WASHINGTON STATE
DEPARTMENT OF
ECOLOGY

# Guidelines for Preparing *Quality Assurance Project Plans* for Environmental Studies

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# Abstract

Each environmental study conducted by or for the Washington State Department of Ecology (Ecology) must have an approved Quality Assurance (QA) Project Plan. The QA Project Plan describes the objectives of the study and the procedures to be followed to achieve those objectives.

The preparation of a QA Project Plan helps focus and guide the planning process and promotes communication among those who contribute to the study. The completed plan is a guide to those who carry out the study and forms the basis for written reports on the outcome.

This document presents detailed guidance on the preparation of QA Project Plans. It describes 14 elements to be addressed in the plan and provides supporting information and examples relevant to the content of each element.

This document replaces Ecology Document 91-16, *Guidelines and Specifications for Preparing Quality Assurance Project Plans*, May 1991.

# Introduction

Washington State Department of Ecology (Ecology) Policy 1-21 requires the preparation of a Quality Assurance (QA) Project Plan for each study that acquires environmental measurement data. This document describes the content of a QA Project Plan for studies conducted by or for Ecology. The QA Project Plan integrates the contributions of everyone involved in the study into a statement of exactly what needs to be accomplished, how it will be done, and by whom. It is a guide for those who implement the study as well as a basis for preparing reports on the outcome. The content and level of detail in a QA Project Plan depend on the type of project and the intended use of the data.

The preparation of a QA Project Plan should be a team effort coordinated by the project manager. The team includes (where applicable) the client, representatives of the analytical laboratory, field staff, and anyone else who will contribute to the study. The team might also include specialists in QA, information management, and statistics in an advisory capacity. Once the goals of the study have been formulated, a meeting of the project team should be held to develop specific objectives for the project and to decide on the best methods to achieve them.

Field work should not begin until the plan has been approved and distributed for implementation by the appropriate personnel.

Some Ecology staff conduct studies that are similar in nature, and others are involved in emergency response activities.

- Once a good QA Project Plan has been prepared for one study, it may be used as a template for planning similar studies. Information specific to a new study can be inserted into the original plan.
- For emergency response activities, the QA Project Plan should be prepared in advance based on available knowledge and experience, and then updated as needs evolve. In this case, the plan becomes a valuable training tool for emergency response staff.

Some programs require preparation of Sampling and Analysis Plans (SAPs). These documents generally cover the details of sampling and analysis required in a QA Project Plan and include a Health and Safety Plan. SAPs do not adequately address background, goals, objectives, and data assessment. The authors recommend that a QA Project Plan be prepared with the SAP included as an attachment.

Preparation of a QA Project Plan requires an understanding of some basic concepts of sampling, field and laboratory procedures, statistical analysis, and data quality assurance. This document includes appendices covering some of these concepts, beginning with a glossary of terms in Appendix A.

This document replaces Ecology Document 91-16, *Guidelines and Specifications for Preparing Quality Assurance Project Plans,* May 1991.

# What is Quality Assurance?

In this document, Quality Assurance means a process for ensuring the reliability of measurement data. QA principles and practices enable you to acquire data of the type and quality you need. Data must be of documented quality in order to be scientifically and legally defensible.

Data Quality Assurance in the Department of Ecology includes:

- The agency QA Policy (Executive Policy 1-21) and Quality Management Plan
- Manchester Environmental Laboratory QA Manual
- Manchester Environmental Laboratory *Lab Users Manual*
- Staff training in the principles and practices of Data Quality Assurance
- Preparation and use of QA Project Plans
- Preparation and use of Standard Operating Procedures (SOPs)
- Use of appropriate Quality Control (QC) Procedures
- Review, verification, and validation of data
- Assessment to determine whether the data support the project objectives
- Quality improvement through audits of systems and performance
- Accreditation of environmental laboratories providing data to Ecology

Ecology staff make important decisions on strategies for protecting the environment and dealing with pollution. Physical, chemical, and biological data often form the basis for these decisions. Quality Assurance helps ensure that data acquired by and for Ecology support correct decisions.

The potential consequences of inadequate data quality include:

- Faulty decisions
- Wasted resources
- Legal liability
- Increased risk to human health and the environment
- Inadequate understanding of the state of the environment
- Loss of credibility
- Unnecessary regulation

# Quality Assurance Project Plans

## What is a QA Project Plan?

A project or study is a logical sequence of activities grouped into three categories:

Planning → Implementation → Assessment

A QA Project Plan documents the planning phase and guides implementation and assessment.

A QA Project Plan

- Lists the objectives of a study
- Identifies the type and quality of data needed to achieve those objectives
- Describes the sampling, measurement, quality control, and assessment procedures needed to acquire those data

## Why Prepare a QA Project Plan?

The purpose of preparing a QA Project Plan is to ensure that all necessary steps are taken to acquire data of the type and quality needed. Systematic planning is essential to the successful acquisition of useful environmental data. Once you begin field work, your options are limited by what you know and what you have with you.

Systematic planning should be based on the scientific method and professional expertise. The levels of effort and detail in the planning process should be commensurate with the importance of the study and available resources. The planning process generates acceptance criteria for the quality of the data and for the quality of decisions made on the basis of those data.

Preparation of a QA Project Plan serves these important functions:

- Focuses the project team on issues affecting data quality while they can still do something about them (i.e., before data are acquired).
- Promotes and facilitates communication among those involved in the project.
- Compiles some of the information needed for reports on the outcome of the study.

The credibility of your data may be compromised if the procedures used to acquire them are not adequately documented. The QA Project Plan provides important initial documentation of your study and identifies other necessary documentation such as:

- Standard operating procedures (SOPs)
- Field logs
- Chain-of-custody records
- Lab records and reports
- Photos and drawings
- Project reports

Ultimately the QA Project Plan can only be considered a success if it is fully implemented and the required data are obtained. It is necessary to assess projects to verify whether this is the case.

## When is a QA Project Plan Required?

A QA Project Plan is required for any study that acquires environmental data that will be used by Ecology.

## Who Should Prepare a QA Project Plan?

Those with responsibility for QA Project Plans include:

- Ecology staff with overall responsibility for conducting a project (project managers) prepare QA Project Plans with input from their project team.

- Staff who administer grants or contracts for projects which acquire environmental data ensure that satisfactory QA Project Plans are prepared by the grantees or contractors.

- Staff with oversight responsibility for projects conducted to comply with regulations or agreements ensure that satisfactory QA Project Plans are prepared by the responsible parties.

Agency QA staff are available to assist with the preparation and review of project plans and with the development of QA requirements for inclusion in grants and contracts.

## Who Reviews and Approves a QA Project Plan?

QA Project Plans are generally reviewed by the project manager's supervisor, the client, laboratory QA staff (if laboratory services are required), and the program QA coordinator

or agency QA officer. Some programs have standing procedures governing review and approval of QA Project Plans. Reviewers check the plans for errors or omissions and provide comments and suggestions for improvement. Environmental Assessment Program staff with specialized expertise may be available to review your plan. Appendix B is a checklist for reviewing QA Project Plans.

The project manager makes any necessary changes to the plan based on reviewers' comments and submits the revised plan for approval signatures. The plan should be approved by the project manager's supervisor, the client, a representative of the laboratory (if laboratory services are required), the program QA coordinator or agency QA officer, and other key staff as appropriate. The agency QA officer must approve all project plans submitted to EPA. For projects conducted under a grant or contract, the Ecology grant or contract administrator approves the plan as well.

Copies of the approved QA Project Plan are distributed to the signatories and to everyone responsible for implementing the study. If the study is unusual or particularly complex, the project manager should convene a meeting of the project team to discuss and answer questions about the plan.

The QA Project Plan should be approved and distributed before field work is started. The plan is a living document that should be updated during the course of a study whenever it is appropriate to do so.

## What is the Role of the Laboratory in a Project?

The management and staff of the laboratory contribute to the success of the project by:

- Advising on selection of analytical methods
- Reviewing and approving the QA Project Plan
- Providing containers and other sampling supplies
- Analyzing samples using the methods selected for the project
- Carrying out appropriate QC procedures
- Reporting results for samples and QC procedures
- Reviewing and verifying results

# What are the Elements of a QA Project Plan?

The following elements comprise a complete QA Project Plan.

1. Title Page with Approvals
2. Table of Contents and Distribution List (optional)
3. Organization and Schedule
4. Background and Problem Statement
5. Project Description
6. Data Quality Objectives
7. Sampling (Experimental) Design
8. Field Procedures
9. Laboratory Procedures
10. Quality Control
11. Data Management Procedures (optional)
12. Audits and Reports (optional)
13. Data Review, Verification and Validation
14. Data Quality Assessment

All of the above elements, except 2, 11, and 12, are required in every QA Project Plan. The project manager may decide that the three optional elements can be omitted or merged into other elements. Factors which influence these decisions include the scope and complexity of the project, the number of staff involved and their level of expertise, and past problems which could be avoided by clearly stating expectations in the plan. Criteria to help the project manager make these decisions are provided in the discussion of the individual elements below.

The level of detail in a QA Project Plan depends on the type and complexity of the project and the intended use of the data. The information in the QA Project Plan must be sufficiently detailed to allow those responsible for review and approval of the plan to understand what is to be done and the reasons for doing so.

Documents containing information relevant to the study are referenced in, or appended to, the QA Project Plan.

Project plans prepared to meet EPA requirements must address the elements described in EPA Documents QA/R-5, *EPA Requirements for Quality Assurance Project Plans* (EPA, 1999), and QA/G-5, *Guidance for Quality Assurance Project Plans* (EPA, 1998). See Appendix C for a list of those elements. The information in this guidance will be helpful in meeting those requirements as well.

# 1. Title Page with Approvals

The following information is presented on the cover page of the plan:

- Title
- Author
- Author's organization
- Date the plan was prepared or revised
- Other information useful in identifying the study (e.g., a document, grant, geographic location, or contract identifier)

At the bottom of the page, provide spaces for approval signatures and dates. The plan should be approved by:

- Project manager
- Project manager's supervisor
- Client
- Representative of the laboratory, if a lab is involved in the project
- Program QA coordinator or agency QA officer
- Other key staff as appropriate

The agency QA officer must approve all project plans submitted to EPA. For projects conducted under a grant or contract, the Ecology grant or contract administrator approves the plan as well.

## 2. Table of Contents and Distribution List

Include a Table of Contents if it would be helpful to those using the plan. The longer the plan, the more useful the Table of Contents. It directs the user to the project plan elements and to tables, figures, references, and appendices.

Those who will receive copies of the approved plan, along with their affiliation and address, may be listed after the Table of Contents.

## 3. Organization and Schedule

Begin by identifying the members of the project planning team whose input is necessary to develop the plan. Also identify the decision-makers and the stakeholders, those directly affected by the outcome of the study.

Study participants need a clear understanding of their roles and their relationship to the overall effort. A planning team meeting is a good place to discuss individual roles and responsibilities and the schedule for implementing the plan.

Identify everyone involved in implementation of the study and use of the data and describe their responsibilities. Include names, organizations, and phone numbers of key personnel.

For large studies, an organization chart showing the lines of communication among participants should be included.

Include a timetable for the project. Provide dates for

- Reconnaissance visits
- Field activities
- Delivery of samples to the laboratory
- Reporting laboratory results
- Data entry to the EIM database
- Progress, draft, and final reports, as needed
- Disposal of samples

Describe limitations imposed on the schedule by factors such as weather, seasonal conditions, availability of equipment, etc. Be sure to keep the laboratory informed of your schedule for delivery of samples.

Finally, the budget for the study, as well as credit for financial support, may be presented here.

# 4. Background and Problem Statement

This element documents the historical basis for the project and the problem to be studied. Provide enough background information so that the reasons for conducting the study are clear.

The idea is to give the reader a perspective of the present situation and the events leading up to it. It may be necessary to make a reconnaissance visit to gather information on conditions, accessibility, and activity in the area before completing this element of the plan.

- Describe the site and surroundings in sufficient detail that reviewers can determine whether the study design and field procedures are appropriate. Include maps, photos, or drawings showing sampling locations and salient features of the site or area.

- Relate the history of the site, emphasizing sources, forms, quantities, and fates of known or suspected contaminants. This is called a "conceptual model" of the problem and may be described with the help of a drawing or photograph.

- Identify applicable regulatory requirements or criteria.

- Summarize existing data, using tables and charts if necessary, to demonstrate that the problem is correctly defined and has not been solved previously. Reference reports from previous studies conducted in the area.

- Mention any logistical problems with the site, such as limited access or the presence of hazardous substances, which require unusual procedures.

