Welcome to the CLU-IN Internet Seminar

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

Delivered: February 27, 2012, 2:00 PM - 4:00 PM, EST (19:00-21:00 GMT)

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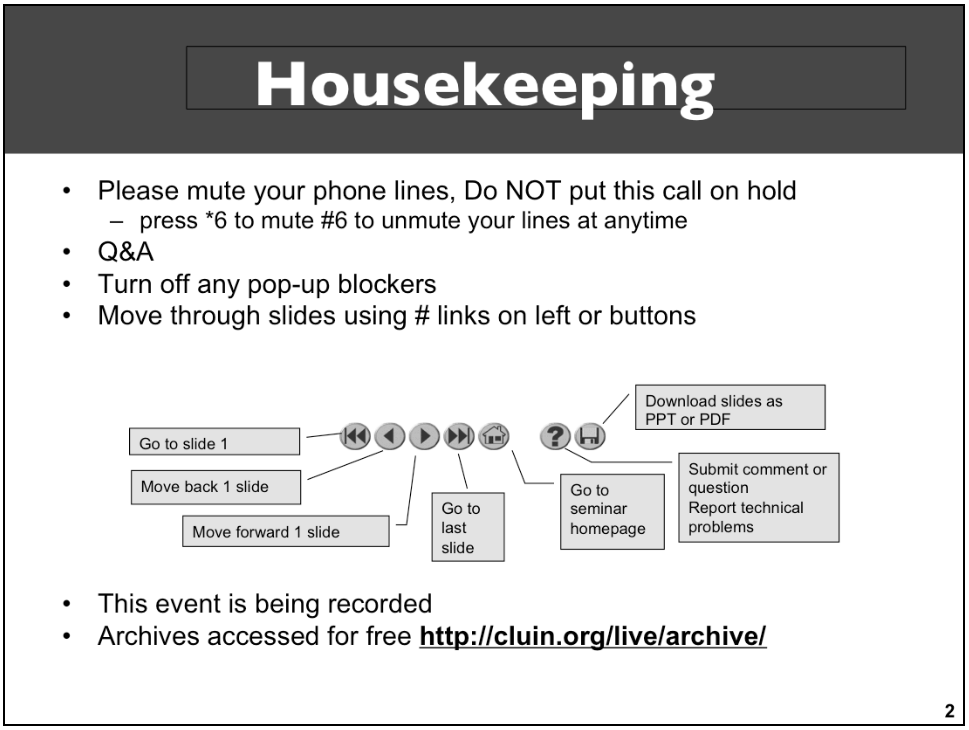

Although I'm sure that some of you have these rules memorized from previous CLU-IN events, let's run through them quickly for our new participants.

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 4.1

Incremental-Composite Sampling Designs for Surface Soil Analyses

Introduction to Last Day

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Today's Agenda

- Case Study: Dept. of Energy's Paducah nuclear facility use of composite searching for PCBs
  - 10-min Q & A
- Case study: An experimental project for incremental averaging at a firing range site
  - 10-min Q & A
- Resources and final Q & A for 20-min

Instructors

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Module 4.2

Incremental-Composite Sampling

Case Study - Paducah

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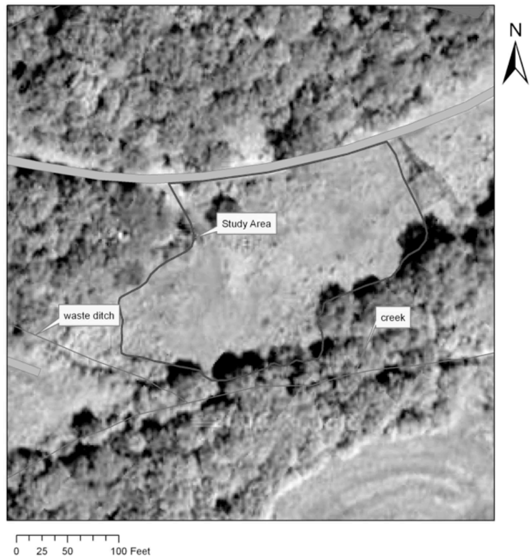
Background

- The Paducah site was/still is a uranium enrichment facility
- Historical processes resulted in release of PCBs and uranium to the environment
- For this example, a ditch and stream with contaminated sediments were dredged with the spoils placed along the banks almost 30 years ago
- Present concern is PCBs and uranium contamination in soils where dredged materials were placed
- Assumption is that uranium and PCBs are commingled

Area of Concern

- Approximately 1 acre
- Mostly grassland
- Bordered by waste ditch on west and creek to the south
- Concern is sediment spoils from ditch and creek
- Spoils placement probably 20 to 30 years ago



Applicable Criteria

- Because a radionuclide is present (uranium), MARSSIM applies (Multi-Agency Radiation Survey and Site Investigation Manual)
- MARSSIM assumes two criteria, a wide-area averaged criterion applied to an exposure unit and a hot spot criterion applied to much smaller areas
- For this site, those criteria were:

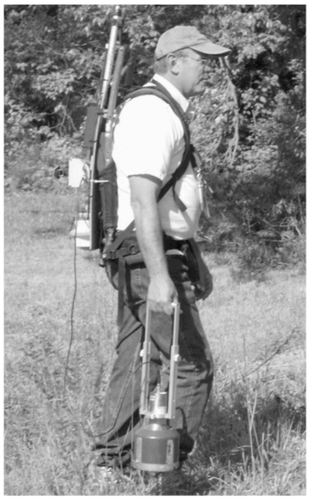
	Area-Averaged	**Hot Spot (25 m^2)**
Uranium:	10 ppm	90 ppm
Total PCB:	3.6 ppm	33 ppm

Analytical Options

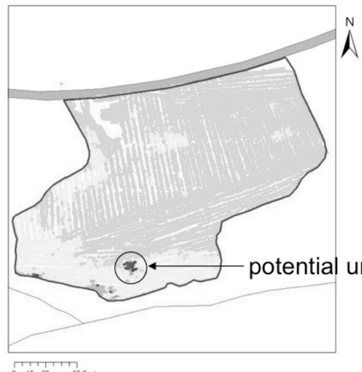
- Uranium (background ~ 3 ppm)
  - Gamma walkover scans (qualitative, very cheap)
  - XRF (quantitative, MDC ~ 10 ppm, cheap)
  - Alpha spectroscopy ("definitive", expensive)

- Total PCBs (not in background)
  - Test kits (semi-quantitative, MDC ~ 0.5 ppm, cheap)
  - GC ("definitive", expensive)

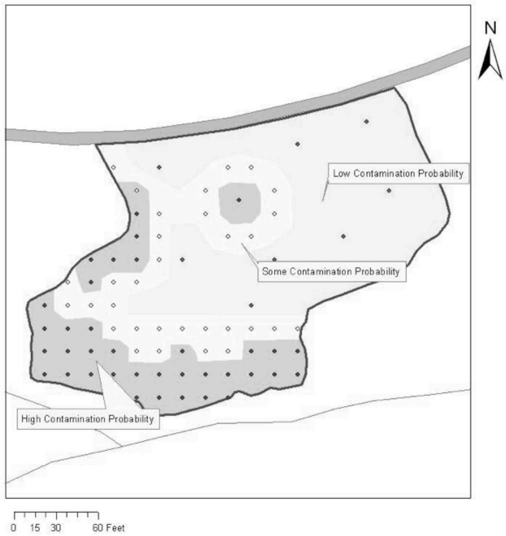
Gamma Walkover Surveys Provided Unique Data Set



More than 20,000 measurements providing wonderful spatial resolution regarding the presence/absence of uranium contamination in surface soils

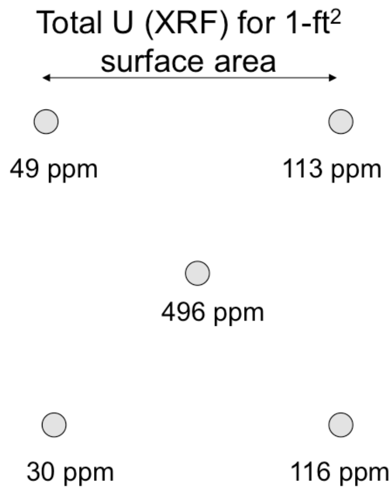


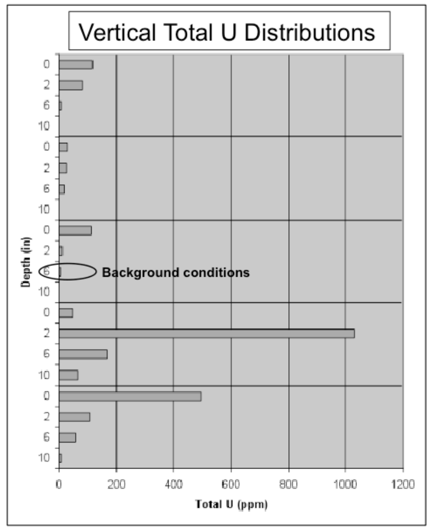
Decision Unit Layout Based on CSM



- Total area = 0.98 acre
- 3 exposure (decision) units, each reflecting a different level of concern about whether contamination present above criteria
- Decision units formed to avoid diluting contamination, if it was present
- CSM based on assumption of how contamination got there, and on gamma walkover survey results
- Hot spots were considered a potential issue for the two units with a more likely chance of contamination being present

Contamination Heterogeneity was a Recognized Problem

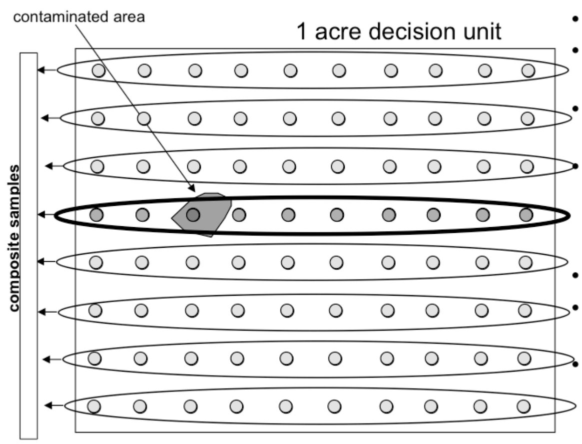




Sampling Strategy Requirements

- Show compliance with wide area-averaged criteria for uranium and PCBs for each exposure unit (95%UCL comparison)
- Demonstrate that hot spot concerns are not present for the two exposure units with a higher probability of contamination being present
- Provide data to support surgical soil removal if necessary

