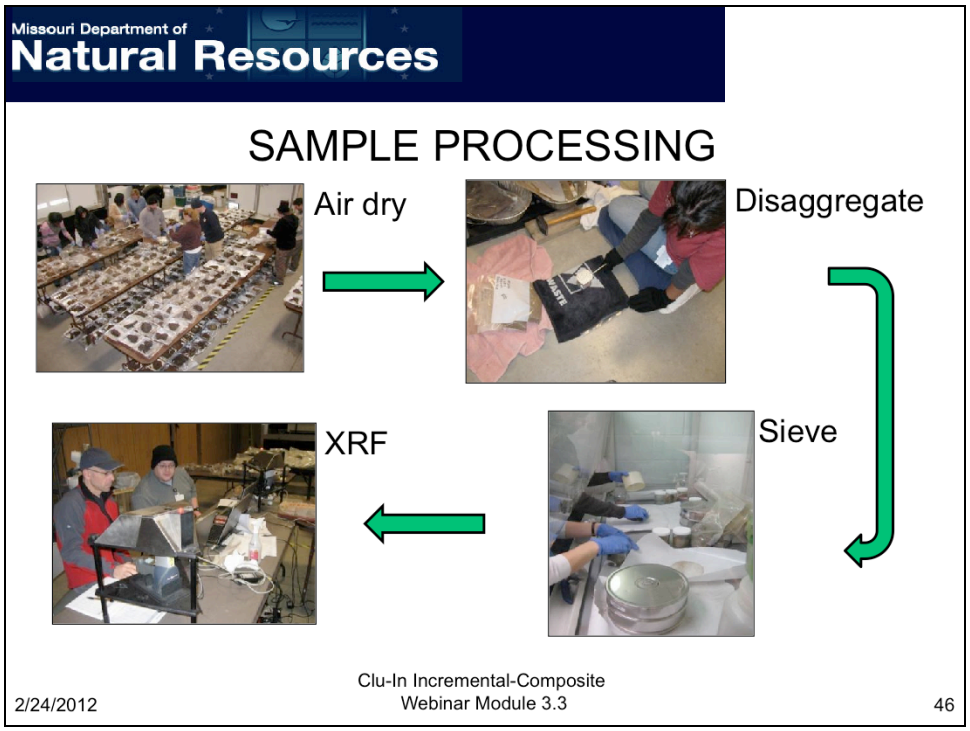
- This is a screen shot of VSP showing the results for a single 1-acre SU.
- Again, the VSP analysis was all done on total Cr results and was used only to determine sampling density.
- We entered in our level of confidence (95%), and then the WGR which is just the action level minus the measured average from the discrete samples.
- We need an action level for total Cr, but we only had one for hex Cr, so we had to convert hex Cr AL using 3x worst case ratio observed during DMA.
- We also enter in the mean and SD from the discretes and VSP provides an estimate of how many samples are needed to make this decision.
- Note in this case it is less than 10 so we can simply combine the 10 discretes already collected to form our ICS
- This was then repeated from the other two 1-acre Sus.

Missouri Department of Natural Resources

FARM FIELD DESIGN – STEP 2



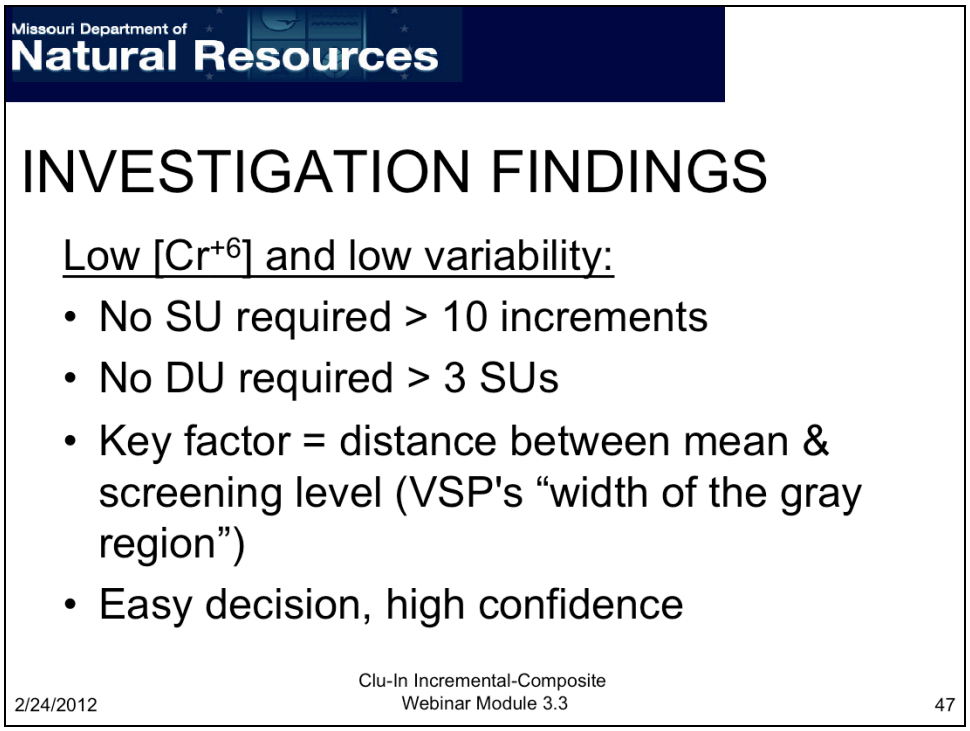
- The second step in our design was to determine how many of the 1 acre SUs we needed to sample in the DU
- Our DMA told us 5 would be pretty close, so we started with the 3 bags of soil from step 1.
- As before we analyzed each SU ICS by XRF and calc. mean and SD.
- VSP was used to determine whether 3 SUs were enough or if we needed to go get more.
- Once we had enough, all SU ICS sent to lab for Cr 6 analysis
- For our final decision, a 95% UCL on the mean Cr6 conc. Was calculated from the SU ICS results.



