Advanced Design Application & Data Analysis for Field-Portable XRF

A Series of Web-based Seminars Sponsored by
Superfund's Technology & Field Services Division

Session 3

Q&A for Session 2
Module 3.2 – Representativeness Part 2

3.2-1

How To . . .

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- Control slides as presentation proceeds
  - » manually advance slides
- Review archived sessions
  - » http://www.clu-in.org/live/archive.cfm
- Contact instructors

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Notes

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Q&A For Session 2 – Representativeness Part 1

3.2-3

Module 3.2:

Representativeness – Part 2

3.2-4

Review: Sample Representativeness

- "A representative sample is one that answers a question about a population with a given confidence."
- "A sample that is representative for a specific question is most likely not representative for a different question."
- From Ramsey & Hewitt, "A Methodology for Assessing Sample Representativeness," published in *Environmental Forensics* (2005)
- Also quoted in SW-846 Method 8330B (App A.1.3 p. A-6)

3.2-5

Notes

- **Review: Sample Representativeness:** Module 3.1 identified the preferred definition for sample representativeness which links the concept of representativeness with the decision being made or the question being answered. The source for this definition is:

  Ramsey C. A. and A. D. Hewitt, (2005). A methodology for assessing sample representativeness. *Environmental Forensics* 6:71-75.

  This definition is also quoted in SW-846 Method 8330B (App A.1.3, p. A-6).

Sample Support is the Foundation of Sample Representativeness

- Module 3.1 explained what sample support is and why it is so critical to data quality
- Controlling sample support helps reduce the effects of micro-scale (within-sample) and short-scale (between-samples) matrix heterogeneity
- Sample support MUST ABSOLUTELY be controlled when splitting samples to assess analytical method comparability

3.2-6

Notes

- **Module 3.1 explained what sample support is and why it is so critical to data quality:** Sample support is the defined physical properties of the sample that are relevant to the representativeness of the sample, such as the size (mass or volume), shape, and orientation of a physical sample drawn from a matrix population (such as soil, sediment, or water).

- **Controlling sample support helps reduce the effects of micro-scale (within-sample) and short-scale (between-samples) matrix heterogeneity:** By controlling sample support, the heterogeneities associated with within-sample variability, micro-scale, and between-sample variability, short-scale, can be reduced. Increasing sample volume and sample preparation (such as grinding to a homogenous particle size) reduces the effects of heterogeneity. Collocated samples provide a measure of the degree of short-scale matrix heterogeneity. The distance between collocated samples should always be stated in sampling plans and project reports.

- **Sample support MUST ABSOLUTELY be controlled when splitting samples to assess analytical method comparability:** If micro-heterogeneity is not controlled when a single sample is split between two labs or between two analytical methods, the two splits may actually be different, and accurate analysis will show they are different. Poor matches between field duplicates, lab duplicates, and split samples are usually an indication that there has been poor control over matrix heterogeneity during sample handling.

Fictional Example of a "Support Chain" for Grab Samples: Step 1

Determine the Decision Support

- Clarify project decision: Determine average conc of metal analyte (Me) over a **decision unit** defined according to the data needs of the eco-risk assessor
- The eco-risk assessor has defined the decision unit as an **exposure unit**, which is the soil encompassed by a 1-acre area and 1-ft depth. Relevant eco-receptors are assumed to be equally exposed to all soil particle sizes.
- So, the **decision support** = ***1-acre*** soil area (2-dimensions) from ***0 to 12-in depth*** (3rd dimension). The total Me conc for the ***bulk soil*** is assumed to be representative of receptor exposure to Me. EPC* will be calculated over this decision support.

3.2-7

Notes

- **Clarify project decision:** The support chain begins with the decision to be made. In this example, the decision to be made is to determine the average concentration of metal analyte (Me) over a decision unit which is defined according to the needs of the eco-risk assessor.
- **Decision unit:** In this example, the eco-risk assessor has defined the decision unit as an exposure unit, which is the soil in a 1-acre area to a depth of 1 foot. It is assumed that the relevant eco-receptors are equally exposed to all soil particle sizes.
- **Decision support:** In this example, the decision support is a 1-acre area (2-dimensions) from 0 to 12-inches in depth (3rd dimension). The total Me concentration for the bulk soil is assumed to be representative of receptor exposure to Me. The exposure point concentration (EPC) will be calculated over this decision support. EPC is the best estimate of the true mean for the decision unit.

"Support Chain" Fictional Illustration: Step 2

Determine the Desired Degree of Data Confidence & Develop the Preliminary CSM

- For input into the risk equations, the risk assessor would like to have a 95% UCL for the exposure unit that is within +10% of the calculated mean
- Preliminary CSM: Release of Me to exposure unit occurred 10 yrs ago when a nearby lagoon overflowed onto this flat meadow area. So the distribution of Me is expected to be reasonably homogeneous at a macro-scale across the exposure area. An initial guesstimate of the true mean is in the vicinity of 300-400.

3.2-8

Notes

- **For input into the risk equations, the risk assessor would have to have a 95% UCL for the exposure unit that is within +10% of the calculated mean:** The 95% UCL is a statistically-derived conservative estimate of the mean. Because it is very unlikely that the calculated mean is equal to the true mean, the 95% UCL takes that uncertainty into account to provide an upper limit on what the true mean is expected to be. There are 3 things that are used in the statistical equations that calculate the UCL:
  - » If there is a lot of variability [measured as standard deviation (SD)] in the data set (i.e., the data results bounce around a lot), the statistical calculation will cause the UCL to be much higher (i.e., farther away from the mean) than if the variability is less. This makes sense since the wider the range of values in the data set, the more uncertainty there is about what the true mean really is.
  - » The more data points in the data set (n), the lower the UCL (i.e., the closer the UCL will be to the mean). Again, this makes sense since more data points provide more confidence that the calculated mean is close to the true mean.
  - » The higher statistical confidence desired (say 95% confidence, instead of 80 or 90 % confidence), the higher the UCL will be. This also is intuitive since the farther the UCL is from the mean, the more confidence there is that the true mean has "lots of room" in which to fall.