Simple Example…



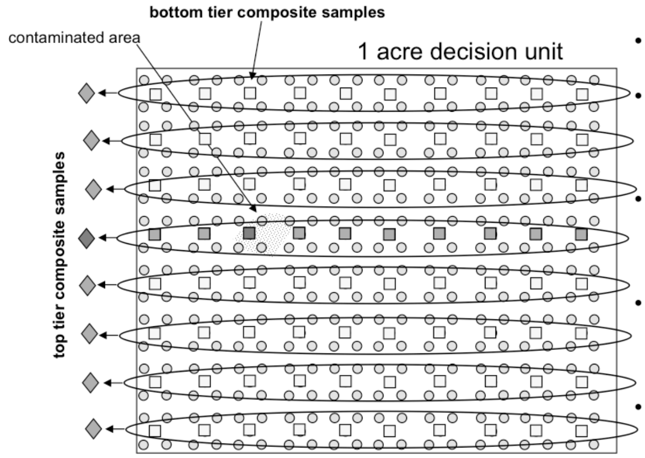
- Looking for PCBs > 50 ppm
- Could be anywhere in area of concern 1 acre in size
- Discrete sample/analyze all approach – 80 samples
- Alternative: take 80 samples and organize into 8 composites consisting of 10 samples each
- Decision criteria: **5 ppm**
- Would need to analyze 8 composites
- Plus analyze 10 archived samples from the guilty composite
- Find hotspot & calc average over all or portion of DU

More than 75% analytical cost reduction!!

Incremental Averaging & Composite-Searching Can Be Combined

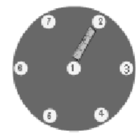
- Purpose
  - provide area average over larger decision units while detecting hot spots at the same time
- Design
  - A “bottom-tier” of incremental-averaging is done on a small “local” scale within a larger “top tier” strategy
  - “Top-tier” strategy of area-averaging over the decision unit
  - Area-wide composite-searching for hot spot/pattern detection
- Provides overall mean estimate for the DU (or portions) while controlling analytical costs

Simple Example Expanded…



- 400 soil increments ○ grouped by 5's,
- Form 80 bottom tier □ composite samples representative of 80 small areas
- 10 top tier composites combined to form 8 2nd tier composites, which are analyzed (◇ &◆).
- 10 of the original composite samples required re-analysis of the 1st tier composites
- Rationale: improve likelihood of "seeing" contamination of interest

Review Outputs from Combined Design



1. High density sampling coverage: controls short-scale heterogeneity & its problems
2. Finds hot spots: can go back & do finer delineation if desired
3. Can calculate DU average over all (or selected parts)
4. Provides vastly improved information for about same, or less, cost than much less informative sampling designs
5. Supports high confidence, high precision remedial designs

Strategy

Combine Incremental-Averaging with Composite-Searching

- Gamma-walkover data already indicated at least one uranium hot spot was likely present
- There was also more general elevated U in one exposure unit that might pose a concern
- Composite-searching to cost-effectively address PCB hot spot concerns
- Incremental-averaging across exposure units used to show wide area-average compliance

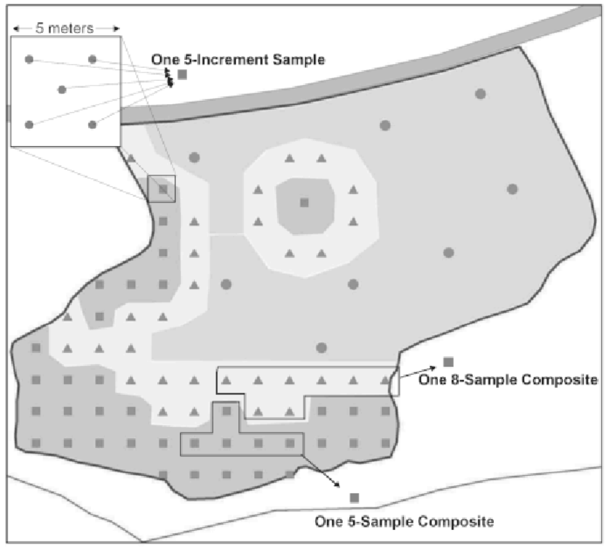
Sample Compositing Took Place Over Two Different Spatial Scales

- One 5-increment composite sample per 25 m^2
  - Each bottom-tier composite sample was homogenized & split
  - One half archived, the other used to form top-tier composites
- # of samples contributing to the top-tier composites depended on possibility of contamination
  - 5 for decision unit with the greatest chance of contamination
  - 8 for the decision unit with a medium chance of contamination
- Composites analyzed by XRF and PCB test kits, with results compared to decision criterion
  - Decision criterion = (hot spot criterion)/(# of samples in composite)
  - Composite results averaged across EU & average compared to the wide-area average criteria

Compositing Strategy…

Area to be checked for hotspots = yellow & pink with a total area of 1,700 m^2

(68 25-m^2 areas)



Results…

- As expected, one composite failed for U, requiring analysis of the original contributing samples
- Its decision unit as a whole also failed its average comparison (95%UCL > action level)
- Split analysis identified one 25 m^2 "hot spot" that corresponded to the hot spot identified by gamma walkover survey (GWS)
- Hot spot remediated, exposed soil re-sampled
- Re-sampled results pooled with original data, exposure unit now passed 95%UCL comparison

Summary of Increment & Composite Numbers

- 385 soil increments total
  - 190 from 1st exposure unit (EU)
  - 155 from 2nd EU
  - 40 from 3rd EU
- Resulting in 77 bottom-tier increment-average samples
  - 38 from 1st EU
  - 31 from 2nd EU
  - 8 from 3rd EU
- Producing 11 top-tier search-composites for analysis
  - 7 from 1st EU
  - 4 from 2nd EU
- 8 increment-average (single tier) composites from 3rd EU
- A total of 24 sample analyses
  - Cleared 68 25-m^2 areas of hot spot concerns
  - Demonstrated wide-area average compliance for 3 EUs

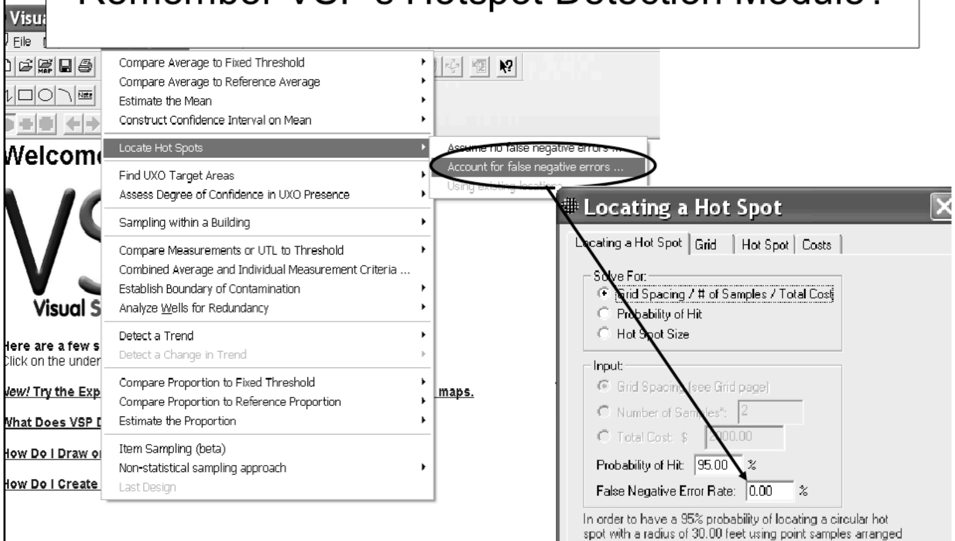
Hot Spot Detection Performance: Why 5 Increments per 25 m^2?

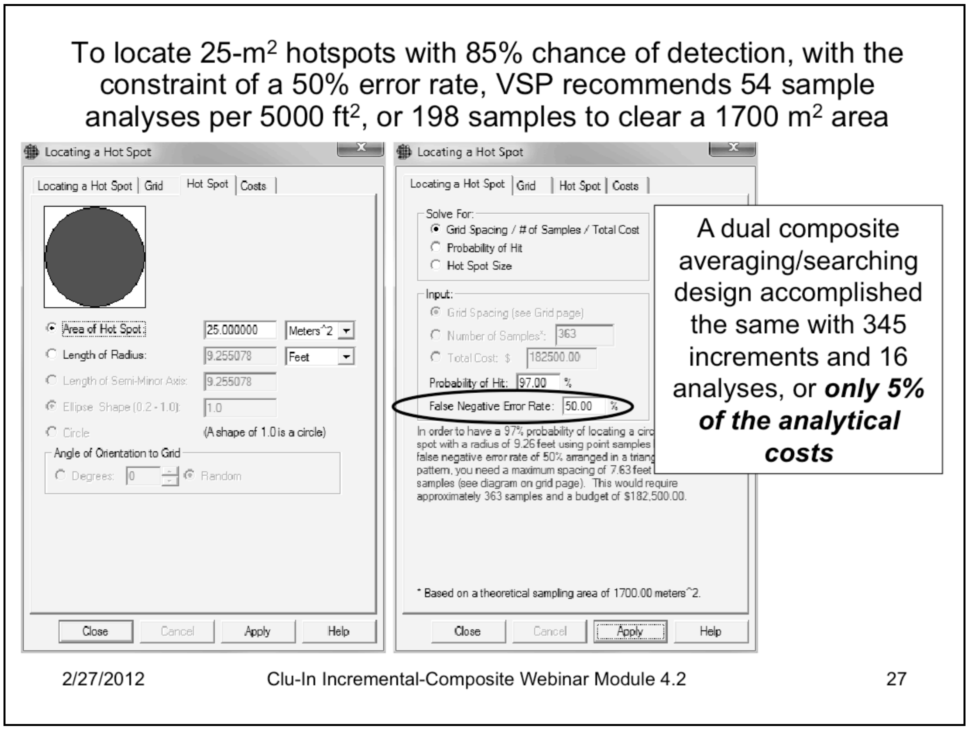
- Assume that within a hotspot (defined as ≥ 25 m^2), chance of any single increment > criterion is 50%
- Assume that if a composite contains even one increment above the criterion, the composite result will be > criterion
- <u>Theoretical</u> chances of a composite catching a hot spot:
  - Discrete sample: 50% (possible outcome = **>** or **<** = 1 of 2)
  - 2-increment composite: 75% (**<<, <>,><,>>** = 3 out of 4)
  - 3-increment composite: 87.5% (**<<<, <<>, <>>, <><, ><>, >><, ><<, >>>** = 7 out of 8)
  - 4-sample composite: 93.75% (**<<<<**, etc. for 15 out of 16)
  - ***5-sample composite: ~97%*** (**<<<<<**, etc. for 31 out of 32)