The photos on this slide illustrate our sample processing proceedure.

Samples were air dried and then disaggregated manually using a mallet

The samples were then sieved to .25mm to obtain the fine fraction particle size of interest prior to XRF & lab analysis



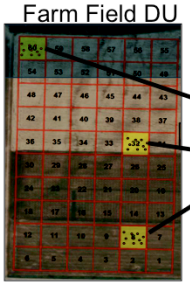
- We sampled in 60 SUs located in 20 farm field Dus.
- No Sus needed more than 10 increments and no farm fields needed more than three 1-acre Sus
- The key factor to this low sampling density was the distance between the mean we measured and the SL. Recall that this is called the WGR in VSP.

Missouri Department of Natural Resources

ESTIMATES OF DU MEANS

- Calculation of DU UCL from the SU ICS sample results

Farm Field DU

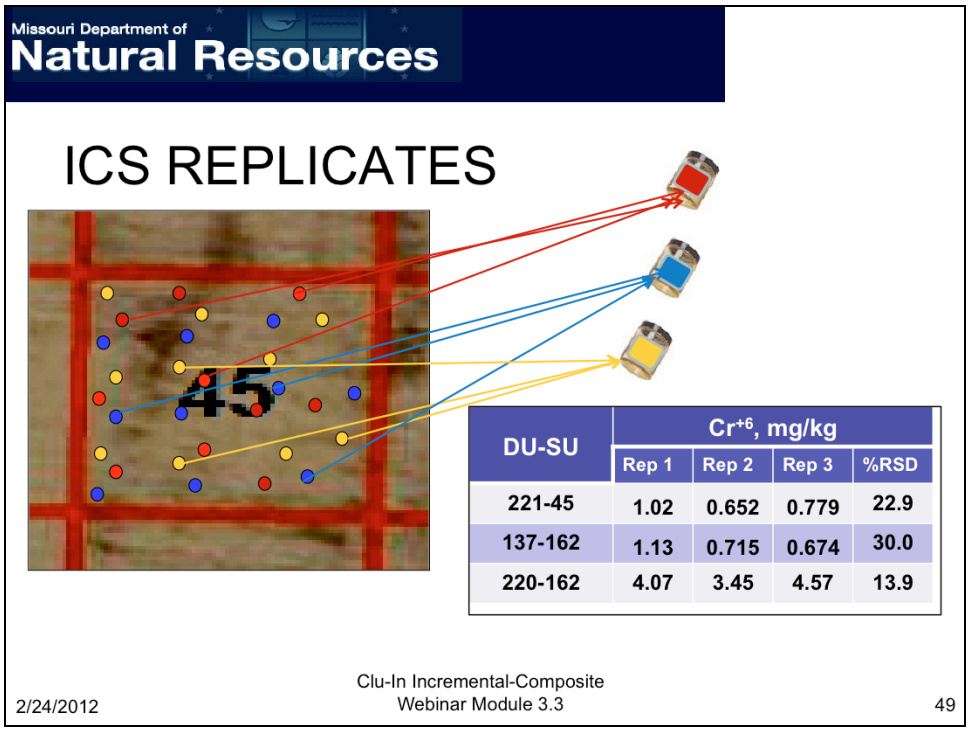


SU	Cr^{+6}, mg/kg
60	3.4
32	4.3
8	2.4
Mean	3.3
SD	0.8

$$UCL_{1-\alpha} = \overline{X} + t_{1-\alpha,n-1}\left(\frac{s}{\sqrt{n}}\right)$$

$$UCL = 3.3 + 2.9\left(\frac{0.8}{\sqrt{3}}\right) = 5.3 mg/kg$$

- This slide shows the calculation of 95% UCL for a particular farm field
- Lab results for Cr6 were used to calculate a mean and SD which were entered into this equation for UCL using the student's t
- For this DU, we calculated a mean of 3.3 and a UCL of 5.3 ppm (far below the 86 ppm SL)

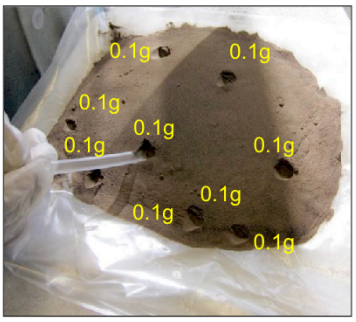


- In some of the Sus, we collected replicate ICS to measure overall sampling and analytical precision
- Three separate ICS consisting of 10 increments were collected as shown in this diagram
- A RSD was calcuated from the lab results of the replicates as shown in the far right column of this table.
- Conventionally, ICS replicates are collected across an entire DU and used to calc a UCL. Here though, we used it for QC as a measure of overall sampling and analytical error since we were using the SU ICS to calc. the UCL.
- It was at below the 30% criteria established for this project in all cases indicating that the overall sampling and analysis error were well controlled

Missouri Department of Natural Resources

LABORATORY DUPLICATES

- How well does 1 gm analyzed by lab represent the entire jar of soil?



