National Contaminated Sites Remediation Program Guidance Manual for Sampling, Analysis, and Data Management

Volume One

Prepared for:

Environment Canada
Contract No. KE144-1-7026

DCN No. 92-703-001-01

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Under Contract No. KE144-1-7026

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October 1992

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ABSTRACT

This document is one of a series of technical support documents being prepared under the Canadian Council of Ministers of the Environment's National Contaminated Sites Remediation Program. Use of this manual will provide a consistent approach to sampling, analysis, and data management from contaminated sites on a national basis. The two primary objectives of this document are:

- To provide guidance for sampling and analysis of complex environmental matrices, such that the data obtained will be representative and of known quality; and
- To reduce selection of the many available methods in use to a few of the best so that future analytical data from multiple participating laboratories will be more consistent and comparable.

Throughout the document, the significance of QA/QC and planning is stressed. Another theme emphasized is the interdependence of sampling, analysis, and data management objectives on the planning and execution of tasks within each of these three areas. The focus of the document revolves around specific analytes identified in the CCME's, "Interim Environmental Quality Criteria for Contaminated Sites", which were published in September of 1991.

In Volume 1, Chapter 1 generally introduces the subject matter covered in this document. Chapter 2 is devoted to the principles and problems involved with obtaining representative samples from the four matrices, viz. soils, sediments, surface waters and groundwater. Topics include problems unique to each matrix, considerations in obtaining representative samples, selecting sampling locations and equipment, and preserving samples after they have been collected.

Chapter 3 provides a brief discussion of the criteria that are important in selecting appropriate analytical methods. In Chapter 4, the criteria for selecting analytical methods are described. Chapter 5 discusses data management. This includes topics such as data recording and documentation, data custody and transfer, data validation, completeness, comparability, compatibility, review, verification, handling and transmission. A final section addresses data reporting by laboratories and data presentation in final reports.

Chapter 6 lists all the references that have been used in the compilation of this document. A glossary of scientific terms used is included in the Appendix. Also, included in the

Appendix is a list of unpublished analytical methods that are used by various federal, provincial and commercial laboratories.

In Volume 2, method summaries are provided for the analytes in a consistent format which identifies all the information needed to make a decision as to whether to use that method in preference to another, and if so, what major analytical instrumentation would be required. A complete description of each method is provided including sample preparation, potential interferences, QC requirements, comments on use, and, where applicable, comparison with other methods. For detailed information, however, users are recommended to look-up the original references. This Volume is available in hard copy format, or on a computer diskette.

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Chapter 1 - Introduction

Background and Objectives of the National Contaminated Sites Remediation Program

The National Contaminated Sites Remediation Program was established in October of 1989 by the Canadian Council of Ministers of the Environment to deal with contaminated sites in Canada. The program has essentially three main objectives:

- to apply the "polluter pays" principle to the clean-up of contaminated sites;
- to clean-up high-risk orphan sites, i.e., the sites where the responsible parties for the contamination of the site cannot be identified and/or unable to pay for the clean-up; and
- to work with industry to stimulate the development and demonstration of new and innovative clean-up technologies.

The program operates on a cost-shared 5-year $250 million budget based on matching funding by the federal government and the provincial/territorial governments. Of the total amount, $200 million will be directed to the remediation of orphan high-risk contaminated sites, and the remaining $50 million will be used to develop and demonstrate new remediation technologies.

In the first year of the program, two major activities were begun in support of a consistent national approach to dealing with contaminated sites. Those activities were the development of a National Classification System and the development of Interim Environmental Quality Criteria. Both of these provide information which is important to the organization of this document, particularly the latter upon which the analytical groupings of contaminants are based (Table 1).

The CCME National Classification System[1] will be used to classify contaminated sites into three broad categories of concern according to their level of risk. A site is designated high-risk when site contamination is such that it represents a real or imminent threat to human health or to the environment. In this case an immediate action will be required to reduce the threat. The other two categories will be assigned lower priority in clean-up.

The Interim Canadian Environmental Quality Criteria[2] establishes numerical limits for the assessment and remediation of soil and water based on the safe use of reclaimed land for agricultural, residential/parkland and commercial/industrial purposes. They are based on a review of existing criteria used by the Canadian provincial/territorial jurisdictions. These criteria also include the Canadian Water Quality Guidelines (CCREM 1987), and Guidelines for Canadian Drinking Water Quality (Health and Welfare Canada 1989) for specified uses of water likely of concern at the contaminated sites.

The guidance provided concerning sampling, analysis, and data management in this manual represents a further integral step towards development of a consistent national approach to dealing with contaminated sites in Canada. The two primary objectives of this document are:

(i) To provide guidance for sampling and analysis of complex environmental matrices in such a way that the data obtained will be representative and of known quality; and

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Table 1. Target Analytes for the National Contaminated Sites Remediation Program

General Parameters

pH
conductivity
sodium adsorption ratio

Inorganic Parameters

antimony
arsenic
barium
beryllium
boron (hot water soluble)
cadmium
chromium (+6)
chromium (total)
cobalt
copper
cyanide (free)
cyanide (total)
fluoride (total)
lead
mercury
molybdenum
nickel
selenium
silver
sulphur (elemental)
thallium
tin
vanadium
zinc

Monocyclic Aromatic Hydrocarbons

benzene
chlorobenzene
ethylbenzene
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
styrene
toluene
xylene

Phenolic Compounds

non-chlorinated[1] (each)
chlorophenols[2] (each)

Polycyclic Aromatic Hydrocarbons (PAHs)

benzo(a)anthracene
benzo(a)pyrene
benzo(b)fluoranthene
benzo(k)fluoranthene
dibenz(a,h)anthracene
indeno(1,2,3-c,d)pyrene
naphthalene
phenanthrene
pyrene

Chlorinated Hydrocarbons

chlorinated aliphatics[3](each)
chlorobenzenes[4](each)
hexachlorobenzene
hexachlorocyclohexane
PCBs[5]
PCDDs and PCDFs[6]

Pesticides

aldrin and dieldrin
chlordane
DDT
endrin
heptachlor (+metabolites)
lindane
methoxychlor
carbaryl
carbofuran
2,4-D
diazinon
parathion
diquat
paraquat

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[1] Non-chlorinated phenolic compounds include: 2,4-dimethylphenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, nitrophenol (2-, 4-), phenol, cresol.

[2] Chlorophenols include: chlorophenol isomers (ortho, meta, para), dichlorophenols (2,6- 2,5- 2,4- 3,5- 2,3- 3,4-), trichlorophenols (2,4,6- 2,3,6- 2,4,5- 2,3,5- 2,3,4- 3,4,5-), tetrachlorophenols (2,3,5,6- 2,3,4,5- 2,3,4,6-), pentachlorophenol.

[3] Aliphatic chlorinated hydrocarbons include: chloroform, dichloroethane (1,1- 1,2-); dichloroethene (1,1- 1,2-); dichloromethane; 1,2-dichloropropane, 1,2-dichloropropene (cis and trans); 1,1,2,2-tetrachloroethane, tetrachloroethene; carbon tetrachloride; trichloroethane (1,1,1- 1,1,2-), trichloroethene.

[4] Chlorobenzenes include: all trichlorobenzene isomers; all tetrachlorobenzene isomers; pentachlorobenzene.

[5] PCBs includes mixtures 1242, 1248, 1254, and 1260.

[6] PCDDs and PCDFs:

2,3,7,8-T_4CDD
1,2,3,7,8-P_5CDD
1,2,3,4,7,8-H_6CDD
1,2,3,7,8,9-H_6CDD
1,2,3,6,7,8-H_6CDD
1,2,3,4,6,7,8-H_7CDD
O_8CDD

2,3,7,8-T_4CDF
2,3,4,7,8-P_5CDF
1,2,3,7,8-P_5CDF
1,2,3,4,7,8-H_6CDF
1,2,3,7,8,9-H_6CDF
1,2,3,6,7,8-H_6CDF
2,3,4,6,7,8-H_6CDF
1,2,3,4,6,7,8-H_7CDF
1,2,3,4,7,8,9-H_7CDF
O_8CDF

(ii) To reduce selection of the many available methods in use to a few of the best so that future analytical data from various laboratories will be more consistent and comparable.

Data Quality Objectives

Data quality objectives (DQOs) are an important aspect of Quality Assurance (QA) for the entire process from collecting and analyzing samples to the data processing and reporting. DQOs are statements that provide critical definitions of the confidence required in drawing conclusions from the entire project data. These objectives will determine the degree of total variability (uncertainty or error) that can be tolerated in the data. Limits of variability must be incorporated into the sampling and analysis plan and are achieved by using detailed sampling and analysis protocols. DQOs differ from measurement quality objectives (such as precision and accuracy) in that they are limits for the *overall* uncertainty of results, while the latter are only limits for the uncertainty of specific measurements.[4]

Data Quality Objectives can be qualitative or quantitative. Qualitative DQOs are specific descriptions of actions that are to be taken if an answer does not meet the desired outcome. They contain no quantitative terms but reflect general decisions that must be made. On the other hand, quantitative DQOs contain specific quantitative terms. These may include standard deviations, relative standard deviations, percent recovery, relative percent difference, and concentration.[4] Often, desired data quality objectives must be balanced against the cost of sampling and analysis, and more realistic objectives must be established with concurrence of the data users. Three factors that most influence the cost of sampling are (1) site location and accessibility to sampling points, (2) the numbers, kind, complexity, and size of samples to be collected, and (3) the frequency of sampling. The extent to which these factors will influence cost depends on particular aspects of each sampling project.

When environmental data are collected for making regulatory decisions concerning contaminated sites, the decision makers must understand the level of assurance associated with these data. To determine the level of assurance necessary to support the decision, an iterative process should be used by decision makers and project planners.

Data Quality Objectives are the full set of constraints needed to design a study, including a specification of the level of uncertainty that a data user is willing to accept in the decision. DQOs are developed using a process that encourages the sequential consideration of relevant issues. Figure 1 shows the principal stages in the DQO process.[5] Each of the stages results in an important criterion (or 'product') for the study that describes:

- The problem to be resolved at the site;
- The decision needed to resolve the problem;
- The inputs to the decision;
- The boundaries of the study;
- The decision rule; and
- The uncertainty constraints.

These constraints or products are the DQOs that will be used to formulate a study design that achieves the desired control on uncertainty, allowing the decision to be made with acceptable confidence.[5] There are several benefits to establishing DQOs:

- The data generated are of known quality.
- DQOs help data users plan for uncertainty. All projects have some inherent degree of uncertainty. By establishing DQOs, data users evaluate the consequences of uncertainty and specify constraints on the amount of uncertainty they can tolerate in the expected study results. The likelihood of an incorrect decision is estimated *a priori*.

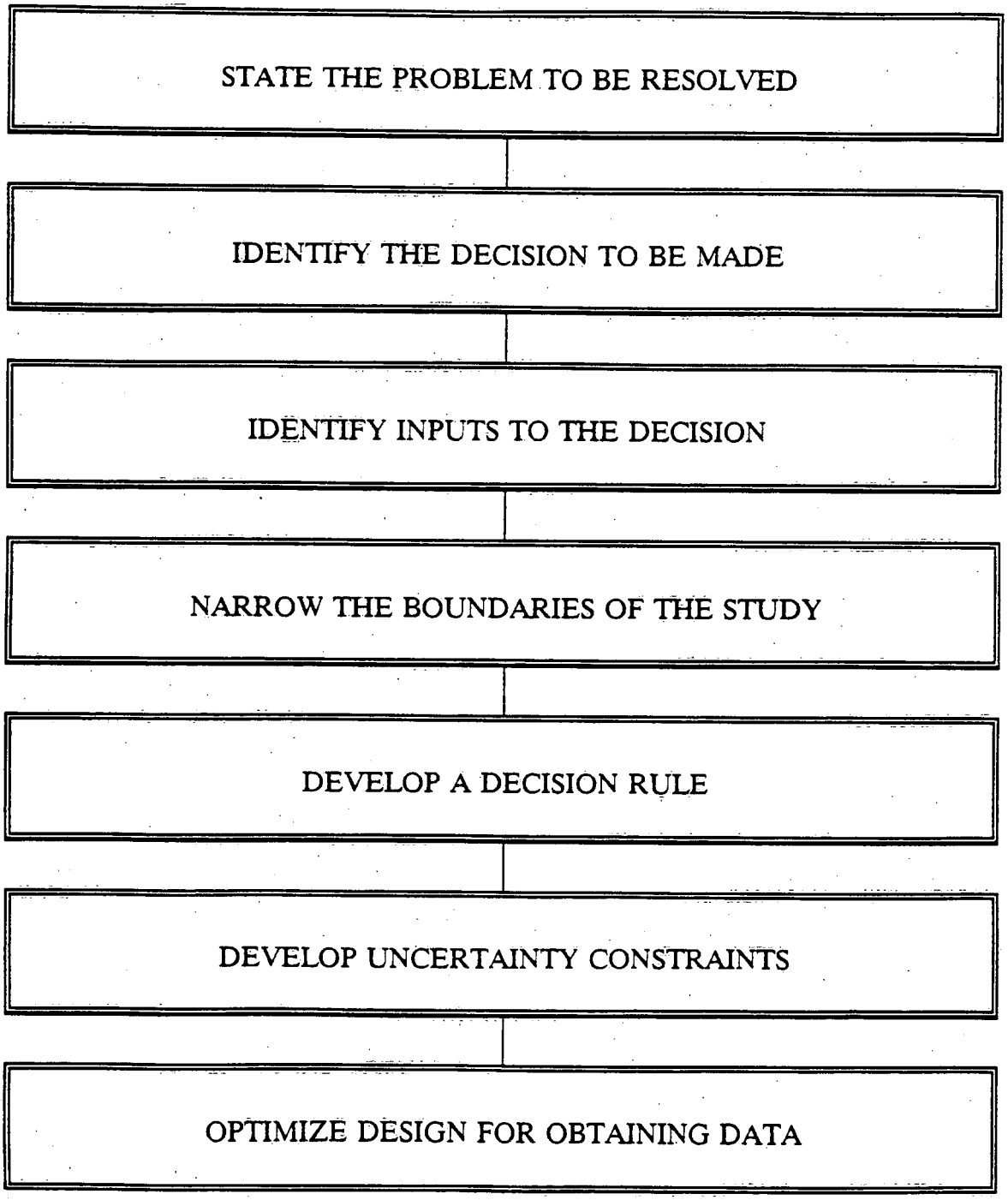

Figure 1. Steps in the Data Quality Objectives Process

- The DQO process facilitates communication among data users, data collectors, managers, and other technical staff before time and dollars are spent collecting data.
- The DQO process provides a logical structure for study planning that is iterative and that encourages the data users to narrow many vague objectives to one or a few critical questions.
- The structure of the process provides a convenient way to document activities and decisions that can prove useful in litigation or administrative procedures.
- The process establishes quantitative criteria for knowing when to stop sampling.

In establishing DQOs, it is important to follow the sequence of stages because the product of one stage is often an input to later stages. However, this process should be regarded as both flexible and iterative; as the study team sees the implications of different products, it should go back as necessary and revise products of earlier stages to incorporate the new concerns.

The Importance of Quality Assurance/Quality Control

The objective in collecting samples for analysis is to obtain a small and informative portion of the population being investigated. Usually, representative samples are sought, i.e., samples that can be expected to adequately reflect the properties of interest of the population being sampled. However, targeted, or nonrepresentative, samples are sometimes needed. An example might be a particular spot at a contaminated site which appears to be discoloured. However, samples taken at that spot should be representative of it at the time samples were taken. If samples, individually or collectively, cannot provide representative information, they are seldom worth the time and expense of analysis. Therefore, planning for informative sampling must be an integral part of any study.

Table 2. Sampling Plan Checklist

What are your Data Quality Objectives (DQOs)?
- What will you do if your DQOs are not met (i.e., resample or revise DQOs?)

Do Program Objectives need exploratory, monitoring, or both sampling types?

Have arrangements been made to obtain samples from the sites?
- Have alternate plans been prepared in case not all sites can be sampled?

Is specialized sampling equipment needed and/or available?

Are samplers experienced in the type of sampling required available?

Have all Analytes been listed?
- Has the Level of Detection (LOD) for each been specified?
- Have methods been specified for each analyte?
- What sample sizes are needed based on Method and desired LOD?

List specific Good Laboratory Practice, Federal, Provincial, or Method QA/QC protocols required.
- Are there percentages or required numbers and types of QC samples?
- Are there specific instrument tuning or other special requirements?

What type of sampling approach will be used?
- Random, Systematic, Judgmental, or combinations of these?
- Will the type of sampling meet your DQOs?

