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SAMPLE HANDLING STRATEGIES FOR ACCURATE LEAD-IN-SOIL MEASUREMENTS IN THE FIELD AND LABORATORY

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ABSTRACT

The inhomogenous lead-in-soil matrix can present serious obstacles to accurate sample collection and handling. In typical lead-in-soil measurement, particle size related errors in sampling and sample handling often exceed all other sources of error. The magnitude of error can vary widely depending on the particulate nature of the lead contaminant and the effectiveness of control measures. Large particle contaminants, such as lead bearing paint chips, pose a much greater challenge to accurate sample handling than do small particle contaminants, such as air dispersed industrial emissions. A sample handling protocol demonstrated to give reliable, valid data in small particle situations may prove entirely inadequate for large particle cases.

This paper focuses on the importance of fundamental error, a statistical consequence of particulate sampling. We discuss in quantitative terms the significance of fundamental error on the measurement of paint chip contaminated soils near a 400 ppm action level. On the basis of error estimates, we recommend that sample handling protocols control particle related errors by ensuring adequate sample size and sample definition, and by accomplishing sufficient particle size reduction and homogenization before subsampling. We discuss particle related errors and their effect on laboratory, field, and in-situ analytical methods. We recommend that quality assurance protocols aim to determine the overall measurement quality by evaluating error at all stages from sampling and sample handling through analysis.

SAMPLING DESIGN AND GEOSTATISTICS

The prerequisite of a well-designed study is a clear statement of the study's objectives for data quantity, quality, reliability, speed, and cost. The planner develops objectives with careful attention to the data's ultimate utility and the available resources of people, technology, and money. The objectives should be stated in quantitative terms, with exact figures to indicate the necessary precision and accuracy at and around the action or decision concentrations.

In large projects with multimillion dollar budgets, such as some Superfund cleanups, statisticians develop a sampling design with the aid of geostatistical theory and preliminary data indicating the spatial variability of site contamination. The sampling design defines the number points to sample and the pattern. The statistician attempts to design a sampling effort that achieves the lowest possible cost of the total sampling, analysis, and remediation effort.[1,2,3] Geostatistics is an art of some subtlety; its effectiveness varies widely with the skill of the statistician.[4] Although, the application of geostatistics to sampling design is well beyond the scope of this paper, some of its principles (e.g. sample support) can be used to improve the effectiveness of small sampling projects.

SAMPLE HANDLING OPERATIONS

A typical soil sample experiences a number of physical manipulations at the sampling site and in the laboratory. According to the sampling plan, the field technician extracts soil from the ground, often by means of a core sampling device. The technician may combine soil collected from several points to form a composite sample. To avoid transporting unnecessarily large quantities of sample material, the technician may thoroughly mix, then split the sample, taking only the minimum necessary for the lab.

The laboratory technician unpacks the sample, weighs the sample, dries the sample (by oven or air-drying), re-weighs the sample, then screens the sample to remove stones, vegetable matter, and other particles larger than 2 mm in size. At this point the technician re-weighs the sample,

then grinds the sample to reduce the particles to small enough size to pass a fine mesh sieve. When all of the sample passes the fine mesh sieve, the technician mixes and splits the sample for final sample preparation, or executes an additional stage of grind, sieve, mix, and split. The technician then carefully weighs the final sample for the analysis. If the analysis is to be performed by atomic absorption spectroscopy (AAS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES) then the technician will prepare the sample by acid digestion or extraction. If the analysis is to be performed by x-ray fluorescence spectrometry (XRF) then then sample may be prepared by flux fusion, press pelletizing, or simply by packing the ground sample in a plastic XRF sample cup. The technician then analyses the final prepared sample by instrument, and calculates the final result using the sample data and instrument output.

Accurate execution of these sample handling operations requires a great deal of skill and care. Every step of handling introduces a degree of error to the overall result. But every step is needed to ensure consistent overall precision, accuracy, and repeatability.

Errors Combine

Errors are generally expressed in terms of standard deviations, or "sigmas". Variance is the square of the standard deviation. The overall, or total, variance is the additive sum of the many individual variances created in each step of the process. The overall error (square root of overall variance) includes the contributions of sampling error, sample handling errors, sample preparation errors, and analytical error. Generally, you can most effectively reduce the overall error by reducing the largest contributing error.

