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Project Summary

A Rationale for the Assessment of Errors in the Sampling of Soils

J. Jeffrey van Ee, Louis J. Blume, and Thomas H. Starks

The sampling of soils in RCRA and Superfund monitoring programs requires associated quality assurance programs. One objective of any quality assurance program is to assess and document the quality of the study data to ensure that it satisfies the needs of the users. The purpose of this report is to describe the nature and function of certain quality assurance samples in the assessment and documentation of bias and precision in sampling studies of inorganic pollutant concentrations in soils. A foundation is provided for answering two basic questions:

How many, and what type of, quality assurance (or, to be more specific, quality assessment) samples are required to assess the quality of data in a field sampling effort?

How can the information from the quality assessment samples be used to identify and control the principal sources of error and uncertainty in the measurement process?

This document has been developed to provide people who plan, implement, or oversee RCRA or Superfund soil sampling studies with information on quality assessment samples so that they will have a better basis for decisions concerning the employment of such samples in their quality assurance programs.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The four principal contributions of this document are as follows:

(1) a list of names and descriptions of quality assessment samples;
(2) a rationale for determining the number of quality assessment samples to employ in a study;
(3) a description of the function of various types of quality assurance samples in determining estimates of components of measurement error variance; and
(4) a basis for the development of a computer program for computation of components of measurement error variance.

The list of names and descriptions of types of quality assessment samples in Table 1 is considered as a major contribution in that there is great need for standardization of nomenclature and terminology in soil-sampling quality assurance. The named sample types in Table 1 are classified as double blind, single blind, or non blind. A double-blind sample is one that the laboratory chemist will not recognize as a quality assurance (QA) sample. A single-blind sample is one that the laboratory chemist will recognize as a QA sample but will not know the pollutant concentration in the sample. A non-blind sample is one that the laboratory chemist recognizes as a QA sample and one for which the chemist knows the reference value for the pollutant concentration. Principal emphasis in this document is given to the double-blind and single-blind types of quality assessment samples.

***Table 1.** Type of Quality Assessment Samples or Procedures*

Double-Blind Samples

1. *Field Evaluation Samples (FES)*

These samples are of known concentration, subjected to the same manipulations as routine samples and introduced in the field at the earliest stage possible. They can be used to detect measurement bias and to estimate precision.

2. *Low Level Field Evaluation Samples (LLFES)*

These samples are essentially the same as field evaluation samples, but they have very low or non-existent concentrations of the contaminant. They are used for determination of contamination in the sample collection, transport, and analysis processes. They can also be used for determination of the system detection limit.

3. *External Laboratory Evaluation Samples (ELES)*

This sample is similar to the field evaluation sample except it is sent directly to the analytical laboratory without undergoing any field manipulations. It can be used to determine laboratory bias and precision if used in duplicate. We recommend using the same sample as the FES to allow isolation of the potential sources of error. Spiked soil samples have been used as external laboratory evaluation samples in past studies for dioxin, pesticides, and organics, and natural evaluation samples have been used for metals analysis in soil and liquid samples.

4. *Low Level External Laboratory Evaluation Sample (LLELES)*

This sample is similar to the LLFES except it is sent directly to the analytical laboratory without undergoing any field manipulations. It is used to determine method detection limit, and the presence or absence of laboratory contamination. We recommend using the same sample as the LLFES to allow isolation and identification of the source of contamination.

5. *Field Matrix Spike (FMS)*

This is a routine sample spiked with the contaminant of interest in the field. Because of the inherent problems associated with the spiking procedure and recovery it is not recommended for use in field studies.

6. *Field Duplicate (FD)*

An additional sample taken near the routine field sample to determine total within-batch measurement variability. The differences in the measurements of duplicate and associated samples are in part caused by the short-range spatial variability (heterogeneity) in the soil and are associated with the measurement error in the field crew's selection of the soil volume to be the physical sample (i.e., two crews sent to the same sampling site, or the same crew sent at different times, would be unlikely to choose exactly the same spot to sample).

7. *Preparation Split (PS)*

After a routine sample is homogenized, a subsample is taken for use as the routine laboratory sample. If an additional subsample is taken from the routine field sample in the same way as the routine sample, this additional sample is called a preparation split. The preparation split allows estimation of error variability arising from the subsampling process and from all sources of error following subsampling. This sample might also be sent to a reference laboratory to check for laboratory bias or to estimate inter-laboratory variability. These samples have also been called replicates.