- In the context of the above background information, describe in general the problem(s) to be studied. Two examples are:

  *Determine whether nitrate is present in the ground water under the site.*

  *Determine whether marine sediments in the area are contaminated with cadmium.*

# 5. Project Description

## Goals and Decision Statement

Identify the decision(s) to be made based on the data you will acquire. List the question(s) the study will attempt to answer and the actions that may result. The types of questions a study might resolve include:

- Do the concentrations of contaminants in the discharge meet permit limits?
- Does the concentration of the pollutant in the soil pose a human health risk?
- Is the concentration of the contaminant above background levels?

Combine the study question and alternative actions into a decision statement.
The answer to the study question will provide the basis for determining the course of action that should be taken to solve the problem.

Examples of decision statements:

> *Determine whether the concentration of nitrate in the groundwater poses an unacceptable health risk that requires notification of nearby residents to monitor their drinking water.*
>
> *Determine whether the concentration of cadmium in the sediment exceeds the Sediment Quality Standard and requires removal of the sediment, or is close enough to the standard to merit systematic monitoring.*

These are your goals for the project, and they must be specific, realistic, and measurable.

## Objectives

It is essential to document your objectives carefully, because they are the basis for the rest of the plan. Clear objectives preclude unrealistic expectations and facilitate planning and communication. Do not attempt to complete any of the subsequent elements of the plan until your objectives are stated clearly and completely.

On the basis of the problem identified in Element 4 and the decision statement above, state the objectives for the study. Use explicit statements of exactly what the study will accomplish. Objectives lead to achieving your goal.

Identify the information needed to meet those objectives and potential sources of that information. Determine which information is already available and which requires environmental measurements.

Identify the target population. The target population might be one of the strata in a lake in the springtime, contaminated soil at an abandoned industrial facility, or tissue from the shellfish in a particular estuary. The population is characterized by its boundaries in time and space as well as its relationship to its surroundings.

Define the study boundaries in time and space to help ensure that data will be representative of that population.

An objective of many environmental studies is to acquire data for comparison to specific regulatory criteria or to existing data. The comparison then forms the basis for a decision on whether some action is required. Decisions are rarely made on the basis of a single result.

For each parameter that you intend to measure, define:

- the statistic you will use to describe the target population (e.g., mean)
- the scope of the decision in space and time
- the applicable action level
- alternative courses of action

Write a statement that defines how the decision-maker will choose among the alternative courses of action (EPA calls this a "decision rule"). Examples are

> *If the mean of the concentrations of nitrate-nitrogen in the monthly samples from any of the test wells exceeds 10 mg/L, well owners down gradient of the site will be informed of the results and advised to monitor their wells monthly. If the concentration does not exceed 10 mg/L, well owners will be informed of the results but no warning will be issued.*
>
> *If the mean concentration of cadmium in the samples of the top six inches of sediment exceeds 50 mg/kg (wet weight), recommend immediate removal of that layer of sediment to an approved disposal site. If the mean concentration of cadmium in those samples is between 10 and 50 mg/kg, recommend periodic monitoring of the sediment layer on a specified schedule. If the mean concentration of cadmium in those samples is less than 10 mg/kg, recommend that no action be taken.*

When the mean concentration equals the criterion or regulatory limit, there is only about a 50% chance an individual measurement result will equal or exceed the limit, because the distribution of results around the mean is symmetrical. The level on which the ultimate decision is based may be different from the criterion or regulatory limit when the data quality objectives are developed as described later. See Appendix D for a discussion of the effect of errors on decisions.

Finally, identify any practical constraints on the study design, such as seasonal or meteorological conditions, limited access, or availability of personnel or equipment. Use existing information and professional judgement to stratify or segregate the population into categories with homogenous characteristics.

# 6. Data Quality Objectives

There are several factors that affect the quality and usefulness of data, and impact the decisions made on the basis of those data. The overall quality of your data is determined by a combination of those factors. Data may be affected by systematic errors in the form of bias and are always subject to random errors. Appendix D provides additional information on the effects of errors on decisions.

## Bias

A measurement result is a numerical estimate of a population parameter obtained by carrying out the procedures specified in a method. If a physical or chemical measurement is repeated many times using sufficiently sensitive procedures, the results will be distributed symmetrically about their mean value. Bias is the difference between the mean of an infinite number of replicate results (population mean) and the true value of the parameter being measured.

Potential sources of bias include:

- Sampling procedures
- Instability of samples during transportation, storage, or processing
- Interference effects
- Inability to measure all forms of the parameter of interest
- Calibration of the measurement system
- Contamination of equipment, reagents, or containers

Bias due to sample collection, transportation and storage must usually be inferred through alert observation and professional judgement. These errors can be avoided or minimized through careful use of standardized procedures by properly trained staff. Bias affecting measurement procedures can be inferred from the results of quality control (QC) procedures involving the use of blanks, check standards, and spiked samples described in Element 10, *Quality Control*. It is not generally possible to directly estimate the total bias of analytical results. Instead, each of the potential sources of bias is assessed based on QC results and other observations.

When a measurement result is to be used to decide whether the true value exceeds a criterion or standard, the possibility of bias must be considered since unidentified bias can lead to an erroneous conclusion. The most effective way to deal with bias is to select sampling and measurement procedures that are not likely to introduce systematic error in the first place.

Note that if a decision will be based on the difference between two results that are likely to be equally biased, that difference may not be biased. An example might be the comparison of semivolatile organics results for samples from upstream and downstream of an outfall.

## Precision

Precision is a measure of the variability in the results of replicate measurements due to random error. Random errors are always present because of normal variability in the many factors that affect measurement results. Precision can also be affected by the variations of the true concentrations in the media being sampled.

The dispersion (width) of the normal probability distribution represented by the standard deviation provides an estimate of precision. See Appendix E for the equations for estimating precision. Note that any estimate of a population parameter can be improved by increasing the number of results used to calculate it.

Existing data may offer an indication of the precision you can expect from the data you plan to acquire.

It may be more efficient to use less precise and less expensive screening techniques if they can meet your data quality objectives. Remember that the standard error (i.e., precision) of the mean is given by $s/\sqrt{n}$, where s is the estimated standard deviation for the population of individual analytical results. Therefore, if you use the mean of n values as your result, the precision of that result improves by a factor of $1/\sqrt{n}$ over that of an individual result (see Appendix E). Thus, a result obtained by averaging the values from several replicate measurements may be as precise as a single value obtained by a procedure with better precision.

## Reporting Limits

An important consideration for data quality is selection of procedures capable of producing accurate results at the concentration used for decision-making (i.e., the standard, criterion, or regulatory limit). It is important that the method used for analysis has a reporting limit well below this level, since precision near the detection limit is not good and decisions should not be based on imprecise data. A rule of thumb is that the reporting limit should be at least 10 times lower than the reference concentration. Specify the required reporting limit for the project, and have the laboratory confirm their ability to report results down to the reporting limit.

## Measurement Quality Objectives

Data Quality Objectives (DQOs) answer the question of how accurate data need to be in order to make correct decisions. Measurement Quality Objectives (MQOs) answer the question of how accurate the measurements need to be in order to get accurate data. DQOs are the driver for MQOs.

The total error E in result R is given by E = R – T, where T is the true value. Accuracy is a measure of the magnitude of E and is a function of precision and bias such that

$$\text{Accuracy} = \text{Bias} + 2 \times \text{RSD}$$

where accuracy and bias are expressed as percentages of the true value, and RSD is the percent relative standard deviation. See Appendix E for the equation. Accuracy is said to improve as the total error decreases.

Prepare a table listing targets for accuracy, precision, bias, and required reporting limits for each parameter. These are your MQOs. If you intend to draw conclusions or make decisions based on individual measurement results, they are also your DQOs. This table provides the basis for subsequent selection of field, laboratory, and quality control procedures. An example of a completed table is found in Appendix F.

The MQOs depend on the particular application, and each case needs to be considered individually. For example, in water quality monitoring a target of 20% total error, equally divided between random and systematic errors, may be used for many parameters.

It may not be possible to meet the percentage targets for MQOs at very low concentrations because the relative error increases rapidly near the detection limit. MQOs expressed in concentration units may be needed for projects involving trace analyses.

For some projects, it may be advisable to have an experimental design for preliminary estimates of precision and some sources of bias. This ensures that MQOs are met before any of the project samples are collected for analysis. *The Chemical Analysis of Water* (Hunt and Wilson, 1986) includes an experimental design for this purpose.

In addition to the MQOs for precision, bias, and lower reporting limit, MQOs can be specified for quality control acceptance or performance criteria. Whether or not these criteria are specified as MQOs, they are the basis for assessing whether the MQOs for precision and bias have been met.

## EPA's Data Quality Objectives Process

Many projects will only need to specify MQOs, which correspond to the objectives for individual measurement or analytical results. In this case, the objectives for sampling error are not quantified. Instead, operational procedures are specified that will control sampling error, and total precision is documented in terms of the results for field duplicates.

Some projects require a more precise estimate of the population parameter than is provided by individual results. Then another approach is needed, such as the seven-step

Data Quality Objectives Process developed by EPA. That improved estimate can be obtained by taking additional measurements or collecting and analyzing additional samples and averaging the results. For example, if you compare the mean of the results for several soil samples to a cleanup standard, the uncertainty in the mean will be less than the uncertainty in any individual result. This is the basis for the DQO Process. Note that bias is not reduced by taking more measurements.

The DQO Process is described in detail in EPA documents QA/G-4 (EPA, 2000a) and QA/G-4HW (EPA, 2000b). In that process, a decision rule is used as the basis for specifying statistical limits on decision errors. EPA's DQO Process considers only random error in measurement results and assumes those results are unbiased. Systematic planning processes have been adopted by other federal agencies, but they differ somewhat from EPA's DQO Process. For example, the U.S. Army Corps of Engineers adopted a four-step Technical Planning Process to implement systematic planning for cleanup activities.

# 7. Sampling (Experimental) Design

Design your study using the information developed in Elements 4, 5 and 6. It may be helpful to evaluate alternatives and select the most efficient design that will satisfy your objectives. Some regulatory programs have specific requirements for sampling design; these should be described or referenced in this element.

Your description of the study design should cover:

- Measurements to be taken and samples to be collected
- Locations and schedule for sampling and measurements
- Chemical, physical, and biological parameters to be determined

Include maps or diagrams showing the physical boundaries of the study area as well as measurement and sampling locations.

Some studies may need to include reconnaissance sampling to aid in the selection of sampling locations, and this also should be included in the study design.

In addition, discuss any assumptions that underlie the study design as well as how the design relates to the study objectives and to characteristics of the site/area described in the background information. Explain how the proposed sampling frequency and locations relate to the expected temporal and spatial variability of the parameters of interest.

Measurement results are an estimate of the value of a characteristic of a target population. The validity of that estimate is affected by the location, timing, and procedures selected for field measurements, sampling, and analysis.

Sometimes sampling locations are defined by the project objectives (e.g., characterize the effluent at the outfall). In other cases, a sampling strategy must be developed. Sampling may be based on probability or professional judgement. Remember that statistical methods are tools to be used in support of common sense and professional judgement, not as a substitute for either.

When decisions on sampling will be made in the field, describe the determining factors.

## Representativeness

Obtaining representative measurements or samples requires a good sampling design as well as good execution of that design. A result is representative of a population when it reflects accurately the desired characteristic of that population. This sounds like a simple concept, but obtaining representative data requires careful planning. First of all, the target population must be clearly defined in Element 5, *Project Description*. The sample must be taken, or measurement made, at the appropriate time and place using an

appropriate procedure. Finally, the sample must be handled in such a way that it remains unchanged until it is analyzed. Procedures for obtaining representative results are described in Element 8, *Field Procedures*.

If the order of sampling is important, it should be described here. For example, it is a good idea to try to collect the samples in order of increasing concentration to minimize cross-contamination from the sampling equipment. It is also advisable to sample from downstream to upstream to avoid contaminating the downstream samples. An exception to this would be time of travel sampling, which has the objective of sampling the same block of water. There may be holding time considerations as well.

Sample collection should be scheduled to best characterize the problem. For example, non-point impacts on water quality often are related to certain land use activities and weather conditions. If samples are not collected when those activities are going on or during typical weather patterns, the results may not be representative of their impact on water quality.

Be aware of ancillary parameters that are necessary to evaluate a contaminant of interest against a criterion or standard. For example, hardness is a factor in calculating the water quality standard for several metals.

Information on representative sampling designs is available in several of the references listed at the end of this document. For example, EPA Document QA/G-5S, *Guidance for Choosing a Sampling Design for Environmental Data Collection* (EPA, 2001) provides information on environmental study design. Also, Ecology Document 91-78, *Technical Guidance for Assessing the Quality of Aquatic Environments* (Ecology, 1994a) includes chapters on planning and study design, water quality assessment, TMDL analysis and biological surveys.

Many Environmental Assessment Program staff are experts in sampling environmental media and may be consulted for advice.