Analytical errors are usually well-characterized, well-understood, and well-controlled by laboratory quality assurance and quality control procedures. By contrast, sampling and sample handling errors are not usually well-characterized, well-understood, or well-controlled. Sampling programs frequently neglect to implement quality assurance measures. To control overall error, one must control sampling and sample handling errors as well as analytical errors.

THE PARTICULATE NATURE OF SOIL

Soil particles range widely in size from clay (less than 0.0039 mm diameter) to silt (0.0039 mm to 0.0625 mm) to sand (0.0625 mm to 2.0000 mm). Particles larger than 2 mm in diameter are classified as gravel.[5] Natural soils are mixtures of different particle types and sizes.

By general agreement and tradition, particles larger than 2 mm in diameter should be removed (by U.S. number 10 sieve) from a soil sample before analysis. The excluded particles are large enough to be examined and classified by eye or by magnifying glass. Contaminants can also be particulate. Lead-bearing particles in soil can vary in size from sub-micron aerosol deposits (less than 0.001 mm diameter) to lead paint chips and lead shot (up to the maximum 2 mm diameter). Generally, the largest particles create the greatest challenge in sample handing.

Particulate Sampling Theory

A theory of particulate sampling was developed by geologist Pierre Gy to improve the quality of data gathered in support of mineral exploration and mining.[6,7] The theory has since been adopted by environmental scientists. The theory recognises two major categories of sampling error: sampling bias and fundamental error. Both types of error are measureable and controllable.

In general, a sample is intended to represent the a particular sampling unit, or volume of material. The sampling unit may be a particular plot of land (e.g. a certain 10 foot by 10 foot square), to a particular depth (e.g. surface to 4 inches). Or a child's sand box. Or a rail car load of ore. A single sample represents the entire sampling unit.

The sampling methodology is considered unbiased and correct if all of the particles in the sampling unit have exactly the same probability of being selected for inclusion in a random sample. The perfectly unbiased methodology is a practical impossibility. To reduce sampling bias, we must recognise the difficulties presented by the sampling unit. It may exhibit grouping or segregation of particles. Denser particles may have settled toward the bottom. New contaminants may have recently settled onto the unit, and may not be mixed into the volume. The contaminants may be heavily concentrated on one side of the unit, or concentrated in "clumps".

One method for sampling from a plot of land is to go to the center of the unit and shovel out the requisite amount of sample. However, we can reduce bias substantially by using a core sampling probe to control the depth and profile of the sample. More importantly, we can take soil from several different parts of the unit and mix it together as a composite to "increase sample support". By increasing sample support, we create a composite sample which more accurately reflects the average contaminant concentration of the unit than that of any single point sample. The composite sample reduces bias and improves accuracy over single point sampling without the expense of additional analysis.

FUNDAMENTAL ERROR IN SAMPLING

Fundamental error results directly from the particulate nature of the material sampled. For a given distribution of particle sizes and particle compositions, a random sample of fixed mass can never perfectly match the overall composition of the larger sampling unit. Even if every particle in the sample has been selected at random without bias from the sampling unit, the sample composition can differ from that of the overall sampling unit. The difference is randomly distributed according to statistical therory (see Appendices A and B).

You may find fundamental error easiest to understand in the case that the number of contaminant particles is small. Suppose that your sample size and contaminant particle concentration are such that the expected number of contaminant particles in a randomly selected sample is exactly 1.00. Then if you were to draw many repeat samples of the same size from the same sampling unit, the average contaminant particle count would be close to 1.00. But not every sample would have a count of 1. Some of the samples would have 0, others would have 2 or more.

According to the Poisson formula (Appendix A) we can calculate the probability P_x of a particular count x when the expected, or mean, value is $\overline{x}$. In our example $\overline{x}$ = 1.00, so P_0 = 36.8%, P_1 = 36.8%, P_2 = 18.4%, P_3 = 6.1%, P_4 = 1.5%, and so on. Therefore 63.2% (100% - P_1) of the samples are probably going to give counts that are not 1, and are therefore off the mean by *at least* 1. If we calculate the standard deviation of the counts from many samples, it will approach the square root of the mean. In our example the error band of one standard deviation (1-sigma confidence) is therefore square root of 1.00, which is 1.00, or 100% of the expectation, or mean, value of 1.00. In other words, if you expect very few contaminant particles in your sample, expect very large relative errors.