Single-Blind Samples

1. *Field Rinsate Blanks (FRB)*

These samples, also called field blanks, decontamination blanks, equipment blanks, and dynamic blanks, are obtained by running distilled, deionized (DDI) water through the sampling equipment after decontamination to test for any residual contamination.

2. *Preparation Rinsate Blank (PRB)*

These samples, also called sample bank blanks, are obtained by passing DDI water through the sample preparation apparatus after cleaning in order to check for residual contamination.

3. *Trip Blank (TB)*

These samples are used when volatile organics are sampled, and consist of actual sample containers filled with ASTM Type II water, and are kept with the routine samples throughout the sampling event. They are then packaged for shipment with the routine samples and sent with each shipping container to the laboratory. This sample is used to determine the presence or absence of contamination during shipment.

Non-Blind Samples

These samples (e.g. Laboratory Control Samples (LCS)) are used in the Contract Laboratory Program to assess bias and precision. For convenience, these samples are described in Appendix E of the report with the definitions being adapted from the CLP Inorganic Statement of Work #788.

The Rationale

A basic recommendation in the report is that the number of quality assessment samples of any given type that are employed in a study should be a function of how the information from the samples will be employed. For example, if a type of QA sample is to be used in the estimation of the total measurement error variance for the study (i.e., to determine the measurement precision), then it is important that a sufficient number of the samples be employed so that the estimate of the total measurement error variance can be used with confidence in the evaluation of study results and in defending possible court challenges to study conclusions. The quality of the common estimate, s^2 of a variance depends on the number of degrees of freedom (a number directly related to the number of QA samples used in the computation) for the estimate. For example, from Table 2, if the number of degrees of freedom for a variance estimate, s^2, is only 2 and the distribution of the measurements is normal, a 95 percent confidence interval for the true variance, σ^2, is from $0.27s^2$ to $39.21s^2$ whereas, if the estimate had been based on 20 degrees of freedom, the 95 percent interval for the true variance would be $0.58\ s^2$ to $2.08\ s^2$.

Now suppose the data quality objective (DQO) for total measurement error variance is that this variance be not greater than 5, and after the survey the total measurement error variance estimate s^2 is based on only 2 degrees of freedom and $s^2 = 1$. One could not be confident that the true variance is not greater than 5 since the upper 95 percent confidence limit for the true variance is 39.21. However, if the estimate, $s^2 = 1$, had been based on 20 degrees of freedom, one could be reasonably confident that the true total measurement error variance is considerably less than 5 since the upper limit for the 95 percent confidence interval is 2.08. In establishing soil survey DQOs, one should establish data quality objectives for the estimates of data quality and use these quality objectives in determining the number of QA samples required to reach the objectives.

While estimates of measurement precision may be obtained by estimating appropriate variance components, estimates of bias are much more difficult to obtain. Bias caused by contamination is a positive bias, but may occur in such a small proportion of samples as to have little chance of being detected in the QA samples used to detect contamination. Bias related to causes other than contamination, such as incomplete recovery, will often depend on the individual sample pollutant concentration and on the individual soil sample matrix. Hence, estimates of bias based on field evaluation samples or external laboratory evaluation samples may only reflect the amount of bias for the reference concentrations and types of soil matrix of those samples and not the bias in the routine samples. Bias detection rather than bias estimation should be the primary purpose of assessment of bias. The quality assurance process should eliminate bias rather than try to estimate and adjust for it.

Unfortunately, variance estimates from any one type of QA sample will seldom provide an estimate of a variance component of interest (e.g., the variance caused by variation in the process of actually taking the physical soil sample from the earth). It often takes a combination of variance estimates from different types of QA samples to obtain an estimate of a variance component of interest. For illustrative purposes, consider a study in which soil samples are taken, submitted, prepared, and analyzed in n (≥ 2) batches each containing r routine samples, one field duplicate sample, and two field evaluation samples. The field duplicate and its associated routine sample encounter all the possible sources of error from that of locating the physical volume of soil to be extracted to the analytical error. However, the error component associated with the batch effect is the same for both samples. Hence, the difference of the measurements on the two samples contains no information about the batch effect but is a sum of the differences in errors from all other sources of error. It is for this reason that the variance estimate calculated from the pair differences over all batches,