What type of data analysis methods will be used?
- Geostatistical, control charts, hypothesis testing, etc.
- Will the data analysis methods meet your DQOs?
- Is the sampling approach compatible with data analysis methods?

How many samples are needed?
- How many sample sites are there?
- How many methods were specified?
- How many test samples are needed for each method?
- How many control site samples are needed?
- What types of QC samples are needed?
  - Will the QC sample types meet your DQOs?
- How many of each type of QC samples are needed?
  - Are these QC samples sufficient to meet your DQOs?
- How many exploratory samples are needed?
- How many supplementary samples will be taken?

Number of Samples = Test + Control + QC + Exploratory + Supplementary
- Test Samples = Methods x Sample sites x Samples per site
- Control Samples = Methods x Sample Sites x Samples per site
- QC Samples = Methods x Type of QC sample x % needed to meet DQOs
- Exploratory Samples = (test samples + control samples) x 5 to 15%
- Supplementary Samples = (test samples + control samples) x 5 to 15%

From the beginning of sampling to the phase where the collected data undergo analysis, interpretation, and evaluation, there must be clear and precise documentation encompassing quality assurance (QA) guidelines and principles which cover every aspect of data collection[3]. Table 2 provides a convenient check list of the subjects that should beconsidered when planning for sampling contaminated sites[4]. Table 3 lists the minimum documentation needed for sampling activities[4].

Table 3. Minimum Requirements for Documenting Environmental Sampling

- Sampling Date
- Sampling Time
- Sample Identification Number
- Sampler's Name
- Sampling Site
- Sampling Conditions or Sample Type
- Sampling Equipment
- Preservation Used
- Time of Preservation
- Relevant Sample Site Observations (auxiliary data)

Another important consideration in planning for sampling and analysis of contaminated sites is the type and number of quality control (QC) samples to take. There are many different kinds of QC samples and each perform certain specific functions. Some are used to estimate bias and others to estimate precision. Some are useful for determining different sources of sampling errors, and others various sources of laboratory or analytical errors. It is critical that the correct types of QC samples be selected to meet DQOs or else the time and money spent gathering data will be wasted by obtaining data of unknown quality (i.e., it may be good, bad, or mediocre but no one will know the true quality). Advice should be sought from experts in planning QC strategies for environmental sampling and analysis at the beginning of each project. Additionally, software is also now readily available to help select the proper types of QC samples needed and to advise on the specific use of QC samples to compliment sampling and analysis processes for the production of known quality data.[7]

The bottom line of the importance of quality assurance (QA) and quality control (QC) to sampling is that if samples are not representative of the contaminated site being investigated, it doesn't matter how good the QA/QC of the analysis or of the data management is -- the information will be largely useless.

When samples arrive at a laboratory, another set of QC procedures must be observed as part of the laboratory's QA protocol. Each method may contain certain specific QC requirements. However, complete documentation of all records associated with laboratory analyses is also an important part of laboratory QC procedures. The records listed in Table 4 are the minimum requirements for documenting laboratory work.[6]

Table 4. Minimum Requirements for Documenting Laboratory Work

- Method of Analysis
- Date of Analysis
- Analyst's Name and Laboratory
- Calibration Charts & Other Measurement Charts (e.g., spectral)
- Method Detection Levels (or Limits)
- Confidence Limits
- Records of Calculations
- Actual Analytical Results

After analyses are completed, the third phase consisting of data handling and reporting begins. Data handling and data management QA programs focus on production of data which have characteristics of accuracy, precision, completeness, and representativeness[3]. The processes involved are summarized in Table 5 and are discussed in detail in Chapter 4.

Measurement results must be reported with clear units of measurement such as μg/L (for water and liquids) or μg/Kg (for soils, sediments and other solids) instead of parts per million, parts per billion, etc. The latter are less definitive than the specific units of measurement in the examples above and are SI units.

Table 5. Processes Involved in Data Handling and Management

- Data Recording and Documentation
- Data Transmission, Custody, and Transfer
- Data Validation
- Data Verification
- Data Analysis
- Data Handling
- Data Reporting

Not all factors that can influence the reliability and representativeness of data are measurable. Those that are measurable will usually be found if the data handling processes listed in Table 5 are followed. However, there are also many unmeasurable factors (Table 6) that can severely bias data and which are not necessarily readily identified even by good data handling and data management procedures.[8]

Table 6. Examples of Nonmeasurable Factors

Biased sampling,
Sampling the wrong area,
Sampling the wrong matrix,
Switching samples prior to labeling,
Mislabeling sample containers,
Incorrectly preserving the sample,
Incorrectly aliquoting or weighing samples,
Incorrectly diluting or concentrating samples,
Incorrectly documenting any procedure,
Matrix-specific interferences not recognized, and
Using the wrong method for analysis.

When good QA/QC procedures have been used in the total monitoring process, then the information derived from investigation of a contaminated site will be both reliable and of known quality. Failure to follow good QA/QC procedures within any of these activities may seriously jeopardize the quality and/or reliability of the data needed to

make critical decisions and may adversely affect costs for remediation of a contaminated site.

The Interrelation of Sampling, Laboratory Analysis, and Data Management

In addition to applying good QA/QC procedures to sampling, analysis, and data management, careful thought must be given to planning and carrying out the work that is involved within each of these activities. Often, each of these activities is planned somewhat independently but sampling, analysis, and data management are all interrelated and the objectives of each must be known to all of the participants involved with the monitoring of a contaminated site. Written protocols for sampling, analysis, and data handling must document the way in which each of the many individual tasks will be performed and also serve as a source of information for all of the participants in these interrelated efforts.

Pollutant Migration Pathways

Most environmental pollutants at a contaminated site will not remain stationary. If they are in a water, air, soil, sludge, solid, or liquid matrix they are almost certain to migrate. The physical characteristics of each matrix, meteorological conditions, the amount of pollutant present, the rate of release into the environment, the source of release and human intervention all affect the pathway and rate of migration.

The most common transport mechanisms for environmental pollutants are wind, rain, surface water, groundwater, and human intervention (wastewater pipes, drainage ditches, roads, etc.). In addition to transport mechanisms, physical and biological influences may also affect migration of pollutants. Physical influences include topographical features (valleys, mountains, slopes, lakes, rivers, etc.) and geological features (aquifers, soil composition, mineral composition, etc.). These physical influences can either aid or impede chemical migration. Biological influences usually consist of food pathways. Bioaccumulation

of environmental pollutants, from low concentrations in water, air, and soil to increasingly higher concentrations through the food pathways of plants and animals, is well documented and must be carefully considered when sampling biota at contaminated sites.[4]

Often an important objective of a contaminated site study will be to determine how far pollutants have migrated from their source and to measure their concentrations at various distances from their source. Regardless of the objective of a study, migration is always an important issue when obtaining blanks from nearby control sites. Analytes of interest migrating into the control site blanks, when the blanks are supposed to contain only background amounts of those analytes, will superimpose low values on test results when high background levels are subtracted from test sample data.

The Importance of Reporting Laboratory Data

How results are reported is one of the most controversial areas in environmental analytical chemistry because it affects how data are received, and perhaps equally importantly, how data are perceived and used by the public. Analytical chemists should always emphasize that the single most important characteristic of any result is a statement of its uncertainty interval.[9] Just as important is the sensitive issue of the level of data omission or inclusion in analytical reports. Deciding what limits should be used to report a measurement and how analysts and users should handle the resulting data are discussed in Chapter 5.

Decisions involving the presence or absence of pollutants are very important when their concentrations are near method detection levels (MDL). The first question is whether or not the analyte of interest is present in the sample. What has to be understood is that an MDL is a calculated concentration level that is indirectly selected. The concentration level of an MDL is calculated based on the risks of reporting false positives. What constitutes the appropriate level of risk is selected by either the analyst or the user of the data. Unfortunately, the criteria used for these risk selections are not always

understood. Furthermore, the value selected for determining that an analyte is reported as present may be different from the value selected for determining that an analyte is not reported as present.[10,11]

It must be emphasized that the MDL and other related calculations are not intrinsic constraints of the analytical methodology but depend upon the precision attainable by a specific laboratory working with a specific matrix when using that methodology.[12] Thus, MDLs can be very diverse. Unfortunately, this fact is generally not considered when evaluating environmental analytical data. Published values of MDLs in Volume Two must be considered only as typical. Each laboratory involved in reporting data should evaluate its own precision and estimate its own MDL values for analytes of interest for each type of matrix it analyzes. A common and acceptable alternative when method-specified limits are available (for example, with many methods summarized in Volume Two) is to verify that each instrument used can meet or exceed these published limits. If there is any possibility of a link between sensitivity of a method to operator performance or proficiency, then the instrument and method verification should be performed by each person who will use it.

Laboratory reports must contain sufficient data and information so that users of the conclusions (even years later) can understand the interpretations without having to make their own interpretations from raw data. Unless this objective is achieved, the samplers and analysts have not done their jobs properly. Laboratory reports also must make clear which results, if any, have been corrected for blank and recovery measurements. If published methodology (such as those in Volume Two) is used, it must be cited and any modifications made must be fully documented.

The Importance of Presenting Integrated Project Information

Sampling personnel are responsible for fully describing the precise conditions under which samples are collected. This includes all deviations from the sampling protocols for any reason.

Analytical chemists are responsible for fully describing and reporting the analytical data in an appropriate manner. It may be necessary to employ the help of a statistician in the data evaluation and interpreting stages. Measurement results should be expressed so that their meaning is not distorted by the reporting process.

Data handlers and managers are responsible for verifying and validating the data and providing evaluations of its consistency, integrity, and reliability. They rely upon information from both sampling and laboratory personnel to perform their evaluations. An integrated understanding of the problems presented by a contaminated site is possible only after the data have been evaluated and presented within the context of a report that integrates caveats documented during sampling, estimated during analysis, and placed in overall perspective from data management and review.

Report formats will vary but the content of each should contain the following:

- A summary of the problem being investigated;
- A summary of the data quality objectives and whether they were met or modified;
- A description of the sampling effort complete with contaminated site maps showing sampling locations;
- A description of the analytical approach with methods referenced and summaries of any analytical problems;
- A summary of the completeness and representativeness of the data; and
- Interpretations and conclusions from the integrated information provided in the report.

The following chapters treat each of these topics in greater detail. Chapter 2 discusses the sampling of contaminated sites and provides specific guidance for sampling contaminated soils, sediments, surface water (i.e., rivers, streams, and lakes), and

groundwater. Special considerations for sampling ice and/or surface waters under winter conditions are also included.

Chapter 3 discusses the general conditions involved with analysis of environmental samples with a focus on QA/QC aspects.

Chapter 4 provides a synopsis of the methods selected for recommendation and briefly discusses which methods are applicable to the list of target analytes in Table 1. They are discussed in the eight major groupings identified in the Interim Canadian Environmental Quality Criteria for Contaminated Sites.[2]

Chapter 5 provides a detailed discussion of the considerations needed for data management. This includes guidance on recording, documentation, data verification and validation, handling and transmission of data, etc. Key sections also include discussions on reporting data involving low level concentrations of pollutants and data presentation in final reports.

The document is concluded with a listing of all references and a glossary of common terms used in the document and also in environmental sampling and analysis. Also, included in the Appendix is a list of unpublished analytical methods that are used by various federal, provincial and commercial laboratories.

A summary of each of the recommended methods is provided in Volume Two. Each summary provides critical information that can be used to decide whether to select a specific method or not and, if selected, what will be required in terms of samples, equipment, and quality control.

Chapter 2 - Sampling Contaminated Sites

Defining Objectives

The first step in planning a contaminated site sampling activity is to define its objectives. Objectives of environmental sampling are broadly divided into exploratory (surveillance) or monitoring (assessment) goals.[4] Exploratory sampling is designed to provide preliminary information about the site or material being analyzed. Monitoring, on the other hand, usually is intended to provide information on the variation of specific analyte concentrations over a particular period of time or within a specific geographic area. A sampling plan for monitoring usually is more effective if it is preceded by exploratory sampling or if there is historical data on the analytes of interest at the sampling site.

Obtaining Representative Samples

Samples representative of a site (or of that portion of a site being investigated) provide information which is often extrapolated to include the whole area under investigation. This is true whether the entity being sampled is a contaminated section of land, a stream, an industrial outfall, or a drum containing waste material. Therefore, samples which are collected must be representative of the entity being sampled but not necessarily representative of the entire area of which that entity is a part.

Bias caused by sampling is often difficult to measure accurately but it can be detected by using field blanks fortified with the analytes of interest. On the other hand, it is also difficult to show that bias from sampling activities is absent because of an inability to measure it rather than its absence. When they do occur, sampling errors are usually much larger than those associated with analysis. Yet, the focus of errors in most sampling and analysis projects continues to be on laboratory and data handling sources, probably because these are the easiest to measure and control.

Sampling Approaches

Sampling program designs must consider the quality of the data needed, i.e., the degree to which total error must be controlled to achieve a required level of confidence. The data collection planning process should provide a logical, objective, and quantitative balance between the time and resources available for collecting the data and the data quality based on intended use of the data. One of the most important aspects of a planning process is the joint involvement of the data users, samplers, and analysts. Initial and continued involvement, and the perspective of each, is critical to defining data quality and quantity requirements.[4]

The choice of a data analysis method is an important decision that also should be made in the planning stage. It must facilitate, and be facilitated by, goals, DQOs, and experimental design. Both analyses and sampling approaches require prior information to meet data quality objectives. Any random variable method of data analysis (such as hypothesis testing, estimation interval, tolerance interval, control charts, etc.) requires random sampling. The number of samples for random variable methodology must be determined by the population variance and the desired size of a "significant change" in the test parameter.[4]

Systematic sampling is preferable for geostatistical data analysis, but random or even judgmental sampling may achieve greater accuracy within specific local areas of contaminated sites. Geostatistical data analysis accounts for the time and space dependence of data, and it is usually used to produce site maps (with qualification of interpolation errors) showing analyte locations and concentrations.[4]

Two basic sampling decisions, that must be resolved during the planning stage and documented in the protocol, are the types and number of QC samples to take.[13] The answers depend on the nature of the errors to be assessed (i.e., systematic and/or random) and the accuracy desired in their assessment. Additional considerations include the

contribution of sampling error relative to total error, the relative cost of sampling and analysis, and the sensitivity and selectivity of the analytical method in relation to the concentration of the analytes.[4]

There are three basic sampling approaches: random, systematic, and judgmental. There are also three primary combinations of each of these: stratified-(judgmental)-random, systematic-random, and systematic-judgmental.[4] Also, there are further variations that can be found among the three primary approaches and the three combinations of them. For example, the systematic grid may be square or triangular; samples may be taken at the nodes of the grid, at the center of the spaces defined by a grid, or randomly within the spaces defined by a grid. Table 7 summarizes the differences among the three basic approaches.

Table 7. Basic Sampling Approaches

Approach	Relative No. of Samples	Relative Bias	Basis of Selecting Sampling Sites
Judgmental	Smallest	Largest	Prior history, visual assessment and/or technical judgment
Systematic	Larger	Smaller	Consistent grid or pattern
Random	Largest	Smallest	Simple random selection

Often a combination of judgmental, systematic, or random sampling is the most feasible approach; however, the sampling scheme should be sufficiently flexible to permit adjustments during field activities. Problems such as lack of access to preselected sampling sites or unanticipated subsurface formations or weather conditions at a contaminated site may necessitate major adjustments to sampling plans.

Deciding How Many Samples to Take

There are numerous factors that influence how many samples need to be taken at a contaminated site. These include:

- How many distinct areas are there within the site?
  - If there are several, are samples desired from each?
  - If there are none, how widely dispersed within the single area are the sampling spots to be?
- How many different analytical methods are needed?
  - If more than one, will all sampling spots require all methods?
  - Typically, different analytical methods are needed for various types of organic pollutants (e.g., halogenated or non-halogenated, volatile or nonvolatile, metals or general parameters).
  - Typically different analytical methods are also needed for different sample matrices (e.g., surface or groundwater, solid or liquid wastes, industrial wastewaters, and air or soil gases).
- How many samples are needed for each analytical method?
  - This depends on the DQOs of the project, the size and complexity of the site, etc.
- How many control site samples are needed?
  - Typically, one or more from each matrix type is needed if a differentiation between polluted and non-polluted samples is being made.
  - If all samples contain concentrations of pollutants that are above specified action levels then no control site samples may be needed because the action results won't change. Also, in the case of heterogeneous solid or liquid waste materials (e.g., from drums) it may not be possible to obtain control samples.