With a larger sample size the expected contaminant particle count will increase, but the relative error will decrease. If we make our sample 4 times as large, then the mean particle count will be 4.00. The standard deviation will then be the square root of 4.00, or 2.00, which is 50% of 4.00. So if we quadruple the sample, the relative error is halved. Similarly, if we make our sample 100 times as large, the mean particle count will be 100 and the relative error will drop to 10%. To reduce fundamental error to below 10% (1-sigma confidence) we must ensure that our expected contaminant particle count is at least 100.

A Plausible Real-World Example

Are small particle counts possible in lead measurements at or above action levels? Yes. The worst case situation involves lead shot. Lead has been used for centuries in firearms ammunition. A very common traditional use of lead, projectile "shot" or small spheres, are packed by the hundreds into individual shotgun cartridges, or "shells". Shot range from 1 mm to about 5 mm in diameter, depending on the intended usage. Every shotgun blast, whether for hunting or trapshooting, scatters several hundred shot to the environment. The traditional alloy used for shot is around 95% lead by weight, with small amounts of arsenic and antimony added to improve manufacturability and increase hardness.[8]

Imagine a plot of land that was once used as a skeet shooting range. Suppose the average shot size was 2 mm diameter. From the diameter, you can calculate the volume of each shot and multiply by lead's density (11.3 g/cm^3), and arrive at an average shot mass of 0.047 gram. Using 95% as the lead concentration in the alloy, the average lead content of a shot is 0.045 gram. Say we sample soil with a sample size of 100 grams, typical for lead-in-soil sampling. At an action level of 400 ppm, or 0.04%, we would have an expected shot count per sample of 100 grams times 0.04% divided by 0.045 shot per gram, or 0.89 shot per sample. So soil contaminated with an average of 400 ppm lead may have an average of less than one contaminant particle (shot) per 100 grams. This result is actually even worse than the single particle example that gave a 100% error. The relative error is greater than 100% due to fundamental error alone. Other errors only add to the fundamental error.

The only way to reduce fundamental error in sampling is to take a larger sample size. In this example, to reduce fundamental error to a manageable 10% (or 40 ppm), we must increase sample size by a factor of 112, which would amount to more than 11 kilograms (24 pounds)! What laboratory would be willing to process such a sample in its entirety?

A Single Chip

Paint on older buildings often has a lead loading of 20 mg/cm^2 or more. Imagine that a single chip of such paint the size of your thumbnail (2 cm^2) falls into in a 100 gram soil sample. The chip contains 40 mg, or 0.040 grams of lead, nearly the same amount of lead as in a 2 mm shot. Take 0.040 grams and divide by 100 grams and multiply by 1,000,000 to get 400 ppm. Your single paint chip raised the lead concentration of an entire 100 gram sample by 400 ppm. If the soil has a background level lead content of 20 ppm without the chip, then the chip raises it to 420 ppm, and above the 400 ppm action level.

Now imagine you are kneeling down next to a house to take a soil sample. You see the paint chip. Take it, or leave it? According to HUD's Soil Sampling Protocol,[9] "If paint chips are present, they should not be avoided and should be included in the sample." (item C.5) Later, under the heading "Laboratory Analytical Procedure", the same protocol states "Samples are to be sieved once with a number 10 sieve with a mesh size of 2 millimeters." (item E.3) So far, so good. It continues "Visible paint chips are disaggregated by forcing the paint chips and other large particles through the sieve by a rubbing motion." Disaster. Whether the sample passes or fails depends entirely on whether you take the chip. Or whether you notice the chip. What if the chip is just below the surface, invisible? Go back to the same spot and sample again, and again. You may never obtain the same result again.

The author suggests a different approach. Leaded paint chips are always a potential hazard; the hazard increases over long periods of time as chips decompose into the soil. To knowingly include large chips of leaded paint in a soil sample accomplishes nothing; the result is foregone. If you do not already know the lead content of the paint chips, do have the paint chips analysed, but separately. As for the soil itself, pass it through the 2 mm mesh, but without trying to break up the paint chips. Include only the soil that passes through the mesh. If you find paint chips that do not pass through, study them carefully; find out where they came from; test them for lead content; but do not include them in the soil sample.