$$s^2_{FD} = \sum_{i=1}^{n} (FD_i - RS_i)^2/(2n),$$

is an estimate of the total measurement error variance minus the between-batch error variance, $(\sigma^2_m - \sigma^2_b)$. It is important to have a good estimate of the total measurement variance, σ^2_m, but it cannot be obtained from the field duplicate QA samples alone if the study contains more than one batch and there are nonzero batch effects (i.e., $\sigma^2_b \geq 0$). The difference between the measurements of the pair of field evaluation samples (FES) is a sum of differences of all error components except batch-effect error and the error associated with the physical taking of a sample since they are in the same batch and were not obtained by the sample taking mechanism. Hence, the variance estimate based on the differences of these pairs over the n batches,

$$s^2_{WFES} = \sum_{i=1}^{n} [FES_{1i} - FES_{2i}]^2/(2n),$$

is an unbiased estimate of the total measurement error minus the sum of the sample-taking variance and the between-batch variance, $\sigma^2_m - \sigma^2_s - \sigma^2_b$. To get the between-batch variance, it is necessary to calculate the sample variance of the batch averages, $\overline{FES}_i = (FES_{1i} + FES_{2i})/2$, of the pairs of field evaluation samples.
This sample variance,

$$s^2_{BFES} = 2 \sum_{i=1}^{n} [\overline{\overline{FES}}_i - \overline{\overline{FES}}]^2/(n-1),$$

is an unbiased estimator of $(\sigma^2_m - \sigma^2_s + \sigma^2_b)$. Now unbiased estimates s^2_m, s^2_s, and s^2_b, of total measurement error variance, sample-taking error variance, and between-batch error variance may be obtained by solving for them in the three equations,

$$s^2_m - s^2_b = s^2_{FD}$$

$$s^2_m - s^2_s - s^2_b = s^2_{WFES}$$

$$s^2_m - s^2_s + s^2_b = s^2_{BFES}$$

to obtain

$$s^2_m = s^2_{FD} + (s^2_{BFES} - s^2_{WFES})/2$$

$$s^2_s = s^2_{FD} - s^2_{WFES}$$

and

$$s^2_b = (s^2_{BFES} - s^2_{WFES})/2$$

These equations explain why pairs of field evaluation samples were employed in each batch; for if only one FES had been placed in each batch, it would have been impossible to obtain an unbiased estimate, s^2_m, of the total measurement error variance. It should be noted that if one wants a reasonably accurate estimate of the total measurement error variance, it is necessary to have a large number of degrees of freedom for each of the estimates, s^2_{FD}, S^2_{WFES}, and s^2_{BFES}. Further, it would be wasteful to have a large number of degrees of freedom for one of these three estimates and a small number for another, since the estimate of the total variance cannot be more precise than the least precise term in its formula. In the above example, the variance estimates s^2_{FD}, s^2_{WFES}, and s^2_{BFES}, had n, n, and (n-1) degrees of freedom respectively. The choice of n will depend on the DQO for the precision of these variance estimates. The report suggests that for estimation of total measurement error, an n of at least 20 might be a reasonable DQO requirement for most studies.

Table 2. *Some 95 Percent Confidence Intervals for Variance*

Degree of Freedom	*Confidence Interval*
2	$0.27s^2 \le \sigma^2 \le 39.21s^2$
3	$0.32s^2 \le \sigma^2 \le 13.89s^2$
4	$0.36s^2 \le \sigma^2 \le 8.26s^2$
5	$0.39s^2 \le \sigma^2 \le 6.02s^2$
6	$0.42s^2 \le \sigma^2 \le 4.84s^2$
7	$0.44s^2 \le \sigma^2 \le 4.14s^2$
8	$0.46s^2 \le \sigma^2 \le 3.67s^2$
9	$0.47s^2 \le \sigma^2 \le 3.33s^2$
10	$0.49s^2 \le \sigma^2 \le 3.08s^2$
11	$0.50s^2 \le \sigma^2 \le 2.88s^2$
12	$0.52s^2 \le \sigma^2 \le 2.73s^2$
13	$0.53s^2 \le \sigma^2 \le 2.59s^2$
14	$0.54s^2 \le \sigma^2 \le 2.49s^2$
15	$0.54s^2 \le \sigma^2 \le 2.40s^2$
16	$0.56s^2 \le \sigma^2 \le 2.32s^2$
17	$0.56s^2 \le \sigma^2 \le 2.25s^2$
18	$0.57s^2 \le \sigma^2 \le 2.19s^2$
19	$0.58s^2 \le \sigma^2 \le 2.13s^2$
20	$0.58s^2 \le \sigma^2 \le 2.08s^2$
21	$0.59s^2 \le \sigma^2 \le 2.04s^2$
22	$0.60s^2 \le \sigma^2 \le 2.00s^2$
23	$0.60s^2 \le \sigma^2 \le 1.97s^2$
24	$0.61s^2 \le \sigma^2 \le 1.94s^2$
25	$0.62s^2 \le \sigma^2 \le 1.91s^2$
30	$0.64s^2 \le \sigma^2 \le 1.78s^2$
40	$0.67s^2 \le \sigma^2 \le 1.64s^2$
50	$0.70s^2 \le \sigma^2 \le 1.61s^2$
100	$0.77s^2 \le \sigma^2 \le 1.35s^2$