- What types of QC samples are needed?
  - Is an estimation of bias important?
    - If so, does it need to be determined if it occurs in sampling or in the laboratory as opposed to overall bias?
  - Is a measurement of precision needed?
    - If so, does precision in sampling or in the laboratory (as opposed to overall bias) need to be determined?
  - Is the type of bias important?
    - Distinctions can be made between operator/method sources of bias and low level contamination originating in the laboratory, sampling, or from either operation if the correct type of QC samples are selected to differentiate these sources.
- How many of each type of QC samples are needed?
  - The number may depend on those specified in a particular method and/or the number calculated from statistical considerations to meet data quality objectives.
- If exploratory samples are needed first, how many should be taken from each sampling site area?
- If supplementary samples are needed for possible analyses at a later time, how many should be taken from each sampling site area?

The total number of samples needed can be roughly estimated using the following formula:

Total Samples = No. of Test Samples + No. of Control Samples + No. of QC Samples + No. of Exploratory Samples + No. of Supplementary Samples

where No. of Test Samples = No. Methods x No. of Sample Sites x No. of Samples per Site

and No. of Control Samples = No. of Matrices at the Sample Sites

and No. of QC Samples = % of Test Samples or a Statistically Calculated Number

and No. of Exploratory and Supplementary Samples = % of Test Samples or a Judgmental Number.

A more precise estimation of the number of samples needed is to select the sampling frequency which results in the desired confidence interval width about the mean for the specified analyte variability. Unfortunately, this may not often be available at contaminated sites, but if it is then a statistically derived number can be calculated.[3]

Thus, there is no straightforward, easy answer to the question, "How many samples should be taken?" Data Quality Objectives, discussed in Chapter 1, are intended to cover an entire study, but most often emphasis is given to the measurement phase of the investigation. Precision, accuracy, representativeness, completeness, and comparability are terms used in setting DQOs and are usually addressed in terms of the analytical portion of an investigation. Decision-makers must be concerned with the larger aspects of these terms, however. For example, a decision-maker may want to know whether the reported data are accurate to within 20% of the true value.

Measurement Quality Objectives (MQOs) are meant to apply to the analytical phases of a study. Terms for precision, accuracy, representativeness, completeness, and comparability are more applicable when used with the analytical phase. The distinction between DQOs and MQOs is important because QC samples are taken to determine whether these objectives are being met.

If historical data indicate that inaccuracy or variability is increased in the preparation and handling of a sample, and this decreases the accuracy needed to meet the MQOs, then more frequent sampling is justified. As another example, if the values reported are near an action level, then bias is particularly important in meeting a DQO for accuracy, and the consequences in knowing whether a pollutant is above or below that action level may be large. In this case, greater attention may need to be devoted to sample collection and to the use of field duplicates to assess sampling variability. The number of samples

required will depend on available resources, the required degree of confidence in the data, and the objectives of the study.

The U.S. EPA in Las Vegas, Nevada, has available a public-domain computer program named ASSESS. This program resembles a computer-based spreadsheet and computes measurement errors, provided enough QA/QC samples of the right type have been taken throughout the study. ASSESS indicates when insufficient samples exist and certain variabilities cannot be computed. The program can display graphically the degrees of confidence that exist for the measurement of variability in the individual portions of a study. Certain portions of a study usually receive more QC data than others. For those portions of a study that are monitored to a high degree, the variability may be low and ignored, or the variability may be high and may need to be addressed. For those portions of a study that are not monitored to a high degree, the variability may be low, but more samples may be required, or the variability may be high and more QC samples may be required.

Deciding on Exploratory and Supplementary Sampling

Often, exploratory sampling (screening) is desired to help delineate the extent of contamination and variations in contaminant levels within an affected area. This exploratory sampling may involve 10 to 15% of the overall monitoring effort. It requires an additional step of preliminary data analysis before the remaining samples are collected. When conducting exploratory sampling it is important that both the sampling and subsequent analyses, or preliminary work, be performed under the same sampling, analytical, and QA/QC protocols as those developed for the main body of test samples. Otherwise, the exploratory sampling may produce invalid data and false conclusions.[4]

Frequently, supplementary sampling (resampling) also is desirable; it is used to confirm particularly critical findings and to clarify uncertainties that were discovered

during the monitoring program. Supplementary sampling may also involve 10 to 15% of the monitoring effort.

Control Site Selection

Control sites are important for understanding the significance of monitoring data. Sites should be selected that have common characteristics with the contaminated areas except for the pollution source. Background samples (or control site or matrix samples) are samples taken near the time and place of the sample of interest. They are used to demonstrate whether the site is contaminated and/or truly different from the background in the area. Some sort of background sample is always necessary for a valid scientific comparison of samples suspected of containing environmental contaminants with samples containing no (below detectable or measurable levels) or acceptably low levels of contaminants. Unless background samples are collected and analyzed under the same conditions as the environmental test samples, the presence and/or concentration levels of the analytes of interest and the effects of the matrix on their analysis can never be known or estimated with any acceptable degree of certainty. Therefore, background samples of each significantly different matrix must always be collected when different types of matrices are involved whenever possible.[4]

Examples include various types of water, sediments, and soils in or near a sampling site area. Background air samples would include upwind air samples and perhaps different height samples. The only logical exception to collecting background samples is when drums or containers of materials are involved, as in a landfill; however, if the chemicals are suspected of polluting the land, water, or air around them, then appropriate background samples from those matrices must be taken for analysis.

There are two types of control sites (local and area) and their differentiation is primarily based on the closeness of the control site to the environmental sampling site.

Local control sites are usually adjacent or very near the test sample sites. In selecting and working with local control sites the following principles apply:[4]

- Local control sites generally should be upwind or upstream of the sampling site;
- When possible, local control site samples should be taken first to avoid contamination from the sampling site; and
- Travel between local control sites and sampling areas should be minimized because of potential contamination cause by humans, equipment, and/or vehicles.

In contrast to a local control site, an area control site is in the same area (e.g., a city or country) as the sampling site but not adjacent to it. The factors to be considered in area control site selection are similar to those for local control sites. All possible efforts should be made to make the sites identical except for the presence of the analytes of interest at the site under investigation. In general, local control sites are preferable to area control sites because they are physically closer. However, when a suitable local control site cannot be found an area control site will still allow important background samples to be collected.[4]

Sample Size Considerations

Because different analytical techniques are used for the many different analytes of interest at contaminated sites, sufficiently large samples must be taken for multiple analyses. Also, since analytical techniques are not well developed for some of the analytes in complex matrices, large samples provide laboratories the opportunity to analyze replicate samples or reanalyze samples when the data are suspect. However, disadvantages of large samples include additional costs of storage space, materials, and larger sample disposal costs.

Each analytical method summary selected for inclusion in Volume Two contains specific sample size requirements or guidance on collecting an appropriately sized sample. However, often a single sample may be collected with the intent that it will be used for multiple analytes of the same type. When this is planned, the sampling protocol must clearly define which analyses will be performed with each sample and this must be checked with the sample preparation requirements of each method to insure that they are compatible with such a plan. Sufficient sample must be collected so that there will be enough for each analytical method's requirement.

Deciding Types and Numbers of QC Samples

As discussed in the above section, there are many different types of QC samples from which to select. Choices depend entirely on the data quality objectives of the contaminated site being investigated. Thus, selections should be made depending on whether bias-free and/or precision data are required, whether differentiation between laboratory or sampling sources of error is needed, and whether the degree of error to be estimated is relatively small (i.e., from typical contamination type sources) or large (i.e., from operator and/or procedural sources).

Thus, there are many different types of QC samples to select from and it is important to select only those that are needed to meet the goals of a specific program. If the wrong QC samples are selected then the goals of the entire sampling and analysis program may be compromised. Most of the analytical method summaries described in Volume Two have a section entitled, "Quality Control Requirements." In this section, specific types of QC samples are listed for each method. However, these QC samples are designed primarily to measure laboratory sources of bias and precision and, usually, only bias from contamination-type sources. Thus, additional QC samples will usually be required in order to meet the data quality objectives of a specific contaminated site remediation program.

Because of the complexity of selecting among the many different types of QC samples and the consequences when incorrect QC samples are selected, an expert system was developed to provide advice on this subject. The *QC Advisor* is a simple, inexpensive program that can be run on IBM-compatible personal computers or Macintosh computers with a DOS emulator and is published by Lewis Publishers, Inc.[7]

The number of QC samples to take is best derived from statistical calculations based on the levels of confidence estimated to be obtainable from a specific method used with a specific environmental matrix (water, soil, etc.) to analyze for analytes at an estimated concentration factor above the method detection limit. Unfortunately, these estimates are not readily available so default values are usually selected which relate to a percentage of the environmental test samples analyzed. Specific default value recommendations may be provided with an analytical method summary as in Volume Two. When this occurs they are found in the section entitled, "Quality Control Requirements." A very common misconception is that if this recommended number (or percentage) of QC samples is analyzed in conjunction with the environmental samples, that there is some specified level of confidence in the data (e.g., a 95% confidence that the concentration of the analyte is near the measured value or that less than a 1% false positive or false negative detection will occur). This is not true! No specific confidence level in the data can be assigned when numbers of QC samples are based simply on a percentage of the environmental samples. Therefore, these are only useful as *very general* guidelines when no statistical information is available.

Grab Versus Composite Samples

Grab samples are single samples collected at a specific spot at a site over a very short period of time (typically seconds). Thus, they represent a "snapshot" in both space and time of the pollutants at a contaminated site sampling area. They are usually less expensive to obtain than composite samples and often several grab samples may be taken at the same spot over a period of time when information relating to changes in

concentrations of analytes with time is desired (i.e., with flowing streams or with air samples).

For example, there are two types of grab samples that are used for sampling water matrices: "discrete" and "depth-integrated" grab samples. A "discrete" grab sample is one that is taken at a selected location, depth and time, and then analyzed for the constituents of interest. A "depth-integrated" grab sample is collected over a predetermined part or the entire depth of the water column, at a selected location and time in a given body of water, and then analyzed for the constituents of interest.[14]

Composite samples are derived by combining portions of multiple samples. Compositing can be accomplished simply by collecting and combining multiple grab samples or by using specially designed automatic sampling devices. The latter can be configured to automatically collect and combine a series of "grab" samples or to continuously sample the environmental matrix and combine the samples.

Using the same water matrix as an example, there are two main types of composite samples: "sequential or time" and "flow proportional" composites. "Sequential or time" composites are made by continuous, constant sample pumping or mixing equal water volumes collected at regular time intervals. "Flow proportional" composites are obtained by continuous pumping at a rate proportional to the flow, or by mixing equal volumes of water collected at time intervals which are inversely proportional to the volume of flow, or by mixing volumes of water proportional to the flow collected during or at regular time intervals.[14]

Usually composite sampling techniques are selected in order to provide a more representative sample of heterogeneous matrices (such as rivers or air) in which pollutant concentrations may vary over short periods of time. However, compositing is not always an option; for example, samples of water that will be used for analysis of volatile

organics must always be collected as grab samples in order to avoid negatively biasing the results from loss of the volatile compounds during the compositing process.

Composite sampling is often used to reduce the cost of analyzing a large number of samples. Experimental costs are substantially reduced when the frequency of individual samples containing the analytes of interest is low. In such experiments, individual sample aliquots are combined into composites, and each composite is analyzed. However, composite sampling also has some limitations that must be considered.[4] These include the following:

- When considering multiple analytes in a composite, information regarding analyte relationships in individual samples will be lost.
- When the objective of the monitoring program is a preliminary evaluation or classification, compositing may dilute the analyte to a level below the detection limit, producing a false negative.
- If sampling costs are greater than analytical costs, analyzing each sample individually may be more cost effective.
- If compositing reduces the number of samples collected below the required statistical need of the DQOs, then those objectives will be compromised.

Assessing Safety Requirements

Contaminated sites, by their nature and definition, contain concentrations of chemicals that may be harmful to humans -- including those who collect samples at these sites. Thus, safety must always be considered in the development of any sampling plan. Proper planning and execution of safety protocols help protect employees from accidents and needless exposure to hazardous or potentially hazardous chemicals.

Safety plans should include requirements for hard hats, safety boots, safety glasses, respirators, self-contained breathing air, gloves, and hazardous materials suits if any

of these are needed. In addition, personal exposure monitoring and/or monitoring ambient air concentrations of some chemicals may be necessary to meet safety regulations.

Potential exposure of personnel to hazardous chemicals that can permeate their chemical protective clothing (CPC) causes concern whenever neat chemicals (those not in solution) or chemicals in high concentrations, e.g., from some landfills and wastewater streams, are to be sampled. There are many different manufacturers and many different models of CPC available on the market, but each of these has vastly differing protective capabilities against various chemicals. Thus, one manufacturer's model may offer over 8 hours of protection from a particular chemical while another's model, made from the same polymeric material, may degrade within minutes of exposure to that same chemical. Because of the complexity of selecting good CPC and the large amount of CPC data available, several databases have been published which allow rapid searches to be conducted using personal computers either at the sampling site or at an office/laboratory facility.[15-17]

Documenting Sampling Protocols

Sampling protocols are written descriptions of the detailed procedures to be followed in the collection, packaging, labeling, preservation, transportation, storage, and documentation of the samples. The more specific a sampling protocol is, the less chance there will be for errors or erroneous assumptions. Table 8 provides a convenient checklist of considerations that should be made when preparing sampling protocols.[4]

The overall sampling protocol must identify sampling locations and include all of the equipment and information needed for sampling: the types, number, and sizes of containers, labels, field logs, types of sampling devices, numbers and types of blanks, sample splits and spikes, the sample volume, any composite samples, specific preservation instructions for each sample type, chain of custody procedures, transportation plans, any field preparations (such as filter or pH adjustments), any field measurements (such as pH, dissolved oxygen, etc.), and the report format.[18] Also, it should identify those physical,

Table 8. Sample Protocols Checklist

What observations at sampling sites are to be recorded?

Has information concerning DQOs, analytical methods, LODs, etc., been included?

Have instructions for modifying protocols in case of problems been specified?

Has a list of all sampling equipment been prepared?
- Does it include all sampling devices?
- Does it include all sampling containers?
- Are the container compositions consistent with analytes?
- Are the container sizes consistent with the amount of samples needed?
- Does it include all preservation materials/chemicals?
- Does it include materials for cleaning the equipment?
- Does it include labels, tape, waterproof pens, and packaging materials?
- Does it include chain of custody forms and sample seals?
- Does it include chemical protective clothing or other safety equipment?

Are there instructions for cleaning equipment before and after sampling?
- Are instructions for equipment calibration and/or use included?
- Are instructions for cleaning or handling sample containers included?

Have instructions for each type of sample collection been prepared?
- Are numbers of samples and sample sizes designated for each type?
- Are any special sampling times or conditions needed?
- Are numbers, types, and sizes of all QC samples included?
- Are numbers, types, and sizes of exploratory and supplementary samples included?
- Are instructions for compositing samples needed?
- Are instructions for field preparations or measurements included?

Have instructions for completing sample labels been included?

Have instructions for preserving each type of sample been included?
- Do they include maximum holding times of samples?

Have instructions for packaging, transport, and storage been included?

Have instructions for chain of custody procedures been included?

Have safety plans been included?

meteorological, and hydrological variables that should be recorded or measured at the time of sampling.[19] In addition, information concerning the analytical methods to be used, minimum sample volumes, desired minimum levels of quantitation, and analytical bias and precision limits may help sampling personnel make better decisions when unforeseen circumstances require changes to the sampling protocol.

Selecting analytical methods is an integral part of the sample planning process and can strongly influence the sampling protocol. For example, the sensitivity of an analytical method directly influences the volume of sample required to measure analytes at specified minimum detection (or quantitation) levels. The analytical method may also affect the selection of storage containers and preservation techniques.[20] In documenting sampling protocols there are at least three different types of QA documents to consider, each one covering different aspects of sampling and analysis procedures. These are: a QA Program Plan, a QA Project Plan, and a Program Implementation Plan. Often a fourth document, a Field Sampling QA/QC Manual, is also necessary but, organizationally, this is considered to be a part of the overall QA Project Plan.[21]

The QA Program Plan is a document which commits management to a specific QA policy and sets forth the requirements for data needed to support program objectives. The program plan describes the overall policies, organization, objectives, and functional responsibilities for achieving data quality goals. The five major functions of a QA program plan are:[21]

- A statement of the purpose and importance of a QA plan;
- A description of the procedures that will be used to carry out the QA program;
- A description of the resources committed to perform the QA work;
- An identification of projects which require QA project plans; and
- A description of how QA implementation will be evaluated.