FUNDAMENTAL ERROR IN THE LABORATORY

Now imagine you are the lab technician. You have the soil sample, 100 grams, dried and sieved through the 2 mm screen. You see little paint chips in the sample, all of them just small enough to pass through the sieve, about 2 mm on a side. If they are leaded like the thumbnail sized chip, how many chips will it take to exceed the action level? How much fundamental error should you expect?

The average area is 0.2 cm times 0.2 cm, or 0.04 cm^2. At 20 mg/cm^2, the average lead content per chip is 20 mg/cm^2 times 0.04 cm^2, which is 0.8 mg, or 0.0008 grams. Assuming that there are no other leaded particles in the soil, 400 ppm would imply a chip count of 400 divided by

1,000,000, times 100 grams per sample, divided by 0.0008 grams per chip. A total of 50 chips. For a mean chip count of 50, the standard deviation of the chip is the square root of 50, or about 7.1. Therefore the fundamental error is 7.1 divided by 50, or 14.1%. Remember, this is only 1-sigma confidence!

I have analysed in great detail a actual sample that was very similar to the example given. I do not believe that this type of sample is unusual or uncommon; it was one of the first soil samples that I ever examined in detail. The soil came from the drip line of a train depot built in 1874. Of the portion of the 100 gram sample that passed through the 2 mm mesh, more than half of the lead content was contained in particles between 1 mm and 2 mm in size. See Table 1.

The assumptions that lead to a fundamental error of 14.1% are plausible, but also arbitrary. You may imagine worse cases of fundamental error due to higher lead content per chip or smaller sample sizes. The higher lead content per chip may be caused by higher lead loading in the paint film (40 mg/cm^2, say) or larger area chips (a 4 mm by 2 mm chip can fit through the 2 mm mesh). So it is possible you may experience fundamental errors of worse than 14.1% from 100 gram soil samples with lead paint chips. Since smaller samples only exacerbate this error, I strongly discourage sampling less than 50 grams for lead-in-soil where paint chips may be present.

Subsampling Error

The laboratory has dried the sample and sieved the sample through the 2 mm screen. Sample digestion methods generally require between 0.2 and 1.0 grams of sample material.[10, 11] The sensitivity of atomic spectrometry is more than adequate to analyse such small amounts of material; using a larger quantity of sample material would require larger amounts of acid, increase cost, and raise safety concerns. So the laboratory subsamples.

Subsampling leads to another set of errors. Once again we have bias and fundamental error. Suppose we subsample 0.3 grams from the same example 100 gram sample. If we subsample without any regard to homogenization or particle properties, the result will be analytical disaster. The mean chip count in the subsample will go from 50 in the 100 g sample to 0.15 in the 0.3 g sample. The fundamental error in the subsample will then be the square root of 0.15, which yields 0.39, or 258%. What is worse is that the most likely outcome is that no lead will end up in the subsample at all, and the result will be 0 ppm. In the off chance that a 2 mm by 2 mm chip lands in the subsample, the result will be 0.0008 g divided by 0.3 g, which is 2667 ppm. There is no chance that the result will be even close to the correct 400 ppm.

Fortunately, we can reduce the particle size and homogenize the sample thoroughly before we subsample. Say we grind the 100 gram sample until all the particles pass a U.S. Number 60 sieve (0.250 mm). Then the average particle might be roughly spherical with a diameter of 0.250 mm. The volume of the sphere would be 0.0082 mm^3 or 0.0000082 cm^3. If the lead bearing particles each have a lead loading of 15% and a density of 2 g/cm^3, then each will have a total lead content of 0.00000245 g (or 2.45 g). In a 0.3 g subsample of our 400 ppm lead sample the expected particle count is then 0.3 times 400, divided by 1,000,000, divided by 0.00000245, which is 48.9. The fundamental error would be the square root of 48.9, which is 7.0 counts, or 14.3%. The fundamental error from subsampling (14.3%) is actually slightly worse than what we calculated for the fundamental error from the original sampling (14.1%). Remember that the errors combine together (by adding the variances) to form an overall error that is worse than any of the several individual components. In the case of a sampling error of 14.1% and a subsampling error of 14.3%, the total error is 20.1%.

Realistic scenarios of subsampling could be even worse than those described. The lead content of dry paint film can be as high as 50%, far greater than 15%. Also, laboratories typically grind samples to a U.S. number 35 sieve (0.500 mm) rather than number 60 (0.250 mm) before subsampling. Larger particles translate to larger errors. With 50% lead content and 0.500 mm particles, the 0.3 g sub-sampling error could be as high as 74%!

