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The Roles of Project Managers and Laboratories in Maintaining the Representativeness of Incremental and Composite Soil Samples

This fact sheet discusses concepts and techniques for *processing* soil samples submitted to laboratories for chemical analysis in order to ensure the analytical results are representative with respect to the decisions that are to be made using the data.

Specifically, this fact sheet recommends application of incremental-composite sampling (ICS) as a subsampling technique *in the laboratory* when processing soil samples in order to minimize the influence of within-sample variability.

Appropriate sample processing is particularly important when analyzing for trace concentrations (parts per million and lower) of organic and inorganic contaminants. If appropriate sample processing techniques are not used when subsampling soil samples for chemical analysis, the results cannot be considered representative of the sample or, therefore, of the area or volume of soil the sample is intended to represent.

Effective soil sampling for any contaminant requires consideration of the factors that can affect sample representativeness. These factors include the inherent heterogeneity in soil and subsampling approaches used in many laboratories. The heterogeneity typically observed in soil chemical and physical properties can lead to substantial variability in measured soil contaminant concentrations. This variability can be expressed at various scales, ranging from the field scale to the micro scale. Incremental-Composite Sampling (ICS) is a soil sampling protocol that reduces data variability and reasonably assures all contamination present within a defined area or volume of soil is adequately represented. ICS requires specialized procedures both in the field and in the laboratory. In ICS, many equal mass "increments" of soil collected from multiple locations within a defined area or volume are combined into a single "field" sample that represents the area or volume of soil of interest. It is critical that laboratory processing of ICS field samples follow standard operating procedures (SOPs) that ensure the subsample that is analyzed is representative of the entire field sample. The laboratory can accomplish this by employing ICS protocols at the sample scale to reduce within-sample data variability.[1]

For laboratory sample results to be representative for the intended decision:

Project managers should ensure that

- Sample representativeness is discussed by the technical team during project planning.
- The Quality Assurance Project Plan (QAPP) identifies data quality objectives (DQOs) for sample representativeness and how these DQOs relate to project decisions.
- The QAPP specifies the overall processing and specific subsampling procedures to be used on soil samples to achieve representativeness DQOs.
- Any modifications to sample processing procedures that deviate from the original QAPP are documented in an amended QAPP.
- Requests for quotes (RFQs), requests for proposals (RFPs), work assignments and other contracting documents are clear about the requirements for ICS sample processing techniques.

Analytical laboratories should

- Provide descriptions of their laboratory's methods, space and equipment available to process soil samples using ICS techniques.
- Provide pricing after the project scope estimates the number of samples, analytes, sample processing options, and turn-around time.
- Provide appropriate SOPs to become part of a contracted project's QAPP.
- Discuss sample representativeness DQOs with clients; describe the strengths and limitations of processing options so the project team can select the most appropriate for the end use of the data.
- Alert the project team if samples' properties deviate from those anticipated and described in the project QAPP.
- Discuss the potential effects of unexpected sample properties on the final results, the options to mitigate possible negative effects and the cost implications of modifications.
- Document all deviations from the original QAPP in the laboratory report narrative.

[1] U.S. Environmental Protection Agency (EPA) (2011) User Guide - Uniform Federal Policy Quality Assurance Project Plan Template For Soils Assessment of Dioxin Sites, September. www.epa.gov/superfund/health/contaminants/dioxin/dioxinsoil.html

What is ICS?

ICS is a soil sampling and processing protocol that reduces data variability and reasonably assures all contamination present within a defined soil area or volume is adequately represented. ICS requires specialized procedures both in the field and in the laboratory.

The remainder of this fact sheet discusses the factors that can lead to non-representative results when processing samples in the laboratory and provides information for project managers to consider when developing DQOs to define sample representativeness needs.

Factors That Should be Considered for Representative Soil Sample Results

A number of factors can cause routine laboratory processing and subsampling techniques to yield non-representative results. These factors include micro-scale, within-sample heterogeneity in soil properties (such as differences in particle size and composition within a sample jar), too large an imbalance in the size of subsamples relative to the whole sample, and particle segregation resulting from the mechanics of scooping and weighing subsamples in the laboratory.