## Comparability

If you want to compare your data with other data, the issue of comparability will need to be addressed in the project plan. Comparability is ensured by selection and documentation of standardized procedures and by clearly stating any non-standard requirements.

Describe the critical characteristics of the existing data. Then select procedures that will ensure your project data will match those characteristics. Some critical characteristics might involve timing, type of sampler used, or the analytical or measurement method selected.

Composite sampling (i.e., physically combining and homogenizing environmental samples or subsamples to form a new sample) can also lower the cost of improving precision. Averaging the analytical results of a few composites can produce an estimated mean that is as precise as one based on many more individual sample results.

# 8. Field Procedures

The procedures selected for field measurements and sampling affect the accuracy, representativeness, and comparability of your results. Sampling may account for more variability in your results than the measurement process.

Field measurements and sample collection activities must not significantly disturb the environment being sampled. For instance, sediments in streams, lakes, and estuaries are easily resuspended; the surface microlayer concentrates some contaminants in quiet waters; and exhaust or fluids from a vehicle can contaminate your samples. These kinds of potential problems must be addressed in the planning process in order to obtain representative samples. After collection, samples must remain stable during transport and storage. Careful adherence to documented procedures for sample collection, preservation, and storage will minimize errors due to sampling and sample instability.

Describe in detail or reference the procedures for taking measurements in the field and for collecting samples. Referenced SOPs or published procedures must be up-to-date and readily available. If a referenced method offers various options, specify the particular options to be used in this study.

The Puget Sound Water Quality Action Team publishes procedures for environmental sampling and analysis, *Puget Sound Protocols and Guidelines,* which are available at their web site listed in Appendix H.

Include a table listing containers, sample size, preservation, and holding times for each parameter. Requirements for containers, sample size, preservation and holding times are available from the laboratory. The Ecology Intranet site contains this information at http://aww.ecoweb/eap/pubs/labmanual.pdf. An example of a completed table is found in Appendix F.

Describe the procedures for decontamination of sampling equipment and disposal of waste from field operations. Decontamination waste must be disposed of according to federal, state, and local regulations.

Describe the sample identification scheme. List the information to be recorded on the sample labels, such as identifying number, location, date, time, sampler's initials, parameters and preservatives. Plan to prepare labels and forms before you leave for the field.

Describe the procedures and assign responsibility for transporting samples to the lab. Make sure the samples will arrive in time for analysis before the holding times expire. Include a copy of the form which accompanies the samples to the laboratory with examples of required entries.

If your data may be needed for legal purposes, follow formal chain-of-custody procedures, such as those described in the Manchester Environmental Laboratory *Lab Users Manual*. You have custody of a sample if it is in your possession, under your control, or in a secure area with access restricted to authorized personnel. Describe or reference any such procedures.

Detailed notes on field activities must be kept in a bound notebook with consecutively numbered pages to ensure that data are legally defensible. Notebooks with waterproof paper are available for field notes. Entries must be made in permanent ink and must be initialed and dated. Corrections are made by drawing a single line through the error so it remains legible, writing the corrections adjacent to the errors, and initialing the correction.

Notes on the collection and handling of samples should be sufficiently detailed to allow the data user to understand and evaluate the procedures. It is helpful to include a sample of the required field log entries such as:

- Name of the project and the location
- Identity of field personnel
- Sequence of events
- Changes to the plan
- Site and atmospheric conditions
- Number of samples collected
- Date, time, location, identification, and description for each sample
- Field measurement results
- Identity of QC samples
- Unusual circumstances which affect the interpretation of the data.

Include plans for taking pictures of key features of the site or of the sampling process.

Other activities you may want to describe:

- Briefings and training for field staff
- Calibrating and checking measurement and test equipment
  - ◊ identify equipment
  - ◊ procedures and standards to be used
- Periodic preventive maintenance (PM) of measurement and test equipment
  - ◊ identify equipment
  - ◊ schedule of PM
- Homogenizing non-aqueous matrices
  - ◊ procedures
  - ◊ equipment
- Notifying the lab about sample shipments
  - ◊ procedures
  - ◊ responsibility

# 9. Laboratory Procedures

Before submitting samples to the laboratory, coordinate with lab staff for their services. The first contact might be a phone call or e-mail indicating what you are planning to do. If you hold a planning team meeting, include a representative from the lab. Lab staff can help select analytical methods that will enable you to meet the targets for precision, bias, and required reporting limits stipulated in Element 6, *Data Quality Objectives.*

Some considerations in the selection of analytical methods include potential bias for the particular sample matrix or particular analyte in which you are most interested. In addition, the method should be capable of determining all forms of the analyte (e.g., dissolved and total metals) needed for the study, as stated in the sampling design element. Finally, the method is fully documented either in a publication or in a Standard Operating Procedure (SOP) and validated by the lab before it is used.

The Manchester Environmental Laboratory uses a "Pre-Sampling Notification" form and a "Sample Container Request" form to aid in coordinating analytical services. Manchester Environmental Lab also requires that a completed copy of their "Laboratory Analyses Required" form accompany the samples. Much of the information on these forms is included in this element of the QA Project Plan.

Prepare a table with the following information:

- Analyte
- Sample Matrix
- Number of Samples
- Analytical Method(s), including Prep Method(s) when necessary
- Expected Range of Results (if known)

An example of a completed table is found in Appendix F.

Specify sample preparation procedures if they are not included in the analytical method or when multiple options are offered in the method. Describe or reference any specialized methods or modifications to established methods.

metimes the selection of analytical methods will be limited. For example, some al and state programs require the use of specific methods. If you plan to compare esults with those from another study or to conduct a trend analysis, select ures comparable to those used previously. Remember to select methods with limits at least 10 times below the lowest concentration of interest for the study.

Ecology policy requires that water and water-related (e.g., marine sediment) data come from laboratories accredited for the parameters and methods used. Contact the Environmental Assessment Program Lab Accreditation Unit (LAU) for information on accredited labs. A list of accredited labs is available at www.ecy.wa.gov/programs/eap/labs/lablist.htm.

Keep in mind that accreditation means that the lab has the capability to provide accurate data. However, accuracy requirements for your project must be specified to ensure that the laboratory uses the methods and quality control appropriate to your needs. The specification of MQOs (Element 6) and the use of QC procedures (Element 10) are always required to ensure the quality of your data.

The *Lab Users Manual* includes brief descriptions of the methods available at the Manchester Environmental Laboratory. Other methods may be available by special request. In addition, analyses by other methods may be contracted by the laboratory. The project manager should contact the laboratory with any questions related to analytical methods and sample shipment. Agency QA staff (QA officer as well as program and lab QA coordinators) may be able to advise you on method selection and applicability.

If analytical services are contracted to a private laboratory, be sure that all state and agency requirements for purchasing products or services are followed.

In some cases, contracting procedures require the preparation of a QA Project Plan that includes the laboratory procedures before it is known which laboratory will perform the work, which is decided later through competitive bidding. In those cases, a consultant with expertise in environmental analyses may be engaged, the plan may be revised, or a lab addendum may be prepared after the laboratory becomes part of the project team.

# 10. Quality Control

Targets for accuracy, precision, bias, and reporting limits are established in Element 6, *Data Quality Objectives*. The results for quality control (QC) samples are used to evaluate data quality. These results indicate whether the measurement system is functioning properly and whether the MQOs have been met.

## Laboratory QC

Many of the analytical methods used in the laboratory include QC procedures and acceptance limits. The project manager should be familiar with the terminology and theory of analytical QC so as to be able to discuss them with lab staff. The agency QA officer and program and lab QA coordinators can help with this communication.

Analytical QC procedures involve the use of four basic types of QC samples. QC samples are analyzed within a batch of field samples to provide an indication of the performance of the entire analytical system. Therefore, the QC samples should go through all sample preparation, clean up, measurement, and data reduction steps in the procedure. In some cases the laboratory may perform additional tests that check only one part of the analytical system.

### 1. Check standards

Check standards are QC samples of known concentration prepared independently of the calibration standards. They are sometimes called laboratory control samples (LCS) or spiked blanks. Results are used to verify that analytical precision is in control and that the level of bias due to calibration is acceptable. If the results for the check standards do not fall within established control limits, the measurement system should be re-calibrated. In some analytical methods, sample results may be qualified when associated check standard results are not within acceptable limits.

Check standards are usually prepared in deionized water, though any uncontaminated medium can be used. Their concentration should be in the range of interest for the samples, and at least one check standard should be analyzed with each batch of 20 samples or less.

Reference materials may be used as check standards that more closely match the matrix of environmental samples. Some performance evaluation (PE) samples from commercial vendors can be stored and used as check standards once the true values are known. The acceptance limits for the recovery should not be those set by the vendor but should be established in the lab by replicate analyses of the PE sample. The Lab Accreditation Unit in Ecology can help identify suppliers of standards and reference materials.

## 2. Analytical duplicates

Depending upon the analytical method, the laboratory may analyze duplicate aliquots of one or more samples within a batch. Results are used to estimate analytical precision.

If the samples selected for duplicate analyses do not contain measurable amounts of the analyte of interest, the results provide no information on precision. Further, if the lab selects samples from another study with significantly different levels of the analyte or different matrices, the estimate of analytical precision may not be applicable to the study samples in the batch. Thus the project manager may need to specify which samples are to be analyzed in duplicate.

One of the field duplicates is a good choice for an analytical duplicate since you can then calculate total and analytical variability from the same sample. There is no advantage to "randomly" selecting samples for duplicate analysis.

## 3. Matrix spikes

A matrix spike is an aliquot of a sample to which a known amount of analyte is added at the start of the procedure. Matrix spike recoveries may provide an indication of bias due to interference from components of the sample matrix. Since the percent recovery is calculated from the difference between the analytical results for the spiked and unspiked samples, its precision may be relatively poor. For best results, the amount spiked should be approximately equal to the amount in the sample before spiking. If the spike is too high, any interference effect could be masked. And if too low, random error would make it difficult to accurately estimate the recovery. In some cases, many replicate spikes would need to be analyzed in order to distinguish bias from the effects of random error on the recoveries. Thus, matrix spike results are not used to correct sample results and should only be used in conjunction with other QC data to qualify them.

While the primary use of matrix spikes is to indicate the presence of bias, duplicate spike results can be used to estimate analytical precision at the concentration of the spiked samples. When the samples are not expected to contain measurable amounts of the analyte, duplicate spikes may provide the best available estimate of analytical precision for your samples.

The project manager may indicate to the laboratory which samples might be most appropriate for use as matrix spikes and, if necessary, provide additional sample for this purpose. Also, the project manager may want to specify samples to be spiked since matrix spikes are not automatically included in all analytical methods, and samples from other projects may be selected by the analyst for spiking. Matrix spikes prepared from other types of samples or matrices provide no information on bias due to the matrices in your samples.

In some analytical methods, all of the samples and blanks are spiked with surrogate compounds at the start of the procedure. Surrogate compounds produce responses that can be distinguished from those of the analytes of interest and are not expected to be present in the samples. Surrogate recoveries provide an estimate of accuracy for the entire analytical procedure. The standard deviation of surrogate results provides an estimate of analytical precision, while the mean percent recovery of surrogate results indicates whether or not bias is present.

**4. Blanks**

Blanks are used in the laboratory to document the response of the measurement system to a sample containing effectively none of the analyte of interest. Depending on the analytical method, the analyst will analyze one or more method blanks with each batch of samples and compare the results to established acceptance limits.

A positive method blank response can be due to a variety of factors related to the procedure, equipment, or reagents. Unusually high method blank responses indicate contamination. The method blank response becomes very important when the analyte concentration is near the detection limit. Method blank responses are sometimes used to correct the sample responses or to determine the Limit of Detection (see Appendix E).

## Field QC

The project manager is responsible for selecting QC procedures to be used in the field.

Replicates are two (duplicates) or more samples collected, or measurements made, at the same time and place. Replicate results provide a way to estimate the total random variability (precision) of individual results. If conditions in the medium being measured or sampled are changing faster than the procedure can be repeated, then the precision calculated from replicate results will include that variability as well. Appendix E describes the calculation of precision from replicate results.

Replicate results that are "non-detects" cannot be used to estimate precision. Since there is no advantage to randomly selecting samples for replication, use all available information and professional judgement to select samples or measurements likely to yield positive results.

Samples are sometimes split in the field and sent to separate laboratories for analysis. This has been common practice in compliance situations. However, one should be aware of the limitations of this practice, since there is no way to determine which results are correct when they do not agree. If the project manager doubts the lab's ability to meet the MQOs, those concerns should be resolved through analyses of representative samples and reference materials or PE samples before any commitment is made for analysis of study samples.

Field blanks are samples of "clean" material which are exposed to conditions in the field. They should be analyzed like any other sample. The results for field blanks may indicate the presence of contamination due to sample collection and handling procedures or to conditions in the field. Unless they are intended as blind QC samples, plan to clearly identify field blanks so that they are not selected for analytical duplicates or matrix spikes.