Common sense thinking about probabilities and statistical confidence:

» 95% statistical confidence that your decision is correct is equivalent to a probability of a 1 in 20 (5 in 100) chance of being wrong.

» 80% statistical confidence that your decision is correct is equivalent to a probability of a 1 in 5 (20 in 100) chance of being wrong.

» 50% statistical confidence that your decision is correct is equivalent to a probability of a 1 in 2 (50 in 100) chance of being wrong. A 50% confidence is really saying you have no confidence either way about your decision being right or wrong (we often use the phrase, "there is 50-50 chance"). In other words, your confidence in your decision is no better than if you made your decision by flipping a coin.

» 25% statistical confidence that your decision is correct is another way of saying there is only a 25% chance of being right. That is, there is 75% probability (3 in 4 or 75 in 100) chance of being wrong.

◆ **Preliminary CSM:** In this example, the preliminary CSM found that the release of Me to the exposure unit occurred 10 years ago when a nearby lagoon overflowed onto the flat meadow area in which the exposure unit is located. The distribution of Me is expected to be reasonably homogeneous at a macro-scale across the exposure area. The true mean is estimated to be in the range of 300 to 400 ppm.

"Support Chain" Fictional Illustration: Step 3

Begin Considering the Sample Support

- The sample support must mimic the decision support for the target population
  - » Equals depth for depth-wise shallower decision supports
- Area-wise, the diameter of the sample support is balanced against n (the # of samples) to control data variability
- For this example:
  - » Depth dimension must be 12 inches
  - » Optimal sample support diameter can be estimated from prior data or a small pilot study

(continued)

3.2-9

Notes

- **The sample support must mimic the decision support of the target population:** For shallow decision supports the sample support depth equals the decision unit depth.
- **Area sample support:** With regard to area, the diameter of the sample support is balanced against "n" (the number of samples) to control data variability.
- **For this example:** The depth dimension of the sample support for this example is 12 inches. The optimal sample support diameter can be estimated from prior data or a small pilot study.

"Support Chain" Fictional Illustration: Step 3

Control of Micro-scale Variability

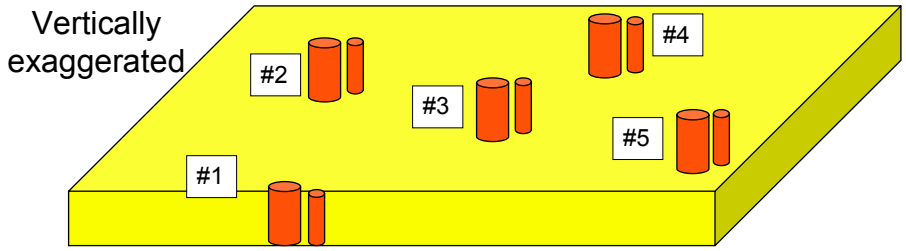
- The degree of micro-heterogeneity for this matrix is unknown at this time, and it costs more to process larger mass samples than smaller ones
- Soil samples will be crushed manually and subsampling will be consistent with EPA's Gy-based guidance
- The adequacy of this sample preparation will be evaluated by running a triplicate lab split on a site sample that is the most difficult to crush to a uniform appearance
- If the triplicate within-sample variability exceeds between-sample variability and impedes statistical confidence, additional sample preparation procedures will be evaluated

3.2-10

Notes

- **The degree of micro-heterogeneity for this matrix is unknown at this time:** The degree of within-sample heterogeneity for the matrix at this site is not yet known, and it cost more to process larger mass samples than smaller mass sample.
- **Soil samples will be crushed manually and subsampling will be consistent with EPA's Gy-based guidance:** Soil samples will be crushed to a visible uniform appearance and then subsampling of the crushed soil will be conducted in accordance with EPA's subsampling guidance.
- **The adequacy of this sample preparation will be evaluated by running a triplicate lab split on a site sample that is the most difficult to crush to a uniform appearance:** The adequacy of the sample preparation will be tested by analyzing triplicate laboratory splits on a site sample that is the most difficult to crush to a uniform size.
- **If triplicate within-sample variability exceeds between-sample variability and impedes statistical confidence, additional sample preparation procedures will be evaluated:** The data from the triplicate analysis will be used to determine if the within-sample variability is impeding statistical confidence. If this if the case, additional sample preparation procedures (such as better grinding and/or sieving) will be evaluated. As noted on the chart on the next slide, for a worst case scenario, the standard deviation (SD) of the triplicate analysis was 10. Since this is the smallest of the 3 SDs, the amount of variability due to micro-heterogeneity is acceptable as long as the same sample preparation is applied to every sample.

Optimize Sample Support vs. Samples # via Pilot Study (aka, DMA*)



Parameter	Small Sample Support Set	Large Sample Support Set	Within-Sample Triplicate
Std Dev for fictional data set of n = 5	SD = 90	SD = 20	SD = 10 (isolates the within-sample variability)
Sample # (n) to achieve desired data quality	n = 20	n = 4	

3.2-11

Notes

- Note that for the large sample support, the pilot study (also called a "demonstration of method applicability" (DMA) within the Triad framework) for this example completes the project, since the data variability for the large sample support was low enough to achieve the project's desired decision confidence.
- Under some circumstances, it may also be possible for a real project to be completed using the data from the larger sample support data set. When this happens, the data set from the smaller sample supports turns out not to be necessary. If the sampling and analytical budget for a project is very tight, this possibility can be used to save money: although the large- and small-support samples should be concurrently collected, initially only the large samples need be analyzed. (The small-support samples can be stored.) If the decision can be made without needing anymore data, there is no need to analyze the small samples.
- The stored small-support samples may be retrieved and analyzed if it becomes advantageous to have that data. One reason to need that information is when additional samples need to be collected during the main investigation event. It will be helpful to know the cost trade-off between the number of additional data points needed to reach a decision vs. the extra cost of labor and any equipment to process the larger sample supports. If the analysis is relatively inexpensive compared to the effort to dry, crush, and grind the soil to get a representative analytical sample (such as can be the case with heavy clays), the stored small-support samples should be analyzed. It may be that the cost of collecting and analyzing 10 more small-support samples is actually less than the cost of collecting, processing, and analyzing 5 more large-support samples. If you estimate the sample handling and analysis costs (on a per-sample basis) for the

large- and small-support sample sets, along with the SD associated with each data set, it is straightforward to calculate the optimal sampling and analysis plan that can achieve decision goals.