An analytical subsample obtained by opening a sample container and scooping some material off the top, or by shaving soil from a clump, will not reflect the composition of the whole sample. "Mixing" by stirring and cone-and-quartering are seldom effective and should be replaced with more appropriate procedures.[2] Techniques such as ICS subsampling at the laboratory scale need to be employed for a data result to be representative of the whole sample. Incremental subsampling requires that the sample first be processed as discussed on pages 4 and 5 of this fact sheet. After processing, the sample is flattened and approximately 30 increments are taken from it using a square scoop (see Figures 1 and 2). All of the increments are combined to form the analytical sample which is then extracted or digested in preparation for analysis.

Soil samples exhibit heterogeneity within the sample container because soil consists of solid particles of different sizes that are composed of different materials. These micro-scale heterogeneities are important because the masses used for chemical analysis are small. Typically about one gram of soil is analyzed for inorganic constituents and five to 30 grams are analyzed for organic contaminants. It is important to recognize that soil does not behave as a liquid with evenly dissolved contaminants. Trace-level contamination (concentrations of parts per million and less) in soil is often attached to a relatively few discrete particles that are "sprinkled" unevenly throughout a bulk matrix of uncontaminated particles. Figure 3 illustrates such a trace contaminant distribution in a sample container.

Figure 1. Photograph of a "2-D slabcake."[3,4] The processed field sample has been spread out and incrementally subsampled to create a single analytical sample.

Figure 2. A laboratory duplicate requires another incremental subsample to be collected in the same way as the first.

[2] EPA (2003) Guidance for Obtaining Representative Laboratory Analytical Subsamples from Particulate Laboratory Samples, November. www.clu-in.org/download/char/epa_subsampling_guidance.pdf

[3] Interstate Technology and Regulatory Council (ITRC) (2012) Incremental Sampling Methodology (ISM) website (www.itrcweb.org/ISM-1)

[4] ITRC Soil Sampling and Decision Making Using Incremental Sampling Methodology – Parts 1 and 2 Archived Internet-based Training (www.clu-in.org/live/archive/default.cfm?display=all&group=itrc)

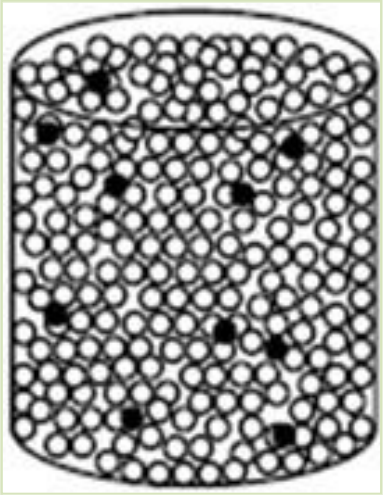

Figure 3. Depiction of the particulate nature of trace amounts of contaminants in soil as a small number of high-concentration particles (dark color) present in a "sea" of uncontaminated particles (light color).[5]

Contaminants in soil behave as discrete particles for several reasons. Sometimes contaminants can be released as tiny, solid particles comprised entirely of the contaminant (such as dust-sized lead particles in shooting ranges and explosives residues in bombing ranges), or having a high loading of contaminants (such as smelter dust emissions). Even contaminants initially released in a dissolved form eventually exhibit particle-like behavior because they bind to specific types of soil particles. Particles composed of organic carbon and selected minerals, such as clays and iron oxides, have large surface areas to which contaminant atoms and molecules bind through interactions mediated by electrical charges and non-ionic molecular forces. These adsorbent particles are usually very small (less than 0.2 mm), but may take up high loadings of contaminant. Larger soil particles are generally composed of uncharged minerals such as quartz and feldspars that bind little or no contaminant. As a result, trace contamination typically is concentrated in the very small particle size fractions.

The smaller an analytical subsample (recall that trace metals analyses typically use only one gram), the more likely the subsample will misrepresent the concentration of the sample as a whole. Figure 4 illustrates why small analytical subsamples have more variable results than larger ones. The true concentration in the container is related to the ratio of contaminated-to-uncontaminated particles. A concentration result is calculated from the mass of analyte (measured by the instrument) divided by the mass of soil from which that analyte was extracted. Larger subsamples, shown as the large, red subsample at the upper-left of the figure, are more likely to capture the same ratio as in the container. Small subsamples are likely to miss contaminated particles (see the blue, bottom-left subsample), giving very low or nondetect results after the subsample is digested or extracted for analysis (flask). In some cases, however, a small subsample may yield a higher ratio of contaminated particles (the green subsample to the right of the container). In the latter example, the smallness of the subsample's mass increases the reported concentration. For example, if 50 nanograms (a nanogram is 10^{-9} gram) of analyte is extracted from 10 grams of soil, the contaminant concentration [when expressed as milligrams (mg) analyte per kilogram (kg) soil] is 5 mg/kg. If the same 50 nanograms was extracted from one-tenth that mass of soil (i.e., 1 gram), the reported concentration is 50 mg/kg, ten times higher.