Field blanks are used when there is reason to expect problems with contamination or to meet programmatic or contractual requirements. The use of good operational procedures in the field and thorough training of field staff reduces the risk of contamination.

Several types of field blanks are described below. The reagent water or other "clean" material used to prepare them is usually obtained from the laboratory.

- A *transport blank* is prepared at the lab and carried unopened to the field and back with the sample containers to check for possible contamination in the containers themselves or for cross-contamination during transportation and storage of the samples.

- A *transfer blank* is prepared by filling a sample container during routine sample collection to check for possible contamination from the surroundings. The transfer blank will also detect contamination from the containers or during transportation and storage of the samples.

- A *rinsate (equipment) blank* is prepared by exposing clean material to the sampling equipment after the equipment has been used in the field and cleaned. The results provide a check on the effectiveness of the cleaning procedures. The rinsate blank may also detect contamination from the surroundings, from containers, or from transportation and storage of the samples and is therefore the most comprehensive type of field blank.

Ideally, the results for your field blanks will be "not detected." If they are not, you will need to take them into account in determining whether your MQOs have been met.

Check standards and spiked samples usually are not prepared in the field due to the hazards of working with concentrated solutions of contaminants under field conditions. It may be appropriate to submit a reference material to the laboratory along with the samples.

Describe the field QC procedures to be used for the study. Specify the source of clean material or reference material and the number of each type of QC sample to be prepared.

Prepare a table listing the field and laboratory QC samples required for the study. An example of a completed table is found in Appendix F.

QC results may indicate problems with data quality during the course of the project. The lab will follow procedures described in the methods or in their SOPs and QA Manual to resolve the problems. Describe here any additional procedures to be followed to correct or compensate for these problems if they occur.

Options for corrective action might include:

- Retrieving missing information
- Re-calibration of the measurement system
- Re-analyzing samples
- Modifications to the analytical procedures
- Collecting additional samples or taking additional field measurements
- Qualifying results

# 11. Data Management Procedures

Data management addresses the path of data from acquisition in the field or laboratory to final use and archiving. Experience has shown that roughly half of the errors in results reported for performance evaluation (PE) samples have been due to mistakes in recording results, calculations, or transcription.

Describe the procedures to be used for recording and reporting data acquired in the field. Include procedures for detecting and correcting errors and for compiling and analyzing the data, including software requirements.

Describe requirements for the data package from the laboratory. Documentation should always include a case narrative discussing any problems with the analyses, corrective actions taken, changes to the referenced method, and an explanation of data qualifiers.

The lab data package should also include all QC results associated with your data. This information is needed to evaluate the accuracy of the data and to verify that the MQOs were met. This should include results for all method blanks and check standards included in the sample batch, as well as results for analytical duplicates and matrix spikes prepared from your samples.

List requirements for electronic transfer of data from the field or lab to your database. Provide or reference information necessary to enter the data in Ecology's Environmental Information Management (EIM) system. Information on the EIM system is available on the Ecology Intranet at http://aww.ecoweb/is/iip.htm.

Identify data to be obtained from existing databases and literature files. State acceptance criteria for these data in terms of precision, bias, representativeness, and comparability. Discuss any qualifiers associated with the data.

# 12. Audits and Reports

A process is needed to ensure that the QA Project Plan is implemented correctly, that the quality of the data is acceptable, and that corrective actions are implemented in a timely manner.

## Audits

Describe any audits that will be conducted during the project. Discuss the information expected and the success criteria. Identify the auditors and define their scope of authority. Provide the schedule and describe how the results will be reported.

Two types of useful audits are:

- *Technical Systems Audit* (TSA) – a qualitative audit of conformance to the QA Project Plan. The TSA is conducted soon after work has commenced, so that corrective actions can be implemented early in the project.
- *Performance Evaluation* (PE) – the quantitative determination of an analyte in a blind standard to evaluate the proficiency of the analyst or laboratory.

## Reports

Project plans for large or repetitive projects should describe a mechanism for periodic reports to management on the performance of measurement systems and on data quality. These reports should include:

- Assessment of data accuracy and completeness
- Results of performance and/or technical systems audits
- Significant QA problems and corrective actions taken
- Any other information requested by management

The project manager should list the reports required for the project and identify those responsible for preparing them.

The final report for each project should include a QA section that describes data quality. The final report should undergo peer review, a scientific review of the project report by staff with appropriate expertise who are not directly connected with the project. Peer reviews ensure that project activities were technically sound and properly documented. Guidelines for technical document review are provided on the Ecology Intranet at: http:/aww.ecoweb/eap/pubs/guidelinesforTDreview-4-24-00.pdf

# 13. Data Review, Verification, and Validation

Once the measurement results have been recorded, they should be examined to ensure that:

- Data are consistent, correct, and complete, with no errors or omissions
- Results for QC samples described in Element 10 (*Quality Control*) accompany the sample results
- QC results indicate that acceptance criteria were met
- Data qualifiers are properly assigned where necessary
- Data specified in Element 7 (*Sampling Design*) were obtained
- Methods and protocols specified in the QA Project Plan were followed

Describe procedures for reviewing data acquired in the field. The review should be conducted before leaving a site where samples are collected or measurements made.

Data review involves examination of the data for errors or omissions. Data verification involves examination of the QC results for compliance with acceptance criteria. Laboratory results are reviewed and verified by qualified and experienced lab staff and documented in the case narrative.

Data validation involves detailed examination of the complete data package using professional judgement to determine whether the procedures in the methods, SOPs, and QA Project Plan were followed. Validation is the responsibility of the project manager, who may wish to arrange for a qualified specialist to conduct the validation and document it in a technical report.

Once the data have been verified and validated, you can examine the data to determine if the MQOs have been met. It is good to coordinate with the laboratory at this point. In addition to the QC samples associated with your data package, the laboratory has historical QC data that may help in judging whether MQOs have been met.

MQOs were established in Element 6 (*Data Quality Objectives*) for precision (%RSD), bias (% of true value), and required reporting limit. An experimental design for preliminary estimation of precision and bias and the use of control charts provide the best way to determine whether MQOs have been met. If these will not be done, results of QC samples analyzed during the project can provide an indication as to whether the MQOs have been met

To evaluate whether the %RSD target has been met, the following QC samples can be used.

> The check standard and surrogate results should be within ±2 times the target for %RSD of the true value. Sometimes it is necessary to control precision around the mean of these results (i.e., mean ±2 times the target for %RSD) if calibration bias is present.
>
> If enough pairs of duplicate sample results are available within a narrow concentration range, a pooled estimate of the standard deviation can be calculated. This estimate, divided by the mean concentration of these duplicate results and converted to percent, can be used to judge whether the %RSD target has been met.

To evaluate whether the bias target has been met, the following QC samples can be used.

> The mean percent recovery of the check standards and the surrogates should be within ±%bias target of the true value (e.g., true value ± 10%).
>
> To check individual spike recoveries for an indication of bias due to interference or matrix effects, the percent recovery should be 100 ± 2.8 times the target for %RSD. But the power of the spike recovery test to detect interference is low, so normally only results that significantly exceed the limits are considered to indicate bias.
>
> Unusually high blank results indicate bias due to contamination that may affect your low-level results.

To evaluate whether the target for reporting limit has been met, examine the results for "non-detects" to determine if any of the values exceed the required reporting limits.

# 14. Data Quality Assessment

At this point in the process, the project manager knows whether the data are complete and meet requirements for precision, bias, and required reporting limit and whether the procedures that ensured representativeness and comparability were performed correctly. Assuming that the data are satisfactory, the project manager must decide whether they can be used to make the determination or decision for which the project was conducted (i.e., whether the DQOs have been met).

This step may be as simple as noting that no contaminants were found in any of the samples, that all the DQOs were met, or that the data are suitable for archiving in a database for comparison with data to be obtained in the future.

However, good planning requires that a procedure be described for demonstrating statistically that the decision based on the data has an acceptable probability of being the correct decision. The process is called "hypothesis testing" and some procedures for applying it to decide whether a regulatory level has been exceeded are described in Appendix D and in EPA document QA/G-9, *Guidance for Data Quality Assessment, Practical Methods for Data Analysis* (EPA, 2000d). Computer models may also be used to interpret data and meet the DQOs.

EPA's Data Quality Assessment process involves the following steps:

1. Review the DQOs and Sampling Design
2. Conduct a Preliminary Data Review
3. Select the Statistical Test
4. Verify the Assumptions of the Statistical Test
5. Draw Conclusions from the Data

Describe the process that will be used for deciding whether the data can be used to meet the project objectives.

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# Appendices

# Appendix A

## Glossary of Terms Related to Environmental Measurements

**Accreditation** - "Formal recognition by (Ecology)...that an environmental laboratory is capable of producing accurate analytical data...(Ecology) does not, by certifying or accrediting any laboratory...vouch for or warrant the accuracy of any particular work done or report issued by the laboratory." [WAC 173-50-040]

**Accuracy** - An estimate of the closeness of a measurement result to the true value.

**Bias** - The difference between the mean of the results of an infinite number of replicate measurements (limiting mean) and the true value.

**Blank** - A sample expected to contain none of the analyte of interest.

**Calibration** - The process of establishing the relationship between the response of a measurement system and the level of the parameter being measured.

**Check standard** - A QC sample prepared independently of calibration standards and analyzed along with the samples to check the accuracy of the measurement system. Sometimes called a lab control sample (LCS).

**Control chart** - A graphical presentation of the precision of QC results indicating whether the measurement system is in statistical control.

**Control limits** - Statistical warning and action limits calculated for control charts.

**Data Quality Objectives** - Statements of how accurate the data need to be in order to serve their intended use for decision-making.

**Data review** - The process of checking data for errors and omissions.

**Data validation** - Examination of the data package to determine whether the required procedures were followed.

**Data verification** - Evaluation of QC results for compliance with acceptance criteria.

**Detection limit** - That concentration of an analyte which can be determined to a specified level of certainty to be different from zero.

**Duplicates** - Two samples collected or measurements made at the same time and location, or two aliquots of the same sample prepared and analyzed in the same batch.

**Field blank** - A blank used to obtain information on contamination introduced during sample collection, storage, and transport.

**Laboratory Control Sample (LCS)** - See "Check standard."

**Matrix spike** - A QC sample prepared by adding a known amount of the target analyte(s) to an aliquot of a sample to check for bias due to interference or matrix effects.

**Measurement quality objectives** (MQOs) - Targets for the performance of a measurement system in terms of precision, bias, and required reporting limit.

**Measurement result** - An estimate of a population characteristic obtained by carrying out once the procedures described in a method.

**Method blank** - A blank prepared to represent the sample matrix and analyzed in a batch of samples.

**Parameter** - A specified characteristic of a population or sample.

**Precision** - A measure of the variability in the results of replicate measurements due to random error.

**Quality assurance (QA)** - A system for assuring the reliability of measurement data.

**Quality assurance project plan (QA Project Plan)** - A document that describes the objectives of a project and the procedures necessary to acquire data that will serve those objectives.

**Quality control (QC)** - The routine application of statistical procedures to evaluate and control the accuracy of measurement data.

**Relative standard deviation (RSD)** - Standard deviation divided by the mean.

**Relative percent difference (RPD)** - Difference between two values divided by their mean and multiplied by 100.

**Replicates** - Two or more samples collected or measurements made at the same time and place.

**Required reporting limit** - The lowest concentration of a substance reported by the lab established to ensure that the results will meet the requirements for the specific project. The reporting limit is set by the project manager in consultation with the lab.

**Standard deviation** - A statistic which is a measure of the dispersion of a population distribution (see Appendix E).

**Standard operating procedure (SOP)** - A document that describes in detail the approved way in which a routine procedure is to be carried out.