- Visual Sample Plan (VSP) is a software package that can be used to make these calculations (http://vsp.pnl.gov/). On the top menu, choose "Sampling Goals", then "Construct Confidence Interval on Mean". Besides standard deviation (SD), the other inputs needed to calculate n (i.e., the number of samples needed) are

  - the desired statistical confidence level (often 95%, but doesn't have to be),

  - whether this is a 1- or 2-sided interval (if only the UCL is to be calculated, it is a 1-sided interval--as opposed to using both the UCL and LCL, which would call for a 2-sided interval), and

  - the highest acceptable distance between the calculated mean and the UCL. In the case of this simplified illustrative example, those inputs were determined by the risk assessor.

  Recall that the risk assessor wanted to have a 95% UCL that was within +10% of the calculated mean. Therefore, VSP inputs are "1-sided" and "95%". For the "Maximum acceptable width of confidence interval," this input value is derived by taking the expected mean (guesstimated at 300-400) + 10% of the expected mean (= 30 to 40). To be on the safe side when calculating n, the smaller of the two (30) was input into the VSP dialog box.

- After the data are collected, the data are assessed to see if the decision goals were achieved. The 10% will now apply to the mean that is calculated from the actual data. For example, if the calculated mean is 350, then the highest acceptable UCL is 350 + (0.10 x 350) = 385. If the UCL calculated on the actual data set is lower than 385, the desired decision confidence has been achieved.

"Support Chain" Fictional Illustration: Step 4

Going from a large sample support to analysis (from sample support to subsample support)

- Field sample supports are very large compared to the mass of soil digested for the ICP analysis
  - » Mass digested for ICP = 0.5 to 2 g
  - » This soil mass might be called the "subsample support" or the "analytical sample support"
- Need to go from a large field sample support (i.e., mass) to very small analytical sample support/mass
  - » How? See 2003 EPA subsampling guidance that discusses Gy-based particulate sampling

(continued)

3.2-12

Notes

- **Field sample supports are very large compared to the mass of soil digested for the ICP analysis:** The actual amount of soil from the large field sample that is digested and analyzed by the ICP method is between 0.5 and 2 grams. This smaller soil mass might be called the "subsample support" or the "analytical sample support."

- **Need to go from large field sample support (i.e., mass) to very small analytical sample support/mass:** Gy-based subsampling techniques, which provide a subsample that is representative of the average bulk concentration, are discussed in the 2003 EPA subsampling guidance (EPA 600/R-03/027). The guidance be found at http://cluin.org/download/char/epa_subsampling_guidance.pdf

  Pierre Gy's theories were developed to help the mining industry generate accurate data from highly heterogeneous ores. Gy-based sample handling takes particle size into account when determining the volume of a representative subsample and when selecting the proper subsampling implement to use (such as a flat-bottomed scoop). The larger the particle size in the sample, the larger the subsample and the larger the scoop needs to be to avoid preferential selection of certain particle sizes over others. That is why using tiny subsamples requires having a very small particle size.

"Support Chain" Fictional Illustration: Step 4

Representative Subsampling

- Options for our fictional story
  - » Grind large samples to uniform particle size and take ~1 g subsample
    - — Equipment able to efficiently grind large sample masses might not be readily available
  - » Use Gy-based sample handling to progressively subsample in a representative way
    - — Reduces sample mass to a small subsample that is easily ground
    - — Take 1-g for analysis

3.2-13

Notes

- **Options for our fictional story:** Subsample representativeness or "a representative subsample" means that for each particle making up the target population within the sample container, there is an equal chance of it being included in the analytical sample. The two options for obtaining a representative subsample are:

  - » Grind large samples to uniform particle size and take ~1 g subsample – The equipment that can efficiently grind such a large sample mass might not be readily available.

  - » Use Gy-based sample handling to progressively subsample in a representative way – This method reduces sample mass to a small subsample that is easily ground and then the 1-gram subsample is taken for analysis.

Gy-based Subsampling: a 1-kg Field Sample

Crush aggregates; avoid non-uniform distribution of particles

Scoop through entire depth over surface

3.2-14

Gy-based Subsampling

Distribute soil evenly in a line by emptying scoop in a back & forth motion

Use properly sized*, flat-bottomed scoop

3.2-15

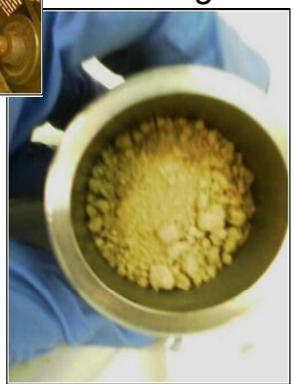
Notes

- Read EPA's Subsampling Guidance for how to determine the proper dimensions for a scoop. The process of forming a line and subsampling with a scoop can be repeated sequentially until the final subsample is of the desired mass, but still representative of the particle size distribution and other properties of the original material.
- The desired mass should be optimized to be large enough to retain the same particle size distribution of the material being subsampled, but small enough to be amenable to further processing of the sample. For this soil, the subsample mass was reduced to 25 g. (Each cross-line scoop of soil was about 5 g (5 cross-scoops times 5 g = 25 g). 25 grams was a good fit for the size of the ball mill cartridge that was available.

The Ball Mill (Ring & Puck Mill Better!)