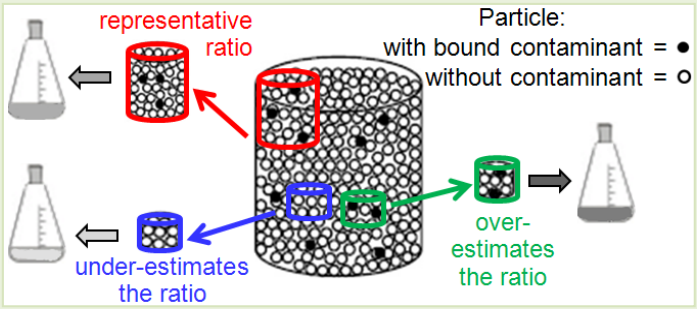

Figure 4. Graphic illustrating possible subsampling outcomes for a container filled with a certain ratio of contaminated-to-uncontaminated particles. Smaller subsamples are more likely to misrepresent the ratio. When the subsample is extracted prior to analysis, the concentration of the extract (represented by the flasks) is proportional to the ratio captured by the subsample.[5]

The contaminant concentration would be the same no matter how big or small the subsample only if contaminants were uniformly distributed throughout the sample, like salt dissolved in water. An additional complication is that soil particles easily segregate in dry samples. As soil samples are shaken and bumped during the trip to the laboratory, smaller particles work their way downward under the influence of gravity, leaving larger particles near the top. Segregation also occurs during stirring and other manipulations of the sample that allow gravity to influence particle movement. Figure 5 shows the difference between non-segregated and segregated soil. Since contaminant molecules typically

[5] Adapted from EPA (2002) RCRA Waste Sampling Draft Technical Guidance, 530-D-02-002, August. Page 92. www.epa.gov/osw/hazard/testmethods/sw846/pdfs/rwsdtg.pdf

associate with smaller particles, and since larger particles segregate near the top, subsampling by scooping off the top biases the subsample towards less contaminant-laden particles and analytical results that are lower than the true concentration of the sample. On the other hand, other subsampling activities, such as selectively tapping fine particles into the subsample while it is gradually brought toward the target subsample weight, can introduce bias in the other direction.

Figure 5. Freshly collected soil sample (left) versus the same sample after the jar was shaken for 15 minutes (right), showing particle segregation caused by gravity.

The Project Manager: Defining What the Sample is to Represent

"A representative sample is one that answers a question about a decision unit with an acceptable level of confidence. This requires…selecting the appropriate sampling design and strategy, and including proper quality controls to assess sample representativeness…A sample that is representative for a specific question is most likely not representative for a different question."[6]

Many different kinds of characterization and cleanup decisions with serious risk and cost consequences depend on reliable soil data. A sampling and analysis plan (SAP) to provide representative data cannot be designed until the intended decisions are well understood. Different decisions often require different sample collection and processing procedures. To illustrate, contrast the following two decisions in relation to the question of target soil particle size:

1) Does the lead concentration in residential yard soil pose a risk to children?
2) If the soil lead concentration requires it to be removed, can the soil be disposed of in an unlined landfill in Massachusetts?

Since the concentration of lead in soil varies with particle size, the particle size to be analyzed must be selected to be representative of the intended decision. For Question #1, the EPA recommends that soil lead be measured on the <0.25 millimeter (mm) or smaller soil fraction to estimate exposure point concentration since this is the particle size most likely to stick to a child's hands.[7] Thus the soil needs to be sieved through a 60-mesh (or smaller) sieve; the soil passing through the mesh is analyzed. For Question #2, Massachusetts regulations allow lead-contaminated residential soil to be disposed at state unlined landfills if the total lead concentration is less than 1,000 mg/kg.[8] Since soil disposal involves bulk soil, the bulk soil is what should be analyzed. In most cases, this means that disaggregated soil is passed through a 10-mesh sieve to exclude stones and particles larger than 2 mm. Soil scientists consider the material passing through a 10-mesh sieve as "soil" for analysis purposes.[9] However, this target particle size could be changed if lead shot larger than 2 mm were present and would be landfilled as part of the soil, since the measure is "total lead."