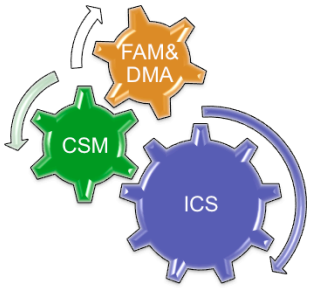
DU-SU	Cr^{+6}	Cr^{+6} Lab repl.	RPD
201	0.06	0.063	4.9
209-96	1.05	0.942	10.8
205-88	1.110	0.938	16.8
212-53	0.605	0.750	21.4
213-44	0.833	0.788	5.6
214-25	1.610	1.620	0.6
215-55	0.069	0.080	14.8
217-103	0.793	0.775	2.3
221-162	4.38	3.76	15.2

- We were also interested in what portion of the overall sampling and analysis precision was coming from subsampling procedure at the lab.
- The lab needed 1 gm for digestion/analysis.
- Rather than the typical “dig a spot” method we requested they obtain the 1gm analyzed from 10 x 0.1g subsamples collected thruout the sample mass. This process is shown in the photo to the left.
- The table to the right shows the results from the lab replicate pairs and the %RSD between them.
- You can see from the low RSDs that the subsampling process contributes relatively little to the overall sampling error. So this was not turn an important source of error for this site, but it may be at sites where the overall S & A precision is interferring with your ability to make a decision, and you need drill down and find out which step in the process needs to be improved.

Missouri Department of Natural Resources

SUMMARY – TANNERY SITE

- Hybrid increment averaging approach
- Strong CSM
- DMA (pilot study) was key
- FAM and VSP guided ICS density
- Low conc. & SD allowed decision with low density sampling

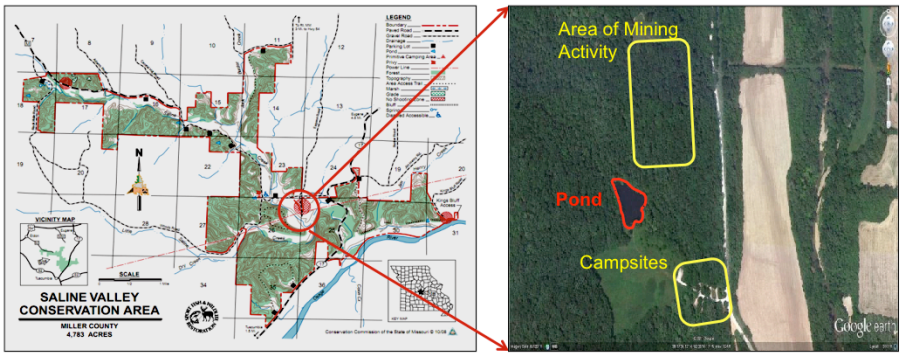


The key points about this case study are

1. the use of a strong CSM to focus on worst case farm fields and then have confidence making decision for the others
2. Using a pilot study revealed problems with our analytical method which were corrected before implementing full scale sampling.
3. The use of field analytical (XRF) together with an ICS strategy streamlined our investigation saving time and money.

Missouri Department of
Natural Resources

CASE STUDY #2
FORMER LEAD SMELTER SITE



The second case study is a small historic lead smelting operation located near what is now a campground in a public recreational area.

Missouri Department of Natural Resources

SMELTER HISTORY

Example of a reverberatory furnace

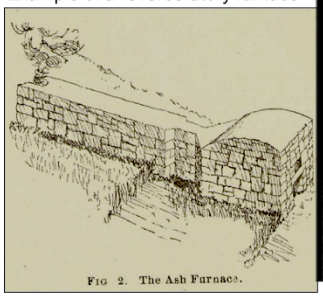
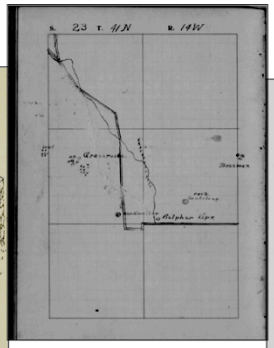
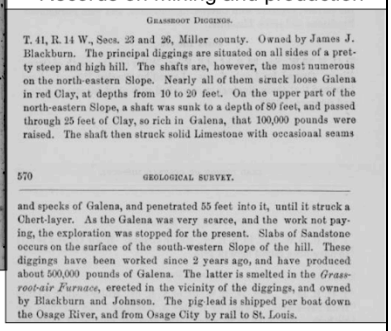


FIG 2. The Ash Furnace.