Inside of ball mill with cartridge inserted into shaker

Un-ground soil in cartridge



The steel balls, lying in a cartridge cap

3.2-16

Notes

- A ball-mill is all that was available for this project, however, it is often not the best choice. A ball-mill may be adequate for certain soils, such as those that are predominantly clays and do not have many larger mineral particles. Ball-mills are not good at grinding the larger, harder mineral materials common to most soils. Ring and puck mills are better grinders. They are able not only to grind to a uniform particle size, but they also produce particles with a uniform shape, which is important to avoid particle size segregation when pouring or transporting sample material.

Soil Ground to Uniform Particle Size

High clay soil ground in a ball mill

Lower clay soil ground in a mortar & pestle

3.2-17

Notes

- Twenty-five grams of soil was put into a ball mill cartridge (for hard dry clays) or into a mortar & pestle (for more loamy or sandy soil) for grinding to a uniform particle size before subsampling to obtain the analytical sample. Hard dry clays are very difficult to grind by hand with a mortar & pestle.

"Support Chain" Fictional Illustration: Step 5

Measurement Support

- The analytical instrument "sees" only what is injected into it in liquid form
- Analytical sample preparation
  - » Digestion or extraction must be appropriate for (i.e., be representative of) the parameter of interest.
- ICP* metals analysis does not always report total metals
  - » Digestion w/ nitric acid does not solubilize all of the minerals that may be binding metals in the soil matrix
  - » Certain metals routinely recover poorly (e.g., antimony)

3.2-18

Notes

- **The analytical instrument "sees" only what is injected into it in liquid form:** The ICP or inductively-coupled plasma instrument, is commonly used to analyze a wide range of metals in the same injection.
- **Analytical sample preparation:** The digestion or extraction used must be appropriate for (i.e., be representative of) the parameter of interest.
- **ICP metals analysis does not always report total metals:** Knowing whether a method reports total or partial metal content is crucial to establishing data comparability. Digestion with nitric acid does not solubilize all of the minerals that may be binding metals in the soil matrix. Certain metals, such as antimony, routinely recover poorly.

Quick Review

- Control sample support to reduce within- and between-sample heterogeneity:
  - » improves data quality
  - » reduces data variability
  - » reduces incidence of "outliers"
- Sample support MUST be controlled when splitting samples
- Controlling sample support increases agreement between field and lab duplicates which improves QC
  - » QC is a mechanism to estimate data uncertainty

3.2-19

Notes

- **Control sample support to reduce within- and between- sample heterogeneity:** Outlier results are those which appear to be outside the bulk of the data set. Statisticians often recommend that outlier results be discarded because they "mess up" (skew) statistical analysis of the data. However, blindly subjecting a data set to statistical tests for outliers, and then discarding data points solely on the basis of statistical conclusions, can create misleading data sets.

  The reason for outlying results should be investigated. If due to a mistake, such as a clerical error, analytical or sample handling "goof," then the data point should be discarded. However, outliers are usually providing important quality assurance (QA) information about the project.

  » Outliers may be a symptom that within-sample variability is not adequately controlled. This problem is an artifact of analytical sample supports that are too small for the matrix being subsampled. The source of the problem should be determined, along with what corrective actions to take (such as larger analytical samples or more thorough sample handling, like Gy-subsampling and grinding).

  » Outliers may be an indicator of excessive between-sample variability (i.e., short-scale matrix heterogeneity), which is an artifact of field sample supports that are too small for the degree of variability within the decision unit. Grab sample results can be severely affected by short-scale heterogeneity (recall the collocated samples in the TNT "wheel" slide in the previous module). This creates misleading data sets and problems with statistical analysis of the data set. Corrective actions include multi-increment sampling and using larger sample supports for the field samples.

» Outliers may indicate that unanticipated true variation (such as "hotspots") exists on a larger spatial scale. This indicates that your CSM for your site is incomplete. It is possible that more than one contaminant population exists, where you assumed there was only one. Further sampling is required to determine the size and shape of the hotspot or contaminated region.

In all cases, the presence of outliers is an indication that something is going on that you don't know about, but need to. Ignoring the problem by simply throwing away inconvenient data puts you at risk for decision errors.

- **Sample support must be controlled when splitting samples:** Control of sample support when splitting samples is critical to establishing comparability between analytical methods.

- **Controlling sample support increases agreement between field and lab duplicates which improves QC:** Controlling sample support will increase the agreement between field and lab duplicates because heterogeneity is accounted for. This improves the quality control. Quality control is the mechanism to estimate data uncertainty.

Review of "Supports"

- **Decision Unit Support** - the spatial dimensions and other physical properties (such as particle size) that define the population of interest targeted by the decision.
- **Sample Support** - the spatial dimensions and other physical properties (such as particle size) of a physical sample; it needs to be selected to mirror the decision unit support.
- **Measurement Support** - the choice of analytical sample preparation (laboratory subsampling & digestion/ extraction prior to instrumental measurement) that determines how much of the original sample content is actually "seen" and measured by the instrument

3.2-20

Notes

- **Decision unit support:** Decision unit support identifies the spatial dimensions and other physical properties (such as particle size) that defines the population of interest targeted by the decision.
- **Sample support:** Sample support encompasses the spatial dimensions and other physical properties (such as particle size) of a physical sample; it needs to be selected to mirror the decision unit support.
- **Measurement support:** Measurement support is the choice of analytical sample preparation (laboratory subsampling and digestion/extraction prior to instrumental measurement) that determines how much of the original sample content is actually "seen" and measured by the instrument.

Question:
Why do we need to understand all this?