One way to reduce subsampling error is to simply subsample and digest a larger amount. The ASTM method for sample digestion of soils for lead analysis[11], which is based on USEPA SW-846 Method 3050, calls for a 1.0 g subsample, more than three times larger than the 0.3 g subsample we calculated. In taking the larger subsample, the fundamental error from subsampling should be reduced by nearly half. But the method fails to deliver better performance, because it relaxes the grinding requirement from number 60 mesh (0.250 mm) to number 35 (0.500 mm). Doubling the particle diameter increases the volume of the spherical particle by a factor of 8, more than compensating the larger subsample. The fundamental subsampling error grows to 22.1%, and the total fundamental error becomes 26.2%.

Besides increasing subsample size, the laboratory can improve subsampling error by grinding the sample to a smaller particle size. Grinding to a 0.125 mm particle diameter, the laboratory reduces the fundamental error of the 0.3 g subsample from 14.3% to 5.1%. But grinding 100 grams of soil to such small particle size by hand methods (e.g. mortar and pestle) can be tedious and difficult. A method for speeding the particle size reduction without greatly increasing fundamental error is to grind and subsample in stages. If you grind the 100 g sample to 0.250 mm and subsample not 0.3 g, but 5 g, the fundamental error will be only 3.5% If you then grind the 5 g subsample to 0.125 mm and sub-subsample 0.3 g, the fundamental error will be 5.1%. Combining the subsampling and sub-subsampling errors, you have an overall error of 6.2%. By reducing only 5 g of the 100 g sample to the smallest particle size, you avoid much of the effort of grinding and sieving the whole sample.

Other errors related to subsampling include bias and homogenization errors. An accurate subsample must be unbiased; every particle should have an equal probability of being subsampled. If the ground, sieved sample is not properly homogenized, there can be substantial segregation of particles by composition, shape, size, and or density. Some types of particles (e.g. magnetic or electrostatic particles) tend to group or clump together. An improper method for homogenizing a sample can actually create segregation. Agitation or shaking a sample with particles of different size, shape, or density will likely cause stratification. With agitation, denser, smaller and rounder particles tend to drop to the

bottom, while less dense, larger and flatter particles tend to rise to the top. Finely ground samples do not stratify as readily as the raw, unground sample.

One way to avoid homogenization error in subsampling is to make use of mechanical sample splitting devices. A riffle splitter, for example, can efficiently eliminate segregation errors in subsampling. If mechanical splitters are not available, then the manual cone-and-quarter method can reduce bias in subsampling.

OTHER LABORATORY ERRORS

A number of other laboratory errors affect the analysis of lead-in-soil. The sample should be dry; water content should be no more than around 2 or 3% of the sample mass. For atomic spectroscopy requiring acid digestion of the sample, the the laboratory must measure the sample mass and solution volume, and record the data accurately. To avoid sample to sample cross contamination, the laboratory must clean tools and containers between samples. The lab must track each sample and follow every preparation step according to protocol, using the proper tools and properly maintained and calibrated equipment. Overall, laboratory error should be small and well controlled; otherwise, lapses in quality can easily lead to substantial error.

Sample Dissolution

An acid digestion or extraction procedure must achieve reproduceable results for the contaminant of interest in any of its likely physical or chemical forms. The procedure should allow ample time for the dissolution of the sample to finish. In general, reducing particle size speeds the dissolution to completion. Some chemical forms of lead tend to be difficult to dissolve. Of particular difficulty in this regard are the lead chromates, colored pigments commonly used in marine, exterior, and signage paints. Standard acid digestion procedures and suitable quality control will likely provide consistency to within a few percent under most circumstances.[10]

Instrumental Error

Instrumental errors generally fall into the categories of signal-to-noise and interference. Atomic spectrometry methods (AAS, ICP-AES) generally provide excellent sensitivity for the lead-in-soil application, with detection limits of 10 ppm or lower. Signal-to-noise ratios are correspondingly high. Matrix related interferences are also fairly low and well controlled in modern atomic spectrometry instruments. The overall instrumental sensitivity, precision, and accuracy are excellent, with errors in the range of nearly negligible compared to the other sources of error already discussed.