Actual Hotspot Search Performance

- U hotspot identified by GWS also caught by soil sampling
- 10 discrete samples were collected from within the hotspot footprint & analyzed by XRF
  - Results ranged from 4 to 649 ppm, with average of 174 ppm (well above hotspot criterion of 90 ppm)
  - 5 > 90 ppm & 5 < 90 ppm (= 50% hotspot detection rate)
  - If the 10 were considered increments & randomly combined into composites using actual conc values, what is the probability (via Monte Carlo) of hotspot detection
    - 1 increment (1 of the 10 randomly selected) – 50% detection rate
    - 2 increments (2 selected & “composited”) – 66% detection rate
    - 3 increments (3 selected & “composited”) – 74% detection rate
    - 4 increments (4 selected & “composited”) – 78% detection rate
    - ***5 increments – 85% detection rate (actual performance)***

Remember VSP's Hotspot Detection Module?





Beige color = R(239), G(235), B(225); Hue(30), Sat(78), Lum(232)

Overall Performance

The use of compositing strategies provided significant cost savings

- Analytical burden for 1st exposure unit reduced by 68%
- Analytical burden for 2nd exposure unit reduced by 88%

Achieved 85% probability of 25-m^2 area hotspot detection for only 12% the analytical cost of a traditional hotspot search strategy

Any Questions?

Experimental Field Study of Incremental Averaging and Sample Processing

4 Questions Addressed by this Field Study

- Does grinding a sample increase the leaching of metals that would normally not be measured and that probably would not be bioavailable in the native material?
- Is there a benefit to grinding?
- Does incremental sampling produce data comparable to what would be obtained by a reasonably dense discrete sampling design?
- What about cost?

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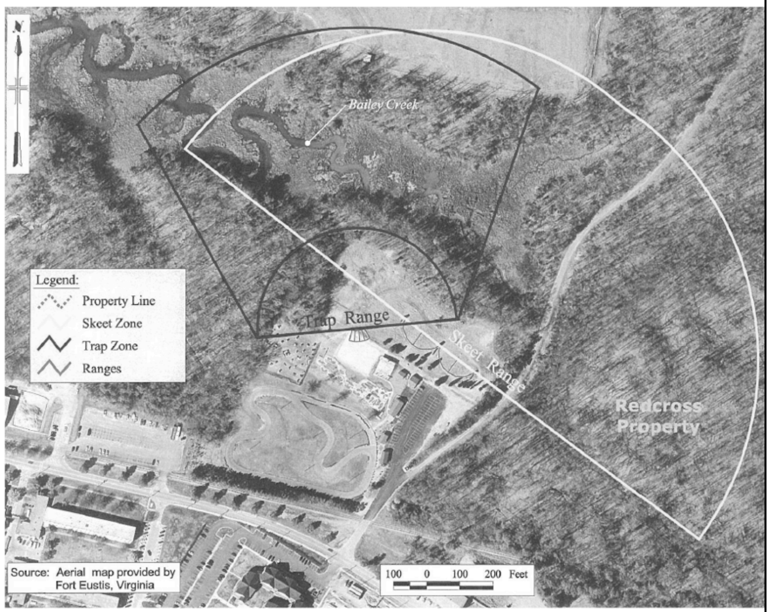
First, Some Study Particulars

- Performed by EPA Region 3
- Former skeet & trap range (PAHs, Pb, As, Sb)
- Only present the metals data here
- DUs based on different ecozones
- Pb is major component of shot-bullets (85% or more)
- Sb is added (up to about 4-6%) to increase bullet hardness
- As also added (up to about 1%) to help increase bullet hardness

Site Layout



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Skeet range outlined in yellow; trap range outlined in red.

DU1 – 2.32 acre forested tidal wetland characterized by a predominately flat topography

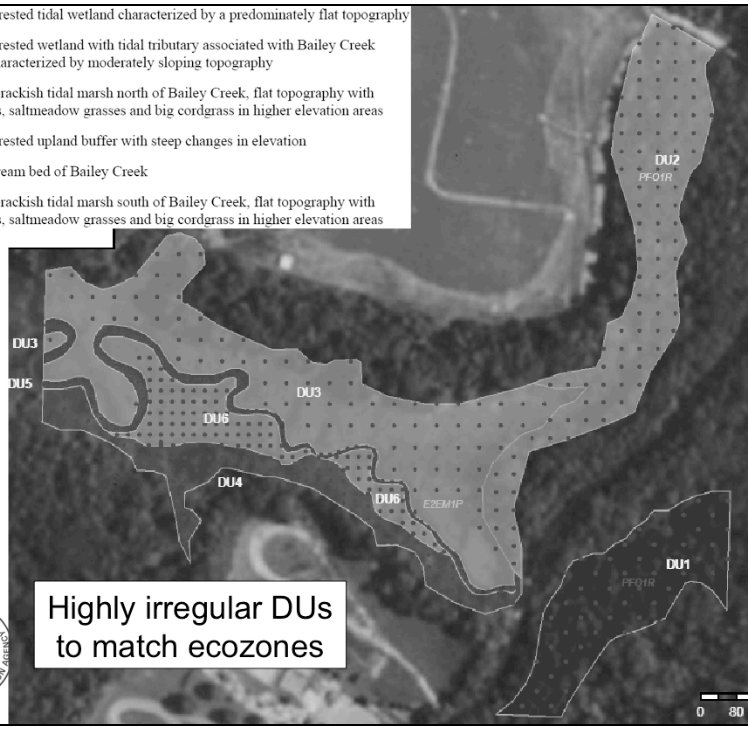
DU2 – 3.49 acre forested wetland with tidal tributary associated with Bailey Creek moving through, characterized by moderately sloping topography

DU3 – 5.203 acre brackish tidal marsh north of Bailey Creek, flat topography with saltmarsh cordgrass, saltmeadow grasses and big cordgrass in higher elevation areas

DU4 – 1.62 acre forested upland buffer with steep changes in elevation

DU5 – 0.88 acre stream bed of Bailey Creek

DU6 – 1.346 acre brackish tidal marsh south of Bailey Creek, flat topography with saltmarsh cordgrass, saltmeadow grasses and big cordgrass in higher elevation areas



Highly irregular DUs to match ecozones

Going out to get samples in soft, marshy conditions.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The incremental sampling tool used for this project.

Sampling tool use demonstrated.

Using the lever to expel the increment (a small core) into the incremental sample collection bag. The collection tool does not need to be decon'd between increments; only between different incremental samples. The soils are from DU4 (forested upland)

FATE OF PB-SHOT IN THE ENVIRONMENT

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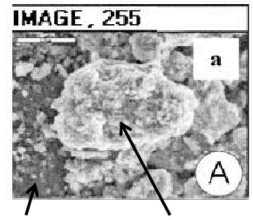
Contamination from Shot Bullets

- Background Information: How does soil contamination from shot bullets occur?
  - Shot is not stable in soil, but corrodes
  - Constituents transform into minerals, some of which dissolve in water
  - The more organic carbon, water and oxygen present, the faster the shot corrodes

Fate of Pb Shot in Soil



Bullet surface with Pb carbonate crusts

- Surface corrosion creates Pb mineral particles (e.g., oxides, carbonates) (Cao et al, 2003)
- They flake off & integrate into soil matrix as particles containing concentrated Pb
- Water-soluble minerals dissolve & Pb atoms can sorb onto native soil minerals & organic carbon particles
- May eventually form insoluble Pb minerals

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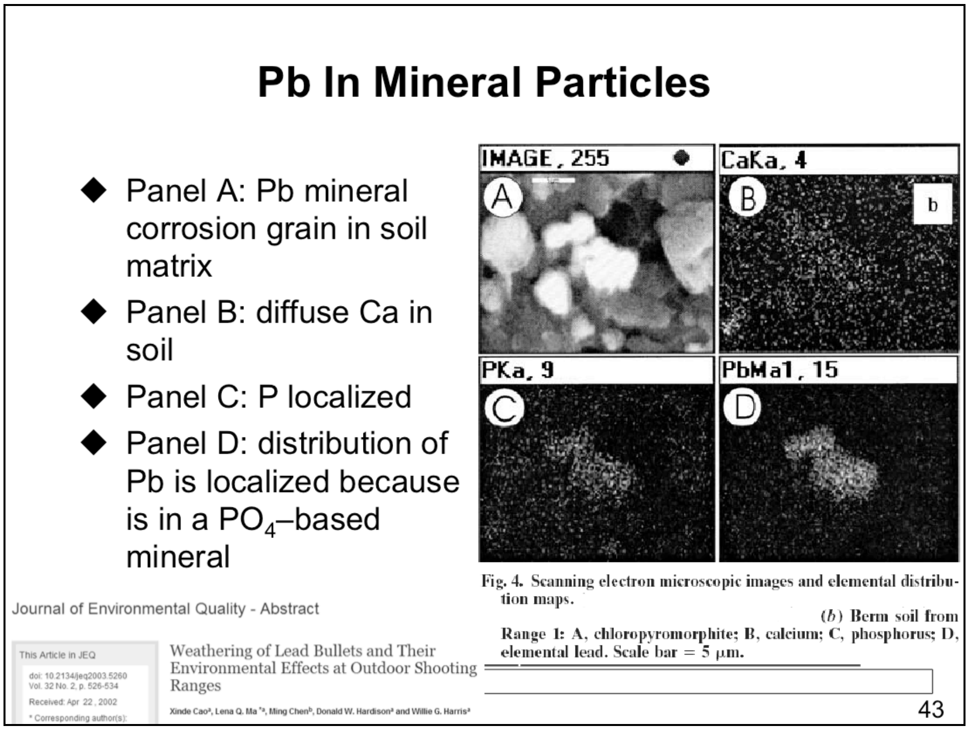
Cao, X., L.Q. Ma, M. Chen, D.W. Hardison, W.G. Harris. Weathering of Lead Bullets and Their Environmental Effects at Outdoor Shooting Ranges in *Journal of Environmental Quality Vol 32,* No. 2, page 526-534 (2003).