# Appendix B

## QA Project Plan Review Checklist

REVIEWER _____ DATE _____

| ELEMENT | YES | COMMENTS |
|---|---|---|
| **1 Title Page with Approvals** | ____ | _____ |
| Title, author, organization | ____ | _____ |
| Date prepared or revised | ____ | _____ |
| Dated signatures of project manager, supervisor, laboratory, QA officer or coordinator | ____ | _____ |
| Other signatures, as needed | ____ | _____ |
| **2 Table of Contents and Distribution List** | ____ | _____ |
| **3 Organization and Schedule** | ____ | _____ |
| Key individuals and their responsibilities (project team, decision-makers, stakeholders lab, etc.) | ____ | _____ |
| Organization chart | ____ | _____ |
| Project schedule | ____ | _____ |
| Budget and funding | ____ | _____ |
| **4 Background and Problem Statement** | ____ | _____ |
| Site and surroundings | ____ | _____ |
| Site history | ____ | _____ |
| Regulatory requirements | ____ | _____ |
| Summary of existing data | ____ | _____ |
| Logistical problems | ____ | _____ |
| Constraints | ____ | _____ |
| Problem to be studied | ____ | _____ |

# QA Project Plan Review Checklist (cont.)

| ELEMENT | YES | COMMENTS |
|---|---|---|
| **5 Project Description** | ____ | _____ |
| Decision(s) to be made | ____ | _____ |
| Decision statement | ____ | _____ |
| States project objectives | ____ | _____ |
| Information needed and sources | ____ | _____ |
| Target population | ____ | _____ |
| Boundaries | ____ | _____ |
| Decision rule | ____ | _____ |
| Practical constraints | ____ | _____ |
| **6 Data Quality Objectives** | ____ | _____ |
| Measurement Quality Objectives (MQOs) in terms of targets for | | |
| Precision | ____ | _____ |
| Bias | ____ | _____ |
| Accuracy | ____ | _____ |
| Required reporting limits | ____ | _____ |
| Data Quality Objectives (DQOs) | ____ | _____ |
| **7 Sampling (Experimental) Design** | ____ | _____ |
| Measurements and samples required | ____ | _____ |
| Locations and frequency | ____ | _____ |
| Parameters to be determined | ____ | _____ |
| Maps or diagrams | ____ | _____ |
| Representativeness | ____ | _____ |
| Comparability | ____ | _____ |
| **8 Field Procedures** | ____ | _____ |
| Measurement and sample collection | ____ | _____ |
| Containers, preservation, holding times | ____ | _____ |
| Equipment decontamination | ____ | _____ |
| Sample ID | ____ | _____ |
| Chain-of-custody, if required | ____ | _____ |
| Field log requirements | ____ | _____ |
| Other activities | ____ | _____ |

# QA Project Plan Review Checklist (cont.)

| ELEMENT | YES | COMMENTS |
|---|---|---|
| **9 Laboratory Procedures** | ____ | _____ |
| Lab procedures table, including | ____ | _____ |
| Analyte | ____ | _____ |
| Matrix | ____ | _____ |
| Number of samples | ____ | _____ |
| Analytical methods | ____ | _____ |
| Expected range of results | ____ | _____ |
| Required detection limits | ____ | _____ |
| Sample preparation, if required | ____ | _____ |
| Specialized methods, if required | ____ | _____ |
| **10 Quality Control** | ____ | _____ |
| Lab QC procedures and frequency | ____ | _____ |
| Field QC procedures and frequency | ____ | _____ |
| Table of lab and field QC required | ____ | _____ |
| Corrective action | ____ | _____ |
| **11 Data Management Procedures** | ____ | _____ |
| Data recording/reporting requirements | ____ | _____ |
| Lab data package requirements | ____ | _____ |
| Electronic transfer requirements | ____ | _____ |
| Acceptance criteria for existing data | ____ | _____ |
| **12 Audits and Reports** | ____ | _____ |
| Number, frequency, type and schedule of audits | ____ | _____ |
| Responsible personnel | ____ | _____ |
| Frequency and distribution of reports | ____ | _____ |
| Responsibility for reports | ____ | _____ |

# QA Project Plan Review Checklist (cont.)

| ELEMENT | YES | COMMENTS |
|---|---|---|
| **13 Data Review, Verification and Validation** | ____ | _____ |
| Field data review, requirements | ____ | _____ |
| responsibilities | ____ | _____ |
| Process for data validation | ____ | _____ |
| Responsibilities of project manager | ____ | _____ |
| Procedures for determining if DQOs have been met | ____ | _____ |
| **14 Data Quality Assessment** | ____ | _____ |
| Process for determining whether DQOs have been met | ____ | _____ |

# Appendix C

## Comparison of QA Project Plan Elements for EPA and Ecology

This appendix lists the elements required for QA Project Plans prepared for EPA projects and then compares the elements in this document to these EPA requirements.

**EPA Document QA/G-5**

A. Project Management

- A1 Title and Approval Sheet
- A2 Table of Contents and Document Control Format
- A3 Distribution List
- A4 Project/Task Organization
- A5 Problem Definition/Background
- A6 Project/Task Description and Schedule
- A7 Quality Objectives and Criteria for Measurement Data
- A8 Special Training Requirements/Certification
- A9 Documentation and Records

B. Measurement/Data Acquisition

- B1 Sampling Process Design (Experimental Design)
- B2 Sampling Methods Requirements
- B3 Sample Handling and Custody Requirements
- B4 Analytical Methods Requirements
- B5 Quality Control Requirements
- B6 Instrument/Equipment Testing, Inspection, and Maintenance Requirements
- B7 Instrument Calibration and Frequency
- B8 Inspection/Acceptance Requirements for Supplies and Consumables
- B9 Data Acquisition Requirements (Non-Direct Measurements)
- B10 Data Management

C. Assessment/Oversight

- C1 Assessments and Response Actions
- C2 Reports to Management

D. Data Validation and Usability

- D1 Data Review, Validation, and Verification Requirements
- D2 Validation and Verification Methods
- D3 Reconciliation with Data Quality Objectives

**Ecology Guidelines**

In this document, most of EPA's 24 elements have been incorporated into the 14 elements as shown below. EPA elements A8 and B8 are omitted since they are not relevant to projects of the scale conducted by or for Ecology. The contents of EPA elements A9 and B9 are incorporated into various elements of this document.

| Ecology Elements | EPA Elements |
|---|---|
| 1. Title Page with Approvals | A1 |
| 2. Table of Contents and Distribution List | A2, A3 |
| 3. Organization and Schedule | A4 |
| 4. Background and Problem Statement | A5 |
| 5. Project Description | A6 |
| 6. Data Quality Objectives | A7 |
| 7. Sampling (Experimental) Design | B1 |
| 8. Field Procedures | B2, B3, B6, B7 |
| 9. Laboratory Procedures | B4 |
| 10. Quality Control | B5 |
| 11. Data Management Procedures | B10 |
| 12. Audits and Reports | C1, C2 |
| 13. Data Review, Verification and Validation | D1, D2 |
| 14. Data Quality Assessment | D3 |

# Appendix D

## Effects of Errors on Decision-making

A decision error occurs when the sample data lead to an incorrect decision. Decision errors occur because the data are incomplete and imperfect. The combination of all the errors affecting your decision is called the total study error or total variability.

Total study error consists of statistical sampling error and measurement error. Statistical sampling error occurs when the sampling design is not able to characterize fully the variability of the population over space and time, including any inherent variability (e.g. stratification) in the media being sampled. Measurement error occurs during the process of collecting, handling, and analyzing the samples.

The following discussion is focused primarily on measurement error, but reference is also made on how to improve sampling design by increasing the number of samples taken and analyzed.

In keeping with the purpose of this guidance document, emphasis is placed on how planning should take into account the effects of errors on decision-making

### Comparison of a Result with a Fixed Numerical Value

It is often necessary in environmental decision-making to compare a result with a fixed numerical value or action level. Examples of this are determining compliance with a water quality standard or in determining whether a hazardous waste site cleanup standard has been exceeded. Projects done by or for Ecology often involve use of the data for these types of decisions.

The "Data Quality Objectives Process" described in EPA Guidance Document QA/G-4 is EPA's recommended systematic planning process when data will be used to select between two alternative conditions or to determine compliance with a standard. Step 6 of the DQO process is to specify tolerable limits on decision errors. EPA QA/G-4 provides practical guidance, but does not give a complete explanation of the statistical basis for decision-making or how the assessment decision relates to the planning process. The following provides additional information on the statistics behind EPA's process for specifying tolerable limits on decision errors.

Decisions are often made without taking into account the effect of error on those decisions. Obviously, if the results are biased (high or low) our decisions may be incorrect. Random error also needs to be taken into account when decisions are made based on environmental data.

**Effect of Random Error**

To begin with, assume that there is no bias in the results, only random error. This is the approach taken in the EPA QA/G-4 document. In this approach, one must take operational steps to ensure that bias in sampling and analysis is negligible. While this may not always be possible, it can provide an initial framework for the planning process.

Assume also that the results are normally distributed around a mean value, which also corresponds to the regulatory limit. Referring to Figure 1, if the action level (AL) (i.e., the maximum acceptable concentration) is set equal to that regulatory threshold (C), then when the true value equals the action level, the probability of deciding that the limit has been exceeded is 50% and equals the probability of failing to decide that the limit has been exceeded, the equivalent of flipping a coin to make a decision.

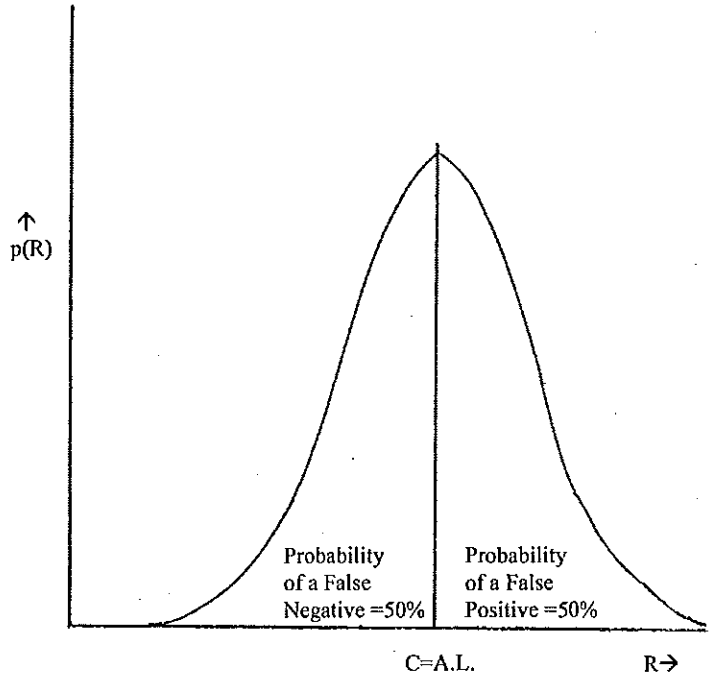



Figure 1. Effect of Random Error when the Action Level (A.L.) is Set Equal to the Regulatory Limit (C)

Often decisions are made without taking into account the probabilities of decision errors, which are referred to as "Type I" and "Type II" errors.

Type I error is deciding that C has been exceeded when it has not. The probability of the Type I error is denoted by $\alpha$.

Type II error is the error of failing to decide that C has been exceeded when in fact it has been. The probability of the Type II error is denoted by $\beta$, and hence $(1-\beta)$ is called the power of the test (i.e., in this example, the power to determine that a standard has been exceeded).

In EPA document QA/G-4, Type I and Type II errors are defined in terms of the null hypothesis. A false rejection (Type I) decision error occurs if the decision-maker rejects the null hypothesis when it is really true, and a false acceptance (Type II) decision error occurs if the decision-maker fails to reject the null hypothesis when it is really false.

To further clarify this, consider the following cases. Fig. 2(a) shows that when the true concentration of a parameter, T, is slightly less than the standard or regulatory threshold, C, random errors will frequently lead to a result, R, that is greater than C. Similarly, Fig. 2(b) shows that when T is a little greater than C, there is a substantial probability that a result less than C will be obtained. Suppose the decision rule is to take corrective action whenever $R>C$. When T is close to C, there are significant probabilities that action will be taken when it is not necessary (when $R>C$ but $T\leq C$)or that action will not be taken when it is required (when $R\leq C$ but $T>C$).
Suppose that we want to reduce the probabilities of these two undesirable decisions so that neither of them occurs at a frequency greater than 5%. To do that, a new action limit C' must be defined and action taken whenever $R>C'$. (See Fig. 2(c).) The value of C' is chosen so that, when $T=C$, the probability of obtaining a result less than C' is no greater than 0.05. From the properties of the normal distribution, $C'=C-1.64\sigma_C$, where $\sigma_C$ is the standard deviation of measurement results at the level C.

Note however that when $T=C'$ action will be called for needlessly 50% of the time. Thus, to ensure that action is not needlessly taken too frequently, the aim must be to make the decision at or below a control limit C", where C" is chosen so that, when $T=C''$, the probability of obtaining a result greater than C' is no more than 0.05. (See Fig. 2(d).)