Answer

Because XRF analytical programs perform much, **much, MUCH** better when XRF sampling and analysis designs apply this knowledge

Let's talk about the supports relevant to field-portable XRF instrumentation

3.2-21

XRF's "Supports"

- Analytical Sample Support
  - » The X-rays pass thru a window that is only a few cm^2 in area
    - — They penetrate 1 - 2 mm depth into the soil surface
    - — The instrument "sees" ~ 2 g or less of a thin soil layer
  - » Soil particle size and its correlation to Me concentration determines how much Me is in the XRF's field of view
- Measurement support (same as analytical sample support)
  - » XRF measures the total element content of the soil volume for analytes it sees

3.2-22

Notes

- **Analytical sample support:** In contrast to the laboratory sample, the XRF measures about a 2 square centimeter area at a depth of a few millimeters, which represents about 2 grams or less of a thin soil layer. This is the XRF's analytical sample orientation. Soil particle size and its correlation to Me concentration determines how much Me is in the XRF's field of view.
- **Measurement support:** The XRF measures the total element content of the soil volume for analytes it sees.

Measurement support: XRF vs. ICP

- ICP analysis requires digestion of soil mineral structure to free metals into solution
  - » The common nitric acid (HNO3) digestion does not free all metal present in the sample. How much is solubilized depends on soil mineralogy, the metal species released and how long ago, the redox and pH soil environment over the years…
  - » Hydrofluoric acid (HF) digests all minerals so total metal is measured by ICP analysis - but it is hard to find environmental labs with HF capability
- XRF directly measures total metals
  - » Results more comparable to HF digestion

3.2-23

Notes

- **ICP analysis requires digestion of soil mineral structure to free metals in solution:** Two digestion methods are available, the common nitric acid (HNO_3) method and the hydrofluoric acid (HF) method. Nitric acid does not free all metal present in the sample. The amount of metal solubilized depends on several factors including, soil mineralogy, the metal species released, the age of the release, the redox of the soil environment, and the pH of the soil environment. HF digests all minerals so total metal is measured by ICP analysis. However, it is difficult to find environmental laboratories with HF digestion capability.

- **XRF directly measures total metals:** The results of the XRF are more comparable to HF digestion than nitric acid digestion.

Controlling XRF Sample Support

- XRF's small sample support (1-2 grams, on the order of a lab subsample) makes it susceptible to non-representative readings (i.e., readings that are very different from the average concentration of the sample)
- The more uniform the distribution of soil particles, the more precise the XRF readings
- Uniformity depends on the adequacy of sample handling and preparation

3.2-24

Notes

- **XRF's small sample support makes it susceptible to non-representative readings:** Because the XRF "sees" only 1 – 2 grams of sample, it is susceptible to readings that are very different from the average concentration of the sample.
- **The more uniform the distribution of soil particles, the more precise the XRF readings:** The precision of the XRF is controlled by how uniformly the element of interest and soil particles are distributed within the XRF's field of view. The more uniform the distribution, the more precise XRF measurements will be.
- **Uniformity depends on the adequacy of sample handling and preparation:** Because of inherent heterogeneity, uniformity is a function of sample preparation. The greater the sample preparation the greater the uniformity.

XRF Sample Handling/Preparation

- There are 3 main types of sample preparation for XRF— the effectiveness of all is influenced by operator effort and consistency
- Sample handling procedures should be defined in detail in the QAPP and followed meticulously
  - » Prepare soil for *in situ* "shots"
  - » Taking shots (i.e., readings) over a bagged sample
  - » Taking shots on a cup containing highly prepared soil

3.2-25

Notes

- **There are 3 types of sample preparation for XRF – the effectiveness of all is influenced by operator effort and consistency:** There are three types of sample preparation available for use with the XRF. Each requiring increasingly more sample preparation. In addition, the effectiveness of the XRF is also influenced by the operator effort and skill and the consistency of sampling handling, sample preparation, and XRF operation.

- **Procedures defined in QAPP and followed meticulously:** The procedures for sample preparation and XRF use (including calibration procedures) should be described in detail in the QAPP and must be followed meticulously by the field team. There will be different procedures for the three types of XRF sample preparation, which are:

  » Prepare soil for *in situ* "shots" – this procedure requires the least sample preparation

  » Taking shots (i.e., readings) over a bagged sample – this procedure requires more sample preparation than the *in situ* method, but less than the cup method

  » Taking shots on a cup containing highly prepared soil – this procedure requires the most sample preparation

Sample Preparation Option 1: *in situ*

- Grades of sample preparation for *in situ* "shots"
  - » Least preparation: "shoot" on bare ground with minimal debris removal & smoothing
  - » Most preparation: Loosen soil to selected depth of interest. Carefully pick out extraneous material. Crush & mix soil *in situ* until uniform appearance. Smooth/compress surface before placing XRF.
  - » Take several shots in the same prepared location. Re-position the XRF between shots to estimate matrix variability (evaluate the adequacy of sample prep)

3.2-26

Notes

- **Grades of sample preparation for *in situ* "shots":** There are different levels of sample preparation for *in situ* use of the XRF:
  - » Least preparation – The least sample preparation involves "shooting" on bare ground with minimal debris removal and smoothing.
  - » Most preparation – The most sample preparation involves loosening the soil to a selected depth of interest. Extraneous material is then carefully picked out of the loosened soil. The loosened soil is then crushed and mixed *in situ* until it is uniform. The uniform soil is then smoothed and compressed before placing the XRF.
  - » Multiple shots – Several shots can also be taken for a single sample area, with repositioning of the XRF between the shots, to estimate sample variability and to evaluate the adequacy of sample preparation.

Sample Preparation Option 2: Bagged

- Bagged samples
  - » Increases sample support compared to *in situ* shots, especially when multiple shots are taken per bag
  - » Remove extraneous material. If necessary, crush soil before placing into bag (crushing a hard soil in a bag can damage the smoothness of the plastic).
  - » Mix bag by kneading (also breaks up aggregates) and/or turn bag end-over-end. Visually inspect to ensure uniform appearance. Do not just shake bag—will cause particle segregation and increase data variability.
  - » Do not shoot through significant dimples or creases in the plastic—can cause increased reading variability

3.2-27

Notes

- **Bagged samples:**
  - » Increases sample support compared to *in situ*, especially when multiple shots are taken per bag.
  - » Remove extraneous material and, if possible, crush the soil before placing it into the bag – this helps to increase uniformity.
  - » Mix bag by kneading to reduce particle size and/or turn bag end-over-end. Visually inspect the soil sample in the bag to judge the uniformity of the particle size. Shaking the bag does not effectively reduce particle size and can cause particle segregation and increase data variability.
  - » Do not shoot through creases or crinkles – The operator should take care not to shoot through creases or crinkles in the bag itself.