Cao, X., L.Q. Ma, M. Chen, D.W. Hardison, W.G. Harris. Weathering of Lead Bullets and Their Environmental Effects at Outdoor Shooting Ranges in *Journal of Environmental Quality Vol 32,* No. 2, page 526-534 (2003).

Iron Minerals Absorb Unmineralized Metals

"the iron in a cubic yard of soil [1-1.5 tons] is capable of adsorbing 0.5 to 5 lbs of soluble metals …or organics" (Vance 1994).

Contaminants adsorbed to particulate minerals create "nuggets"

Arsenic sorbed to iron hydroxides (the light-colored particles)

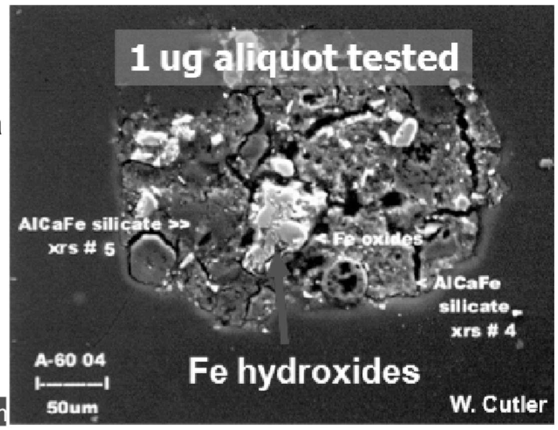


Figure courtesy of Roger Brewer, HDOH

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Particulate iron minerals are very good at binding contaminants. One researcher stated that the Fe in a cubic yard of soil can adsorb ½ to 5 lbs of soluble metals or organics. By the way, a cubic yard of soil is more than a ton. The picture shows microscopic iron hydroxide grains with a high loading of arsenic. The As appears as a light-colored deposit covering Fe-OH grains. The silicate minerals making up most of the mass in the background do not adsorb arsenic and remain dark.

Quote from a journal article: "Given the average concentration in soil, the iron in a cubic yard of soil is capable of adsorbing from 0.5 to 5 pounds of soluble metals as cations, anionic complexes, or a similar amount of organic[s]." (Vance, 1994). [Reference = David B. Vance. "Iron – The Environmental Impact of a Universal Element," *National Environmental Journal*, May/June. 1994 Vol.4 No. 3 page 24-25.]

Sources of Pure Pb/As/Sb Nuggets

- Metal dust generated when weapon is fired
  - Pb primers
  - Scraping of bullet against barrel rifling
- Abrasion of bullet as it travels through soil
  - Experiment showed average of 41 mg mass lost as bullet traveled through sand
  - Research article:

ELSEVIER

Science of the Total Environment 328 (2004) 175–183

www.elsevier.com/locate/scitotenv

Lead contamination in shooting range soils from abrasion of lead bullets and subsequent weathering

Donald W. Hardison Jr., Lena Q. Ma*, Thomas Luongo, Willie G. Harris

Hardison, D.W., L.Q. Ma, T. Luongo, W.G. Harris. Lead Contamination in Shooting Range Soils from Abrasion of Lead Bullets and Subsequent Weathering in *Science of the Total Environment 328* (2004) 175-183.

STUDY DESIGN

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DU Increment Numbers and Areas

DU #	Increment # per IS sample	Area (acres)	Ecozone
DU1	50	2.3	Forested wetland
DU2	100	3.5	Forested wetland
DU3	80	5.2	Brackish tidal marsh
DU4	100	1.6	Forested upland
DU5	100	0.9	Stream bed depositional areas
DU6	91	1.4	Brackish tidal marsh

Sample Processing

- DU field increments added to large plastic bag which was sent to lab
- In lab, soil was air-dried and crushed (to break up clods)
- Then sieved: retain everything passed thru 10-mesh (2 mm) sieve
- Some sieved samples subsampled before grinding ("pre-grind" or "unground")
- All samples eventually milled ("post-grind" or "ground") to 74 µm (0.074 mm = 200-mesh)

Large Bagged Samples (pic not from this project)

Photo from USACE-Alan Hewitt

Air Drying (pic not from this project)

Photo from USACE-Alan Hewitt

Sieve to Remove >2 mm (pic not from this project)

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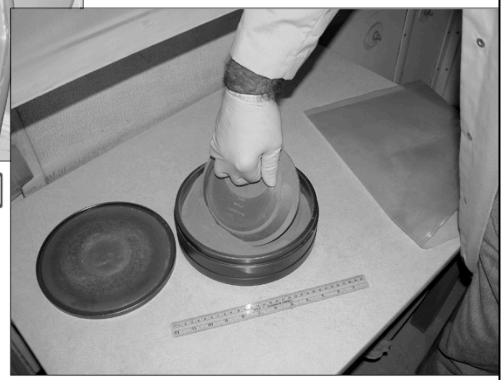
Photo from USACE-Alan Hewitt

Puck Mill Grinder



Photos from USACE-Alan Hewitt

Type of grinder used in Ft Eustis project

Incremental Subsampling (pic not from this project)

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Photo from TestAmerica

Study Design

DU#	Field Replicate Sample (3)	Laboratory Pre-Grind Replicates (5) *	Laboratory Post-Grind Replicates (5)*	Laboratory Post-Grind Replicates (3)*	Discrete Samples (49)
1	✓			✓	
2	✓	✓	✓		
3	✓			✓	
4	✓	✓	✓		✓♦
5	✓			✓	
6	✓	✓	✓		

* - Only 1 of the 3 field replicate samples from each DU was included in this portion of the evaluation. The other field replicates were simply sub-sampled once after sieving, drying and grinding.