The second document is a QA Project Plan. It differs from the former in that it is a technical document that details specific QA and QC requirements for a project. The plan also specifies any QA/QC activities required to achieve the data quality goals of a project and describes how all data are assessed for precision, accuracy, representativeness, completeness, comparability and compatibility. The QA Project Plan further requires that all data generated be thoroughly documented and address the following items in sufficient detail to permit unambiguous evaluation of project results:[21]

- Project description;
- Project organization and designated responsibilities;
- QA objectives for the experimental data in terms of precision, accuracy, completeness, ruggedness and comparability;
- Sampling procedures and sample handling;
- Sample custody, transportation, preservation and storage;
- Calibration procedures and frequency;
- Experimental design and analytical procedures;
- Reference standards and quality control standards;
- Documentation needed;
- Data reduction, validation, verification and reporting;
- Internal quality control checks and frequency;
- Preventive maintenance procedures and schedules;
- Specific routine procedures to be used to assess data quality;
- Corrective actions; and
- Quality assurance reports to management.

To satisfy the requirements for quality data, a QA Project Plan must describe the following activities:[21]

- Network design;
- Selection of specific sampling sites;
- Sampling, analytical methodology, calibration, and standard operating procedures (SOPs);
- Sampling devices, storage containers, and preservatives;
- Special operating conditions (e.g., heat, light, reactivity, etc.);
- Reference, equivalent or alternate test procedures;
- Instrument selection and use;
- Preventive and remedial maintenance;
- Replicate sampling;
- Replicate analyses;
- Blank and spiked samples;
- Intra- and inter-laboratory QC procedures;
- Documentation needed; and
- Sample custody.

A Field Sampling QA/QC Manual is also a component of a QA Project Plan and must provide guidance on policy and procedures. This manual contributes to the quality of the data generated by: [21]

- Providing unified information for all participating agencies;
- Detailing procedures to be used in the field;

- Providing information on project descriptions, project organization and designated responsibility;
- Considering siting criteria for the sampling plan;
- Indicating the QA objectives for precision, representativeness, completeness, and comparability;
- Providing information for calibration and maintaining equipment;
- Providing information on safety practices in sampling and field testing operations;
- Providing accepted procedures designed to control and define errors associated with field measurements;
- Defining statistical techniques for assessing the experimental data; and
- Ensuring that the collected data have met the measurement program objectives.

The third document is a Program Implementation Plan. It documents mechanisms that must be put in place to ensure maximum coordination and integration of QA efforts within the overall program (covering sampling, laboratory analysis and data handling). Resource levels, schedules, turnaround times, responsibility centers, performance indicators, milestones, risk factors, implications, emerging issues, etc., are subjects discussed in program implementation plans.[21]

Sampling Contaminated Soils

Problems Unique to Sampling Soils

In addition to variability of types of pollutants (analytes) and their concentration variations throughout the site, soil samples often exhibit a geological variability. Geological variability is unique to soils and, to a lesser degree, sediments and it imposes some special considerations that sampling other matrices does not have to address. On the other hand, one other characteristic that is unique to sampling soils and,

to a lesser degree, sediments is the slowness of migration of pollutants from one location to another. Thus, a soil site can be sampled and then resampled an hour (or longer) later with no significant change in the pollutants or their concentrations having occurred; this is not generally true of water or air matrices.

Soils are characterized by several types of variation; it is not a homogeneous mass but a rather heterogeneous body of material. Because of this heterogeneity, systems have been set up that attempt to delineate soil classification units which approach homogeneity within themselves, but which, at the same time, are distinctly different from all other units. Differences among these units may be large or small depending, among other things, on the differential effect of the factors which formed the soils. The variation in properties among soils formed from the same parent material under similar conditions, on the other hand, may be rather small even though the soils be classified as different soils. Because of the nature of soil-forming processes, distinct boundaries between soil classification units are rare.

Superimposed on this pattern of slowly changing characteristics, however, may be marked local variations. These local variations may result from natural causes, such as sharp vegetative or topographic variations, or from man-made variations. A similar pattern of variation is found in the subsoil.[22]

Soil properties vary not only from one location to another but also among the horizons of a given profile. The horizon boundaries may be more distinct than are the surface boundaries of a soil classification unit. Here, also, zones of transition are found between adjacent horizons. Furthermore, considerable local variation may occur within a particular horizon.[22]

These characteristics should be kept in mind when sampling soils. The soil population to be sampled should be subdivided, both horizontally and vertically, into sampling strata which are as homogeneous as possible, and the several sources of variation

within the population should be sampled if valid inferences are to be made about the population from the sample.[22]

Another characteristic more unique to soil sampling than most other matrices (except biological sampling) is subsampling. In many types of soil investigations, the use of subsampling, or multistage sampling, is advantageous. With this technique, the sampling unit, selected by one of the previously described methods, is divided into a number of small elements. The characteristic under consideration is then measured on a sample of these elements drawn at random from the unit. For example, a sample of cores may be taken from a field plot, and a number of small samples taken from each core for chemical analysis.[22]

The primary advantage of subsampling is that it permits the estimation of some characteristic of the larger sampling unit without the necessity of measuring the entire unit. Hence, by using subsampling, the cost of the investigation might be considerably reduced. At the same time, however, subsampling will usually decrease the precision with which the characteristic is estimated. At each stage of sampling, an additional component of variation, the variation among smaller elements within the larger units, is added to the sampling error. Thus, the efficient use of subsampling depends on striking a balance between cost and precision.[22]

Review Existing Site Information

Every effort should be made to first review relevant information concerning a contaminated site. A historical data review examines past and present site operations and disposal practices, providing an overview of known and potential site contamination and other site hazards. Sources of information include federal, provincial, and local officials and files (e.g., site inspection reports and legal actions), current and former facility employees, potentially responsible parties, local residents, and facility records or files. For any sampling

efforts, obtain information regarding sample locations (on maps, if possible), matrices, and relevant contaminant concentrations.

When possible, collect information that will describe any specific chemical processes used on site, as well as descriptions of raw materials used, products and wastes, and waste storage and disposal practices. Whenever possible, obtain site maps, facility blueprints, and historical aerial photographs, detailing past and present storage, process, and waste disposal locations.

Site Reconnaissance

A site reconnaissance, conducted either prior to, or in conjunction with sampling, is invaluable to assess site conditions, to evaluate areas of potential contamination, to evaluate potential hazards associated with sampling, and to develop a sampling plan. The reconnaissance should fill data gaps left from the historical review. During the site reconnaissance:

- Interview local residents and present or past employees about site-related activities;
- Obtain information from facility files or records (where records are made accessible by owner/operator); and/or from land registry files, if possible; and
- Perform a site entry, utilizing appropriate personal protective equipment and instrumentation; observe and photo-document the site; note site access routes; note and map process and/or waste disposal areas such as landfills, lagoons, quarries, and effluent pipes and potential transport routes such as ponds, streams, irrigation ditches, etc. Note topographic features, dead or stressed vegetation, potential safety hazards, and visible label information from drums, tanks, or other containers found on the site.

The historical review and site visit are the initial steps in defining the source areas of contamination which could pose a threat to human health and the environment.

However, pollutant migration pathways and the routes by which persons or the environment may be exposed to the chemical wastes at a site are also part of a site reconnaissance.

Migration pathways are routes by which contaminants have moved or may be moved away from a contamination source. Pollutant migration pathways may include pathways such as surface drainage, vadose zone transport, and wind dispersion. Human activity (such as foot or vehicle traffic) also transports contaminants away from a source area. These five transport mechanisms are described below.

- Man-made Pathways -- A site located in an urban and/or rural setting will have a number of man-made pathways which affect contaminant migration. These include: storm and sanitary sewers, drainage culverts, sumps and sedimentation basins, french drain systems, and underground utility lines.

- Surface Drainage -- Contaminants can be adsorbed onto fine sediments, dissolved in surface water runoff, or mobilized via leachate and be rapidly carried by surface runoff into drainage ditches, streams, rivers, ponds, lakes, and wetlands. Consider prior surface drainage routes when formulating a soil sampling design.

- Vadose Zone Transport -- Vadose zone transport is the vertical or horizontal movement of water and contaminants within the unsaturated zone of the soil profile. Contaminants from a surface source or a leaking underground storage tank can percolate through the vadose zone and be adsorbed onto subsurface soil or reach groundwater.

- Wind Dispersion -- Contaminants adsorbed onto soil may migrate from a waste site as airborne particulates. Depending on the particle-size distribution and associated settling rates, these particulates may be deposited downwind or remain suspended, resulting in contamination of surface soils and/or exposure of nearby populations.

- Human Activity -- Foot and vehicular traffic of facility workers and sampling personnel can also move contaminants away from a source although these are usually a minor source of the overall migration.

Incorporating contaminant migration routes and transport mechanisms when designing a representative sampling scheme is often an important consideration in

producing good sampling plans. Field analytical screening techniques can provide direct reading capabilities (e.g., a photoionization detector (PID), or a portable X-ray fluorescence (XRF) unit) which may be utilized to narrow the possible groups or classes of chemicals to support the selection of analytical parameters. Field screening can cost-effectively evaluate a large number of samples for the purpose of selecting a subset for off-site laboratory analysis. When used appropriately, field screening is effective and economical for gathering large amounts of site data. Field screening techniques and confirmatory sampling can be used together to identify or delineate an area requiring evaluation (e.g., extent of contamination). Once this area has been identified using screening techniques, an appropriate confirmatory sampling strategy can substantiate and further define the screening results. The use of field analytical screening data to select and implement confirmatory sampling can provide data which are more representative of problems at a contaminated site than just off-site laboratory analysis alone. Screening strategies in conjunction with confirmation sampling strategies can be used to identify and delineate contamination and to confirm cleanup at a site. In order to minimize the potential for false negatives (not detecting on-site contamination), field analytical screening methods should be selected that provide detection limits below applicable action levels.

Representative Sampling of Soil

Representative soil sampling assures that a sample or group of samples accurately reflects the concentration of the parameter of concern at a given time. Analytical results from representative samples also illustrate the variation in pollutant presence and concentration across a contaminated site. However, because soils are extremely complex and variable, this often requires many different sampling methods. The sampling personnel must select methods that best accommodate specific sampling needs, and that satisfy the stated sampling objectives. In addition, the sample collector is responsible for providing the appropriate samples for laboratory analysis. A soil sample must provide an adequate size sample to meet analytical requirements and supply samples representative of the population to be evaluated.[23]

Deposition of airborne contaminants, especially those recently deposited, is often evident in the surface layer of soils. However, contaminants that have been deposited by liquid spills or by long-term disposition of water soluble materials may be found at depths up to several meters. Also, plumes emanating from hazardous waste dumps or leaking storage tanks may be found at considerable depths.[23]

Because sample heterogeneity often causes problems in soil, and other environmental matrices, representativeness uncertainties frequently far exceed the inherent collection and analysis uncertainties. Often it is not possible to quantify the analyte concentration uncertainties associated with sample selection. In these instances, qualitative descriptions of the uncertainties due to sampling limitations should be clearly described and the associated assumptions fully documented.[4]

Sometimes samples are deliberately collected unrepresentatively. Initial studies at a contaminated site may focus on the most obviously contaminated areas. Although such samples will not represent the average conditions, they may establish the worst case concentrations of the analytes of interest. However, even in these situations it is important to obtain background samples of the soil matrix from either local or area control sites.

Variability arises from the heterogeneity of samples, the size and distribution of the sampling populations, and the bias of the sampling and analysis methods. Because soil samples are heterogeneous, it is best to select as large a test sample as practical for preparation. An extract or digested solution will be more homogeneous, and it will provide more reproducible aliquots, than a smaller portion of the sample.

Composite samples may help overcome the lack of homogeneity over time or in the distribution of chemical species. At the same time, compositing may dilute peak values of concern. Therefore, if peak concentrations of analytes are important, compositing

should be supplemented with grab samples taken at sites and times where higher values are suspected.[4]

Selecting Sampling Locations

Once a sample approach has been selected, the next step is to select sampling locations. For statistical (non-judgmental) sampling, selection of the exact location of each sampling point is crucial to achieve representativeness. For example, factors such as the difficulty in collecting a sample at a given point, the presence of vegetation, or discoloration of the soil could influence (bias) a statistical sampling plan.

Sampling points may be located using a variety of methods. A relatively simple method, which may be used for locating random points, consists of using either a compass and a measuring tape, or pacing off distances, to locate sampling points with respect to a relatively permanent landmark, such as a survey marker. Then, plot aerial coordinates of the sampling points on a map and mark the actual sampling points for future reference. Where the sampling design demands a greater degree of precision, each sample point should be located by means of a survey. After field sample collection, each sample point should be marked so that all the locations can be found again if needed.

Selecting Sampling Equipment

Methods selected for sampling soils may differ in detail but they all make use of one of the following three basic sampling tools: (1) scooping, (2) coring, or (3) augering devices.

Two major considerations must be addressed when selecting a specific sampling tool. These two considerations include soil conditions and the contaminants that are to be analyzed from the collected material. Soil conditions can be extremely variable from location to location. For example, soils can be wet or dry, stony, cohesive (e.g., clay)

or cohesionless (e.g., sand). Similarly, contaminants are extremely diverse, varying between metals, which in most cases are relatively immobile, to highly mobile water soluble substances, to contaminants that are volatile.[23]

Improper use and selection of sampling tools may result in data that are not representative of the soil environment being sampled. Measurement errors can result from a tool being either inappropriate for a particular task, or improperly used. Results based on previous experience, or from an equivalency test, may be used to evaluate and select the proper tool for a specific sampling objective.[23] Table 9 provides a list of commonly used sampling tools for collecting soil samples.

Soil sampling devices should be chosen after considering the depth of the sample to be taken, the soil characteristics, and the nature of the analyte of interest (e.g., organic or inorganic, volatile or nonvolatile). Surface sampling may be chosen for recent spills or contamination and low migration rates of analytes. If the analytes of interest are volatile or have been in contact with the soil for a long period of time, sampling at greater depths may be necessary. Soil characteristics will determine the migration patterns of the analytes of interest and also the characteristics of the usable sampling devices. The nature of the analyte being sampled, e.g., whether it is volatile or soluble, will influence the sampling depth, the sampling device, and sometimes the materials from which the sampling device must be constructed.[4]

When sampling soil at its surface or at shallow depths (less than about 15-30 cm) scoops or shovels may be used; however, they do not obtain very similar samples. Also, these tools are not suitable for sampling soil contaminated with volatile materials, since they may volatilize during sampling and make the samples unrepresentative. As with all sampling devices, careful attention to construction materials is necessary. Generally, scoops and trowels should be stainless steel for soils contaminated with organics and high density polyethylene for soils contaminated with inorganic species.[4]

Table 9. Soil Sampling Equipment

Equipment	Application to Sampling Design	Advantages and Disadvantages
Trier	Soft surface soil	Inexpensive; easy to use and decontaminate; difficult to use in stony, dry or sandy soil.
Scoop or trowel	Soft surface soil	Inexpensive; easy to use and decontaminate; trowels with painted surfaces should be avoided.
Tulip bulb planter	Soft soil, 0 - 15 cm	Easy to use and decontaminate; uniform diameter and sample volume; preserves soil core (suitable for VOA and undisturbed sample collection); limited depth capability; not useful for hard soils.
Soil Coring Device	Soft soil, 0 - 60 cm	Relatively easy to use; preserves soil core (suitable for VOA and undisturbed sample collection); limited depth capability; can be difficult to decontaminate.
Split spoon sampler	Soil, 0 cm - bedrock	Excellent depth range; preserves soil core (suitable for VOA and undisturbed sample collection); acetate sleeve may be used to help maintain integrity of VOA samples; useful for hard soils; often used in conjunction with drill rig for obtaining deep cores.
Shelby tube sampler	Soft soil, 0 cm. - bedrock	Excellent depth range; preserves soil core (suitable for VOA and undisturbed sample collection); tube may be used to ship sample to lab undisturbed; may be used in conjunction with drill rig for obtaining deep cores and for permeability testing; not durable in rocky soils.
Hand operated power auger	Soil, 15 cm - 5 m	Good depth range; generally used in conjunction with bucket auger for sample collection; destroys soil core (unsuitable for VOA and undisturbed sample collection); requires 2 or more equipment operators; can be difficult to decontaminate; requires gasoline-powered engine (potential for cross-contamination).