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Bagged Samples

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Shooting Bagged Samples

Benefits of Bagged Samples

- When sampled from 1 sampling location, bagged samples increase the sample support from that location (this strategy controls within-sample variability)
- Multi-increment sampling can be performed: Placing increments from across the decision unit into 1 bag further increases the sample support and is more representative of the decision unit average (this controls for short-scale matrix variability)
- Taking multiple shots over the bag estimates the degree of within-sample variability (particle size effects) and the statistical average of those readings provides a better estimate of the true concentration for the bag

(continued)

3.2-30

Notes

- **When sampled from 1 sampling location:** When sampled from 1 sampling location, bagged samples increase the sample support from that location controlling within-sample variability.
- **Multi-increment sampling can be performed:** Placing multiple increments from across the decision unit into one bag further increases the sample support and is more representative of a decision unit average controlling short-scale matrix variability.
- **Taking multiple shots over the bag:** Multiple shots over a bag will estimate within-sample variability (particle size effects) and the statistical average of those readings provides a better estimate of the true concentration for the bag. If the bag represents a single sample location then the average will be for that location. If the bag contains multiple increments from a decision unit, the average will be for that decision unit.

Benefits of Bagged Samples

- Sample bagging and readings can be performed in real-time
  - » The number of shots over the bag can be adjusted in real-time (either up or down) to provide statistically valid results
  - » Within-bag variability that is too high can be addressed by additional kneading or other corrective actions, or by examination of bag (ex: paint chips?)
  - » Inexpensive
  - » Supports dynamic work strategy for field work by providing data of known and documented quality

3.2-31

Notes

- **Sample bagging and readings can be performed in real-time:** The XRF is almost unique (if not unique) in providing the ability to non-destructively and quickly evaluate the efficacy of sample preparation by multiple *in situ* readings across a sample's surface. The XRF also provides the possibility of substituting multiple readings across a soil's surface (either through a bagged sample's walls, or across a sample spread on a work area) for sample preparation when trying to obtain an accurate assessment of contaminant levels within the sample. Recall from earlier slides that you can get the same statistical confidence by increasing n (i.e., increasing the number of XRF shots going into calculating an average reading for the bag) or by decreasing the standard deviation (SD) by improving sample homogeneity/uniformity.

  The XRF is unique in providing the ability to inexpensively (no consumables, just labor time), non-destructively and very rapidly evaluate the adequacy of sample preparation by taking multiple readings across a sample's surface (either *in situ* across a work area, or over a bag). Therefore the XRF provides the ability to use multiple readings, rather than more intensive sample preparation, to reduce data uncertainty and increase accuracy.

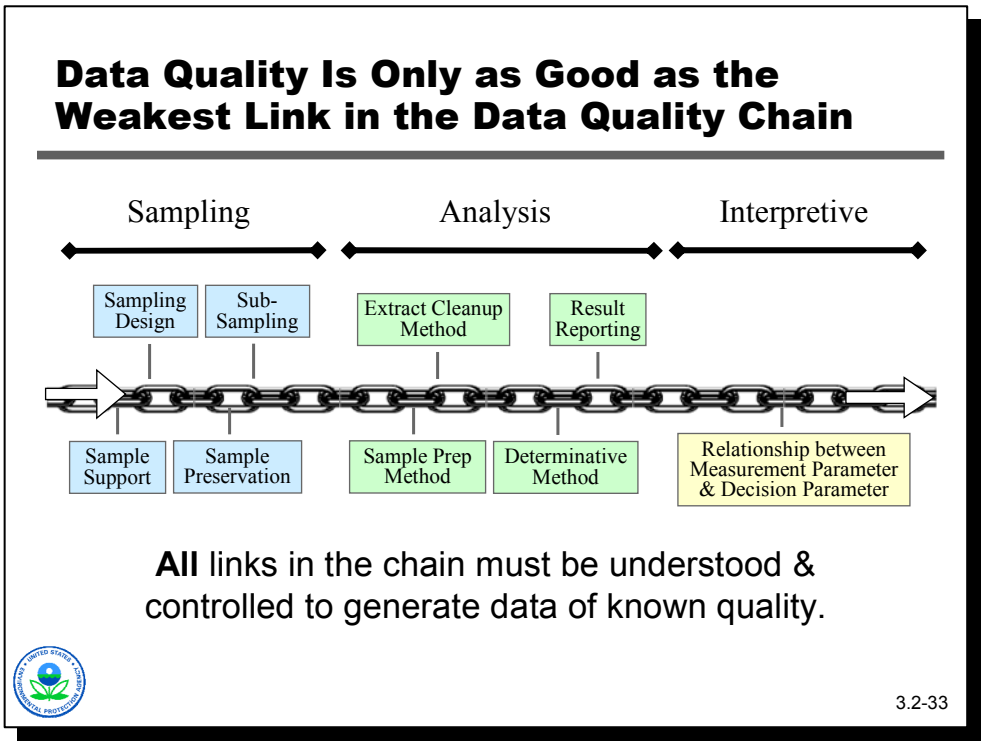
Sample Preparation Option 3: XRF Cups

- Cup samples
  - » Remove debris, dry, grind, and sieve to achieve uniform particle size
  - » Subsample properly and place into XRF cups
  - » Be CAREFUL tapping cups if particle size not completely uniform—will segregate fines.
- Highest homogeneity = best precision
  - » Best for determining method comparability to ICP or AA
  - » Perform XRF and ICP/AA analysis on same cup