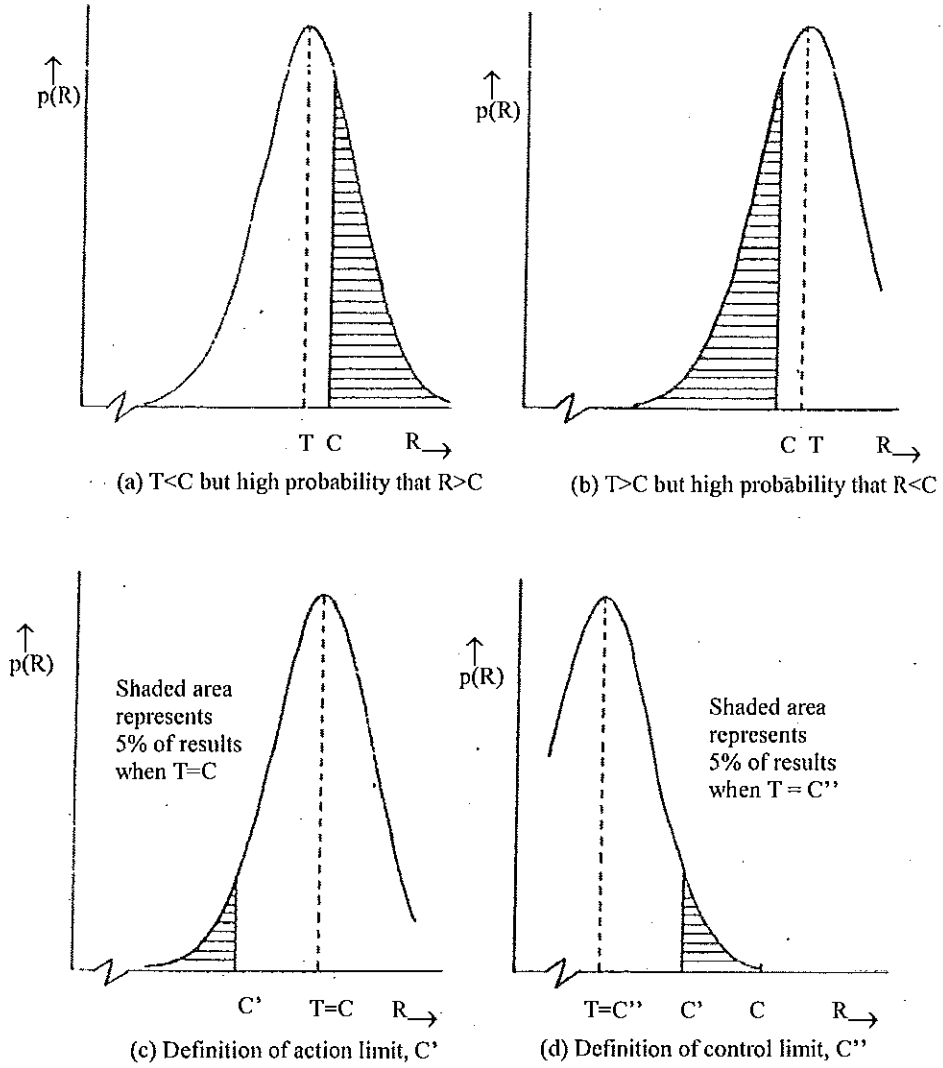



Figure 2(a)-(d). Effect of Random Errors on Decision-Making

Again, from the properties of the normal distribution, $C''=C'-1.64\sigma_{C''}$, where $\sigma_{C''}$ is the standard deviation of measurement results at the concentration C''. It follows that $C''=C-1.64(\sigma_C+\sigma_{C''})$.

If it is assumed that $\sigma$ is independent of the concentration of the parameter in the range between C'' and C, the previous equation can be solved to give $\sigma=(C-C'')/3.28$.

Figure 2(e) combines the two curves presented in Figures 2(c) and 2(d) to show the relationships between the control and action limits.

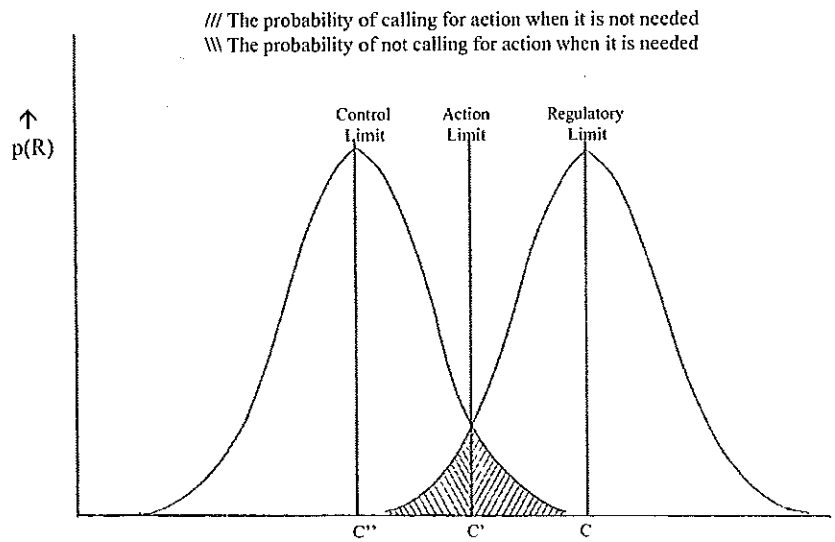



Figure 2(c). Statistical Approach to Decision-Making

Note that C' is the action limit or critical level for decision-making. Decisions are made at the action limit and not at the regulatory limit, in order to reduce Type I errors.

C" is called the control limit because in some environmental situations, such as the operation of a treatment plant or when it is possible to change the inputs of pollution to the environment, one can take measures to control the concentration below C". In other environmental situations such as cleanup of a hazardous waste site, there is no control of the concentration, but C" can be established in order to determine how many samples need to be taken to reduce the effect of Type II errors on decision-making.

The above considerations provide the basis for EPA's procedure for specifying tolerable limits on decision errors, as described in EPA documents (QA/G-4 and QA/G-4HW) and software (QA/G-4D). While the normal distribution curves in Figures 2(a) – 2(e) are not shown in these EPA documents, they provide the theoretical basis for the construction and use of the Decision Performance Curve and Decision Performance Goal Diagrams used by EPA for decision-making.

Figure 3 is an example of a Decision Performance Curve taken from EPA QA/G-4. This curve illustrates how the probability of deciding that the parameter exceeds the standard or regulatory level changes as the true value of the parameter changes. For an ideal decision performance curve where random error is considered to be negligible, the probability is zero until the standard or regulatory level is reached. But for a realistic decision performance curve representing a real-world situation with random error, the probability gradually increases and does not reach 100% until the standard or regulatory level is exceeded. In statistical terms, the realistic decision performance curve is a plot showing how $\beta$ changes as the true value of the parameter changes. EPA refers to this as a power curve, although usually a power curve is a plot of $1-\beta$ against the true value.

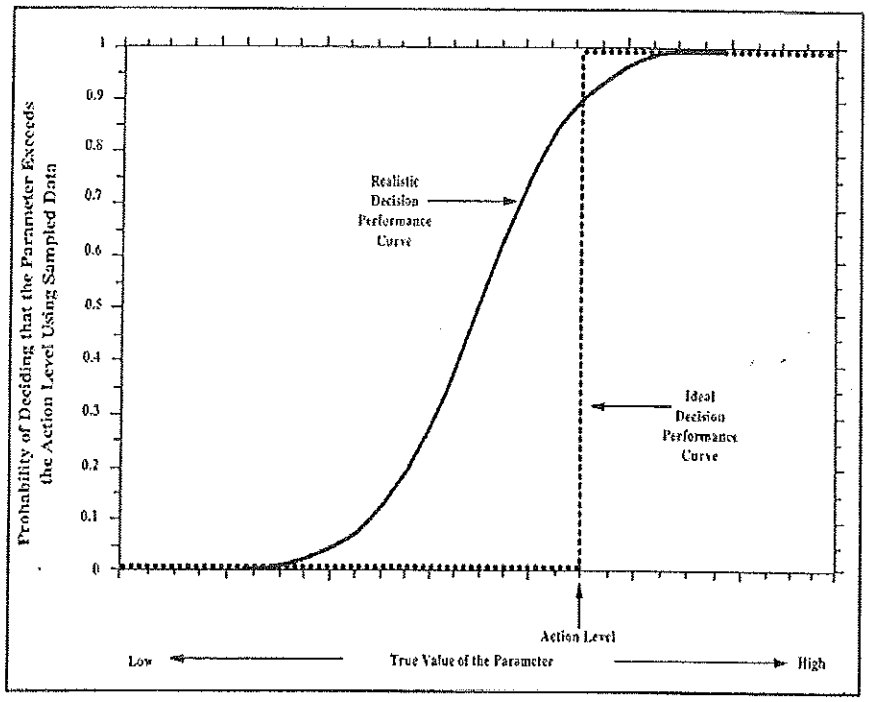



Figure 3. An Example of a Decision Performance Curve

Note that in Figure 3 the action level is equal to the standard level being enforced. This conflicts with the statistical analysis, which showed that the action level must be less than the standard level being enforced in order to reduce the probability of a false positive error. EPA explains this by distinguishing between a theoretical decision rule during the planning stage and an operational decision rule used in the assessment stage. The theoretical decision rule assumes that you know the true value of the parameter, while the operational decision rule is used after you have obtained results for measurements made on the samples.

In the planning process, EPA QA/G-4 specifies that one construct a Decision Performance Goal Diagram (DPDG) which approximates a Decision Performance Curve, based on the choices one makes for tolerable false acceptance decision rates and tolerable false rejection decision error rates.

The American Society of Testing and Materials (ASTM) publication ASTM D5792-95, "Standard Practices for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives" uses an operational decision rule both in the planning and assessment stages. This is consistent with the statistical analysis presented above, and the action level is defined the same way during planning and implementation stages. Figure 4, taken from ASTM D5792-95, shows a Decision Performance Curve. In this case $\alpha = 0.2$ and $\beta = 0.1$ and the regulatory threshold is equal to 1.0 mg/L. It illustrates that the operational action level corresponds to the concentration with a 0.5 probability of taking action, which is the mid-point of the decision performance curve.

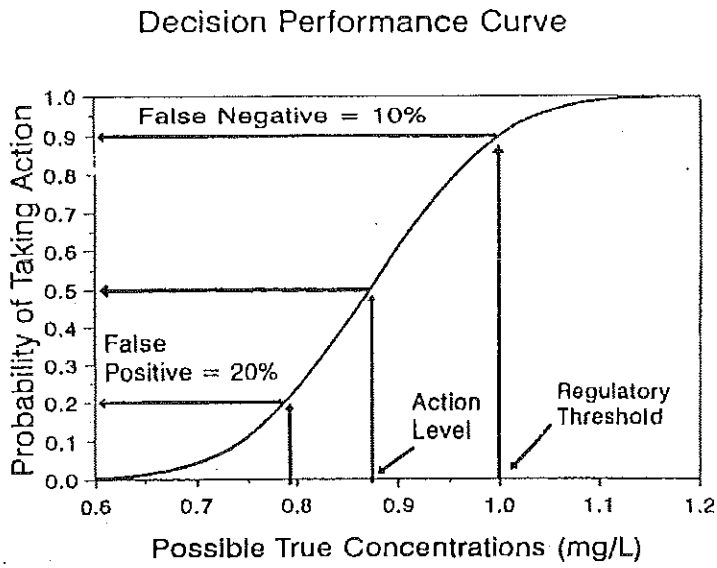


**FIG. 4 Decision Rule Development**

Appendix A of "Data Quality Objectives Process for Hazardous Waste Site Investigations" (EPA QA/G-4HW) presents a comparison of DQO Process Documents, which includes the EPA and ASTM DQO Processes already mentioned, as well as the U.S. Department of Energy "Streamlined Approach for Environmental Restoration" (SAFER) Process.

*A priori* decision-making occurs before the data are collected, during the planning stage. As explained above, when planning projects that involve decisions as to whether a standard has been exceeded, one must choose the desired probabilities of Type I and Type II errors for the data. One must also choose the minimum detectable difference (delta, $\delta$). In Figure 2(e), this minimum detectable difference is the range between C" and C or $3.28\sigma$. In the QA/G-4 document, EPA designates this range as the gray region. It helps to understand that the distributions illustrated in Figure 2(e) determine the gray region.

There are 2 ways of improving precision in order to reduce the minimum detectable difference or gray region:

(1) use more precise sampling and analysis procedures or

(2) take replicate samples for analysis and use the mean result

The standard error of the mean is equal to $s/\sqrt{n}$, so the precision of a mean result as compared with an individual result is improved by a factor of $1/\sqrt{n}$. Taking replicate samples is a very practical way to improve precision for decision-making, and Decision Performance Goal Diagrams help one to decide how many samples must be taken to achieve the precision needed for decision-making.

The number of samples that must be analyzed is determined from the chosen values of $\alpha$, $\beta$, and $\delta$. These, along with the value for $\sigma$, will determine how many samples need to be included in each mean result. Ideally the value assigned to $\sigma$ will be based on an estimate from previous sample analyses at the site. If not, make a preliminary estimate using your best judgement. The bottom line is that one can choose the number of samples needed to ensure that, if the true value is equal to C", the probability of deciding incorrectly that the standard has been exceeded should be equal to $\beta$.