Sampling devices must be decontaminated between successive samples to avoid cross contamination (the decontamination produces QC samples called "equipment blanks"). Sometimes, when using scoops or trowels, it may be easier to use separate devices for each sample and then have them decontaminated in a lab or other facility equipped for that purpose. A soil punch or other thin-walled steel tube device is more suited for obtaining reproducible samples at the soil surface or shallow depths. These devices are pushed into the soil to a desired depth and retain a sample. The sample may be removed for compositing or transferred to other sample containers. Some thin-walled tube samplers are designed as a combination sampling and shipping device, since the ends of the sampler can be sealed for shipment after the outside of the device is decontaminated.[4]

Sampling at depths greater than one foot requires different techniques and devices. Trenching can obtain analyte profiles; however, it usually costs more than other techniques available. Trenches should be excavated approximately one foot deeper than the desired sampling depth. A soil punch or trowel can then be used to dig laterally into the exposed soil to obtain the samples.[4]

Augers, both powered and non-powered, are also useful in obtaining solid samples from depths greater than about one foot. Augers come in different sizes, and samples may be obtained directly from the auger cuttings. However, this technique can introduce cross contamination between soil layers, contamination from drilling material, non-reproducibility in sample size, and loss of volatile components. A more desirable technique is to reach the desired sampling depth with an auger, and then obtain the sample with a soil probe or split barrel sampler. Soil cuttings should be carefully removed after drilling to avoid cross contamination between soil layers.[4]

Soil probes and split barrel samplers work in a similar fashion. The device is driven into the soil to the desired depth and retains the samples as it is withdrawn. A soil sample obtained in this manner may then be transferred to a separate container for shipment to the laboratory. Stainless steel or Teflon® liners are available for split barrel

samplers to minimize adsorption of or reaction with analytes. Some of these devices are designed to be sealed for shipment to the laboratory after the exterior is decontaminated.[4]

Sample Preservation and Storage

In general, sample containers should be tightly sealed as soon as the samples are taken; headspace should be minimized, and the samples refrigerated as soon as possible. The refrigeration should be maintained at about 4° C until analysis, and the samples analyzed as soon as possible.[18]

If extraction or acid digestion is required, these procedures should be carried out as soon as possible; then the extracts or digested solutions can be held for the prescribed holding times. Either entire cores samples or large portions of them should be shipped to a lab, wrapped in solvent washed and dried aluminum foil, or sealed in glass bottles. One pint, wide mouth bottles are useful for core samples -- the samples can be cut so that they nearly fill the bottles.[18]

The most frequent changes in soil, sediment and water samples are loss of volatiles, biodegradation, oxidation, and reduction. Low temperatures reduce biodegradation and, sometimes, volatile loss, but freezing water-containing soil samples can cause degassing, fracture the sample, or cause a slightly immiscible phase to separate. Anaerobic samples must not be exposed to air.[18] However, air drying is generally appropriate for metals and other nonvolatile analytes. Volatile organics would be lost or reduced in concentration if they were present in soils subjected to air drying.

More detailed information on sampling contaminated solids and water can be found in the National Contaminated Sites Remediation Program's, "Handbook on Subsurface Assessment".[31]

Sampling Contaminated Sediments

Problems Unique to Sampling Sediments

Sediments range from sand to clay particles that are under water. They may lie under a flowing stream or deep on the ocean floor. In the context of contaminated land sites they will be at the bottom of ponds, lakes, and streams. Unique sampling problems arise because of the difficulty of sampling generally unseen areas underwater. Additional sampling problems occur when winter time sampling requires cutting holes in ice in order to set up and use sediment sampling equipment.

Access to the sampling area plays an important role in sampling strategy and logistics and selection of sampling equipment. There are basically two options for the collection of bottom sediment samples: sampling from a platform and sampling by a diver. Sampling platforms may be a ship, ice, a plane, a helicopter, etc. Collection by a diver, though usually more costly and difficult than sampling from a platform, often yields better quality samples, particularly sediment cores. In areas with a sufficient ice cover over the sampled water body, sediment samples can be obtained by drilling a hole in the ice and sampling through this hole. The advantage of this technique is a steady platform and a large space at the sampling station for assembling the equipment and processing the samples. In areas with no road access, sediments may be collected from a small float plane or from a helicopter. Availability of a plane or helicopter and cost are factors to be considered.[24]

Review Existing Site Information

Depending on the nature of the project and the site to be investigated, there may be a considerable body of historical information and data relevant to the project objectives. The gathering of historical data with a comprehensive review of literature, reports, and all available previously published data generated by surveys and studies, including the characterization of the sediments, should be completed before the preparation

of a project plan.[24] Historical data can be obtained from a variety of sources. Data specific to the area of a contaminated site may include that derived from:

- Geological investigations;
- Previous sediment analyses;
- Benthic investigations in conjunction with ecological studies;
- Environmental impact studies;
- Analyses of the overlaying water;
- The types of industry and business that used the site; and
- Watershed activities.

Data from regional reconnaissance surveys can sometimes provide information on a broad scale, such as concentrations predicted from the known geology and mineralogy of the area; geochemistry of sediments; general "background" concentrations or concentrations of different chemicals in soil which, through weathering or erosion within a watershed, would contribute material to sediments. Material may enter from a watershed in either dissolved form or associated with eroded soil materials and may include, for example, pesticides or fertilizers from agricultural practices, mining wastes, or excavated materials, or industrial/mining processing by-products/effluents.[24]

An important factor to consider is that even very old or incomplete data can be used to provide a first estimate of the concentration of a parameter or the likelihood of sedimentary processes, or provide sufficient information to warrant additional sampling at the area. In some cases, even simple commentary from local citizens about a site for which there is little documentation can prove to be valuable.[24]

Particular pieces of data which are relevant to project planning for sediments include:[24]

- General information on the watershed, including quantity and quality of runoff, climatic conditions, general or specific land use, types of industries, effluent, and urban runoff;

- Distribution, thickness, and types of sediments, particularly fine-grained sediments (this will assist in assessing the physical extent of sediment accumulation, zones of deposition and erosion, and sediment transport);

- Quantity, particle size, geochemistry, and mineralogy of suspended sediments discharged by tributaries, stormwater runoffs or originating from shoreline erosion (knowledge of the nature and quantity of dissolved and particulate materials entering the area is necessary for the calculation of contaminant and nutrient loading);

- Horizontal and vertical profiles of physical (e.g. porosity, geotechnical properties, water content, bulk density, grain size) and chemical (e.g., organic matter content, concentrations of nutrients, metals and organic contaminants) characteristics of bottom sediments; and

- Biological community structure, composition and diversity, bioaccumulation of contaminants, or bioassay results.

The data and information collected from the above activities must be carefully reviewed as to their:

- Relevancy (to the overall objective of the project);

- Completeness (taking into account that parameters or processes of interest may not have been measured in previous studies, and the objective for previous study was different); and

- Quality of data (based on reported limits of detection and precision compared to precision now required).[24]

Site Reconnaissance

An important aspect which is often overlooked with collection of sediment samples is a site inspection. The visit to the project site permits an assessment of the

completeness of the collected information and identifies any significant changes at the project site.[24]

From the review of collected data, the gaps in the information should be identified and the sampling program designed to fill these gaps to achieve the overall objective of a project. The project plan should describe in detail which objectives will be selected and how these objectives will be achieved within a given time frame and budget for a project. The selection of the number and location of sediment sampling stations, and description of methods for sediment sampling, handling and analyses are a key part of the project plan. Sampling locations affect the quality and usefulness of data in environmental studies.[24] Selection of the sampling locations should be based mainly on the project objective and on the basis of the site reconnaissance.

Sampling hazards should also be identified and documented during the site reconnaissance. These may range from dangers caused by rapidly flowing waters, underwater physical and geological hazardous features, the identification of thin spots in ice covering a sampling site, etc.

Representative Sampling Approaches

In addition to the physical handicaps of collecting representative sediment samples, the sampling procedures and devices must also be considered because they can directly affect the representativeness of the collected samples.

To collect valid suspended sediment samples, samplers and sampling procedures must be designed to represent accurately the water/sediment system being studied. The procedures and apparatus employed for sediment sampling depend on the type of sediment being sampled. The methodology and the equipment used for sampling suspended sediments are different from those required for sediment deposits.[25]

Suspended sediment samples are collected to determine the quantity as well as the physical and chemical characteristics of those sediments in suspension. On the other hand, bottom sediments are sampled to provide the physical and chemical characteristics of those particles that make-up the bed of the system being studied at specific locations.[25]

It is very complex to measure sampling accuracy of sediments, which are, in most cases, heterogeneous. The following two techniques can be used for quality control in sediment sampling. One technique consists of the collection of more than one sediment sample at selected sampling sites using identical sampling equipment (e.g., multicorers) as well as using identical field subsampling procedures, handling and storage of samples, and methods for sediment analyses. The results will show variations which are due to sampling and subsampling techniques, but the heterogeneity of the sediment at the sampling site will still affect the test. The sediment sampler must be selected to suit the sediment texture at the test sampling site.[24]

In the other quality control technique the collected sample is divided into a few subsamples and each subsample is treated as an individual sample The results of geochemical analyses of all subsamples will indicate the variability due to the sampling and analytical techniques and sediment heterogeneity within a single collected sample.[24]

A few control sites should be included in a sampling program for investigation of sediment contamination. They should be selected, after historical data review, at areas where the sediment will most likely not be contaminated. Data obtained at the control sites are important as background values when plotting distribution and concentration gradients of contaminants. Contamination of the sediment samples will also affect the representativeness of the samples and bias the analytical data either positively or negatively both with respect to detection of pollutants as well as with their concentrations in the sediment samples.[24]

Sediment samples can be contaminated with pieces of metal paint or surface corrosion products from samplers or equipment used for the operation of the samplers. Most samplers are metallic; some may be electroplated or painted to prevent corrosion, particularly when sampling in salt water. Samplers with metal parts painted with cadmium or lead paints are not suitable for the collection of sediments for the determination of metal concentrations. Similarly, use of oil and grease on the samplers or sampler lifting equipment should be avoided. Sediment samples for the quantitative determination of metals or organic contaminants should always be obtained from the center of the sampler. Plastic liners and core barrels used with gravity corers may be a source of contamination with various organic compounds. However, no data are available concerning contamination of sediment samples collected with plastic liners and core barrels manufactured from different plastic materials.[24]

Selecting Sampling Locations

Funds spent on sample analyses by the most sophisticated techniques are wasted on samples collected at inappropriate locations or where an insufficient number of samples are taken to represent the project area. Consequently, the selection of the number and positions of sampling stations needs to be carefully designed. There is no one formula for design of a sediment sampling pattern which would be applicable to all sediment sampling programs.[24]

When defining the positions and number of sediment sampling stations, the following factors should be considered:

- The purpose of sampling;
- Study objectives;
- Historical data and other available information;
- Bottom dynamics at the sampling area;
- Size of the sampling area; and

- Available funds vs. estimated (real) cost of the project.

Generally, the reasons for bottom sediment sampling can be divided into the following categories:[24]

- To provide a geochemical survey;
- Environmental assessment of contaminants in sediments;
- Evaluation of sediment for a dredging/disposal permit; and
- Research of sedimentary processes.

Although the strategy and goal of sediment sampling in each category are different, the sampling techniques are similar, and the method for selection of space and number of sampling stations for one purpose may be applicable to the others. The selection and number of sampling stations depend on the project objective, and must be modified for the special sampling situations of each project.[24]

Careful definition of the project objectives is highly critical to the successful completion of the sediment sampling program. Generally, samples will be collected from the study area to investigate the distribution of parameters of interest at a project site. The objectives of a research scientist studying sedimentary processes at an estuary are naturally different from the objectives of a project proponent applying for an open-water disposal permit for sediment to be dredged from a channel within the same estuary. Although both workers will collect samples to characterize the sediment, their sampling strategy will often be distinctly different.[24]

In general, the position of sampling stations should allow for a reliable, rapid repetition of sampling in the future without difficulty. It is imperative that each sampling station be properly referenced to a survey grid on a map and properly labeled.

Scientists involved in the selection of sediment sampling stations should have at least a basic knowledge of bottom dynamics at the project area. Ideally, sediment particle size distribution should be mapped prior to the selection of sediment sampling sites. The distribution of sediment on a lake, river, or ocean floor is affected by energy-controlled processes. Sand, gravel, and boulders are the sediment units on the bottom of a fast flowing river. Fine-grained sediments (i.e., silt and clay) may accumulate in areas of low energy zones, such as bays or the inner side of the main channel of a meandering river. Sediment deposits in large lakes, although strongly influenced by the characteristics of source material, reflect the changes of various energy-controlled processes, such as wave action, current circulation, etc.

A survey of sediment deposits and geochemistry in a lake or pond may be useful for evaluation of contaminated sites. In such a case, sediment mapping should be carried out as a part of the project, and sampling stations selected to provide sufficient information for sediment mapping. The selection of sampling sites dealing with the evaluation of sediment contamination requires a knowledge of sediment distribution to locate the stations of fine-grained sediment accumulation.

Maps of the sediments on sea, lake, and river floors should be prepared with special attention to areas of erosion, transportation, and accumulation. One of the basic tasks of planners is the proper selection of locations considered suitable for sample collection. The goal is to maximize the probability of detecting the areas with the greatest concentrations of pollutants, or conversely, to minimize the cost of collecting improper samples or the loss of collecting no samples.[24]

The number and spacing of sediment sampling stations also depend on the physical size of the project area, and how large an area each sample has to represent. In addition, the density of sampling stations required for the characterization of sediments is determined by the variability or gradients in the processes which control the distribution of the investigated sediment parameter or property. When the distribution of sediment

parameters is relatively homogeneous, stations can be widely spaced. If the distribution of the parameters is heterogeneous, a more dense sampling grid will be required. In projects dealing with environmental pollution of relatively small areas, such as contaminated sites, sediment sampling stations need to be located usually much closer, in particular at areas with heterogeneous distribution of different sediment units and many contaminant sources.[24]

In instances in which sediment transport data are required, sampling sites should be located near a water quantity gauging station, when possible, so that accurate stream discharge information is available at all times. Sampling locations immediately upstream from confluences should be avoided, as they may be subjected to back water phenomena. In streams too deep to wade, it may be advantageous to locate sampling sites under bridges or cableways. When sampling from bridges, the upstream side is normally preferred. Sampling on the downstream side of the bridge presents limited upstream visibility, and care must be taken to avoid sampling in areas of high turbulence, near the piers because sediment samples collected near piers are often unrepresentative of the general sediment transport characteristics. Also, attention must be paid to the accumulation of debris or trash on the piers, as this can seriously distort the flow and hence the sediment distribution. Sampling sites should be accessible during floods, since sediment transport rates are high during these times. Also, it is important that the same transect be used during the entire sampling period so that the variability associated with the sampling procedure is minimized.[25]

Selecting Sampling Equipment

There are two general types of sediments that may be collected: bottom sediments and suspended sediments. In addition, bottom sediments contain two primary zones of sediment which are of interest in contaminant studies: the surficial or upper 10 to 15 cm, and the deeper layers. Sampling of the surface layer provides information on the horizontal distribution of parameters or properties of interest for the most recently deposited material, such as particle size distribution or geochemical composition of

sediment. A sediment column, which includes the surface sediment layer (10 to 15 cm) and the sediment underneath this layer, is collected to study historical changes in parameters of interest or to define zones of pollution. The "typical" geochemical profile shows an exponential decrease of contaminant concentrations with sediment depth to a "background" concentration, since many chemical compounds of environmental concern are of recent origin.[24]

As would be expected, completely different sampling devices are used to collect surface layers of sediments and cores of sediments. And totally different devices are also used to collect suspended sediments and bottom sediments.

For some purposes bed sediment samples can be disturbed, i.e., the individual particles can be rearranged relative to each other and it is unimportant that the volume and shape of the sample are altered from the actual conditions of the deposit. However, for most purposes undisturbed samples are required. For example, when the purpose of sampling is to obtain information related to the vertical composition of the deposits or information on the distribution of contaminants from a certain depth, undisturbed core samples must be taken.[25]

Samplers used for suspended sediments must allow the collection of a sample representative of the water-sediment mixture at the sampling point or sampling zone at the time of sampling. These samplers are of three general types:

- Integrating samplers;
- Instantaneous or grab samplers; and
- Pumping samplers.

Standard suspended sediment samplers used to sample flowing streams and rivers should not be used in lakes, reservoirs or other bodies of water where water is stationary or almost stationary.[25]

Gravity and piston corers are used to collect undisturbed samples of river, lake, reservoir, and pond deposits. Samplers of this type are essentially tubes which are forced into the bed of the system. Samples are retained inside the barrel of the sampler on retrieval by a partial vacuum formed above the sample and/or by a core retainer at the lower end.[25]

Grab samplers are more commonly used than core samplers for collecting deposited sediments, as they are often much lighter and in some circumstances much easier to use. If properly used, a grab sampler encloses a volume of the bed material and isolates the sample from water currents during its ascent to the surface to yield a reasonably good undisturbed sample.[25]

Sampling Bottom Sediments

When sampling bottom sediments, it is preferable to collect samples with high clay and organic matter content instead of rocks and sand, because it is known that pollutants are likely to be observed in the former type of bottom sediment matrices.[3] This approach obviously places a bias on the sampling site selection and is an example of judgmental sampling applied to bottom sediments.