3.2-32

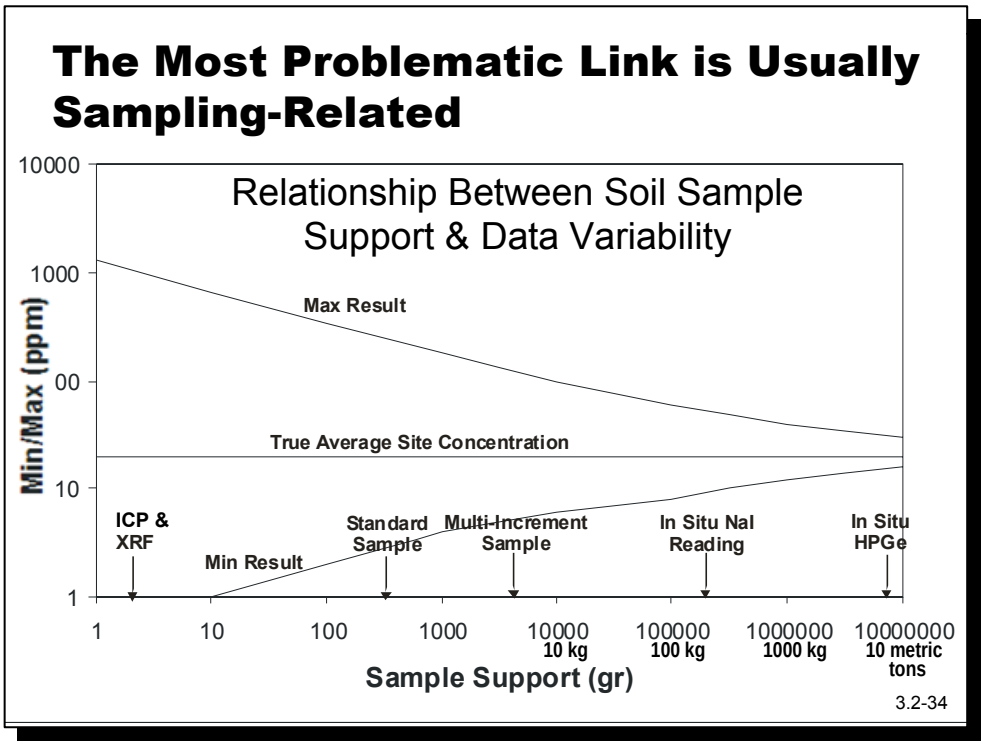
Notes

- **Cup samples:**
  - » Remove debris, dry, grind and sieve sample to achieve uniform particle size – Achieving uniform particle size is very important to increasing precision.
  - » Subsample properly and place subsamples into XRF cups – The subsample should be representative of the whole sample and each particle should have an equal chance of being included in the subsamples. EPA's 2003, "Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples," EPA/600/R-03/027, ranks several laboratory subsampling methods that could also be used in the field.
  - » Be CAREFUL tapping cups if particle size is not uniform – Too much tapping of subsamples that do not have a uniform particle size may cause partitioning of the various particle sizes and affect the ability of the XRF to "see" the total amount of the element of interest.
- **Highest homogeneity = best precision:** The cup method is the best method for determining comparability to ICP or atomic absorption (AA). When conducting comparability analysis of confirmatory samples, it is very important to conduct the laboratory analysis on the same cup on which the XRF measurements were taken.



Notes

- Each link represents a variable contributing toward the quality of the analytical result. All links in the data quality chain must be intact for data to be of decision-making quality.



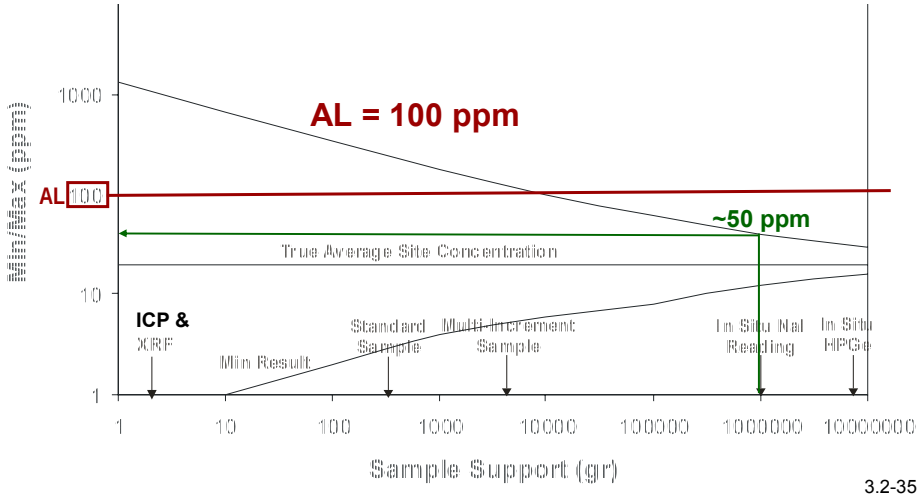
Notes

- This graphic shows the minimum and maximum values present in data from samples taken from a single population with a true mean of 20 ppm and realistic heterogeneity. Clearly, the range of values increases greatly as the sample support (measured by grams of soil contributing to sample) shrinks. An XRF measurement typically "measures" a few grams of soil. A typical soil sample is around 400 grams. A multi-increment sample can range anywhere from one to several kilograms. An *in situ* NaI reading "sees" approximately 150 kg of soils. An *in situ* High Purity Germanium reading sees around 15 metric tons of soil.

  Note: 1 metric ton = 1,000 kilograms

Variability & the Single Data Point #1

If every data point is compared individually to an action level (AL), small sample supports will cause exceedances due to chance even if the true mean is well below the threshold.