X-ray fluorescence (XRF) generally has worse sensistivity than AAS or ICP-AES, but with the compensating advantages of portability and less intensive sample preparation requirements. Matrix effects due to variable elemental composition can be a concern with XRF, but the lead-in-soil application is fairly benign in this regard. Sophisticated matrix correction methods (e.g. "fundamental parameters") have been developed and proven successful;[12,13,14] but even simple techniques, such as Compton Normalization, work surprisingly well in this application.[14,15,16]

XRF has an additional particle-related bias when the particle size becomes large compared to the attenuation length for the analyte's fluorescence x-ray.[15] In lead-in-soil analysis, large contaminant particles cause negative bias. For analysis using the lead 12.6 keV x-ray, particle size should be reduced to 0.125 mm or smaller to control this effect. [Table 2]. Of course, to avoid severe subsampling errors, you should already be grinding samples to small particle size.

Note that the larger subsample required for XRF (3 to 5 grams, typically) does not reduce the subsampling error of XRF relative to digestion based methods. Only about 0.3 grams of the typical XRF soil sample (approximately 1 mm depth in a 25 mm diameter XRF sample cup) produces the major part of the instrument response.[16] Therefore, the subsampling error is about the same as if a 0.3 gram subsample had been drawn rather than a 3 gram subsample.

The analytical error of field portable XRF is around 10 to 15 percent for lead-in-soil samples at 400 ppm. While this analytical error is far worse than that of laboratory atomic spectrometry, the overall error of the methods may be fairly similar after taking into account sampling, sample handling, and sample preparation.[17]

THE SMALL PARTICLE CASE

If all the contaminant particles of the sample unit are very small, then fundamental errors greatly diminish, and sample handling can be simplified. Lead contamination from airborne sources (e.g. automobile emissions, smelter emissions, incinerator emissions, abrasive blasting of painted surfaces) and from chalking (powdery deterioration) of painted surfaces tends to be dispersed as fine particles. If the lead is found only in particles less than 0.032 mm (32 microns) in diameter, then the fundamental error for a 0.3 gram sample or subsample cannot be more than 4% at 400 ppm. In such a sample, grinding and sieving are not likely to make dramatic differences in the laboratory result. Sampling bias resulting from spatial variation is still a concern, so I always recommend careful attention to sampling design, sample support, and homogenization.

Even with the minimal sample preparation (dry, sieve 2 mm, mix), field portable XRF can perform very well in cases of small particle size.[18,19] The minimal sample preparation and high analytical throughput of XRF enable an investigator to collect large quantities of useful data in a short period of time, and at low cost. In many situations, the field XRF provides better overall decision making data than laboratory analysis by virtue of its ability to overcome spatial variability through massively increased sampling density.[20,21]

IN-SITU FIELD XRF

The in-situ capability of some field portable XRF instruments may be especially attractive for high speed, low cost screening and characterization. Depending on the nature of the contaminant and the soil matrix, the in-situ method can offer screening quality data with practically no sample preparation at all. To reduce bias and increase sample support, the field technician can mix and composite a sample on the ground before an in-situ XRF measurement.

Moisture and particle size effects can be especially pronounced for in-situ XRF, so quality assurance is especially important. The field technician may prepare one or more samples by the full protocol (dry, grind, sieve, split) in the field and compare the result to the in-situ measurement to determine if the soil conditions allow the in-situ XRF method to meet the data quality objectives. To back up field measurements, the technician should collect representative samples for laboratory analysis.

QUALITY ASSURANCE FOR SAMPLING AND ANALYSIS

Quality assurance programs usually include sample duplicates, replicates, spikes, blanks, and splits. To assess field based error (that is, error caused by sampling and sample handling), the sampling program should include field duplicates and replicates taken as early as possible in the sampling process. To assess the error due to spatial variation and sampling, the field technician takes duplicates or replicates according to the normal sampling protocol, but from spatially distinct points (sample points should be spread apart from each other) within the representative sampling unit. To assess the error due to sample handling, the technician makes several large field composites and splits them into duplicates or replicates before commencing any sample handling operations.

To assess the error due to final sample preparation and analysis, the field or lab technician splits sample material into duplicates or replicates just before the final sample preparation (e.g. before digestion, or before putting material into XRF cup). Several splits may be sent to an independent laboratory for confirmatory analysis. Spikes and blanks serve to assess analytical recovery and bias. Of course, the quality assurance program should take care to use sample splitting methods that do not introduce significant bias. Chappel and Olsen[22] and Shefsky[23] give practical guidance for using confirmatory data to evaluate the quality of field data.