Appx. location of smelter

Records on mining and production



GRASSROOT DIGGINGS.

T. 41, R. 14 W., Secs. 23 and 26, Miller county. Owned by James J. Blackburn. The principal diggings are situated on all sides of a pretty steep and high hill. The shafts are, however, the most numerous on the north-eastern Slope. Nearly all of them struck loose Galena in red Clay, at depths from 10 to 20 feet. On the upper part of the north-eastern Slope, a shaft was sunk to a depth of 80 feet, and passed through 25 feet of Clay, so rich in Galena, that 100,000 pounds were raised. The shaft then struck solid Limestone with occasional seams

570 GEOLOGICAL SURVEY.

and specks of Galena, and penetrated 55 feet into it, until it struck a Chert-layer. As the Galena was very scarce, and the work not paying, the exploration was stopped for the present. Slabs of Sandstone occurs on the surface of the south-western Slope of the hill. These diggings have been worked since 2 years ago, and have produced about 500,000 pounds of Galena. The latter is smelted in the *Grassroot-air Furnace*, erected in the vicinity of the diggings, and owned by Blackburn and Johnson. The pig-lead is shipped per boat down the Osage River, and from Osage City by rail to St. Louis.

Some historic records available
Operated for 2 years in late 1800s. Minor quantities of lead were produced.
Approximate location of smelter known from an old sketch, but no visual evidence remains.

Photo in lower left shows a shaft.

Photo in upper right shows a campsite near where we believe the smelter was located.

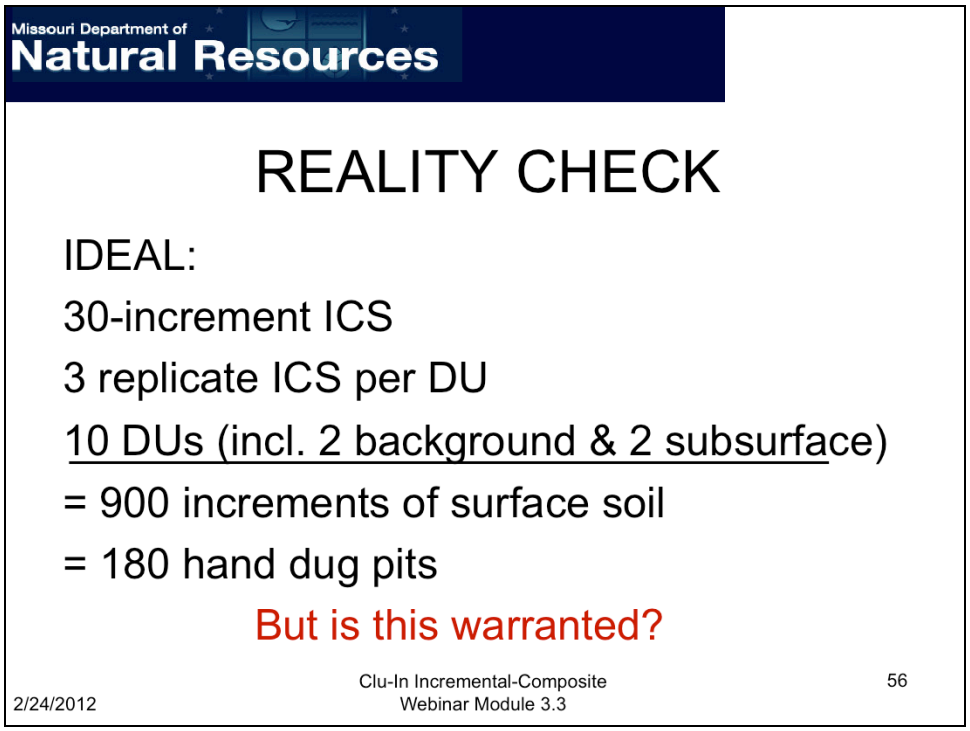
Missouri Department of Natural Resources