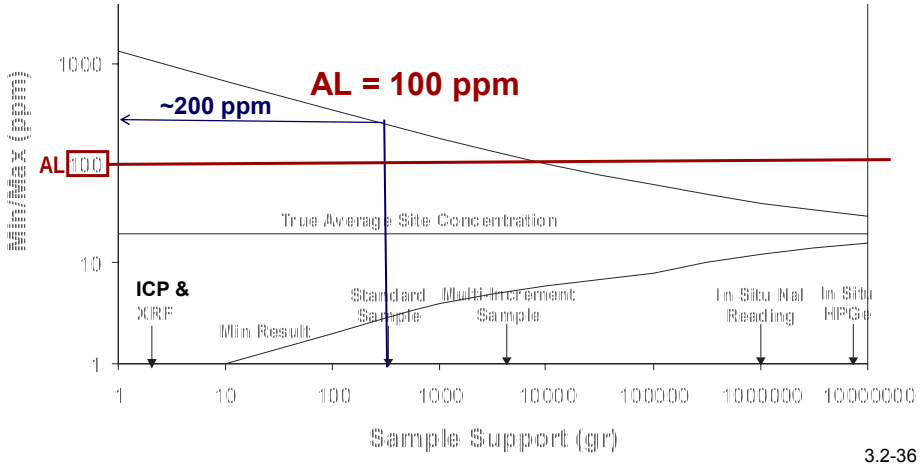
3.2-35

Notes

- As sample support shrinks, the amount of variability grows. This plays havoc with never-to-exceed standards. Note that this graph is specific to a single site, and is used for illustration only. Soils on other sites and other contaminants will have a different graph, although the general pattern would hold true.
- If a never-to-exceed standard was set at 100 ppm for an area of soil having a true mean of 20 ppm, each individual result will be below the action level of 100 ppm if the sample support is about 10 kg or larger. Therefore, data sets based on NaI and HPGe measurements would consistently conclude the area was in compliance.

Variability & the Single Data Point #2

The data variability caused by small sample supports will cause action level exceedances just by chance. Decisions based on single data points have are highly uncertain & subject to scientific challenge.



3.2-36

Notes

- Remember that both the multi-increment and standard samples require proper homogenization and representative subsampling for analysis in order for the actual sample support to match the intended sample support. If, for example, a 400 gram jar sample was sent to the laboratory, but all the lab did was open the jar and take a 1-gram scoop of the top, the actual sample support is not 400 gram, but much smaller.

- Due to their greater range of values, the smaller sample supports of XRF and ICP (0.5 – 2 g), standard sampling (a jar, perhaps 400 g) and multi-increment sampling (the area/volume over which the increments are taken, pooled and homogenized) would produce some values that exceed the 100 ppm threshold, even though the true mean is about 20 ppm. However, if enough samples from the population were analyzed, the average of the data would be close to the true mean. As the variability in data sets increases, more samples would need to be analyzed to get a reasonably close estimate of the mean.

- If you are trying to make decisions using a not-to-exceed strategy, whether you consider the site to be clean or not depends heavily on the measurement technologies deployed and their varying sample supports. One could potentially draw completely different conclusions about site contamination if never-to-exceed decisions are based on small, rather than larger, sample supports.

With these Issues, Can XRF Provide "Definitive Data"?

- Data Quality Objectives Process for Superfund: Interim Final Guidance (Sept. 1993)
  - » Page 43: *"For the data to be definitive, either analytical or total measurement error must be determined."*
- Measuring error requires taking multiple replicate analyses on a sample - this increases analytical costs, which is why error is seldom determined or reported
  - » However, XRF is unique in that replicate readings are very inexpensive
  - » Easy to determine error and meet SF's definition of definitive data

3.2-37

Notes

- **Data Quality Objectives Process for Superfund: Interim Final Guidance (Sept. 1993):** Page 43 for the guidance states: *"For the data to be definitive, either analytical or total measurement error must be determined."*
  - » Analytical error determination - Measure precision on actual sample matrix. A quantitative way to communication uncertainty within decision process, e.g., "the analytical result = 398 ± 10 ppm Pb."
  - » Total measurement error determination - Measure overall precision of entire measurement system (encompasses sample acquisition thru analysis). Ensures decision-makers are provided with full information.
- **Measuring error requires taking multiple replicate analysis on a sample:** Taking multiple replicate analysis on a sample increases analytical costs, which is why error is seldom determined or reported. However, the XRF is unique in that replicate readings are very inexpensive and determining error is easy. Thus, XRF data can meet the Superfund's definition of "definitive data."

Summary: How to Reduce XRF Variability

- Analytical Variability
  - » Increase count time
  - » Use newer instrument
- Sample Handling Variability
  - » Homogenize samples
  - » Aggregate readings
  - » Handle samples consistently
- Sampling Variability
  - » More readings/samples per decision unit
  - » Increase sample support for each sample/reading

3.2-38

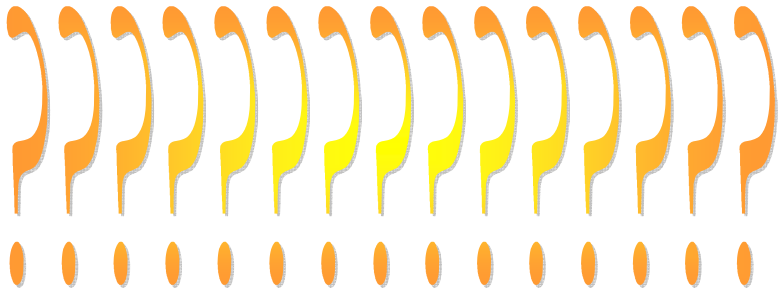
Summary: Controlling Heterogeneity Effects

- In a lab or field trailer
  - » Thoroughly prepare (dry, homogenize, grind) multi-increment bag contents and place sample in a XRF cup
- In the field
  - » XRF measurement aggregation
    - — Aggregate readings over the bag
  - » Multi-increment sampling over a decision unit into large bag

3.2-39

How Many Increments?

Addressed in Module 6



3.2-40

Q&A – If Time Allows

3.2-41