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TECHNOLOGY SUPPORT PROJECT

EPA

Assessment of Errors in Soil Sampling

This fact sheet is based on "A Rationale for the Assessment of Errors in the Sampling of Soils" by J. Jeffrey van Ee, Louis J. Blume, and Thomas H. Starks, 1990.

INTRODUCTION

The sampling and analysis of soils for inorganic contaminants is a complex procedure from experimental design to the final evaluation of all generated data. Sources of error abound but they can be successfully mitigated by careful planning or isolated by intelligent error assessment. Error (or variability) can be either bias or random. Biased error is indicative of a systematic problem that can exist in any sector of soils analysis, from sampling to data analysis. The first step in analysis of variability (or error) is to establish a plan that will identify errors, trace them to the step in which they occurred, and account for variabilities to allow direct corrective action to mitigate them. In anticipation of errors, it is essential to ask two questions:

1 How many and what type samples are required to assess the quality of data in a field sampling effort?
2. How can the information from these samples be used to identify and control sources of error and uncertainty in the measurement process?

Error assessment should be understood by the field scientist and the analyst. To aid scientists in the estimation and evaluation of variability, the Environmental Monitoring Systems Laboratory-Las Vegas (EMSL-LV) has developed a computer program called ASSESS. By applying statistical formulae to data entered, ASSESS can trace errors to their sources and help scientists plan future studies that avoid the pitfalls of the past.

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RANDOM ERRORS

Random errors can result in variations from the true value that are either positive or negative but do not follow a pattern of variability. During the measurement process, random errors may be caused by:

1) sampling variations
2) handling discrepancies
3) transportation vagaries
4) preparation dissimilarities
5) subsampling problems
6) analytical discrepancies
7) data handling eccentricities

The greatest source of error is usually the sampling step. In the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (Superfund) (CERCLA) and the Resource Conservation and Recovery Act (RCRA), site investigations, analytical, and data handling variability are checked by the CLP protocol. When more than one laboratory is involved, handling, transportation, subsampling, and preparation can be checked at the Level IV CLP step, too. But how can the analyst know that the sample in the jar is representative of the surrounding samples at the site? How can the field analyst know that the more (or less) concentrated soil didn't stick to the auger or split-spoon?

It is strongly recommended that the traditional approaches used in mitigating the error in the last six steps be applied to sampling itself, i.e., use of duplicates, splits, spikes, evaluation samples, and calibration standards. A certain amount of random error is inherent in samples themselves. In fact, the total variance equals the measurement variances plus the population variances

$$(\sigma_t^2 = \sigma_m^2 + \sigma_p^2)$$

We can address the variance in measurement; the population variance, however, is a true picture of the complexity of the soil.

BIAS ERROR

Some sources of error are systematic, that is, in a given situation conditions exist that consistently give positive or consistently give negative results. This skewing of data can be initiated early in a sampling regime, e.g., by a sampling device that alters the composition of the soil matrix. It can occur in the middle of the sampling regime, e.g., by the preferential handling of a sampler who isn't trained in the intricacies of sample handling and preparation. Or it can be introduced in the later, analytical stages, where it is easier to trace because of interlaboratory comparisons and frequent calibration checks. The pervasive quality of an early bias error is its resistance to detection and the fact that other variabilities are added throughout the process until, finally, the reported data may be significantly non-representative of the true value. Bias errors can be traced to:

- faulty sampling design
- skewed sampling procedure
- systematic operator error
- contamination
- degradation
- interaction with containers
- displacement of phase (or chemical equilibria)
- inaccurate instrument calibration

PREVENTION

To avoid both random and bias errors (or at least to be able to pinpoint their occurrence and estimate their extent), it is wise to plan a study well, anticipating possible sources of error. The inclusion of quality assurance samples used for quality assessment and quality control can help isolate variability and identify its effect.

An effective technique is to concentrate duplicate sampling early in the study and send the samples off for rapid CLP analysis. Dependent on the results, it may not be necessary to include as many quality assessment samples after these samples demonstrate reliability. This allowance for early detection of sources of error can help the field scientist customize the remainder of the study to meet the specific needs of the project.

QUALITY ASSESSMENT SAMPLES

A Remedial Project Manager (RPM) must ask: how many samples are needed to adequately characterize the soil at this site? The key word is "adequately." By determining the data quality objectives (DQOs) in advance, the RPM can assure adequate sampling at a site. Too little sampling, as well as too much, is a waste of time and money. The extent of QA/QC effort is dependent on the risk to human health, the nearness of action levels to detection limits, and the size, variability, and distribution of contamination. Ultimately, the number of quality assessment samples is determined by the DQOs for the site. The following table explains various types of quality assessment samples and their uses.