♦ 25 of which had 3 unground replicate subsamples in addition to 1 ground

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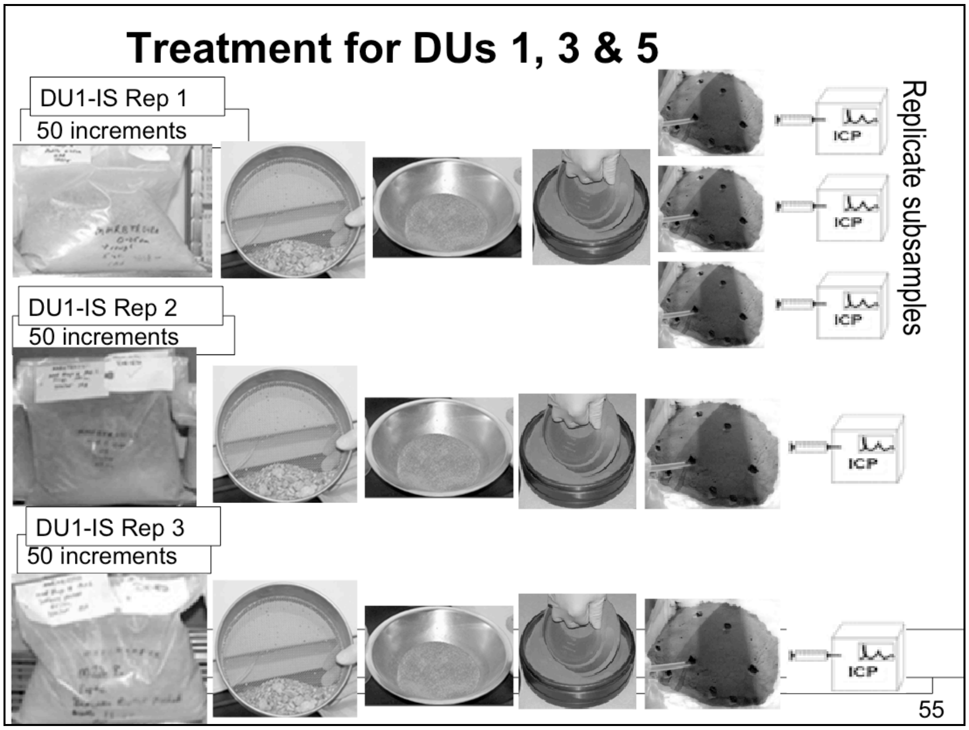
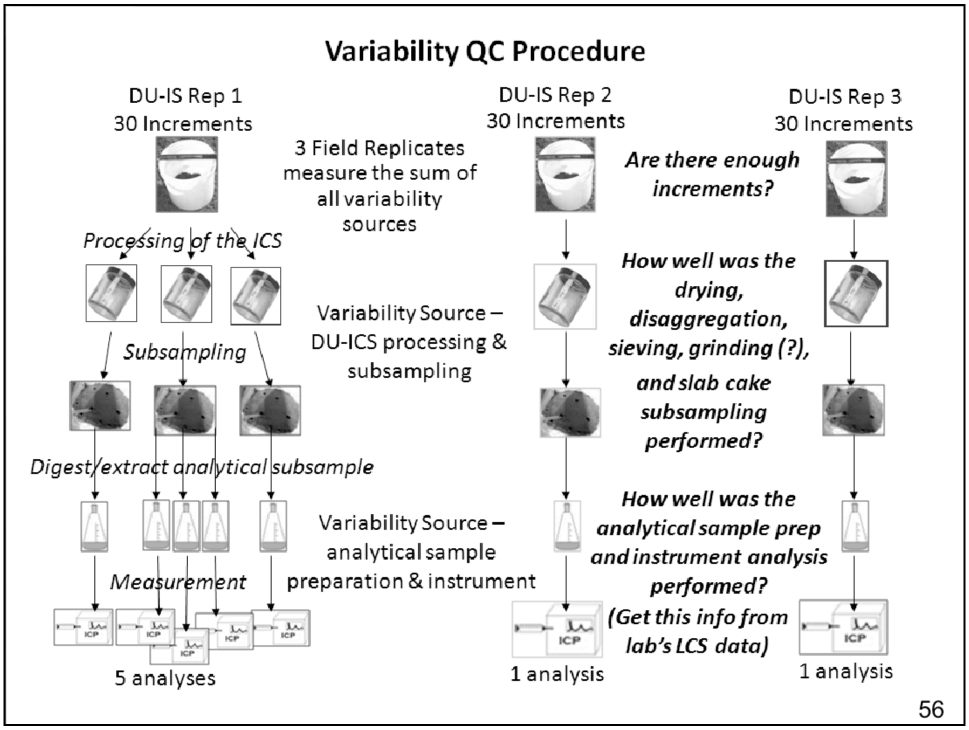
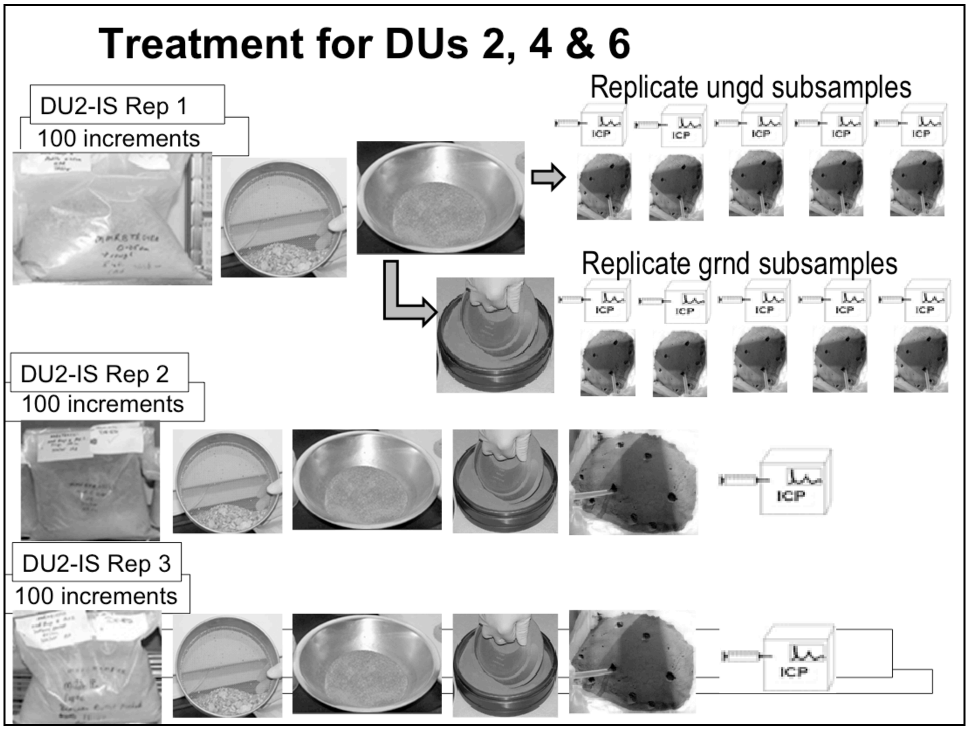
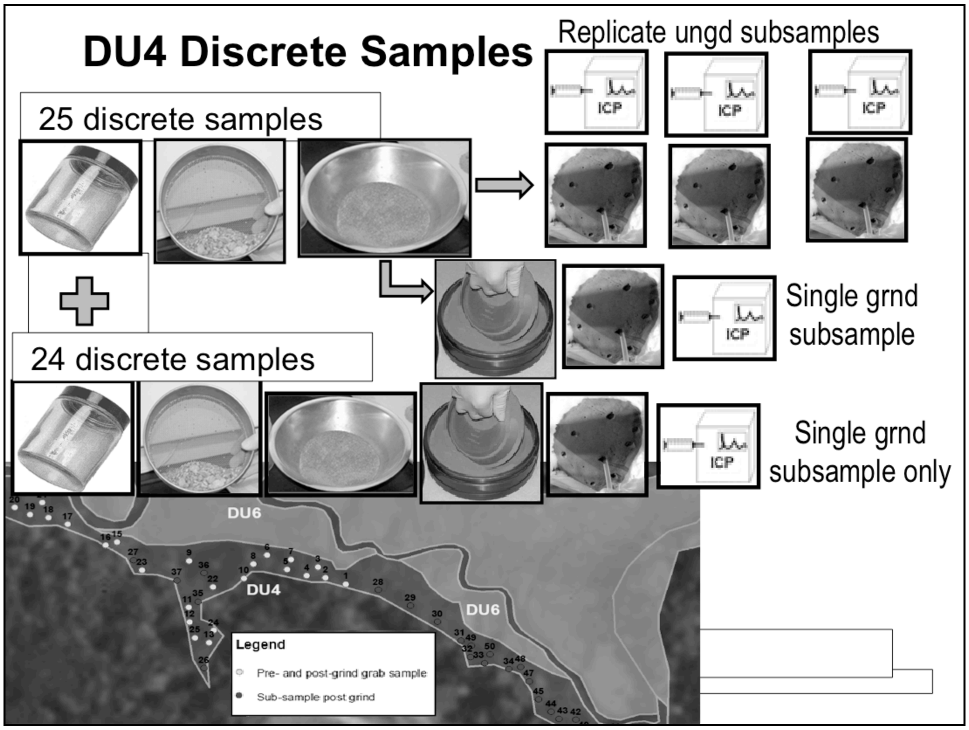

Treatment for DUs 1, 3 & 5
DU1-IS Rep 1
50 increments
DU1-IS Rep 2
50 increments
DU1-IS Rep 3
50 increments
ICP
ICP
ICP
ICP
ICP
Replicate subsamples
55



Treatment for DUs 1, 3 and 5 are the same set-up as the Variability QC Procedure.


Treatment for DUs 2, 4 & 6
DU2-IS Rep 1
100 increments
Replicate ungd subsamples
Replicate grnd subsamples
ICP
DU2-IS Rep 2
100 increments
DU2-IS Rep 3
100 increments


DU4 Discrete Samples
Replicate ungd subsamples
25 discrete samples
24 discrete samples
ICP
Single grnd subsample
Single grnd subsample only
DU6
DU4
DU6
Legend
Pre- and post-grind grab sample
Sub-sample post grind

STUDY FINDINGS

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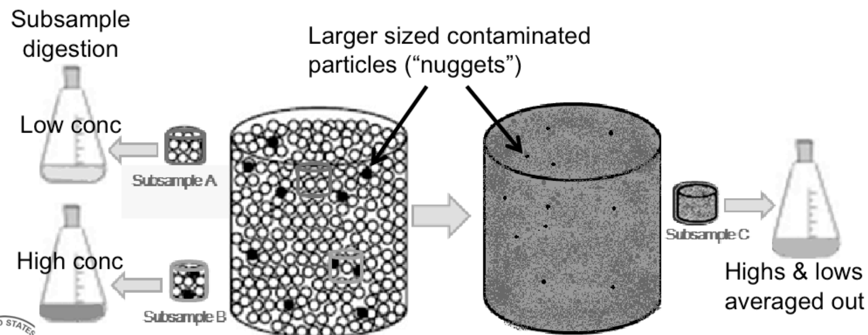
Q: Does Grinding Increase Metal Solubilization During Digestion?

- Short answer: Not consistently; might depend on matrix
- Long answer: For 2 of the DUs (DUs 4 & 6), there is no difference between unground and ground concentrations.
- DU2 (forested wetland) did show statistical elevation of Sb, As and Pb in ground vs unground samples.
  - Cannot rule out that something about the DU2 matrix yields greater solubilization of Sb, As and Pb from ground samples.
    - Some studies suggest matrices with larger pre-grind particle sizes (e.g., sands) are more likely to show higher ground concentrations than matrices with small pre-grind particles (clays & silts)
    - This explanation doesn't fully explain the findings of this study
  - Other metals in DU2's data set did not show this pattern
  - There is another explanation for why higher levels are sometimes seen in ground samples: particle effects

Particle Effects Can Make It Appear that Ground Conc's Are Higher than Unground

Small subsamples & large particles => ↑data variability
Reduction of particle size required for more representative sampling
Can reduce, but not entirely eliminate particle effects



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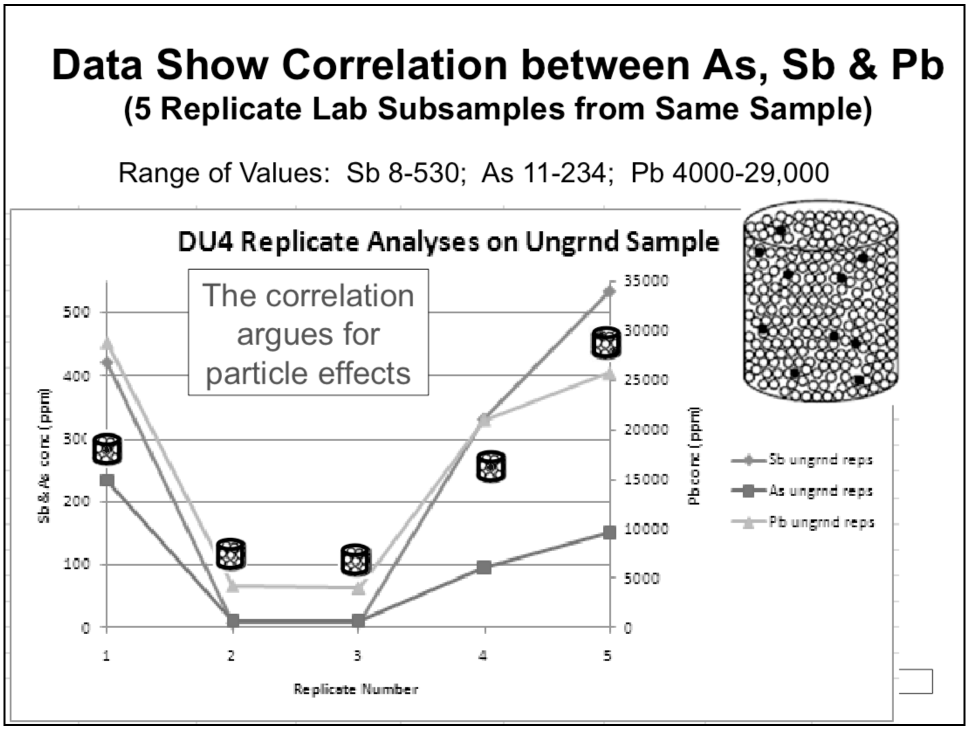


Don't dismiss this data's importance just because all the concentrations are high. Just because these Pb concentrations are much greater than the common risk-related threshold of 400 ppm does not mean that variability at these high concentrations is not important. Decisions about remedy selection and design or soil treatment and disposal may still hinge on differences at these high concentrations.