STUDY QUESTION

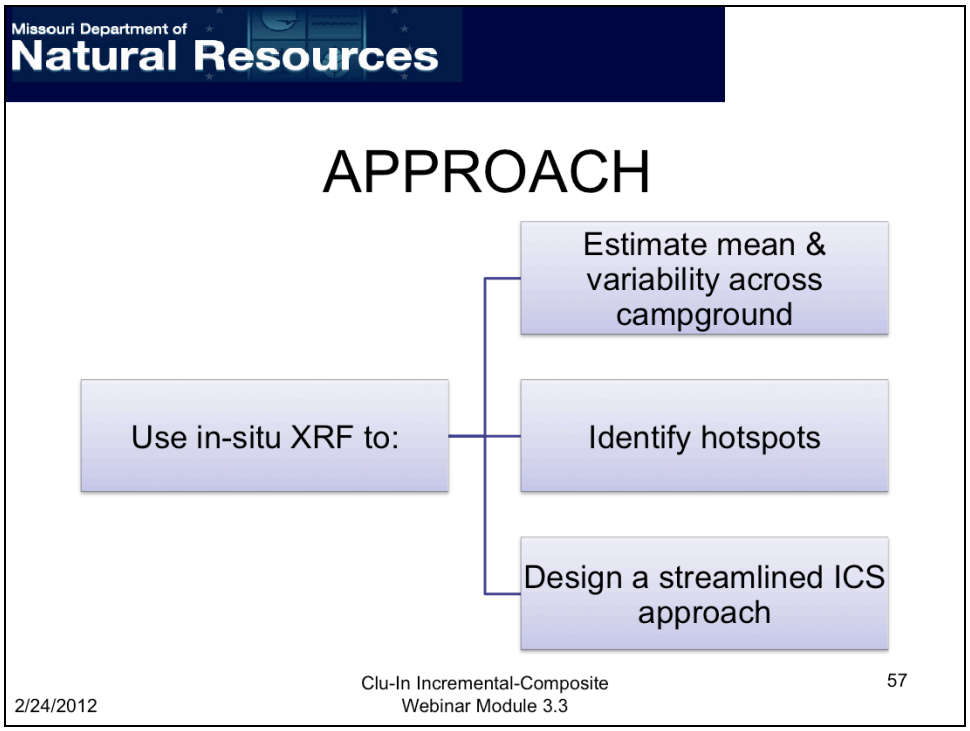
- Does mean [Pb] in fine particulate fraction of surface soil (0-2”) in any campsite exceed screening level?

Here is our study question.

This is investigation has not been completed yet. State risk assessors are currently developing site-specific screening levels for recreational use.



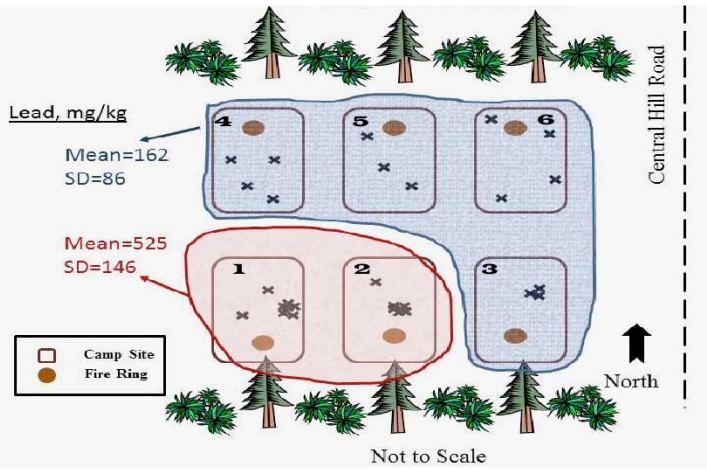
- 30 incr. recommended default to capture spatial variability across a DU when no estimates are available
- 3 replicate ICS allows calc. of a SD which can be used to develop a UCL
- With our 9 Dus, this would require a great deal of field work
- Question the need – this is a screening level assessment of a lightly used recreational site on remote public land



- Chose to use in-situ XRF to get initial estimates of variability and ranges of concentrations
- Also can help identify areas of the campground that may have elevated conc. Such as those near the former smelter.
- Use that data to streamline ICS sample collection

Missouri Department of Natural Resources

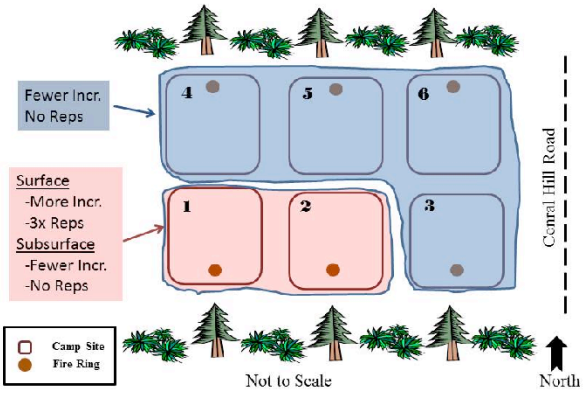
RESULTS OF IN-SITU XRF



- This figure shows the results of in-situ XRF analyses conducted in the 6 campgrounds. There was an additional area not shown here that is planned for development as a future campsite.
- Also, some of these Xs represent locations where we shot shallow (2-12”) depth soil. Lead conc. Trends of surf followed those of subsurf.

Missouri Department of Natural Resources

ICS SAMPLING DESIGN



- Based on the XRF results, we developed an ICS design in which we would collect fewer increments (15vs. 30) in the campsite Dus where we saw lower concentrations and variability. We also collected fewer incr. for the subsurface (2-4”) depths, primarily due to practical constraints of digging holes.