An Alternative Method for Assessing Variability without Field Evaluation Sample

The basic use of the FES in the preceding section was to estimate between batch variance. As an alternative, it is suggested that additional field duplicates may be employed for this purpose. One may go back to a particular sampling location (i.e., a point at which one sample of soil is taken), and take a fresh (collocated) sample to include with each batch (or with at least 21 randomly selected batches if there are a larger number of batches). If it is difficult to take so many collocated samples from one sampling location, one might use two or three such locations and take collocated samples to include in the batches, alternating between locations (e.g., for two sampling locations A and B, batch 1 has a collocated sample from location A, batch 2 from location B, batch 3 from location A, ...). By comparing the variability between collocated samples that are collected and analyzed in different batches, with the variability within the field-duplicate-and-associated-routine-sample pairs, one can estimate the variability contributed by changes in the measurement process between batches. These collocated samples are actually field duplicates, but because they are used in a different way than the field duplicates encountered in the previous section, they will be identified as batch field duplicates (BFD).

As with the process utilizing field evaluation samples,

$$s^2_{FD} = \sum_{i=1}^{n}(FD_i-RS_i)^2/(2n),$$

is an estimate of the total measurement error variance minus the between-batch error variance, $(\sigma^2_m - \sigma^2_b)$.

The estimate of variance obtained from field duplicates inserted in each batch,

$$s^2_{BFD} = \sum_{i=1}^{m}(BFD_i-\overline{BFD})^2/(m-1), \quad (1)$$

or

$$s^2_{BFD} = \frac{\sum_{j=1}^{L}\sum_{i=1}^{m}(BFD_{ij}-\overline{BFD}_j)^2}{\sum_{j=1}^{L}(m_j-1)} \quad (2)$$

provides an assessment of measurement error variance, σ^2_m.

(1) This equation is appropriate when the m batch field duplicate samples are all taken from one sampling location. $\overline{BFD}$ is the sample mean of the m samples.

(2) This equation is appropriate when the batch field duplicate samples are from L locations with m_j (>1) BFDs coming from sampling location j. $\overline{BFD}_j$ is the sample mean of the m_j samples taken for location j.

The difference between the variance estimates utilizing field duplicates and batch field duplicates (s^2_{BFD}-s^2_{FD} provides an estimate of between batch variance, σ^2_b.

Conclusions and Recommendations

Estimation of variance components as has been described above typically involves data transformations so as to stabilize variance of measurements relative to sample pollutant concentrations, and it also involves a considerable amount of computation. To simplify this work and to help eliminate computational errors, a computer program ("ASSESS") has been developed to perform these computations once the data and the nature of the transformation have been entered into the computer. Use of this prototype program is recommended for those who wish to adopt the rationale.

Much emphasis has been devoted to the assessment and reduction of bias and variability in the analytical phases of a study. The rationale presented in the report allows for this variability to be assessed together with variability from other sources. Proper choice and timing of QA materials in a study provide the data to document the *total* quality of the collected data and provide the foundation for judicious corrective actions when the data quality is insufficient to meet the needs of the user.

The EPA authors, **J. Jeffrey Van Ee** (also the EPA Project Officer, see below) and **Louis J. Blume**, are with the Environmental Monitoring Systems Laboratory, Las Vegas, NV 89193-3478. Thomas H. Starks is with the Environmental Research Center, UNLV, Las Vegas, NV 89154.

The complete report, entitled "A Rationale for the Assessment of Errors in the Sampling of Soils," (Order No. PB 90-242 306; Cost: $17.00, subject to change) will be available only from:

National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: 703-487-4650

The EPA Project Officer can be contacted at:

Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Las Vegas, NV 89193-3478

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