Knowing the representative particle size raises another issue: the ability of an analytical subsample to represent the sample is dependent on the relationship between the largest sized particle present in the sample and the subsample's mass. The relationship between maximum particle size, minimum subsample mass and the degree of subsampling imprecision is called "fundamental error," which is a key concept in sampling theory. This is discussed in Appendix D of the EPA's *RCRA Waste Sampling Draft Technical Guidance.*[4] The closeness of analytical results (precision) can be expressed in terms of percent relative standard deviation (%RSD) for repeated subsamples from the same sample. A high %RSD indicates

[6] Ramsey, C.A. and A.D. Hewitt (2005) Environmental Forensics, 6:71-75.

[7] EPA (2007) Short Sheet: Estimating the Soil Lead Concentration Term for the Integrated Exposure Uptake Biokinetic Model (IEUBK), Office of Solid Waste and Emergency Response (OSWER) 9200.1-78, September. www.epa.gov/superfund/lead/guidance.htm#estim

[8] MassDEP (2012) Reuse and Disposal of Contaminated Soil at Massachusetts Landfills, Department of Environmental Protection Policy # COMM-97-001. www.mass.gov/dep/recycle/laws/bwp97001.pdf

[9] U.S. Department of Agriculture (USDA) (2009) USDA Natural Resources Conservation Service *Soil Survey Field and Laboratory Methods Manual*, Soil Survey Investigations Report No. 51, Version 1.0, National Soil Survey Center, Lincoln, NE (Rebecca Burt, ed.) ftp://ftp-fc.sc.egov.usda.gov/NSSC/Lab_References/SSIR_51.pdf

large differences between results from repeated subsamples (i.e., high data variability). This means that there is high imprecision ("noise" or "error") and the precision is poor. Good precision is indicated by a low %RSD. For a typical soil passed through a 10-mesh sieve (so that the maximum particle size is 2 mm), the subsample mass can be no less than 8 grams in order to reduce imprecision from fundamental error to 16% RSD. However, if the subsample mass is only 1 gram (as for most metals analyses), the best precision that can be expected is 50% RSD. If a 1-gram subsample is desired, but precision improvement to 16% RSD is also desired, the sample's maximum particle size can be no larger than 1 mm.

The discussion above addresses only fundamental error (error due to particle size) as a source of imprecision. With real samples there are always additional sources of error. For example, additional subsampling error can come from a non-uniform distribution of sample particles (such as segregation within the jar). This error adds onto the fundamental error. Sources of error add non-linearly such that the greatest error dominates. For example, a fundamental error of 16% becomes inconsequential if subsampling error due to particle segregation is 40%. Total subsampling precision will not improve by reducing the fundamental error below 16% when the segregation error is allowed to remain at 40%. Total subsampling error can be estimated by examining the results for "laboratory duplicates," a routine quality control (QC) check commonly reported with laboratory data.

Subsampling Precision

For a true concentration of 100 mg/kg, 20% RSD means that about 95 out of 100 repeat subsamples can be expected to fall within the range of 60 to 140 mg/kg; with only 5% of subsamples falling below 60 or above 140 mg/kg.

A variability of 50% RSD is poor precision because 95% of repeat subsamples can be expected to fall anywhere between 0 and 200 mg/kg. The "noise" is so high that the measurement system cannot tell the difference between 100 and 0, or between 100 and 200 mg/kg.

In contrast, a 10% RSD is good precision because 95% of subsample results can be expected to fall within the range of 80 and 120 mg/kg. So nearly all subsample results will be close to the true sample concentration of 100 mg/kg.

Relative percent difference (RPD) is a common measure of precision for laboratory duplicates. %RSD and RPD are mathematically interchangeable: $\%RSD = RPD \div \sqrt{2}$.

The project manager, in association with the technical team, is responsible for planning "how good" the data need to be. A simple example follows: If the true concentration in the sample jar is 100 mg/kg, but there is a total subsampling error of 40% RSD, you can expect that results could be reported anywhere between 20 and 180 mg/kg. Would you make a significant decision error if you base your decision on a result of 30 mg/kg (or 150 mg/kg) rather than on a result much closer to the true sample concentration of 100 mg/kg?