The formula for calculating the sample size, assuming simple random sampling, needed to meet the conditions specified for $\alpha$, $\beta$, $\delta$, and $\sigma$ is given by:

$$n = \frac{\sigma^2 (z_{1-\alpha} + z_{1-\beta})}{\delta^2} + \frac{z_{1-\alpha}^2}{2}$$

where $z_p$=the $p^{th}$ percentile of the standard normal distribution.

When $\alpha=\beta=0.05$, this equation can be solved for the minimum detectable difference, $\delta$,:

$$\delta = \frac{3.28\sigma}{\sqrt{n}}$$

Thus, for the example given in Figure 2(e), the value of n can be calculated by solving this equation for n, i.e., $n \cong 10.8(\sigma/\delta)^2$. This aspect of choosing n so that a test is capable of detecting a difference when the population mean differs from a fixed value (e.g. regulatory limit) by a specified amount is known as 'ensuring adequate *power* of the test'.

EPA has provided software that will calculate n for the case described above, as well as for other sampling designs. The latest version of that software, Decision Error Feasibility Trials or DEFT, is available at http://www.epa.gov/quality/tools-prj.html

The U.S. Department of Energy also provides software called Visual Sample Plan (VSP) which provides statistical solutions to sampling design, answering two important questions in sample planning: (1) How many samples are needed? and (2) Where should the samples be taken? VSP is available at http://dqo.pnl.gov/VSP/

*A posteriori* decision-making occurs after the data are collected, during the data quality assessment stage, and is based solely on the probability of Type I error, $\alpha$. The action level (critical level in statistical terminology) should be near the concentration C' established during the planning process. However, the actual decision level will be determined by performing a t-test. The t-test is done to test the null hypothesis that the mean is equal to or greater than the standard or regulatory threshold (C) against the alternative hypothesis that the mean is less than C.

The t-statistic is calculated as follows:

$$t_{calc} = \frac{|\bar{x} - E|}{s / \sqrt{n}}$$

where $E$ = the expected or standard value (C)
$s$ = the estimated standard deviation of a single result
and $n$ results have been used in calculating the mean

The value of $t_{calc}$ is compared with a value of t found in a table ($t_{tabl}$) based on the number of degrees of freedom used in estimating $s$ and the value of $\alpha$ chosen previously. For this test, one rejects the null hypothesis if $t_{calc}$ is less than $t_{tabl}$. Note that this is a one-sided test in which the mean being tested is less than the expected or standard value.

**Effect of Bias**

As a general rule, it is preferable, and sometimes essential, to ensure that bias is negligible. EPA QA/G-4 assumes negligible bias in specifying tolerable limits on decision errors. Unfortunately, it is often the case that significant bias is present in sampling and analysis.

Unrepresentative sampling contributes to biased results, and therefore it is important to have a good sampling plan and ensure that operational implementation of the plan gets representative samples.

Results obtained from the use of many analytical methods, especially those involving extraction of organic compounds from environmental matrices, exhibit negative bias caused by differences in procedures for calibration and sample analyses. Bias may also be caused by interference or failure to allow for blank correction. The project manager should be aware of the bias inherent in the use of some methods, and coordinate with the laboratory to choose methods that are capable of meeting the targets for bias established in the MQOs.

Since there are several possible causes for bias, and bias can vary with concentration as well as from sample to sample and from time to time, it is not generally possible to eliminate bias by measuring it and making a correction to the result for each sample.

When random error is negligible, the only generally effective approach that can be used to account for bias is to change the action level to allow for it. For example, if the standard is C and negative bias is present, one could control at C-$\beta_c$, where $\beta_c$ is the bias present at concentration C.

When both bias and random errors are present, there is no simple and general approach that overcomes the problems involved in the interpretation of results. It is usually possible to obtain an estimate of the random error of a particular result, but much more difficult to estimate the bias. Therefore, emphasis should be placed on ensuring that the magnitude of bias is as small as possible. Finally, one can shift the action level to a lower or higher value, depending on whether

the estimated bias is positive or negative. As already stated, when considering bias alone, one changes the control to $C-\beta_c$. If you consider both bias and random error, one would control random errors below $C-\beta_c-3.29\sigma$, where $\sigma$ is the standard deviation of analytical results and is assumed to be independent of the concentration of the analyte.

## Paired-Comparison Test

The paired-comparison test is a very useful and simple statistical test that can be applied to answer questions that frequently arise in assessing data from environmental projects. Examples include the comparison of pairs of upstream and downstream results over time, the comparison of results before and after cleanup, and the comparison of pairs of results for samples analyzed by two different methods. The paired-comparison test is a variation of the basic t-test, which is used to test whether there is a statistically significant difference at a given probability level between the means of two independent sets of results.

The paired-comparison test is an application of the formula given above, to compare two pairs of results, where the expected difference between each of the pairs of results is zero.

$$\text{i.e., } t = \frac{\bar{x} - 0}{s/\sqrt{n}}$$

The following is an example of the paired comparison test to compare results for samples analyzed using two different methods of analysis and to determine if there is a statistically significant difference between the results.

| Original results | | | | |
|---|---|---|---|---|
| Method A | Method B | Difference B-A | Coded difference, D | $D^2$ |
| 2.5 | 2.8 | 0.3 | 3 | 9 |
| 4.2 | 4.1 | -0.1 | -1 | 1 |
| 7.3 | 8.6 | 1.3 | 12 | 169 |
| 1.4 | 1.7 | 0.3 | 3 | 9 |
| 3.6 | 3.9 | 0.3 | 3 | 9 |
| 5.9 | 6.6 | 0.7 | 7 | 49 |
| 4.5 | 4.5 | 0.0 | 0 | 0 |
| 3.2 | 4.0 | 0.8 | 8 | 64 |
| | | | $\Sigma D=36$ | $\Sigma D^2=310$ |

$(\Sigma D)^2/n = 1296/8 = 162$

$$s = \sqrt{\frac{\sum D^2 - \frac{(\sum D)^2}{n}}{n-1}} = \sqrt{((310-162)/7)} = 4.598 \text{ with 7 degrees of freedom}$$

$$t = (|(\Sigma D)/n - 0|)/(s/\sqrt{n}) = (4.5\sqrt{8})/4.598 = 2.77 \text{ with 7 degrees of freedom.}$$

For a significance level, $\alpha$=0.05, the tabulated value corresponding to $t_\alpha$ for 7 degrees of freedom is 2.36. The observed value, 2.77, is greater than the tabulated value; the difference between Methods A and B is therefore statistically significant.

## References


"Guidance for the Data Quality Objectives Process", EPA QA/G-4, August 2000.

"Data Quality Objectives Process for Hazardous Waste Site Investigations", EPA QA/G-4HW, January 2000.

"The Chemical Analysis of Water", by D.T.E. Hunt &: A.L. Wilson, The Royal Society of Chemistry, 2nd edition, 1986.

"Standard Practice for Generation of Environmental Data Related to Waste Management Activities: Development of Data Quality Objectives", ASTM Designation: D5792-95, American Society for Testing and Materials, January 1996.

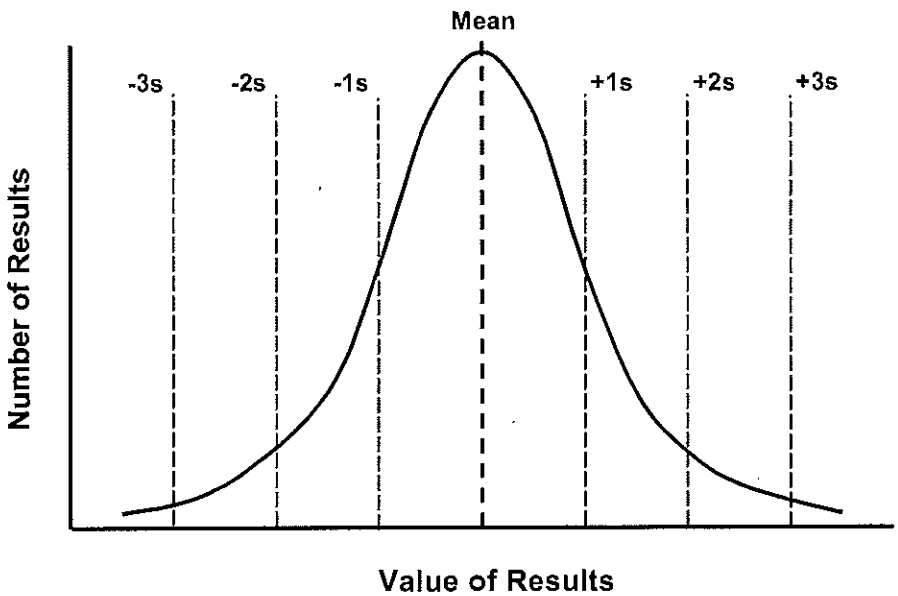
"A Manual on Analytical Quality Control for the Water Industry", by R.V. Cheeseman and A.L. Wilson (Revised by M.J. Gardner), NS 30, Water Research Centre, England, June 1989.

Module 7, "Streamlined Approach for Environmental Restoration (SAFER)" in *Remedial Investigation/Feasibility Study (RI/FS) process, Elements and Technical Guidance,* U.S. Department of Energy (DOE), EH 94007658, December 1993.

# Appendix E

## Statistical Calculations Related to Data Quality

The results obtained from the Quality Control (QC) procedures described in Element 10 can provide an indication, and even a quantitative estimate, of the error associated with measurement data. If a physical or chemical measurement is repeated many times using a sufficiently sensitive procedure, the probability distribution of the results will resemble the familiar bell-shaped curve shown here.




The curve is characterized by its mean value, which defines the center of the distribution, and by its standard deviation, $s$, which describes the width or dispersion of the distribution. The difference between the population mean and the true value is the bias in the results and the standard deviation is the variability due to random error.

Here are some equations you can use to evaluate the quality of measurement data.

### Precision

Precision is estimated as the standard deviation of the results of $n$ replicate measurements by

$$s = \sqrt{\frac{\sum x_i^2 - (\sum x_i)^2/n}{n-1}} \qquad (1)$$

where $x_i$ is the $i$th result in the set of $n$ results. This function is available on most scientific calculators.

For duplicate results, Equation 1 becomes

$$s = \frac{|D|}{\sqrt{2}} \tag{2}$$

where $D$ is the difference between the two results.

If more than one estimate of the standard deviation of a population is available, a pooled estimate, $s_p$, may be calculated from

$$s_p = \sqrt{\frac{\Sigma \nu_i s_i^2}{\Sigma \nu_i}} \tag{3}$$

where $\nu_i = n_i - 1$, the number of degrees of freedom associated with the estimate of $s_i$.

For $m$ pairs of duplicate results, Equation 3 reduces to

$$s_p = \sqrt{\frac{\Sigma D^2}{2m}} \tag{4}$$

The estimate of standard deviation improves as the number of degrees of freedom increases. For a better estimate of $s$, plan to collect and/or analyze more replicates or more pairs of duplicates.

The pooling equations assume that the standard deviations are all from the same population of results. Since the standard deviation varies with the magnitude of the results, the pooling equations should be used only for results of approximately the same magnitude. As a rule of thumb, use results that are within one order of magnitude for pooling standard deviations. If your study involves a wide range of results, it might be necessary to obtain separate estimates of standard deviation for several ranges of concentration.

Precision is often reported as the Relative Standard Deviation (RSD) of the results of replicate measurements, which is calculated as a percentage of the mean by

$$RSD = \frac{s}{\bar{x}} \cdot 100 \tag{5}$$

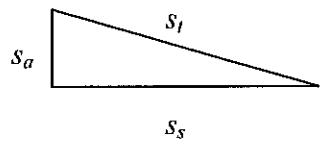
where $\bar{x}$ is the mean of the replicate measurements.

The total precision of results can be estimated from the results of replicate field measurements or replicate samples. Analytical precision can be estimated from the results of replicate analyses of samples or check standards.

The total standard deviation estimated from the analysis of replicate samples, $s_t$, is related to that from analytical replicates, $s_a$, by

$$s_t^2 = s_s^2 + s_a^2 \tag{6}$$

In this equation the variances, $s^2$, are additive, not the standard deviations. This is analogous to the Pythagorean theorem for right triangles as shown by




where $s_s$ is an estimate of the variability due to sampling given by

$$s_s = \sqrt{s_t^2 - s_a^2} \qquad (7)$$

For example, suppose that, for a set of samples, the results of analysis of field replicates yields an estimate of total standard deviation of 0.50 for a particular parameter. Suppose further that the analysis of analytical duplicates yields an estimate of the standard deviation in the analytical procedure of 0.20. Equation 7 provides an estimate of standard deviation due to sampling of 0.46, which means that the sampling procedures are responsible for the majority of the uncertainty in the results.