CONCLUSIONS AND RECOMMENDATIONS

The major goal of measurement in a environmental project is to provide accurate data for assessing risk and deciding on remedial action to lower risk to an acceptable level. The optimal sampling design accomplishes that goal while keeping the total of sampling, analysis, and remediation costs to a minimum. The quality of data provided for decision making depends on the overall error; that is, the combined errors of sampling, sample handling, and analysis. Field analysis often provides the best overall data quality by allowing for low cost, high density sampling of spatially variable sites.

All measurement projects should include a quality assurance program that evaluates error resulting from sampling, sample handling, and analysis. Sampling and sample handling are especially critical components to overall data quality. Sampling protocols must consider the important effects of sample definition, sample support, spatial variability, segregation and grouping bias, and fundamental error due to particulate sampling and subsampling.

In order to control sampling and sample handling errors for lead-in-soil, the author recommends that sampling protocols:

* Ensure data quality objectives (DQO's) are clear.

* Use a low-bias sampling method (e.g. core sampling) to define the sample.

* Use composite samples to increase sample support.

* Collect 100 grams; consider collecting more than 100 grams if paint chips may be present.

* Dry the sample, if possible.

* Exclude particles larger than 2 mm. Examine large particles separately.

* Reduce particle size (preferably to 0.125 mm or less) before subsampling.

* Use low-bias methods for sample splitting (e.g. riffle splitter, cone-and-quarter).

* Implement quality assurance for sampling and sample handling as well as analysis.

* Use confirmatory data to evaluate the effectiveness of field methods.

If the data quality objectives and site characteristics allow for relaxed field sample preparation or in-situ protocols, do take advantage of the higher analytical throughput to collect more data. But always proceed with a degree of caution and support your data with solid confirmatory analysis.

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APPENDIX A: STATISTICAL BASIS OF FUNDAMENTAL ERROR

For a sampling unit containing n contaminant particles, the probability P_x that an unbiased sample will contain x such contaminant particles is given by the binomial distribution**:**

$$P_x = \left(\frac{n!}{x!(n-x)!}\right) p^x (1-p)^{n-x}$$

where *x* is an integer and *p* is the probability that any particular particle will be in the sample. Note that the sum of all probabilities (the sum of

P_x for x running over the range of 0 to n) is always 1. The probability for an individual particle, p, is simply the mass of the sample, m, divided by the mass of the sampling unit, M.

The mean or "expected" value for the number of contaminant particles in the sample, $\overline{x}$ can be found by summing the function xP_x over the range of $x=0$ to n. The resulting mean is simply $\overline{x} = np$, as one would reasonably expect.

The variance σ_{x}^2 of the number of contaminant particles around the mean $\overline{x}$ is found by summing the function $(x - \overline{x})^2 P_x$ over the range of x=0 to n. The resulting variance is $\sigma_{x}^2 = \overline{x}\,(1 - p)$. If the mass of the sample is much smaller than the mass of the sampling unit, then p = m / M will be much smaller than 1, and drops out of the formula, leaving $\sigma_{x}^2 \approx \overline{x}$. The standard deviation of x, or σ_{x}, will then be approximated by SQRT($\overline{x}$).

In calculating fundamental error for an even 50/50 sample split, where n is the number of contaminant particles in the whole sample (now considered the sampling unit for the splitting operation), $p = 0.5$, so

$$\overline{x} = 0.5\, n, \text{ and } \sigma_{x}^2 = 0.5\, \overline{x}.$$

In the limit as the sampling unit becomes extremely large, (n becomes extremely large, p becomes very small) the probability distribution simplifies to the Poisson formula:

$$P_x = \overline{x}^{\,x} e^{-x} / x!$$

where the mean, or expected value, is once again $\overline{x}$. As before, the variance, σ_{x}^2, *simplifies to* $\overline{x}$.

APPENDIX B: PIERRE GY'S PARTICULATE SAMPLING THEORY

An overview of Gy's sampling theory can be found in Ingamells and Pitard.[6] An important element of the theory is the concept of fundamental error. Fundamental error (FE) is an inherent property of the particulate nature of geological samples. FE can never be removed from a sample, but it can be reduced by controlling the maximum particle size allowed into the sample, and increasing the sample size.