Generally, bottom sediment samples are taken from an enlargement of a river, which permits deposition of suspended sediments on the river bottom. In a lake, the situation is usually less critical, and samples are generally collected from the deepest point of the lake, especially when toxic chemical screening is the study objective. However, to obtain a good estimate of the spatial variability of parameter of interest within the bottom sediments, sampling should be performed at as many sites as possible within the given lake or river that is being surveyed.[21]

Many different devices have been designed and used over the years to obtain these types of sediments in a variety of environmental settings. Bed sediment samplers fall

into three broad classifications: 1) grab samplers, 2) corers, and 3) dredges. Corers generally collect both surficial and sediment column samples and show the least amount of disturbance; grab samplers collect large surficial samples; and dredges collect even larger, well-mixed near-surface samples. Usually, dredge samples are considered to be qualitative because their use does not permit adequate control of sample location or sampling depth in the sediment column.[26]

Surficial bed sediments can provide an excellent synoptic picture of pollutant spatial distributions. Typically, such surveys entail random sampling over large geographical areas using stream sediments collected from small, localized streams.[26]

In the case of shallow, wadeable streams, samples are usually collected by hand; in the case of deeper rivers, ponds, or lakes, samples are usually collected with some type of grab samplers. There are numerous grab sampling devices, of various design, that have different advantages and disadvantages depending on the nature of the sediment to be sampled (e.g., coarse versus fine), the water depth, the amount (mass) of sediment required, the size of the area to be sampled, local energy conditions (e.g., sampling in a rapidly flowing stream versus sampling in a relatively quiescent lake), sampling platform (e.g., a boat versus sampling from a bridge), the availability of lifting equipment (e.g., hand-operated versus crane- or winch-operated), etc. Generally, the selection of a particular type of grab sampler for the collection of a sediment-trace element sample is dependent on evaluations against four criteria: 1) degree of physical disturbance during sampling, especially while the device is being lowered to collect a sample (due to the "bow or pressure wave" created by the device which can disperse fine-grained sediment or flocs at the sediment-water interface); 2) loss of material, especially fine-grained sediments, during recovery of the sampler through the water column ("washout"); 3) the efficiency of the grab sampler for collecting sediments of varying textures (e.g., grain size, degree of induration); and 4) potential for sample contamination.[26]

Corers typically are not used for area surveys based on surficial sediment samples, especially in shallow, wadeable aquatic environments. This is because a major disadvantage of most corers is the extremely small area of the bed that is actually sampled. Thus, many more core samples than grab samples usually are required to provide an adequate bottom sediment sample.[26]

One of the most important considerations when collecting surficial sediments is that of obtaining a representative sample. The confidence limit is affected by the number of samples to be collected in a particular study area, how the data are to be used, and the degree of geochemical detail required. As a result of all these factors, regardless of the requisite degree of confidence, it is invariably better to collect a group of subsamples to generate a final composite sample than to arbitrarily collect a single isolated sample as being representative of a sampling site.[26]

Vertical sampling of a sediment column invariably involves the use of some type of coring device. These tend to fall into three broad categories: 1) gravity corers, 2) piston corers, and 3) vibrocorers. Many of the criteria that apply to the selection of a grab sampler also apply to the selection of a coring device. One additional criteria is the length of sediment column to be sampled. Selection of core samples invariably involves subsampling, especially when there are obvious physical differences (e.g., texture or colour) between various sections of an entire core.[26]

Gravity corers, as the name implies, use the force of gravity to penetrate into the sediment column and obtain a sample. Generally, the heavier the corer, the greater the degree of penetration. These devices also require a minimum amount of water depth to achieve sufficient velocity to obtain maximum penetration. To some extent, the amount of weight required can be counterbalanced by the thickness of the core barrel (the thinner the barrel, the lower the resistance to penetration), and by reducing the degree of water resistance to the speed of descent (larger diameter barrels produce less resistance; also, the type of valve at the top of the cover, usually required to prevent sample loss during

recovery, can affect the degree of water resistance). Box corers and "Kastenlots" are special types of "gravity" corers which do not require rapid rates of descent to deeply penetrate a sediment column. However, both devices are usually very heavy. Box corers scoop out a section of the sediment column through the operation of a set of springs which are triggered after the device is lowered to the sediment bed. Kastenlots are extremely heavy and wide barrelled, with the barrel walls being made of extremely thin but very rigid material. These devices are slowly lowered to the sediment bed and achieve high levels of penetration because of their weight working in combination with their lack of frictional resistance due to the thin walls of their barrels. Typical gravity cores do not exceed 2 m in length although Kastenlot cores of up to 6 m have been recovered.[26]

Piston corers are used to obtain long cores in relatively soft sediments. They also are usually very heavy and they are set up so that the piston, which is inserted inside the barrel, stops at the sediment-water interface while the core barrel continues to penetrate the sediment column. The piston creates a vacuum which reduces frictional resistance to barrel penetration. Under the right conditions, piston cores of more than 30 m in length have been collected.[26]

Long cores in fairly indurated sediments are normally obtained with a vibrocorer. These devices can be powered with either electricity or compressed air. Sediment sampling is achieved through the use of thin-walled barrels in conjunction with vibration which tends to 'fluidize' the sediments to facilitate penetration. As a result, vibrocores tend to be more disturbed than piston cores. Vibrocore length is controlled by the size of the system being used, but typically, does not exceed 12 m.[26]

Sampling Suspended Sediments

Sampling and analysis of suspended sediments is a requisite for any study involving the determination of pollutant transport and the calculation of pollutant fluxes. In addition, suspended sediments, along with the sampling and analysis of dissolved samples,

may represent the only available means of determining short-term temporal changes in water quality. Suspended sediment transport is strongly interrelated to both hydrological and geomorphological characteristics. As a general rule, assuming enough material is available, as fluvial discharge or velocity increases, suspended sediment concentrations also increase.[26]

Suspended sediment samplers fall into three general categories: 1) integrating samplers which accumulate a water-sediment mixture over time; 2) instantaneous samplers which trap a volume of whole water by sealing the ends of a flow-through chamber; and 3) pumping samplers which collect a whole-water sample by pump action. Integrating samplers are usually preferred because they appear to obtain the most representative fluvial cross-sectional samples.[26]

Most sampling equipment and sampling designs are established to obtain an "instantaneous" representative sample. However, there is substantial evidence to indicate that temporal changes in suspended sediment concentration and cross-sectional distributions can be quite large and therefore, samples should be obtained over a long period of time to be truly representative (e.g., for 8 to 10 hours). Unfortunately, no single sampling device, nor technique, simultaneously deals with both cross-sectional (spatial) variability and temporal variability. The user must decide which variable is more important to a study, and must select a sampler and technique accordingly.[26]

Sample Preservation and Storage

In general, sediment preservation and storage requirements are similar to those discussed with soils. Procedures for handling and preserving sediment samples depend on the specific analyses needed and on whether the sample is from the suspended or bottom environment. Samples for trace metal analyses require special precautions to prevent contamination and also require preservation.[25] Sample bottles always should be precleaned and thoroughly washed, dried and sealed before being transported to the sampling site.

As soon as possible after collection, sediment samples should be filtered. The filtrate can then be used for measuring the dissolved constituents. Preservations procedures usually involve refrigeration (for organics) and acidification (for metals). Suspended sediment sample analyses are often limited because of the difficulty in obtaining sufficient sediment for the many subsamples required for the different analyses. A composite of a large number of representative samples may be necessary.[25]

Samples of bottom sediments for routine particle size analysis can be transported and stored without refrigeration. Samples for most other types of analysis include refrigeration (for organics) and acidification (for metals). Freezing is not usually employed because it can cause physical-chemical changes, fragment sediment particle structures, and change the representativeness of the sample.

Sampling Water

There are many different types of waters that can be sampled but, other than the sampling equipment itself, most of the samples are treated similarly once they have been collected. In the case of groundwater, the drilling of a well and the contaminants that may be associated with the materials used in well construction are considered to be a part of the overall sampling equipment and are discussed in the subsection on groundwater. The types of water that may be most commonly sampled at contaminated sites include: surface waters (rivers, lakes, artificial impoundments, runoff, etc.), groundwaters and springwaters, wastewaters (mine drainage, landfill leachate, industrial effluents, etc.), and ice. Other types of water that may infrequently be sampled, if at all, include: saline waters, estuarine waters and brines, waters resulting from atmospheric precipitation and condensation (rain, snow, fog, and dew), process waters, potable (drinking) waters, glacial melt waters, steam, water for subsurface injections, and water discharges including waterborne materials. The sampling of these latter water sources will not be addressed since most of them require special equipment that is not likely to be needed for the sources of water found at most contaminated sites.

Problems Unique to Sampling Water

Waters are usually very heterogeneous, both spatially and temporally (with time), making it difficult to obtain truly representative samples. Solids with specific gravities only slightly greater than that of water are usually inorganic. They will remain suspended in the flow but also will form strata in smoothly flowing channels. Oils and solids lighter than water (usually organic) will float on or near the surface. Some liquids, such as halogenated organic compounds, are heavier than water and these will sink to the bottom.[4] The chemical composition of lakes and ponds also may vary significantly depending on the season. The composition of flowing waters, such as streams, depends on the flow and may also vary with the depth.

Stratification within some bodies of water is common. In lakes shallower than about five meters, wind action usually causes mixing, so neither chemical nor thermal stratification is likely for prolonged periods; however, both may occur in deeper lakes.[28] Rapidly flowing shallow rivers usually show no chemical or thermal stratification, but deep rivers can exhibit chemical stratification with or without accompanying thermal stratification. Stratification may also commonly occur where two streams merge, such as the point where an effluent enters a river.

Stratification is also a problem with ocean sampling; various species may be stratified at different depths. In addition, the composition of near shore waters usually differs greatly from waters far from shore. Estuarine sampling is even more complex because stratifications move up rivers unevenly.

Water sample contamination is always a problem, and it increases in importance as the analyte concentration levels decrease. To some extent, contamination sources may depend on the body of water being sampled. For instance, in groundwater monitoring, contamination from well construction materials can be significant and material

blanks become very important. However, many potential contamination sources are common to all water samples.

Groundwater vulnerability to contamination is affected by water depth, recharge rate, soil composition, topography (slope), as well as other parameters such as the volatility and persistence of the analytes being determined. In planning groundwater sampling strategies, knowledge of the physical and chemical characteristics of the aquifer system is necessary (but almost never known). Groundwaters present special challenges for obtaining representative samples.[4]

Review Site Information and Reconnaissance

Site information should be reviewed for sources of possible water contamination in a manner similar to that described above for soils and sediments. The more background information that can be found the better the sampling and analysis programs can be planned.

Also, as described in earlier sections, a preliminary site reconnaissance to inspect the potential locations where water samples will be taken will help significantly in planning the sampling efforts. Surprises can often be avoided and plans can be made to include any special sampling or safety equipment to overcome unusual physical barriers if an adequately planned site visit is made prior to the full sampling effort.

Representative Sampling Approaches

The following general principles apply to the collection of representative water samples[14]:

- Do not include large non-homogeneous particles, such as leaves and detritus, in the sample.

- In flowing waters, place the sampling apparatus upstream to avoid contamination. Sampling from the upstream side of a bridge enables the collector to see whether any floating material is coming downstream and aids in the prevention of contamination of the sample.

- Collect a sufficient volume to permit replicate analyses and quality control testing. If not specified, the basic required volume is a summation of the volumes required for analysis of all the parameters of interest.

The collection of representative water samples requires the use of a variety of sampling equipment depending on the station, the medium to be sampled and the analyte list. The choice of sampler type must be closely related to the analyte list in order to avoid sample contamination. In addition to being analyte and station specific, the sampling equipment must also provide suitable sample volumes, and be suitable for use in a wide variety of environmental conditions.[21] Special guidelines, discussed later, apply to obtaining representative samples from groundwaters, rivers and streams. Additional special guidelines apply to sampling all types of surface waters under winter conditions.

Collecting Representative Water Samples from Rivers and Streams

For water quality sampling sites located on a homogeneous reach of a river or stream, the collection of depth-integrated samples in a single vertical may be adequate. For small streams a grab sample taken at the centroid of flow is usually adequate.[14] When a single fixed intake point is used, it should be located at about 60% of the stream depth in an area of maximum turbulence, and the intake velocity should be equal to or greater than the average water velocity.[27]

For sampling sites located on a nonhomogeneous reach of a river or stream, it is necessary to sample the channel cross section at the location at a specified number of points and depths. The number and type of samples taken will depend on the width, depth, discharge, the amount of suspended sediment being transported and aquatic life present. Generally, the more points that are sampled along the cross section, the more representative

the composite sample will be. Three to five vertical sampling points are usually sufficient, and fewer are necessary for narrow and shallow streams.[14]

Some practical sampling considerations related to location and season of sampling surface waters are outlined below:[14]

Sampling Procedures from Bridges, Abutments, Boats and Aircraft

- Attach sufficient rope to permit the sampler to reach the required maximum depth. The other end of the rope should be secured to a permanent fixture on the bridge, boat or aircraft.
- Ensure that all of the lines that are suspending the samplers remain in the vertical position to enable the accurate estimation of the depth of sample. Depending on the sampler used, weights may be added; the greater the stream velocity, the heavier the weight required.
- When sampling from a boat, sample from the upstream side; if sampling from a float aircraft, sample from the upstream and outer side of the pontoons to minimize the chance of contamination from engine oil leaks.
- When sampling, it is important that the sampling bottle not be permitted to touch the bottom of the river or lake to avoid contamination from stirred-up sediment; predetermine the water depth to prevent this.
- Rinse the sampler three or four times with the water to be sampled unless the bottle contains a preservative or is sterile.

Sampling Procedures from Shores, Stream Banks and Wharves

- A sampling iron is often used when water samples are collected from shores, stream banks and wharves.
- Insert an open clean sampling bottle into the metal holder, ensuring that the ring clamp is securely locked in the holder frame by a key ring or suitable pin. Attach sufficient rope to the holder to permit sampling at the desired depths. Secure the other end of the rope to a

permanent fixture on the bank, wharf, etc. Sampling weights should be added as required, as dictated by stream velocity.

- Throw the bottle with holder well out into the stream. In the case of very shallow streams (approximately 0.5 m), the sampler should collect the sample by hand, wading out if necessary, facing upstream and making sure not to contaminate the sample with sediment, debris and other floating materials.

- Pull the bottle and holder in quickly to prevent the bottle from touching or becoming snagged on the bottom of the stream.

- Rinse the sampling bottle three or four times with the water collected above. It is important that the sample bottle be well rinsed with the water to be sampled before the sample is collected unless preservative has been added to the sample bottle prior to sampling or the bottle is sterile.

Collecting Representative Ice Samples

Representative sampling of ice and snow under winter conditions also requires special considerations:[14]

- Overlying snow should be removed from the ice surface to provide a suitable working area.

- Gas-powered augers are often used for drilling holes. Take extra care to avoid gas, oil and exhaust contamination of sampling equipment.

- Except in the case of shallow flowing streams, samples must not be taken from the hole in the ice but should be taken as a depth-integrated sample below the ice cover.

- The hole in the ice must be cleaned of debris and ice chips; use a dip net or other "deslushing" device.

- Field measurements are not generally taken out on the ice but rather in the warmth of a vehicle, as meters tend to operate poorly in extremely cold conditions. An insulated box should be used and care taken to prevent samples from freezing in sub-zero temperatures.