The prime purpose of this graph is to illustrate the extreme variability that soil contamination can display. Soils that are contaminated are more likely to display a nugget effect which manifests as high variability. Soils that are not contaminated (or very lightly contaminated) are less likely to have particles with high contaminant loading, and so typically show less variability.

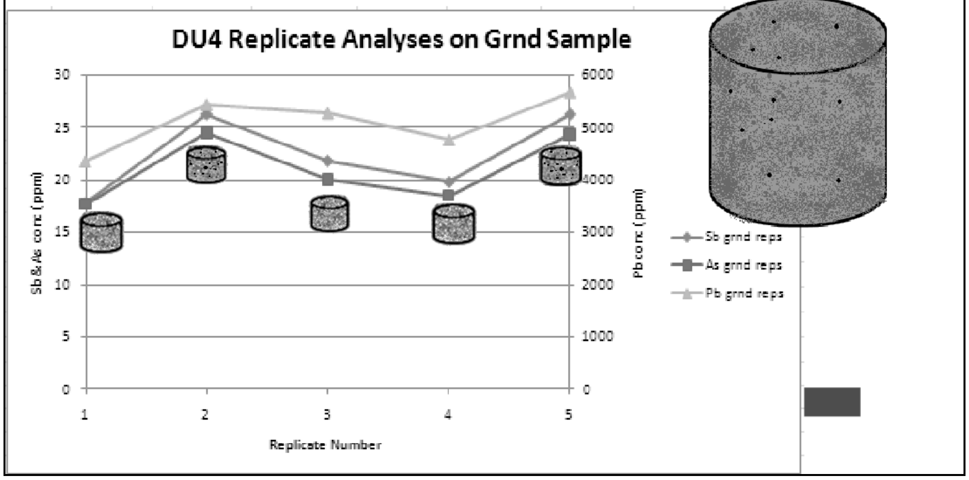
Data variability is striking in this experiment where 5 replicate subsamples were taken from a single unground sample. Each of the 5 subsamples were analyzed for metals. The mass of the subsamples was 2.5 grams. The Pb results varied between 4000 and 28,000. Remember! These are not different field samples…they are 5 different subsamples from the same jar of soil. A small sample mass composed of large particles frequently does not preserve the proportion of constituents as is present in the original population.

Fortunately, routine lab quality control checks provide measures of variability. QC includes co-located samples, field splits, lab duplicates, and matrix spike/matrix spike duplicates. Unfortunately, the information provided by these QC results is greatly under-appreciated and often ignored.

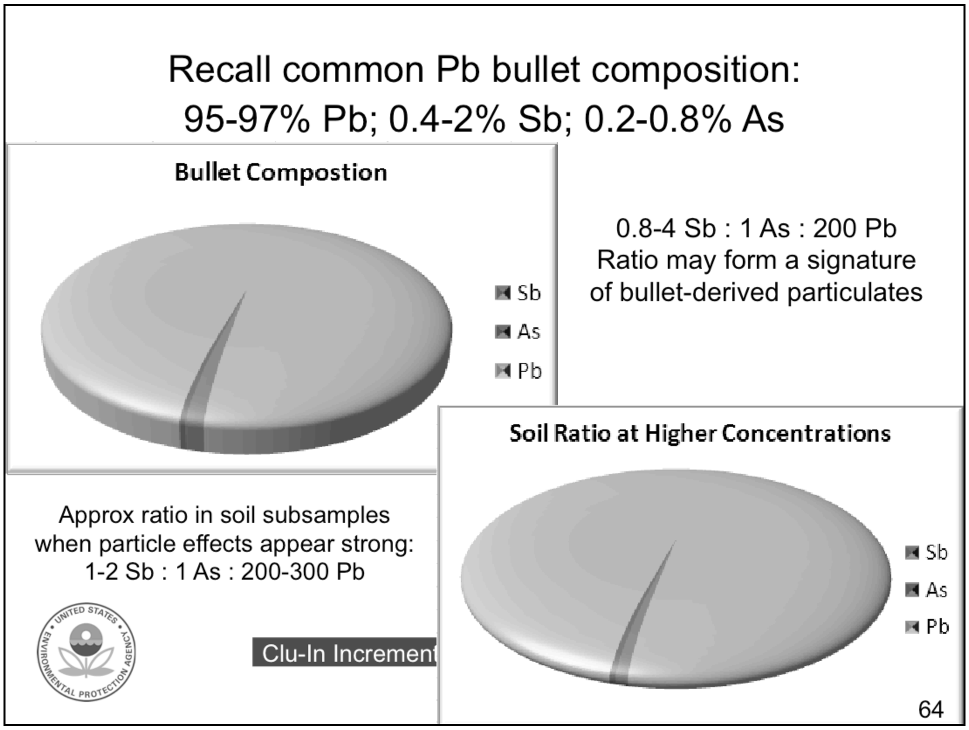
Correlation Still Present After Grinding (altho variability much decreased)

Pre-grind ranges: Sb 8-530; As 11-234; Pb 4000-29,000

Post-grind ranges: Sb 18-26; As 18-25; Pb 4360-5660



After grinding, the low end of the concentration range for each of the 3 elements was higher than low end of the pre-ground concentration range. This shows an “evening out” of the extreme high and low reported concentrations after grinding. It is reasonable to believe (although impossible to know absolutely) that this reflects the ability of grinding to bring each subsample closer to the true concentration of the large sample.



The bottom line is that the evidence points to the existence of pure shot particulates present in subsamples, especially in the unground samples.

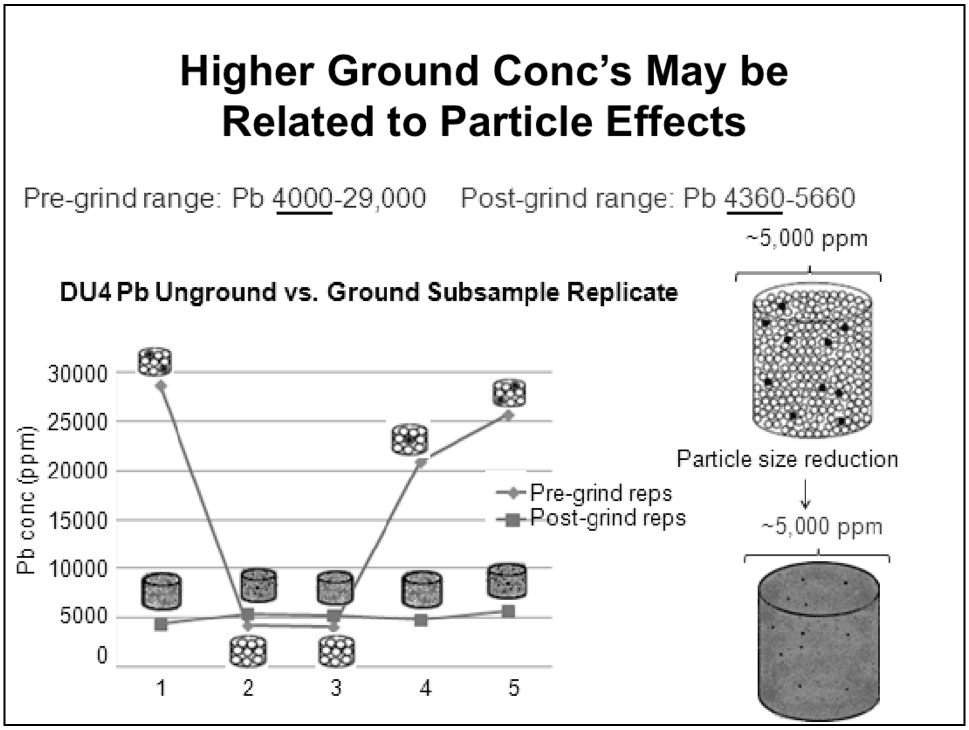
Over the whole study, 4 sub-experiments tested whether analyte concentrations increased after grinding

Number where ground conc is statistically:	higher	the same	lower
Al	3	1	
Sb	3		1
As	2	1	1
Ba		4	
Be	1	2	1
Cd (all conc <0.6, high precision)	3	1	
Ca	1	3	
Cr (grinder "bleed," ignore Cr)	(3)	(1)	
Co	2	2	
Cu	1	2	1
Fe		4	
Pb	2	2	
Mn	1	2	1
Hg		4	
Ni		4	
V	1	3	
Zn	1	2	1
Totals	21	37	6

If solely statistical chance at work, expect "higher" (n = 21) and "lower" (n = 6) to balance out better. Pure chance is likely not the whole story. Particle effects contribute to this observation.

Why Do We Sometimes See Higher Metal Concentrations in Ground Samples?

- Part of the explanation is simple chance. By chance, some ground sample results will be higher than unground sample results.
- This study looked at a large amount of data amenable to statistical analysis
  - The frequency of ground samples being higher is ~½ the frequency of being lower + the same (21 higher vs. 43 not higher)



This is a derivation of the previous slides, now with unground (blue) and ground (pink) results for Pb in the same sample together on the same graph.

5 replicate subsamples were taken for analysis after the sample had been ground. The mass of the subsamples was again 2.5 grams.