QUALITY ASSESSMENT SAMPLES

- ALLOW STATEMENTS TO BE MADE CONCERNING THE QUALITY OF THE MEASUREMENT SYSTEM
- ALLOW FOR CONTROL OF DATA QUALITY TO MEET ORIGINAL DQOs
- SHOULD BE DOUBLE-BLIND:

Types of Samples	Description
Field Evaluation (FES)	Samples of known concentration are introduced in the field as early as possible to check for measurement bias and to estimate precision
Low Level Field Evaluation (LLFES)	Low concentration FES samples check for contamination in sampling, transport, analysis, detection limit
External Laboratory Evaluation (ELES)	Similar to FES but without exposure in the field, ELES can measure laboratory bias and, if used in duplicate, precision
Low Level External Laboratory (LLELES)	Similar to LLFES but without field exposure, LLELES can determine the method detection limit, and presence of laboratory contamination.
Field Matrix Spikes (FMS)	Routine samples spiked with the analytes of interest in the field check recovery and reproducibility over batches.
Field Duplicates (FD)	Second samples taken near routine samples check for variability at all steps except batch.
Preparation Splits (PS)	Subsample splits are made after homogenization and are used to estimate error occurring in the subsampling and analytical steps of the process.

- SHOULD BE SINGLE-BLIND:

Types of Samples	Description
Field Rinsate Blanks (FRB)	Samples obtained by rinsing the decontaminated sampling equipment with deionized water to check for contamination
Preparation Rinsate (PRB)	Samples obtained by rinsing the Blanks sample preparation apparatus with deionized water to check for contamination
Trip Blanks (TB)	Used for Volatile Organic Compounds (VOCs), containers filled with American Society for Testing and Materials Type II water are kept with routine samples through the sampling, shipment, and analysis phases

- MAY BE NON-BLIND: AS IN THE INORGANIC CLP PROTOCOL

SOME STATISTICAL CONCERNS

Confidence in quality assessment sample data can be expressed as an interval or as an upper limit. All confidence levels/limits are based on the number of degrees of freedom and the limits get lower (or the intervals get smaller) as the number of degrees of freedom gets higher. The number of degrees of freedom for any particular statistic is dependent upon the experimental design. For example, if 15 samples are taken at a site, and each is divided into 2 preparation splits, and each split is extracted twice at a CLP laboratory, and 2 injections of each extraction are made into an Inductively Coupled Plasma/Mass Spectrometer (ICP/MS), the total number of degrees of freedom associated with this experimental design would be calculated as:

15 samples x 2 preparations splits	=	30
X 2 CLP extractions	=	60
X 2 injection replicates	=	120

120 degrees of freedom for the whole process. But, if only the population variability in the field samples (which includes the sampling error) is being estimated, the number of degrees of freedom is 15-1, or 14. There are 15 independent samples but one degree of freedom is lost with the estimation of the mean. Therefore, there are 14 degrees of freedom for the sampling variance estimate. As another example, to estimate the variability in the extraction step, one has 30 independent pairs of numbers, each pair associated with one extraction. Thus, there are 30 degrees of freedom associated with the extraction error. In fact, this error represents any error associated with the injection step as well because, obviously, no data are available until injections are made and results are reported.

Consulting the Rationale Document or a statistical manual can give an RPM a feel for how many quality assessment samples must be sprinkled among the routine site characterization samples.

SAMPLE COLLECTION CONSIDERATIONS

If Level IV CLP analysis is performed on the soil, we can assume that very little error is in the analytical stage. This focuses our attention on sources of error in the sampling, handling, and preparation steps. The two major considerations in collection of environmental samples are:

1. Will the collected data give the answers necessary for a correct assessment of the contamination or a solution to the problem?
2. Can sufficient sampling be done well and within reasonable cost and time limits?

ASSESS

The EMSL-LV has developed an easy-to-use program to apply the necessary statistics to the generated data for an accurate determination of precision and bias. ASSESS is a public domain, Fortran program that is available from EMSL-LV. It may be applied to cases where no field evaluation samples are available as well as cases where they are. ASSESS is user-friendly and its use will greatly aid both field scientists and RPMs in decision-making based on soil studies.

FOR FURTHER INFORMATION:

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This document is available in hypertext for IBM PCs to enhance readability and aid users at all levels in knowledge of this material.

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