When collecting representative samples of ice the location of collection devices is especially important. The chemical composition of ice reflects the chemical composition of the surface water and the rate which it forms ice. The dust and/or plankton it entraps has been shown to contribute concentrations of metals such as iron, titanium, and molybdenum. Furthermore, silicon, aluminum, phosphorus, barium, strontium, and manganese (and probably organic contaminants) may show concentration-depth relationships in ice. Therefore, if geochemical (spatially related) data are desired, composite sampling from multiple locations is sufficient, but if data on water composition in relation to the ice in contact are desired, then the ice must be sampled in a series of strata.[28]

Special QC problems also occur during winter sampling, where ice conditions and low temperatures can affect sampling protocols. For example, heavy ice conditions at a site may require the use of power ice augers which can contaminate organic chemical samples with heavy metals, gasolines and oils. Also, during thaw periods, there is often a layer of melt water immediately under the ice, and this water is not representative of the water chemistry of the system. Thus care must be taken to ensure that samples are collected from a stratum that is below the ice-water interface.[21]

The in-situ measurement of the general variables pH and specific conductance (Table 1) during winter conditions, must be carefully scrutinized, since some of the measurement meters do not function well in cold temperatures. For example, conductivity meters may give erroneous results (usually biased low) if slush or ice is allowed to build up around the thermistor or in the conductivity cell.[21]

Another problem associated with winter sampling, involves sample handling. It is essential that water samples are not allowed to freeze prior to analysis. This is particularly important for samples with high concentrations of organic matter, as freezing and subsequent thawing can result in flocculation of dissolved and colloidal organic compounds. Thus, it is necessary to work from a heated vehicle, such as a mobile laboratory during the winter months.[21]

Collecting Representative Groundwater Samples

In order to collect representative groundwater samples, temporal issues need to be considered such as the time of year sampling will be done, whether to sample before or after rainy seasons, etc., and other considerations such as sampling after periods of high agricultural chemical usage. In constructing and using monitoring wells, alteration of the water being sampled must be minimized. Care must be taken during the drilling process not to cross contaminate aquifers with loosened topsoil possibly laden with agricultural/industrial chemicals. Well construction and materials can profoundly influence the chemical composition of samples, so material blanks are important.[4]

Purging wells before sample collection eliminates stagnant water. The method and rate of purging, time between purging and sampling, and sampling itself will depend on the diameter, depth, and recharge rate of a well. Each well should be slug, pressure, or pump tested to determine the hydraulic conductivity of the formation and to estimate the extent and rate of purging prior to sampling.[29] The standard purge volume obtains a stabilized concentration of the parameter of interest. Purge volumes usually range from 3 to 10 well volumes. Sometimes changes in pH, temperature, or conductance measurements can be monitored in consecutive samples to determine when a sample is representative, i.e., when surrogate values stop changing.[4]

Select the material for well construction carefully. Cement used for polyvinyl chloride (PVC) pipe joints can leach into samples from wells; this can be prevented by using threaded pipes. Equipment for monitoring wells should be constructed of stainless steel or other inert materials.[30, 31]

Sampling devices and sample containers are always likely sources of contamination. Carryover between samples from the sampling device also must be prevented. Contaminant leaching from sampling devices and containers is very complex and requires serious attention. Table 10 shows the types of contaminants caused by materials

used in sampling devices and well construction monitoring. Additionally, tin and lead are common contaminants to water transported through soldered pipes. Water containing high calcium levels tends to extract lead preferentially, but tin is removed in small amounts for many years.[28]

Table 10. Potential Contaminants from Sampling Devices and Well Casings

Material	Contaminants Prior to Steam Cleaning
Rigid PVC-threaded joints	Chloroform
Rigid PVC-cemented joints	Methyl ethyl ketone, toluene, acetone, methylene chloride, benzene, organic tin compounds, tetrahydrofuran, ethyl acetate, cyclohexanone, vinyl chloride
Flexible or rigid Teflon® tubing	None detectable
Flexible polypropylene tubing	None detectable
Flexible PVC plastics tubing	Phthalate esters and other plasticizers
Soldered pipes	Tin and lead
Stainless steel containers	Chromium, iron, nickel and molybdenum
Glass containers	Boron and silicon

Sampling protocols often recommend that samples that analyze groundwater monitoring wells for metals be field-filtered under pressure before preservation and analysis. Samples collected for metals are usually acidified; acidification of unfiltered samples can lead to dissolution of minerals from suspended clays. Samples to be collected for organic compounds analyses, however, are never filtered.[4]

As discussed above, blanks are used to assess contamination. Blank samples associated with groundwater samples usually should include equipment, field, and

background blanks. Selections should be made by considering all likely sources of contamination for the specific situation.

Analyte sorption is also a common problem. PVC and plastics other than Teflon® tend to sorb organics and leach plasticizers and other chemicals used in their manufacture. In addition, some pesticides and halogenated compounds strongly adsorb to glass. When analyzing these substances in water samples, therefore, it is important not to prerinse the glass sample bottle with sample before collection. It is equally important at the laboratory to rinse the sample containers with portions of extraction solvent after the water sample has been quantitatively transferred into the extraction apparatus.

Tubing material used in automatic sampling devices is important; depletion of halocarbons from water depends more on the tube material than on the tubing diameter (surface area). However, when a constant flow rate is used, losses are more likely to occur with an increase in tubing diameter. Thermoplastic materials (e.g. polypropylene) appear to sorb many organic analytes efficiently, so they should be avoided in sampling devices.[28]

PVC reportedly containing zinc, iron, antimony, and copper may leach these metals into water samples. Polyethylene has been reported to contain antimony which may also leach into water.[28] Flexible PVC and plastics other than Teflon® usually contain phthalate esters which may also leach into water samples.[30] Phthalate esters interfere with instrument sensitivity by masking other contaminants.

Sorption of metals at low concentrations on container walls depends on the metal species, concentration, pH, contact time, sample and container composition, presence of dissolved organic carbon and complexing agents. Preserving metals samples with acid usually prevents this problem.[28]

Variations in the permeability of an aquifer can affect the representativeness of groundwater samples. If the wells have varying recovery rates, varying concentrations of

the analytes will result. Vertical gradients of flow between permeable strata within an aquifer can result in samples from multiple zones within one well.[30]

Selecting Sampling Locations

The use of proper sampling techniques and good judgment to obtain representative water samples is of utmost importance. In the field various sampling situations occur which require different sampling techniques. Situations in which water is shallow are handled in a manner and with apparatus different from that used at deep water sites. Field technicians must be equipped to handle these situations. In addition, special considerations and precautions mentioned above must also be taken during periods of ice and snow.[14]

Rivers and Streams

Since the fluvial characteristics of a sampling station can change with season, annual maximum and minimum flows and year-round accessibility should be considered when establishing a sampling station on a river or a stream. When visiting an existing sampling station or when establishing a new site, the field investigator should take a variety of sampling equipment so that he or she is prepared for any situation.[14]

Some of the key factors involved when locating sampling stations at rivers and streams include:

- Access to desirable sampling points;
- Entrance and mixing of wastes and tributaries;
- Flow velocities in times of water travel;
- Marked changes in characteristics of the stream channel;
- Types of stream bed, depth and turbulence; and
- Artificial and physical structures such as dams, weirs, and wingwalls.

Variations in water quality with time require that samples from rivers and streams be collected at the proper frequencies and times of day to ensure results that are representative of the variations.[21]

Ready accessibility to sampling stations which extend across the width of a river or stream, can sometimes be difficult, and it is therefore not unusual to collect water and/or sediment samples from bridges. The main sampling location should generally be at the bridge mid-point with additional sampling locations nearby when spatial discontinuities are expected.

Although sampling from bridges has some obvious advantages, there also are some possible contamination problems. Most of these structures are made of metals, concrete or creosoted timer and therefore caution must be exercised to avoid heavy metal, major ion, and organic contamination, respectively. In addition, many of these structures are subject to heavy vehicular traffic and thus there is a possibility of sample contamination by organics, heavy metals (e.g. leaded fuels) and road salts.[21]

In order to avoid sample contamination while sampling from a bridge, all sampling should be conducted from the upstream side of the structure. When sampling from concrete structures, care must be taken to ensure that the movement of the sample rope does not result in concrete dust formation by the abrasive action of raising and lowering the sampler.[21]

Sometimes samples from rivers and streams must be collected from the shore, which also results in QC problems. Before establishing these stations, it may be necessary to perform some cross-sectional sampling to ensure that the littoral samples are representative of overall quality conditions. If samples are collected by wading, water should be taken upstream from the technician's position in order to avoid contamination by re-suspended sediments.[21]

Groundwaters

Groundwater/well water sampling at municipal and domestic wells is best, if possible, at locations prior to any purification/treatment process. This more accurately determines what contaminants are in the aquifer. Chlorination, filters, softeners, and other treatments such as iron, acid, potash, etc., may chemically alter or physically adsorb the analytes of interest. Also, histories and knowledge of any chemical usage in or near wells can provide valuable information. For example, some domestic well owners have been known to pour bleach into their wells as a disinfectant.[4]

Wells at contaminated sites should be drilled above and below the suspected place of contamination. A grid similar to that used for sampling soils also may be employed to gather geostatistical samples at a site. More detailed information on groundwater sampling can be found in the National Sites Remediation Program's, "Handbook on Subsurface Assessment."[31]

Lakes

Lake water sampling often has less temporal variance (but greater spatial variance) than river or stream sampling. This observation favours the use of lakes for long-term trend assessments, as the monitoring costs are potentially reduced. As a general rule, water and sediment sampling stations in lakes should be located near the center, at the greatest depth, to avoid shoreline effects. Lake depth should be at least ten meters, for stable thermal conditions and dystrophic or bog lakes should be voided. Lakes that are fed by large inlets also should be avoided because of the possible dominance of stream characteristics.

Headwater lakes can be affected by atmospheric deposition and therefore sampling stations should be located on the most elevated sites of the basin, away from agricultural lands and urban areas, to avoid local climatic effects.[21]

Samples from lakes often are collected from stations which require the use of aluminum boats, rubber rafts and occasionally, helicopters. Use of these means of transport must be project specific with particular emphasis placed on the analyte list (Table 1). Thus, if heavy metals are the major concern, a rubber boat should be used, while an aluminum boat is more suitable for sampling toxic organics. Regardless of the type of craft used, samples should never be taken off the stern of the boat, where floating oil and gasoline from the outboard motor might contaminate samples.[21] For lakes which have poor accessibility, it may be necessary to use a helicopter; however, this increases the risk of contamination of samples with fuel and kerosene fumes.

Selecting Sampling Equipment

Sampling devices must be constructed of materials compatible with the matrix and target analytes. Hardware should be stainless steel; plated or painted hardware is not acceptable. Equipment (rinsate) blanks are very important. Usually double or triple-distilled water is used to rinse sampling equipment prior to its use.

Medical grade silicone rubber in peristaltic pumps avoids sample contamination by the organic peroxides used in the manufacturing of conventional grade silicone rubber and the tube compression reportedly does not alter or contaminate samples.[32] If organic species are being collected, the rest of the tubing should be Teflon®. When sampling for water quality parameters (pH, colour, chloride, dissolved oxygen, etc.) polyvinyl chloride (PVC) tubing may be used, but it should be of food-grade quality to prevent phenolic compound contamination of samples.[27]

Any sorption of the analytes of interest, in or on the sampling device, must be documented. If such information is not available then analyte sorption with the device must be investigated prior to test sample collection. If the sampling device sorbs the analyte of interest or contributes a significant analytical interference then the samples obviously are not valid, and other means of sampling must be used.

Selection of the sampling device frequently depends on the body of water being sampled. Samples collected from large bodies of water are usually collected manually. Automatic samplers are commonly used for consistent samples of streams and wastewater discharges. The single greatest factor influencing the collection of representative water samples with automatic samplers may be the skill of the user.[27]

Samplers are designed to collect either discrete or composite samples and most are capable of gathering either timed interval samples or samples proportional to flow. Various designs for automatic samplers are available, and selection usually depends on their intended use. Significant selection factors are:[4]

- Intake velocity;
- Watertightness;
- Electrical or insulation quality;
- Explosion proof quality; and
- Ease of field repair.

Samples of water analyzed for volatile organics are always grab samples using glass vials with Teflon®-lined caps; no headspace is allowed.

Glass containers with Teflon®-lined caps should generally be used when organic compounds are the analytes of interest. In contrast, when metal species are the analytes of interest, the samples generally should be collected in plastic (usually polypropylene) or glass containers with added nitric acid for stability.[33]

Characteristics of Various Types of Water Samplers

There is no universally accepted sampler, so the selection of sampling equipment must be made to accommodate the goals of the sampling plan. Vacuum samplers produce higher biological oxygen demand (BOD), chemical oxygen demand (COD), and solids concentrations than peristaltic pumps. If the strainer of a vacuum sampler is allowed to rest on the bottom of the sampling site, the high intake velocity can

scour sediments from around the strainer and enrich the sample. Also, suction life (vacuum) samplers will cause volatile compounds to outgas and be lost. Another potential problem with vacuum samplers is that their metering chambers can serve as a source of cross contamination between samples due to their relatively large wetted surface areas. However, one advantage of vacuum samplers is that they tend to keep heavy solids in suspension. Another advantage of vacuum samplers with metering chambers, and also peristaltic pumps that can compensate for water level changes, is more accurate sampling when the water level varies significantly from one sample interval to the next.[27]

Discrete samplers can take individual samples, usually at uniform time intervals, and retain them in separate containers for analysis. Two optional modes of operation include nonuniform time intervals and time override of flow-proportioned sampling. Nonuniform time intervals give the option of programming different times between samples. They are useful where variations in flow or analyte concentrations occur.[27]

Composite samplers mix samples together in a single container. Their advantage is that many frequent samples can be taken and a time averaged sample is obtained. However, if infrequent events with large concentration variances occur, this information may be averaged out by dilution. A flow-proportioned composite sample, in which small aliquots are collected over small increments of flow, provides the most representative sample of the flow over a given time.[27]

Sampling devices selected for groundwater monitoring should consider the well diameter and yield as well as the limitations in the lift capacity of the devices and the sensitivity of the analytes to construction materials. Groundwater sampling devices should be designed to avoid excessive aeration so that analyte volatilization and oxidation are minimized. Loss or introduction of gases or volatile organics can affect analytes of interest.[30] Commonly used devices include electric submersible pumps, bailers, suction-lift pumps, and positive displacement bladder pumps; the latter being generally considered the best for accuracy and precision under many circumstances.

Bailers are often used for both purging and sampling small diameter shallow wells, but they have the disadvantages of mixing, collecting particulates from the well bottom or casing, and aerating or degassing volatile analytes from samples.[30] Some of these disadvantages can be minimized by modifying a bailer for a bottom draw valve or a dual check valve and gently lowering it into the water. Another problem is having organics from the air absorbed into the water as it is poured from the bailer to the sample container.[30] Thus, field blanks are especially important when using bailers and should always be collected when using this device.

Suction lift and gas displacement pumps often measure the amount of sample delivered inaccurately. In addition, they will cause degassing and the loss of volatile components in the samples.[30]

Common Sampling Equipment

There are many different types of samplers and a few of the most common used in Canada are briefly described below.[14]

- Depth Integrating Samplers

  A depth-integrated sample may be taken by lowering an open sampling apparatus to the bottom of the water body and raising it to the surface at a constant rate so that the bottle is just filled on reaching the surface. This procedure will result in a sample which approximates a theoretical depth-integrated sample. Depth integration may not be possible in shallow streams where the depth is insufficient to permit integration.

- Sampling Iron

  This apparatus is a device which is made of iron and painted with a rust inhibitor. Typically, it uses a 2-L sample bottle but smaller bottles also may be used.

  The sample bottles are placed in the sampler and secured by a neck holder. In some cases, sampling irons may have provision for

additional weights to ensure a vertical drop in strong currents. A depth-integrated sample is taken by permitting the sampler to sink to the desired depth at a constant rate and then retrieving it at approximately the same rate. The rate should be such that the bottle has just been filled when reaching the surface.

Discrete samplers are used to collect water at a specific depth. An appropriate sampler is lowered to the desired depth, activated and then retrieved. Van Dorn, Kemmerer and pump type samplers are frequently used for this purpose.

- Van Dorn Bottles

The Van Dorn bottle is designed for sampling at depth of 2 m or greater. The sampler is available in both polyvinyl chloride and acrylic plastic materials so that it may be used for general or trace metal sampling. End seals are made of semi-rigid moulded rubber or rigid machined plastic with gaskets and a drain valve is provided for sample removal. Sampler volumes from 2 to 16 L are available.

Although operation of a Van Dorn bottle varies slightly depending on its size and style, the basic procedure is the same:

- The sampler is opened by raising the end seals;
- The trip mechanism is set;
- The sampler is lowered to the desired depth;
- A metal or rubber messenger is activated to "trip" the mechanism that closes the end seals of the sampler; and then the water sample is transferred from the Van Dorn bottle to individual sample containers via the drain valve.

- Kemmerer Sampler

The Kemmerer style sampler is commonly used in water bodies with a depth of 1 m or greater. It is available in brass and nickel-plated brass for general water sampling. For trace metal sampling, Kemmerer samplers are made of polyvinyl chloride and acrylic plastic with silicone rubber seals. Both metal and plastic samplers are available in volumes ranging from 0.5 to 8L.

The operation of the Kemmerer sampler is the same as that for the Van Dorn bottle.

- Pumps

  Three types of pumps - diaphragm, peristaltic and rotary - are available to collect samples from specified depths. In general, diaphragm pumps are hand-operated; the peristaltic and rotary pumps require a power source and consequently they have limited field utility. All pumps must have an internal construction that does not contaminate the water sample. Input and output hoses must also be free from contaminants.

- Multiple Samplers

  A "multiple" sampler permits the simultaneous collection of several samples of equal or different volumes at a site. Each sample is collected in its own bottle. When the samples are of equal volume, information concerning the instantaneous variability between the replicate samples can be obtained.

  The sampler may be altered to accommodate different sizes and numbers of bottles according to the requirements of specific programs. This may be done by changing cup sizes, length of cup sleeves and the configuration and size of openings in the clear acrylic top.