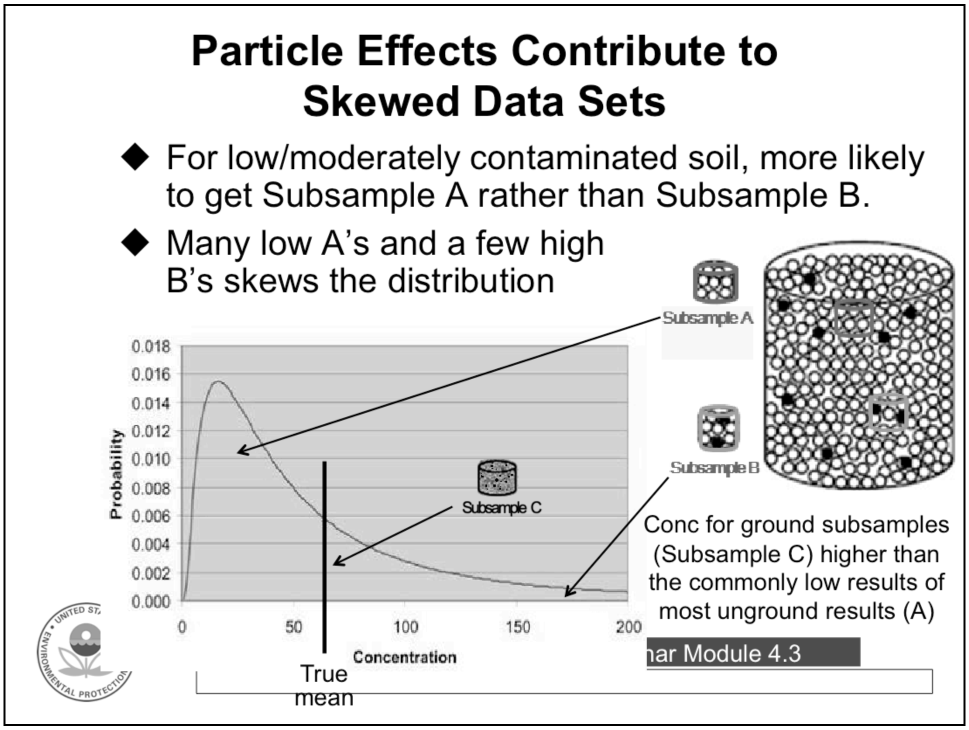
Variability was markedly reduced, which is the same as saying precision was markedly increased.

The dramatic influence of nugget effects in the unground sample is evident by comparing the 2 sets of replicates.

This data illustrates how grinding provides the smaller particles and mixing needed to better preserve the sample's constituent proportions even when small subsamples are used.

The larger the particle size in the sample, the more subsample mass is needed to produce a representative subsample.

Note that the low end of the concentration range rises for ground vs. unground samples.



For low to moderately contaminated soil with particle effects, the distribution of unground subsample data usually takes a lognormal-appearing right-skewed distribution. This occurs because unground samples + small subsamples are more likely to undersample nuggets, such as tiny bullet fragments/dust (illustrated by Subsample A). Thus, lower concentration results are more common than high results (from subsamples that oversample nuggets—Subsample B). But the high concentrations of Subsample B are less likely in the ground sample.

This means that the majority of subsamples will have concentrations that are below the true mean. In other words, most unground samples will have concentrations in the "hump" (Subsample A). If a ground subsample has a concentration near the true mean (Subsample C), there is a good chance that the ground subsamples' concentrations will look elevated compared to results from the unground subsamples. This might be misinterpreted to mean that grinding increases accessibility of tightly bound metal to digestion acid during analytical sample prep.

DID GRINDING PROVIDE A BENEFIT IN THIS PROJECT?

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The purpose of grinding is to reduce laboratory subsampling variability (by reducing within-sample heterogeneity/particle effects).

Summary of 3 Variability Trial Results

- Across all analytes and all DUs, variability differed statistically after grinding by
  - decreasing 15 out of 51 times (29%);
  - increasing 4 out of 51 times (8%); and
  - remaining unchanged 32 out of 51 times (63%).
- For the 3 primary analytes of interest (Sb, As, and Pb), variability similarly
  - decreased 4 out of 9 times (45%)
  - increased 3 out of 9 times (33%)
  - remained unchanged 2 out of 9 times (22%)

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DUs 2 & 6 showed no statistically significant reduction of variability; DU4 did

Did Grinding Reduce Variability?

- Sometimes
  - Hg and Ni consistently saw decreased variability across all 3 trials
  - Other metals were variable
- DUs 2 & 6 showed no statistically significant reduction of variability; DU4 did
- <u>All</u> samples had been sieved (including unground)
  - Possibly sieving was as effective as grinding for these mostly fine-grained soil/sediments

Conclusions from Variability Experiments

- Overall, data variability was unchanged or reduced by grinding; occasionally analyte variability increased after grinding.
- Sieving, particle size, and organic carbon level are factors in addition to grinding that might influence micro-heterogeneity and thus data variability.
- The IS procedures gave RSDs (for the 3 replicate field ISs) that were <20% for metal analytes except Sb, As and Pb. For them the RSDs ranged up to 82%.
  - Consider how **ANY** of your samples are processed or subsampled by lab, regardless of IS or discrete.

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Chromium's RSD was 66% due to stainless steel grinder "bleed," so Cr was ignored.

COMPARABILITY BETWEEN DISCRETE AND INCREMENTAL DATA SETS

Only 1 DU (DU4) Addressed this Question

- Are incremental sample (IS) results within the confidence interval of the dense discrete data set?
  - DU4: had 49 discrete samples
  - ProUCL used to determine statistical distribution of each analyte's data set, mean and 95% UCL
- IS results were independent triplicates: calculated a DU mean and 95% t-UCL for each analyte

DU4 Ground Discrete to Ground MIS Comparability for Sb, As and Pb

Parameter (DU4)	Sb	As	Pb
Mean for 49 discrete samples (grnd)	**38**	**28**	**6817**
Mean for triplicate ISs (grnd)	**38**	**28**	**6680**
RPD between means	1%	1%	2%
Std Dev for 49 discrete samples	**51**	**32**	**8740**
Std Dev for triplicates ISs	**33**	**16**	**3745**
Discrete data distribution	**Gamma**	**Nonparametric**	**Gamma**
ProUCL recommended 95% UCL	**53**	**47**	**10185**
95% t-UCL for triplicate ISs	**94**	**54**	**12994**
Are the 2 results statistically equivalent?	yes	yes	yes

Comparability Summary for All Elements (49 DSs vs 3 ISs; Ground Results Only)

Parameter	Elements
RPD between mean of 49 DS & mean of triplicate ISs <10%	Al, Sb, As, Be, Pb, Hg, Ni, Co, Fe, V, Zn
RPD between 49 DS & IS means >10 & <35%	Ba, Cu, Mn
RPD between 49 DS & IS means >50 & <100%	Ca, Cd, Cr
RPD between 49 DS & IS means >100%	None
DS & IS data sets that are statistically equivalent	Al, Sb, As, Ba, Be, Ca, Co, Cu, Fe, Pb, Mn, Hg, Ni, V, Zn
DS & IS data sets that are statistically different	Cd (DS mean = 0.3; IS mean = 0.1), Cr (transfer from grinder)

Grinding Summary

- The concern that grinding samples would produce non-representative high metals results is not resolved by this study
  - Until more experience is accumulated, you should check your matrix & consider your CSM
- If the native particle size is already small, grinding may provide little additional benefit, especially if larger analytical mass used
- Incremental sampling produces data comparable to a discrete sampling design when there is a sufficiently high density of discrete samples to accurately reflect the population

Total Costs – MIS vs. Discrete
Actual Costs to Sample DU4 (1.6 acre)

Costs	Discrete (n = 49)	MIS (n = 3 of 100 increments each)
Field labor (includes paperwork)	$3,180	$586
Analysis	$15,092	$3,400
Total	$18,272	$3,986

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Any Questions?

Module 4.4

Assorted Technical Resources

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General On-Line Resources

- Clu-In Web site
  http://www.cluin.org
- Brownfields Technology Support Center
  http://www.brownfieldstsc.org
- Triad Resource Center www.triadcentral.org
- Field Analytics Encyclopedia Web site
  http://clu-in.org/char/technologies
- Archived Internet seminars http://cluin.org/live/archive/
- ITRC Web site
  http://www.itrcweb.org
- Argonne National Laboratory ASAP Web site
  http://www.ead.anl.gov/project/dsp_topicdetail.cfm?topicid=23

More General On-Line Resources

- Free geostatistical-based decision assistance software (SADA) http://www.tiem.utk.edu/~sada/
- DOE DQO/statistics training materials Web site & VSP links http://vsp.pnl.gov/
- USACE Engineering Manuals (EMs) [Especially see manuals for CSM (EM 1110-1-1200) & systematic planning (TPP) (EM 200-1-2)] http://140.194.76.129/publications/eng-manuals/

Sampling Design Assistance

- Collected items on the Clu-In Web site (www.cluin.org)
  - Analytical Technologies http://cluin.org/characterization/
- RCRA Waste Sampling Draft Technical Guidance http://www.epa.gov/epawaste/hazard/testmethods/sw846/samp_guid.htm
- EPA statistical sampling guidance (USEPA QA/G-5S) http://www.epa.gov/quality/qs-docs/g5s-final.pdf
- FRTR long-term monitoring optimization http://www.frtr.gov/optimization/monitoring/ltm.htm

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USEPA ERT = EPA's Emergency Response Team webpage (http://www.ert.org/media_resrcs/media_resrcs.asp) offers many Standard Operating Procedures (SOPs) for sampling various kinds of media.

TIO's Clu-In statistical reference section contains various EPA statistical documents available for download, and also links to other sites offering information and software programs (such as DQO-PRO). http://clu-in.org/char1_edu.htm (Statistics section)

EPA is requesting Peer Review of Draft *Guidance for Choosing a Sampling Design for Environmental Data Collection* (EPA QA/G-5S). This draft contains information on innovative sampling designs, such as ranked set sampling, which is an excellent design to take advantage of screening methods. Composite sampling is also discussed in detail.

U.S. Dept. of Energy Pacific Northwest National Laboratory/Oak Ridge National Laboratory Visual Sample Plan (VSP) Demo is available through the DQO Homepage http://www.hanford.gov/dqo/index.html.