To improve the total precision of these results, you will have to find a way to reduce the variability introduced by the sampling procedures because improving the analytical precision has little effect on total precision. In this case, reducing the analytical standard deviation by half to 0.10 reduces the total standard deviation by only 6% to 0.47.

If you plan to base a decision on a mean of several sample results, you can estimate the confidence interval on that mean by

$$CI = \bar{x} \pm t_{(1-\alpha,v)} s_x/\sqrt{n} \qquad (8)$$

where $t$ is the appropriate value of Student's-t statistic for the desired level of confidence $(1 - \alpha)$ and the number of degrees of freedom (v).

If the standard deviation has been estimated from a reasonable number of sample results (at least 10), confidence intervals can be assigned to individual results. The confidence interval for a result, $x$, is given by

$$CI = x \pm t_{(1-\alpha,v)} s_x \qquad (9)$$

Suppose that the mean of the results of 10 replicate determinations is 11.3 and the standard deviation is 1.0. To determine the 95% confidence interval on the mean, look up the value of the 5% point (double-sided test) of the Student's t-statistic for 9 degrees of freedom, which happens to be 2.26. Using Equation 8,

$$95\%CI \text{ on the Mean} = 11.3 \pm 2.26(1.0)/\sqrt{10}$$

$$= 11.3 \pm 0.7$$

$$= 10.6 - 12.0$$

Thus there is a 95% chance that the actual value of the mean lies between these values, assuming no bias in the results.

On the other hand, suppose you need to estimate the confidence interval on just one of those 10 results, say $x = 12.4$. Then Equation 9 gives

$$95\%\text{CI on } x = 12.4 \pm 2.26(1.0)$$

$$= 12.4 \pm 2.26$$

$$= 10.1 - 14.7$$

and there is a 95% chance that the actual value for that sample lies between these values.

This example demonstrates that the mean of several results gives a much more precise estimate of the population mean than can be obtained with any single result, a consequence of the fact that the standard error of the mean is equal to $s/\sqrt{n}$.

Precision must be considered when comparing results to other data or to fixed limits. For example, if the CI for a result includes the regulatory limit, then no decision can be made as to whether the limit was exceeded and an objective of the study may not be achieved. Also, if the CIs for the results from two locations or time periods overlap, then the two sets of results are not statistically different at the probability level selected for the comparison.

If replicate measurements are not greater than the reporting limit, precision cannot be estimated for that parameter. Thus, it is important to select samples to be analyzed in replicate which are likely to give results greater than the reporting limit. There is no reason to select measurements or samples for replication randomly. The more information and professional judgement you can bring to the selection process, the more likely you are to obtain useful information from the results.

## Bias

The determination of bias due to sampling procedures requires special studies designed to examine the various sources of error. Such studies have led to the recommended procedures for sample collection, preservation, etc. currently in use. Careful adherence to the procedures selected for the project should maintain bias within acceptable limits.

Two potential sources of systematic error (bias) in a measurement are calibration and interferences due to the sample matrix. The results of the analysis of check standards can be used to estimate bias due to calibration error. The results of the analysis of matrix spikes can be used to detect interference effects due to the sample matrix.

An estimate of bias due to calibration is given by

$$B(\%) = \frac{\bar{x} - T}{T} \cdot 100 \qquad (10)$$

where $\bar{x}$ is the mean of the results of (at least 10) replicate analyses of the check standard and $T$ is the true concentration. If the confidence interval on the mean includes $T$, the difference is probably due to random error rather than bias. The analyst should monitor check standard results and recalibrate the instrument when the difference exceeds the laboratory's control limits.

For matrix spikes, the percent recovery (%R) is given by

$$\%R = \frac{x_s - x}{C_s} \cdot 100 \qquad (11)$$

where $x_s$ is the result for the matrix spike, $x$ is the result for the unspiked sample, and $C_s$ is the concentration of the spike added to the sample.

Bias is judged to be present when the %R falls outside the control limits established by the laboratory based on historical data. When this occurs, the analytical procedure should be modified to eliminate the interference effects if possible.

Since the %R is a function of the difference between two results, its uncertainty is relatively large and the power of the spike recovery test to detect bias is therefore low. For this reason, correction of the sample results based on matrix spike recovery is not recommended.

If QC results exceed their criteria and no corrective action is taken by the laboratory, the sample results should be qualified as estimated or unusable. If data verification reveals signifieant bias indicated by QC results, the project manager may need to conclude that the data cannot be used or that they should be qualified for the purpose of the project.

# Appendix F

## Tables

### Measurement Quality Objectives

**Example of Completed Measurement Quality Objectives Table**

| PARAMETER | ACCURACY | PRECISION | BIAS | REQUIRED REPORTING LIMIT |
|---|---|---|---|---|
| | *% deviation from True Value* | *RSD** | *% of True Value* | Concentration Units |
| pH | 0.20 SU | 0.05 SU | 0.10 SU | N/A |
| Alkalinity | 15 | 5% | 5 | 10 mg/L |
| Orthophosphate | 20 | 5% | 10 | 0.01 mg/L |
| Cd in water | 30 | 10% | 10 | 4 µg/L |
| Cd in sediment | 50 | 20% | 10 | 0.5 mg/kg |
| BNAs | 60 | 20% | 20 | 10 µg/L |
| Fecal coliforms | N/A | 25% (log transformed) | N/A | 2 cfu |

* Precision MQOs can also be stated in terms of RPD

## Field Procedures

**Example of Completed Field Procedures Table**

| PARAMETER | SAMPLE SIZE | CONTAINER | PRESERVATION | HOLDING TIME |
|---|---|---|---|---|
| Alkalinity | ≥ 200 mL | 500 mL Wide-Mouth Poly | 4° C | 14 Days |
| Orthophosphate | 125 mL | 125 mL Amber Wide-Mouth Poly | 4° C | 48 Hours |
| Cd in Water | 350 mL | 1 L HDPE with Teflon-Lined Lid | PH < 2, 4° C | 6 Months |
| Cd in Sediments | 50 g | 8 oz. Wide-Mouth Glass with Teflon-Lined Lid | 4° C | 6 Months |
| BNAs | ≥ 1 Gallon | 1 Gal. Glass with Teflon-Lined Lid | 4° C | 7 Days |
| Fecal Coliforms | ≥ 250 mL | Sterile Poly | 4° C, Sodium Thiosulfate if Chlorine Residual | ≤30 Hours |

The information required for this table is available in the following publications:

- ◊ Manchester Environmental Laboratory, *Laboratory Users Manual*, 5th Ed., October 2000
- ◊ 40 CFR 136.3, Table II
- ◊ SW-846 Methods, Section 6.0
- ◊ EPA/600/R-93/100, *Methods of the Determination of Inorganic Substances in Environmental Samples*, August, 1993

## Lab Procedures

**Example of Completed Lab Procedures Table**

| ANALYTE | SAMPLE MATRIX | SAMPLES [Number/ Arrival Date] | EXPECTED RANGE OF RESULTS | SAMPLE PREP METHOD | ANALYTICAL METHOD |
|---|---|---|---|---|---|
| Alkalinity | Surface Water | 20 on 11/22/00 | 50 - 100 mg/L | N/A | SM 2320 Titration |
| Chlorophyll a | Marine Water | 10 in August | 0 - 1 µg/L | N/A | SM 10200H Fluorometric |
| Total Phosphorus | Surface Water | 20 week of 7/5/00 | 0 - 0.05 mg/L | N/A | EPA 365.3 Colorimetric Ascorbic Acid |
| Total As | Surface Water | 5 + 5 + 5 on 1st week of May, June, July | 0 - 5 µg/L | PSEP Total Acid Digestion | EPA 200.9 GFAA |
| Dissolved Cu | Marine Water | 12 on 4/7/00 | 0 - 5 µg/L | 0.45 Micron Filter | EPA 6020 ICP/MS |
| Al | Marine Sediments | 8 first week of August + 8 two weeks later | 10 - 100 mg/kg (dry) | | EPA 200.7 ICP/AES |
| Volatile Organics | Ground Water | 10 last week of June | 0 - 200 µg/L | | EPA 8260 GC/MS |
| Fecal Coliforms | WTP Effluent | 4 on 12/8/00 | 2 - 2000 CFU/L | N/A | SM 9222D Membrane Filter |

## QC Samples

**Example of Completed QC Procedures Table**

| | FIELD | | LABORATORY | | | |
|---|---|---|---|---|---|---|
| **Parameter** | Blanks | Replicates | Check Standards | Method Blanks | Analytical Duplicates | Matrix Spikes |
| | | | | | | |
| pH | N/A | 1/Day | 1/Day in Field | N/A | N/A | N/A |
| | | | | | | |
| Orthophosphate | 1/Site | 1/Site | 1/Batch | 1/Batch | 1/Batch | None |
| | | | | | | |
| Cd in Water | 1/Day | 1/10 Samples | 1/Batch | 1/Batch | 1/Batch | 1/Batch |
| | | | | | | |
| Cd in Sediment | 1 Background | 1/10 Samples | 1/Batch | 1/Batch | 1/Batch | 1/Batch |
| | | | | | | |
| BNA | 1 Transfer/ Day | 1/Day | 1/Batch | 1/Batch | 1/Batch | 1/Batch |
| | | | | | | |
| FC | N/A | 1/20 Samples | N/A | 1/Batch | N/A | N/A |

# Appendix G

## Calibration

Calibration relates the response of the measurement system to the property of the sample being measured. It is an essential component of the measurement system itself, necessary before any QC procedures can be performed. In general, calibration standards should be analyzed by the same procedure used to analyze the samples. Failure to do so can introduce bias. This principle is often not followed, and calibration bias is found in many methods, particularly for organics parameters. It shows up as low percent recoveries for check standards and surrogates analyses.

Practical considerations sometimes result in the use of calibration procedures different than sample analysis procedures, in order to use the same calibration procedure to analyze samples in different matrices.

For most analytical procedures, calibration is required each day, shift, or sample batch. This is called within-batch calibration. Calibration with a blank and four standards is recommended for most systems.

Some measurement systems (e.g., UV-VIS Spectrophotometers) are sufficiently stable that a calibration curve can be used for a long period of time. This is called fixed calibration. It is recommended that fixed calibrations be based on a blank and at least seven standards. The fixed calibration is not repeated until the results for the check standards indicate the need to do so.

Most measurement systems are calibrated with external standards. The response of one or more standards is recorded and used to evaluate the response of the samples.

Internal standards are used in some analytical methods such as gas chromatography/mass spectrometry (GC/MS). One or more standards are added to each sample or sample extract. Calibration and sample quantification are based on the ratio of the response of the compound of interest to that of the associated internal standard.

The Method of Standard Additions (MSA) is used in some methods, such as metals analysis by Graphite Furnace Atomic Absorption Spectroscopy (GFAA) to correct for bias due to interference. The interference effects must be proportional to the concentration of the target analyte for MSA to provide accurate results. Standards at several concentrations are added to aliquots of the sample, and the resulting calibration curve is used for quantitation.

Sample responses must fall within the range of the calibration curve. This is why it is important to provide any available information on the expected levels of contaminants along with the samples.

# Appendix H

## Web Sites

| Home Page | URL |
|---|---|
| Links | |
| **American Society For Testing And Materials (ASTM)** | http://www.astm.org |
| QA Programs | http://www.astm.org/STATQA |
| **National Institute Of Standards And Technology (NIST)** | http://ts.nist.gov |
| Standard Reference Materials (SRMs) | http://ts.nist.gov/ts/htdocs/230/232/232.htm |
| **Pacific Northwest Laboratory (Battelle)** | http://www.pnl.gov |
| Statistics | http://www.pnl.gov/Statistics |
| Data Quality Objectives | http://dqo.pnl.gov/index.htm |
| **Puget Sound Action Team** | http://www.wa.gov/puget_sound |
| PSEP Protocols | http://www.wa.gov/puget_sound/Publications/protocols |
| **US Department Of Energy** | http://www.hanford.gov |
| Data Quality Objectives | http://www.hanford.gov/dqo |

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| **US Environmental Protection Agency** | http://www.epa.gov/ |
| Quality Staff | http://www.epa.gov/quality/ |
| Test Methods Index | http://www.epa.gov/epahome/index/ |
| (Includes links to sources of EPA methods) | |
| Stream Monitoring Methods | http://www.epa.gov/owow/monitoring/volunteer/stream |
| **Washington State Department Of Ecology** | http://www.ecy.wa.gov |
| Environmental Assessment Program Bibliography | http://www.ecy.wa.gov/programs/eap/#bibliography |
| List of Accredited Laboratories | http://www.ecy.wa.gov/programs/eap/labs/lablist.htm |
| Sediment Sampling and Analysis Plans | http://www.ecy.wa.gov/programs/tcp/smu |
| Manchester Lab Users Manual | http://aww.ecoweb/eap/pubs/labmanual.pdf |
| (Available only to Ecology staff on the agency Intranet) | |