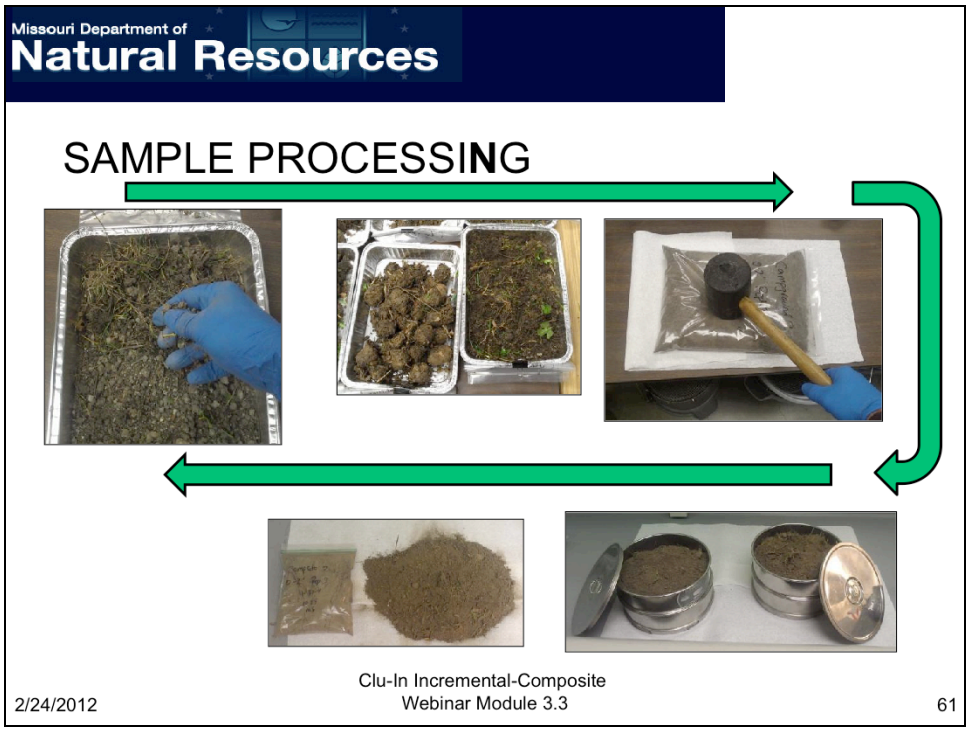
- Additionally, we would collect 3 replicates in the two campsites where we suspect levels may be close to or exceed SLs, but none in the other campgrounds or in the depth Dus.

- These choices reduce the level of effort required in the field, but as you will see there are some consequences in higher data variability.

Missouri Department of Natural Resources

COLLECTING ICS SAMPLES

- These photographs show surface and subsurface increment collection.
- We used one of the commercially available incremental sampling tools which allowed us to complete sampling in all DUs one day including in-situ XRF work.



- This series of photographs show the sample processing steps.
- Immediately upon return to the lab, sample cores were disaggregated by hand.
- Middle photo shows before and after.
- They were then air dried for 2 days, returned to the sample bags and further disaggregated by pounding with a rubber mallet.
- Samples were then sieved to 0.25 mm and analyzed by XRF.

Missouri Department of Natural Resources

95% UCL for DUs 1&2 Surface

- Calculated from results of 3 replicate ICS
- Example for DU1:

DU 1 Repl.	Pb, mg/kg
1	1,320
2	1,390
3	1,240
Mean	1,320
SD	75
%RSD	6

$$UCL_{1-\alpha} = \overline{X} + t_{1-\alpha,n-1}\left(\frac{s}{\sqrt{n}}\right)$$

$$UCL = 1{,}320 + 2.9\left(\frac{75}{\sqrt{3}}\right) = 1{,}440 mg/kg$$

- As Deana mentioned earlier, Pro UCL is not designed to work with ICS data and it will not calculate a UCL from only 3 data points. So, instead we used this standard equation for t-test UCL as we saw in the previous case study.
- First thing to note here is how much higher these concentrations are than what we saw with in-situ XRF which were all <600ppm. Two reasons: soil was wet, and bulk soil vs small particle size.
- Also, notice how close the ICS replicate results are to each other indicating excellent precision.
- Because of this low SD, the UCL is only about 8% higher than the mean.
- This campsite will likely require a cleanup based on SLs used at other rec. sites.

Missouri Department of Natural Resources

95% UCLs for DUs 1&2 Subsurface

Steps 1 & 2

- No replicates collected, so no SD
- Derive SD using relationship between SD of the mean & SD of the samples:

Step 1

$$SD_{90incr} = SD_{repls}\sqrt{n}$$

$$SD_{90incr} = 75\sqrt{90} = 710\,ppm$$

SD of the three ICS surface soil replicates

Step 2

Now we need SD for 15 incr.

$$SD_{15incr} = \frac{SD_{90incr}}{\sqrt{n}}$$

$$SD_{15incr} = \frac{710}{\sqrt{15}} = 183\,ppm$$

- There is a problem with this using this approach for the subsurface samples in Dus 1&2. We didn't collect replicates.
- Without an estimate of est. of var, cannot calc a UCL.
- But if we assume that lead is distributed in the subsurface similarly as in the surface, we can derive an SD using the relationship of the between-reps SD and the between-incr. SD as shown in these two steps
- The equation below step 1 on this slide shows the relationship between the SD between estimates of the mean (repl.) and the SD between increments making up the ICS.
- We can use this to derive a SD for 3 simulated replicate subsurface ICS.
- Also we only collected 15 incr/DU vs. 30.
- In Step 2, we can rearrange this same equation to obtain an estimate of SD for a simulated 15-increment ICS.