VSP is a software tool for evaluating the trade-offs between decision errors, sampling costs, and remediation costs. Permits the evaluation of alternative sampling designs during the planning process. Software should be available through http://terrassa.pnl.gov:2080/DQO/software/vsp/

SADA = Spatial Analysis and Decision Assistance

SADA is free software from the University of Tennessee that integrates modules for visualizing contaminant concentrations, geospatial analysis, statistical analysis, human health risk assessment, cost/benefit analysis, sampling design, and decision analysis. SADA can be used to address site-specific concerns when characterizing a contaminated site, assessing risk, determining the location of future samples, and when designing remedial action. http://www.tiem.utk.edu/~sada/

Sampling Assistance

- USEPA ERT web page for sampling and analytical SOPs http://www.ert.org/mainContent.asp?section=Products&subsection=List
- EPA ORD Soil Sampling Quality Assurance User's Guide http://www.triadcentral.org/ref/ref/documents/soilsamp.pdf
- EPA ORD Subsampling Guidance www.epa.gov/esd/tsc/images/particulate.pdf

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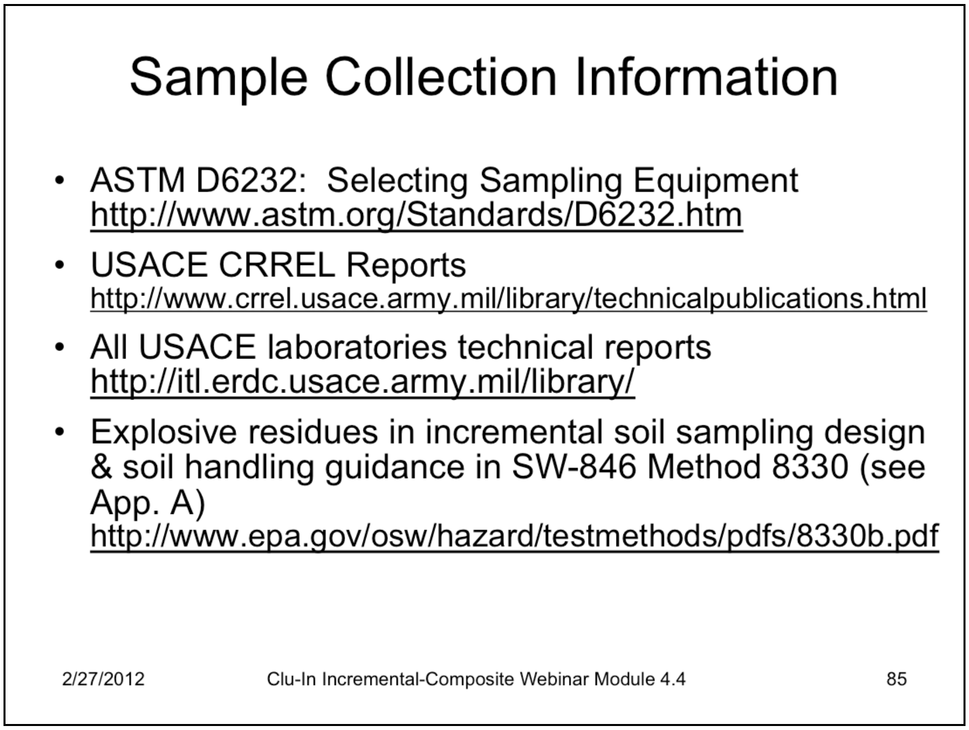
ASTM D6232-98 Standard Guide for Selection of Sampling Equipment for Waste and Contaminated Media Data Collection Activities (developed with input from USEPA's Office of Solid Waste)

USACE CRREL = U.S. Army Corps of Engineers Cold Regions Research & Engineering Laboratory publishes many technical documents related to the sampling and analysis of contaminated sites.

Office of Solid Waste Methods Group (SW-846) is currently developing a sampling guidance for collecting and preserving VOCs in solid media (soil and sediment matrices). Visit http://cluin.org/chartext_edu.htm#samp for the latest update, and links to other references, such as a USACE Strategies for VOC sampling guide. CRREL has another report available at

http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/SR99_16.pdf

See also the US Army Corps of Engineers Waterways Experimental Station website: http://www.wes.army.mil/el/t2info.html



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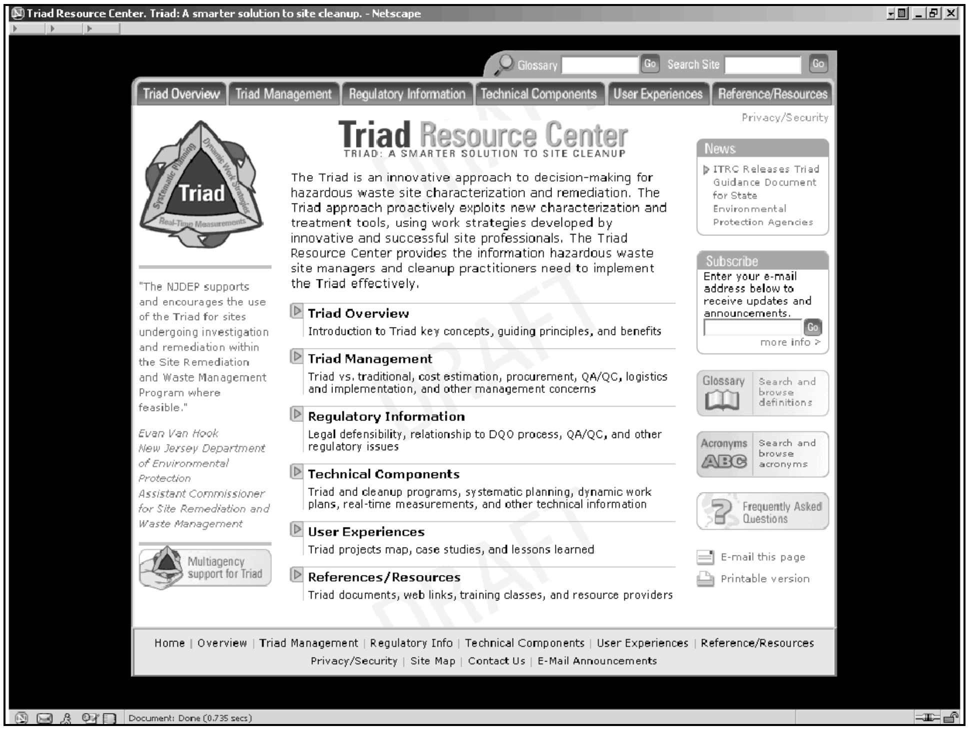
http://www.crrel.usace.army.mil/techpub/CRREL_Reports/reports/SR99_16.pdf

See also the US Army Corps of Engineers Waterways Experimental Station website: http://www.wes.army.mil/el/t2info.html


Triad Resource Center. Triad: A smarter solution to site cleanup. - Netscape
Glossary
Go
Search Site
Go
Triad Overview
Triad Management
Regulatory Information
Technical Components
User Experiences
Reference/Resources
Privacy/Security
Triad Resource Center
TRIAD: A SMARTER SOLUTION TO SITE CLEANUP
Triad
Systematic Planning
Dynamic Work Strategies
Real-Time Measurements
The Triad is an innovative approach to decision-making for hazardous waste site characterization and remediation. The Triad approach proactively exploits new characterization and treatment tools, using work strategies developed by innovative and successful site professionals. The Triad Resource Center provides the information hazardous waste site managers and cleanup practitioners need to implement the Triad effectively.
"The NJDEP supports and encourages the use of the Triad for sites undergoing investigation and remediation within the Site Remediation and Waste Management Program where feasible."
Evan Van Hook New Jersey Department of Environmental Protection Assistant Commissioner for Site Remediation and Waste Management
Multiagency support for Triad
Triad Overview
Introduction to Triad key concepts, guiding principles, and benefits
Triad Management
Triad vs. traditional, cost estimation, procurement, QA/QC, logistics and implementation, and other management concerns
Regulatory Information
Legal defensibility, relationship to DQO process, QA/QC, and other regulatory issues
Technical Components
Triad and cleanup programs, systematic planning, dynamic work plans, real-time measurements, and other technical information
User Experiences
Triad projects map, case studies, and lessons learned
References/Resources
Triad documents, web links, training classes, and resource providers
News
ITRC Releases Triad Guidance Document for State Environmental Protection Agencies
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Home | Overview | Triad Management | Regulatory Info | Technical Components | User Experiences | Reference/Resources
Privacy/Security | Site Map | Contact Us | E-Mail Announcements
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Selected Articles Describing the Triad Approach

See the Technical Components & References sections in the Triad Resource Center:

http://www.triadcentral.org/ref/index.cfm

- Interstate Technology & Regulatory Council TechReg Guideline for Triad: http://www.triadcentral.org/ref/ref/documents/SCM-1.pdf
- 2001 ES&T "Managing Uncertainty in Environmental Decisions" article: http://www.triadcentral.org/tech/documents/oct01est.pdf
- 2001 Quality Assurance journal "Representativeness" article: http://www.triadcentral.org/tech/documents/dcrumbling.pdf

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Selected Articles Describing the Triad Approach

- 2003 Remediation journal “Next Generation Practices” article: http://www.brownfieldstsc.org/pdfs/spring2003v13n2p91.pdf
- 2003 Remediation journal “Insurance” article: http://www.triadcentral.org/ref/doc/Remediation_preprint_Triad-Insurance.pdf
- Fall 2004 Remediation journal “Triad Myths” article: http://www.triadcentral.org/ref/doc/Fall04RemediationArticlePostprint.pdf

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Additional Articles Describing the Triad Approach

- Winter 2004 Remediation journal articles:
  - "Triad as Catalyst" article: http://www.triadcentral.org/ref/doc/RemediationCatalystPostprint.pdf
  - Triad Case Study: Rattlesnake Creek: http://www.triadcentral.org/ref/doc/TriadCaseStudy_RattlesnakeCreek.pdf
  - Triad Case Study: Marine Corps Base Camp Pendleton http://www.triadcentral.org/ref/doc/Winter_04_Remediation_Preprint_Navy_Case_Study.pdf
  - Triad Case Study: Former Small Arms Training Range http://www.triadcentral.org/ref/doc/ShawTriadCaseStudypreprint.pdf

Matrix effects example: moisture greater than 20-30% can impact performance. Usually a low bias.

For in-situ operation good window contact and surface preparation are key.

Final Questions?

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.

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