FE is the product of a several factors. In terms of the variance, σ_{FE}^2,

$$\sigma_{FE}^2 = f\, g\, m\, b\, (u')^3 / w$$

where w is the sample weight, f is the shape factor, g is the particle size distribution factor, m is the mineralogical composition factor, b is the liberation factor, and u' is the maximum allowed particle dimension.

The shape factor f accounts for the typical shape of particles in a particular sampling unit. For cubes, f is exactly 1. For spheres, f is /6 (about 0.5). For flattened particles and flakes, f is less than 0.5, and for elongated particles f can be greater than 1.

The particle size distribution factor g accounts for the different sizes of particles in the sample. If all particles were the same size as the maximum allowed, g would be exactly 1; otherwise, g lowers with the presence of fine particles. Generally, g is much less than 0.5 for the original soil sample, rises to between 0.5 and 1.0 upon sieving. The factor g can never exceed 1.

The mineralogical composition factor m accounts for the presence of analyte (lead) in the ore mineral (contaminant material) and in the gangue mineral (background soil), as well as the density of the mineral components. If the contaminant particles contain much higher concentrations of lead than background and account for the largest share of the total lead, then m is approximately the density of the contaminant material times the ratio of the lead concentration in the contaminant to the concentration of the lead in the total sample.

The liberation factor b allows the ore mineral to be contained in completely separate particles from the gangue mineral (b is exactly 1), or in attached particles (b is less than 1).

The maximum allowed particle dimension u' for soil testing is 2 mm, the opening size of the U.S. Number 10 sieve. Reduction of particle size by grinding and sieving reduces maximum particle dimension u'.

Table1: Distribution of lead by particle size in a lead-in-soil sample from the dripline of an 1874 train depot. The sample contained visible paint chips.

Min. size (mm)	Max. size (mm)	mass (g)	ppm Pb	mg Pb
2.000	& above	8.605	NA	NA
1.000	2.000	7.530	7531	56.7
0.500	1.000	13.814	1317	18.2
0.250	0.500	24.315	297	7.2
0.125	0.250	21.716	236	5.1
0.063	0.125	10.996	323	3.6
0.000	0.063	12.462	630	7.9
	Totals:	99.438		98.7

Table 2: XRF particle effect for lead-in-soil derived from lead bearing paint. The original sample from the dripline of an 1874 train depot was separated by sieve into seven particle size ranges prior to independent analysis of the fractions. Recovery (%) is the response of the sample unground relative to the same sample ground to pass 0.032 mm. Note that analytical recovery is generally poor for the largest particle sizes.

Min. size (mm)	Max. size (mm)	Recovery (%)
1.000	2.000	3
0.500	1.000	31
0.250	0.500	46
0.125	0.250	70
0.063	0.125	90
0.000	0.063	100

Table 3: Example calculations of fundamental error in lead-in-soil sampling and subsampling based on realistic assumptions of concentration and density. Note that σ_{FE} is the calculated 1-sigma relative error at an average contaminant lead concentration of 400 ppm. We assume particles to be spherical, except for paint chips, which we assume to be flat squares. Since real-world contaminants vary widely in particle size, shape, and concentration, one should view these figures as rough approximations.

Contaminant particle	Assumptions	Sample or subsample size (grams)	σ_{FE} (%)
Lead shot, 2 mm dia.	95 % Pb, density 11.3 g/cm^3	100	>100
Paint chips, 2 x 2 mm	20 mg/cm^2 Pb	100	14.1
Paint chips, 1 x 1 mm	20 mg/cm^2 Pb	100	7.1
Paint, .500 mm (#35)	15 % Pb, density 2 g/cm^3	0.3	40.5
Paint, .500 mm (#35)	15 % Pb, density 2 g/cm^3	1.0	22.2
Paint, .250 mm (#60)	15 % Pb, density 2 g/cm^3	0.3	14.3
Paint, .250 mm (#60)	15 % Pb, density 2 g/cm^3	1.0	7.8
Paint, .125 mm (#120)	15 % Pb, density 2 g/cm^3	0.3	5.1
Paint, .125 mm (#120)	15 % Pb, density 2 g/cm^3	1.0	2.8

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