Missouri Department of Natural Resources

95% UCLs for DUs 1&2 Subsurface

Step 3

- We now have an estimate for SD in (simulated) 3 replicate 15-increment subsurface ICS in DUs 1&2
- Using equation for t-test UCL as before:

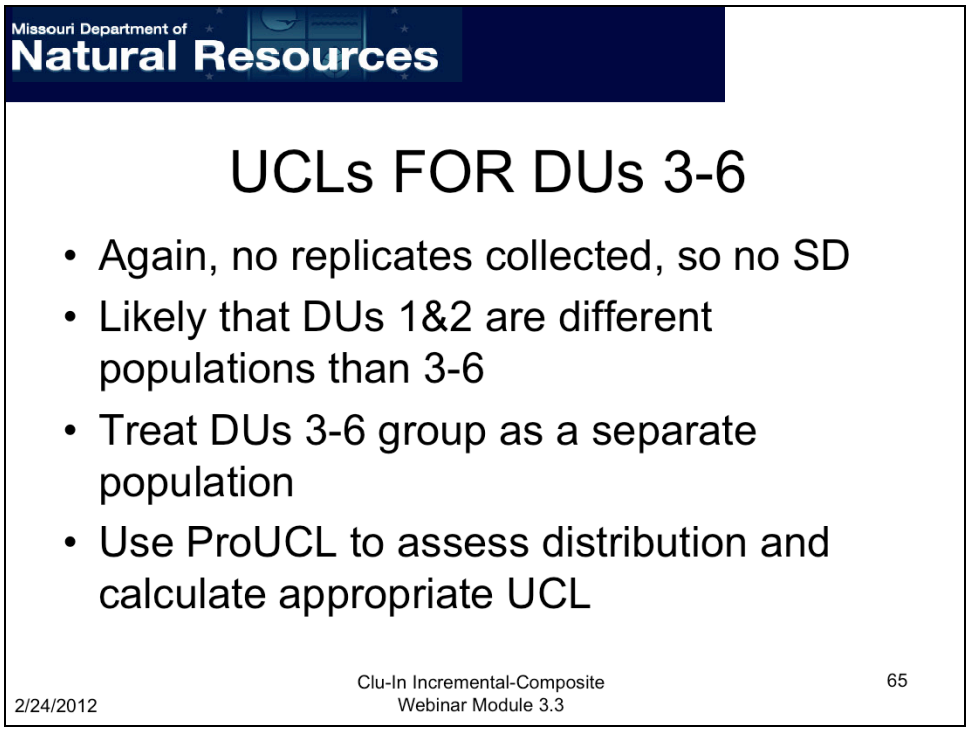
$$UCL_{1-\alpha} = \overline{X} + t_{1-\alpha,n-1}\left(\frac{s}{\sqrt{n}}\right)$$

For DU 1:

$$UCL = \underset{\uparrow}{1{,}720} + 2.9\left(\frac{183}{\sqrt{3}}\right) = 2{,}033\,ppm$$

[Pb] in 15-incr. ICS in DU1

- Now that we have an estimate of variability for the subsurface Dus, we can use the same equation as before to calc a UCL.
- Notice that the UCL is about 20% higher than the estimate of the mean; about 20% vs. only about 8% higher in the surface ICS
- That is the penalty for not collecting subsurf replicates and having to settle for a very conservative estimate of variability from surf samples.

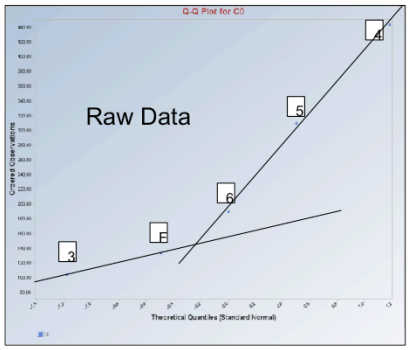


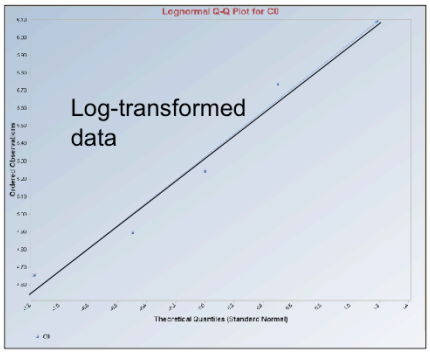
- Now, looking at the other campsites, again, we have no replicates for Dus 3-6 so no way to calc a UCL.
- Based on what we saw with the in-situ XRF data, it is less likely that the conc. And variability in Dus 1&2 are similar to those in 3-6, so not as defensible to extrapolate SD from 1&2.
- So instead, we can treat the entire 3-6 group as a separate population and use Pro UCL tools to develop a UCL for the group.
- The group UCL can then be used to derive uncertainty estimates for each individual DU.
- So let's step through that.