On the other hand, what if the true concentration is 1,000 mg/kg? Subsampling precision of 40% RSD means that results could range between 200 and 1,800 mg/kg. Is that level of data quality sufficient so that you will make correct decisions? Quite clearly, it depends on the value of the decision threshold. If the action level is 75 mg/kg, 40% RSD variability on a true concentration of 100 mg/kg creates opportunity for decision error. A result less than 75 mg/kg is possible even though the true concentration is greater than the action level. On the other hand, 40% RSD on a true concentration of 1,000 mg/kg likely will not cause a decision error, since a low result of 200 mg/kg is still greater than the 75 mg/kg action level. If sample variability can create misleading data that could lead to unacceptable decision errors, improved sample processing and subsampling procedures are required.

Detailed advance planning is required to collect soil data that are representative for project decisions. The properties and activities the technical team needs to consider when developing a QAPP include:

- Clearly describe what decisions the soil data are to support.
- Select the appropriate volume and dimensions of field soil decision units (DUs) for which the true field concentration is to be estimated and on which a decision will be made.
- Will toxicological testing be done on some soil samples? If so, consider collecting those samples separately from samples for chemical analysis.
    - Samples that are ground for chemical analysis are likely not appropriate for toxicological testing.
    - Splitting a sample between different analyses requires sample preparation to be done before splitting and/or specialized splitting procedures.
- Determine the number of increments to comprise each incremental sample (and the number of incremental samples per DU) or the number of discrete samples in the DU's data set.

- Specify the mass and dimensions of increments (or of discrete samples), the field increment collection devices and the increment layout pattern in the field.
- If "hot spots" smaller than DUs are of concern, define the volume, dimensions and concentration that qualifies as a hot spot. Consider whether:
    - The concern is to ensure that hot spots will be incorporated into the DU sample's concentration (this will govern increment spacing); or
    - The goal is to spatially locate hot spots [this may require DUs to be resized, the use of sampling units (SUs), or a switch to a "composite-search" sampling strategy.[5]]
- Determine how an incremental (or discrete) sample should be processed so that it is representative for the decision(s) to be made on the data:
    - Ensure that subsampling of the processed sample will use an incremental subsampling approach.
    - Identify the special sample collection and processing required for ICS field sampling for volatile organic compounds (VOCs).[3,4]
    - Include or exclude above- and below-ground plant parts.
    - Select the soil particle size(s) that is(are) representative for decisions and determine how to appropriately sieve to isolate that target particle size fraction.
    - Consider possible weather and field conditions: will field samples likely be collected as dry, moist or saturated samples? How will soil clods be disaggregated before sieving (i.e., free particles that are simply stuck together)?
    - Will samples be dried as part of processing (with consideration of how drying is performed, such as air-dry versus oven, with respect to the volatility of analytes)?
    - Select the mass of the analytical subsample with consideration of the maximum targeted particle size and allowable fundamental error: might that mass be larger than the laboratory can digest or extract for analysis?
    - Determine whether the isolated targeted particle size fraction needs to be milled (ground) to reduce particle size so that a smaller analytical sample can be accommodated.
        - Could grinding/milling render the sample non-representative through increased leaching from milled particles during subsample digestion?
        - Could the grinding equipment add target contaminants (such as chromium) to the sample?
    - If sample milling is undesirable, could subsampling imprecision be controlled through replicate subsample analyses?
    - Consider whether performing any or all of the sample processing in the field is logistically desirable.
- Define the QC that measures the quality of sample processing:
    - Keep in mind that the goal of QC is to provide evidence that the data are reliable for making project decisions.
    - Select the type of QC to be used (for example, field replicates and subsampling replicates), select how often and when.
    - Set acceptance limits for QC results and the corrective actions to be triggered when acceptance limits are exceeded.
- Ensure the SAP/QAPP document(s) contain sufficient details about the sampling design and sample collection, processing, and subsampling procedures so that these procedures will be carried out as envisioned by the project planning team, and can be understood by reviewers.

There is a wide range of options for how soil samples can be collected and processed. The decisions that will be based on the data will determine what soil properties should be measured. Sample representativeness is achieved by selecting sample collection, processing and analysis options that will produce unbiased and sufficiently precise measurements.

"Representativeness" cannot be left to chance or remain undefined. Seldom will a single person be able to resolve all the variables that must be addressed when sampling and analyzing soil. That is why a technical team with diverse skills is needed. Field staff and the contracted laboratory should be consulted when selecting soil collection and processing procedures. The project manager is responsible for ensuring that up-front, thorough systematic project planning assembles the correct package of options, and that the appropriate technical skills are involved in refining and implementing that package.