Missouri Department of Natural Resources

DISTRIBUTION

Pro UCL Q-Q Plots





Not so good

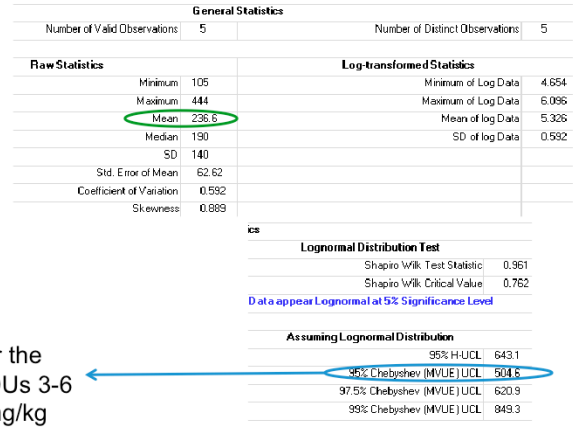
Better

- First it is important to know what sort of distribution we might be dealing with.
- ProUCL has a tool that will generate Q-Q plots.
- A QQ plot is a just a graphical way to look at your data. It plots the data against quantiles generated from a theoretical normally distributed population.
- A straight 45 deg line indicates the data is from a normal distribution.
- A break in the slope can indicate non-normal distr. Or that there are two separate populations.
- The graph to the left is the raw data for each DU ICS. Not normal.
- The graph to the right is for log-transformed data. Straight line here suggests the data are lognormally distributed
- ProUCL can calculate UCL for a number of different distributions incl. lognormal

Missouri Department of Natural Resources

DU GROUP UCL CALCULATION

Pro UCL output



General Statistics

Number of Valid Observations	5	Number of Distinct Observations	5

Raw Statistics		Log-transformed Statistics	
Minimum	105	Minimum of Log Data	4.654
Maximum	444	Maximum of Log Data	6.096
Mean	236.6	Mean of log Data	5.326
Median	190	SD of log Data	0.592
SD	140		
Std. Error of Mean	62.62		
Coefficient of Variation	0.592		
Skewness	0.889		

ics

Lognormal Distribution Test

Shapiro Wilk Test Statistic	0.961
Shapiro Wilk Critical Value	0.762

Data appear Lognormal at 5% Significance Level

Assuming Lognormal Distribution

95% H-UCL	643.1
95% Chebyshev (MVUE) UCL	504.6
97.5% Chebyshev (MVUE) UCL	620.9
99% Chebyshev (MVUE) UCL	849.3

UCL for the group of DUs 3-6 = 505 mg/kg

- This slide is a screen shot of Pro UCL output.
- A UCL for the group of DUS 3-6 is calculated at about 500ppm
- Notice that is about 50% higher than the mean for the group.

Missouri Department of Natural Resources

PUTTING AN UPPER BOUND ON UNCERTAINTY FOR EACH OF DUs 3-6

- Mean of ICS from DUs 3-6 = 237mg/kg
- Distance between UCL & group mean: 505-237 = 268

(measure of uncertainty)

DU	ICS Result Pb, mg/kg	Measure of Uncertainty	Mean + Uncertainty Pb, mg/kg
3	134	268	402
4	105	268	373
5	190	268	458
6	310	268	578
F.C.S.	444	268	712

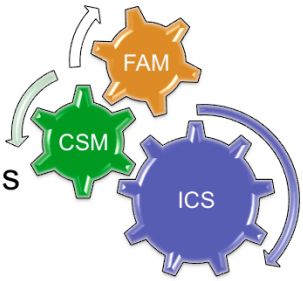
These will be compared with the screening level

- Now we can pull this all together.
- We can use the difference between this group UCL and group mean as a measure of uncertainty for the data set.
- We can then add that measure of uncertainty to each DU ICS result to obtain an conservative estimate of the mean for each DU as shown in the rightmost column of this table.
- Notice how much higher these estimates are than the individual ICS results. Up to 70% higher for DU 4.
- So there is a big penalty paid in data variability here for not having collected replicate ICS in each DU.
- However, if the SL comes out above these conservative estimates of the mean, this penalty will not interfere with our decision to conclude the campsites do not pose a risk.

Missouri Department of Natural Resources

SUMMARY
SMELTER CAMPGROUND SITE

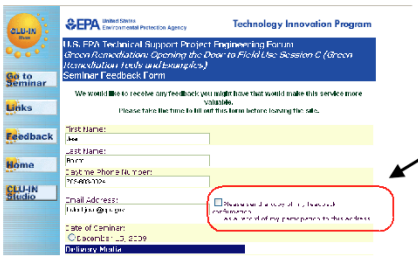
- Increment averaging goal
- FAM → CSM & guide ICS design
- Lower density ICS
- Variability extrapolated across Dus
- Penalty paid in higher UCLs



The key concepts for this case study are
•The use of FAM can refine a CSM and direct sampling efforts
•Using fewer increments and replicates saved time in the field and lab which can be a big factor with limited budgets, but
•Penalty to be paid in higher estimates of the mean

Resources & Feedback

- To view a complete list of resources for this seminar, please visit the **Additional Resources**
- Please complete the **Feedback Form** to help ensure events like this are offered in the future



Need confirmation of your participation today?

Fill out the feedback form and check box for confirmation email.

70