Sample Preservation and Storage Guidelines

Efforts must be made to minimize errors that can be introduced as a result of collecting and handling the sample. The objective is to provide the laboratory with a set of samples which closely represent the aquatic environment from which they are taken. To ensure consistency and efficiency, sample handling (filtration, decantation, centrifugation, sample splitting, etc.) preservation, storage and transportation procedures must be properly and accurately documented, and adhered to by field personnel.[21]

Preservatives should be prepared from Ultrex Grade or similar grade chemicals, and care must be taken to ensure that the water sample is not contaminated by impurities residing in the added preservative. In adding preservatives to field blanks, the same level of caution exercised with actual samples, should be extended to the blanks. The practice of adding ultrapure distilled water to the field blank bottles in the laboratory prior

to the field trip, should be encouraged. The preservation of blanks can then be carried out in the field.[3]

The stability of analytes of interest depends on how well the samples are preserved. Preservation instructions must specify proper containers, pH, protection from light, absence of headspace, chemical addition, and temperature control. The chemistry of all analytes must be considered, and it should be recognized that certain reactions, e.g., hydrolysis, may still occur under recommended preservation conditions.[4]

Holding time is the length a sample can be stored, after collection and preservation and before preparation and analysis, without significantly affecting the analytical results. Holding times vary with the analyte, preservation technique, and analytical methodology used. Usually maximum holding times (MHTs) are specified by the method and they must be considered and planned for when sampling and analysis protocols are being developed.

MHTs of volatile organic compounds are usually 14 days using EPA methods. However, most of these (with the exception of the aromatic compounds that are prone to biological degradation and some highly halogenated compounds that may undergo dehydrohalogenation) have proven stable in water samples for much longer times.[34]

Water samples are in a chemically dynamic state, and the moment they are removed from the sample site, chemical, biological, and/or physical processes that change their compositions may commence. Analyte concentrations may become altered due to volatilization, sorption, diffusion, precipitation, hydrolysis, oxidation, and photochemical and microbiological effects.[33]

Free chlorine in a sample can react with organic compounds to form chlorinated by-products. Drinking water and treated wastewaters are likely to contain free chlorine. Sodium thiosulfate should be added to remove free chlorine.[33]

Samples with photosensitive analytes (such as polynuclear aromatic hydrocarbons and bromo- or iodo-compounds) should be collected and stored in amber glass containers to protect them from light.[33]

The composition of water samples may also change because of microbiological activity. This is especially prevalent with organic analytes in wastewaters subjected to biological degradation. These samples (and samples containing organic analytes in general) should be immediately cooled, stored, and shipped at low temperature (about 4° C). Sometimes extreme pH conditions (high or low) or pentachlorophenol are used to kill microorganisms, but this is not common because of their potential for reacting with other analytes.[33] Recent studies have indicated that sodium bisulfite addition may be just as effective for preserving water samples for organic analytes as the addition of hydrochloric acid.[34]

Samples preserved by cooling should be cooled first in a refrigerator or with "wet" ice (frozen water); "blue ice", a synthetic glycol packaged in plastic bags and frozen, is acceptable for maintaining low temperatures. Initially, blue ice cools less efficiently, and it may take longer to lower sample temperatures.[30] A maximum temperature thermometer will document whether temperatures exceeded desired values during storage.

Analytes also may form salts that precipitate. The most common occurrence is precipitation of metal oxides and hydroxides due to metal ions reacting with oxygen. This precipitation is usually prevented by adding nitric acid; the combination of a low pH (less than 2) and nitrate ions keeps most metal ions in solution. Other acids (especially hydrochloric and sulfuric) may cause precipitation of insoluble salts and/or analytical interferences.[33]

Waters with cyanides or sulfides require added sodium hydroxide to ensure that hydrogen cyanide or hydrogen sulfide gas is not evolved. Waters with ammonia are preserved by adding sulfuric acid. However, addition of sodium hydroxide or sulfuric acid

may precipitate other cations (especially metals), so separate test samples are necessary when cyanides, sulfides, or ammonia are target analytes.

Water samples must be well stoppered and packed, to prevent spillage and/or breakage. Labels bearing the sample identification, destination, and the word "FRAGILE" must be attached to each container. The top of the carton must be clearly identified as "THIS END UP", and the containers in a shipment must be numbered. Also, a check must be made to ensure that all samples bottles recorded on the field sampling sheets have been placed in a given carton, before shipping is effected. The shipping date and mode of transport must be indicated on the field sampling sheet.

Samples from any one location should be kept together, except in cases where all bottles of one size must be shipped together because of container size. When samples from one station must be separated and placed in more than one carton, a copy of the field sampling sheet pertaining to the bottles must be enclosed in each box.

Sample Collection, Preservation and Storage by Method

Most of the analytical methods summarized in Volume Two also have instructions for collecting, preserving and storing samples. A summary of these requirements for each of those methods is provided in Table 11A, 11B, and 11C. The methods are divided into two groups: those for organic compounds and those for metals and other parameters. Within these two groups the summaries are simply arranged in an increasing alpha-numeric order since many of the methods cover portions of more than one of the eight major categories of the analytes of interest.

Table 11A. Sample Collection Preservation and Storage for Organics

Method No./Type	Sampling and Preservation	Storage
EPA-502.2, Rev. 0 Cap. GC/PID/ELCD (VOA)	Use a 40-120 mL screw cap vial (prewashed with detergent, rinsed with distilled water and oven dried at 105°C) with a polytetrafluoroethylene (PTFE) faced silicone septum. If residual chlorine is in the water, add about 25 mg of ascorbic acid (or 3 mg of sodium thiosulfate) to each vial before collection of bubble-free samples. Add hydrochloric acid (1:1) until a pH of <2 is achieved. Seal bottles with PTFE faced down and shake vigorously for one minute. Immediately cool samples to about 4°C.	The maximum holding time is 14 days from the date of collection. Do not store samples in a refrigerator where other volatile chemicals are stored as their vapors may contaminate these samples.
EPA-505, Rev. 0 GC	Fill a 40 mL screw cap vial (pre-washed with detergent, rinsed with distilled water and oven dried at 400°C for one hour) with a PTFE-faced silicon septum with sample. Each vial should contain 3 mg of sodium thiosulfate crystals prepared before shipment to the sampling site. Alternatively, add 75 µL of a sodium thiosulfate solution (0.04 g/mL) to the vials just prior to sampling. Cool samples to 4°C at the time of collection.	Store samples at 4°C for maximum of 14 days from the date of collection. If heptachlor is to be determined, the maximum hold time should be 7 days.
EPA-507, Rev. 2 GC/NPD	Grab samples are collected in 1 L glass sample bottles (pre-washed with detergent and hot tap water, rinsed with reagent water, and dried in an oven at 400°C for 1 hour) with screw caps lined with PTFE-fluorocarbon. Add mercuric chloride to the sample bottle in amounts to produce a concentration of 10 mg/L. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collection. After collection, seal bottle and shake vigorously for 1 minute. Cool sample to 4°C immediately.	Store samples at 4°C in the dark until extraction. Samples containing disulfoton sulfoxide, diazenon, pronamide, and terbufos must be extracted immediately. Most of the other analytes were stable for 14 days under these conditions during preservation studies. However, carboxin, EPTC, fluridone, metolachlor, napiopamide, tebuthuron, and terbacil exhibited recoveries of less than 60% after 14 days during preservation studies. Extracts should be stored at 4°C in the dark for a maximum of 14 days.
EPA-515.1, Rev. 4 GC/ECD	Grab samples are collected in 1 L glass sample bottles (pre-washed with detergent and hot tap water, rinsed with reagent water, and dried in an oven at 400°C for 1 hour) with screw caps lined with PTFE-fluorocarbon. Add mercuric chloride to the sample bottle in amounts to produce a concentration of 10 mg/L. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collection. After collection, seal bottle and shake vigorously for 1 minutes. Cool sample to 4°C immediately.	Store samples at 4°C in the dark until extraction. Maximum hold times are 14 days for samples and 28 days for extracts.

Table 11A - Continued

Method No./Type	Sampling and Preservation	Storage
EPA-524.2, Rev. 3 Cap. GC/MS (VOA)	Use a 60-120 mL screw cap vial (pre-washed with detergent, rinsed with distilled water and oven dried at 105°C) with a PTFE-faced silicone septum. If residual chlorine is in the water add about 25 mg of ascorbic acid to each vial before sample collection. Collect bubble-free samples. Add hydrochloric acid until a pH of < 2 is achieved and immediately cool samples to about 4°C.	The maximum holding time is 14 days from the date of collection. Do not store samples in a refrigerator where other volatile chemicals are stored as their vapors may contaminate these samples.
EPA-531.1, Rev. 3 HPLC	Grab samples are collected in 60 mL glass vials (prewashed with detergent and hot tap water, rinsed with reagent water, and dried in an oven at 450°C for 1 hour) with screw caps equipped with a PTFE-faced silicon septa. Add 1.8 mL of monochloroacetic acid buffer to the sample bottle to adjust sample to pH 3. If residual chlorine is present, add 80 mg of sodium thiosulfate per liter of sample to the sample bottle prior to collection. After collection, seal bottle and shake vigorously for 1 minute. Cool sample to 4°C immediately.	Samples must be refrigerated at 4°C from time of collection to storage. Samples must be stored at -10°C until analyzed. Maximum hold time for samples is 28 days when adjusted to pH 3 and stored at -10°C.
SM-6220C GC/PID-Purge & Trap	Use a 25 or 40 mL vial (pre-washed with detergent, rinsed with distilled water, and oven dried at 105°C for one hour) equipped with a screw cap with a PTFE-faced silicone septum. If residual chlorine is present, add about 25 mg/40 mL of ascorbic acid or other appropriate reducing agent, to each vial. For samples that contain volatile constituents but do not contain residual chlorine, add 4 drops of 6N HCl/40 mL to prevent biodegradation and dehydrohalogenation. Collect bubble-free samples in duplicate and prepare replicate field reagent blanks with each sample set.	Immediately cool samples to 4°C. The maximum holding time is 14 days from the date of collection. Do not store samples in a refrigerator where other volatile chemicals are stored as their vapors may contaminate these samples.
SM-6410B Packed GC/MS (B/N/A)	Collect grab samples in 1 L amber glass bottles fitted with a screw cap lined with PTFE. Foil may be substituted if samples are not corrosive. If amber bottles are not available, protect samples from light. Sample bottles should be washed and rinsed with acetone or methylene chloride, and dried before use. Collect composite samples in refrigerated glass containers. Refrigerate sample containers at 4°C and protect from light during compositing. Fill sample bottles and, if residual chlorine is present, add 80 mg sodium thiosulfate per liter of sample and mix well.	Cool samples to 4°C and keep refrigerated from time of collection to extraction. Extract samples within seven days of collection and analyze completely within 40 days of extraction.

Table 11A - Continued

Method No./Type	Sampling and Preservation	Storage
SM-6420B Phenols by GC/FID or ECD	Collect grab samples in 1 L amber glass bottles fitted with a screw cap lined with PTFE. Wash and rinse bottle and cap liner with acetone or methylene chloride and dry before use. Collect composite samples in refrigerated glass containers. Optionally, use automatic sampling equipment as free as possible of plastic tubing and other potential sources of contamination, incorporate glass sample containers for collecting a minimum of 250 mL. Refrigerate sample containers at 4°C and protect from light during compositing. Fill sample bottles and, if residual chlorine is present, add 80 mg sodium thiosulfate per liter of sample and mix well. Cool samples immediately to 4°C.	Maintain samples at 4°C from time of collection until extraction. Extract samples within 7 days of collection and analyze completely within 40 days of extraction.
EPA-8080B, Rev. 2 GC	Liquid Samples: Use a 1 gallon or a 2 1/2 gallon amber glass with a screw-top Teflon lined cover. Pre-wash with detergent, rinse with distilled water and methanol (or isopropanol). Flush glassware immediately before use with some of the same solvent that will be used in the analysis. Cool to 4 C. If residual chlorine is present, add 3 mL of 10% sodium thiosulfate per gallon and cool to 4 C. Soil/sediments and sludges: Use an 8 oz. widemouth glass with a screw-top Teflon lined cover. Pre-wash with detergent, rinse with distilled water and methanol (or isopropanol). Flush glassware immediately before use with some of the same solvent that will be used in the analysis.	Liquid samples must be extracted within 7 days and extracts analyzed within 40 days. Soil/sediments may be stored for a maximum of 14 days prior to extraction. All extracts and samples should be stored under refrigeration away from the presence of exhaust fumes.
EPA-8240B, Rev. 2 Cap. GC/MS (VOA)	Liquid Samples: Use a 40 mL glass screw-cap VOA vial with Teflon-faced silicone septum (pre-washed with detergent, rinsed with distilled deionized water and oven dried at 105°C for 1 hour). If residual chlorine is present, collect sample in a 40 oz. soil VOA container which has been pre-preserved with 4 drops of 10% sodium thiosulfate. Mix gently and transfer to a 40 mL VOA vial. Add 4 drops of concentrated HCL and cool to 4°C. Collect bubble-free samples in duplicate. Soil/Sediments and Sludges: Use an 8 oz. wide-mouth glass with Teflon-faced silicone septum (pre-washed with detergent, rinsed with distilled deionized water and oven dried at 105°C for 1 hour). Tap slightly to eliminate free air space. Collect in duplicate and cool to 4°C.	The two vials/glasses from each sampling should be sealed in separate plastic bags and stored at 4°C for a maximum of 14 days from date of collection.

Table 11A - Continued

Method No./Type	Sampling and Preservation	Storage
EPA-8260A, Rev. 1 GC/MS Cap.	Liquid Samples: Use a 40 mL glass screw-cap VOA vial with Teflon-faced silicone septum (pre-washed with detergent, rinsed with distilled deionized water and oven dried at 105 C for 1 hour). If residual chlorine is present: collect sample in a 4 oz soil VOA container which has been pre-preserved with 4 drops of 10% sodium thiosulfate. Mix gently and transfer to a 40 mL VOA vial. Add 4 drops of concentrated HCL and cool to 4°C. Collect bubble-free samples in duplicate. Soil/Sediments and Sludges: Use a 8 oz widemouth glass with Teflon-faced silicone septum (pre-washed with detergent, rinsed with distilled deionized water and oven dried at 105 C for 1 hour). DO NOT heat septum for more than 1 hour. Tap slightly to eliminate free air space. Collect in duplicate and cool to 4°C.	The two vials/glasses from each sampling should be sealed in separate plastic bags and stored at 4°C for a maximum of 14 days from date of collection.
EPA-8270B, Rev. 2 Cap. GC/MS (B/N/A)	Liquid Samples: Use a 1 gallon or a 2 1/2 gallon amber glass bottle with a screw-top Teflon lined cover. Pre-wash with detergent, rinse with distilled water and methanol (or isopropanol). Flush glassware immediately before use with some of the same solvent that will be used in the analysis. Cool samples to 4°C. If residual chlorine is present, add 3 mL of 10% sodium thiosulfate per gallon and cool to 4°C. Soil/Sediments & Sludges: Use an 8 oz. widemouth glass with a screw-top Teflon lined cover. Pre-wash with detergent, rinse with distilled water and methanol (or isopropanol). Flush glassware immediately before use with some of the same solvent that will be used in the analysis. Cool samples to 4°C.	Liquid samples must be extracted within 7 days and extracts analyzed within 40 days. Soil/sediments and sludges may be stored for a maximum of 14 days. Do not store in the presence of exhaust fumes.
EPA-8280, Rev. 0 Cap. GC/MS (PCDD/PCDF)	Grab and composite samples must be collected in 1L or 1-quart amber glass bottles. The bottles must be acid-washed and solvent rinsed before use. Teflon-lined screw-caps should be used with bottles. If compositing equipment is used, the system must incorporate glass sample containers for the collection of a minimum of 250 mL. No Tygon® or rubber tubing may be used.	Samples must be stored at 4°C, extracted within 30 days and analyzed within 45 days of collection.

Table 11A - Continued

Method No./Type	Sampling and Preservation	Storage
EPA-8290, Rev. 0 HRGC-HRMS	Sample collection personnel should, to the extent possible, homogenize samples in the field before filling the sample containers. The analyst should make a judgment, based on the appearance of the sample, regarding the necessity for additional mixing before taking an aliquot for analysis. Liquid Samples: Use a 1-gallon or a 2 1/2 gallon amber glass bottle with a screw-top Teflon lined cover. Pre-wash with detergent, rinse with distilled water and methanol (or isopropanol). Flush glassware immediately before use with some of the same solvent that will be used in the analysis. Cool samples to 4°C. If residual chlorine is present, add 3 mL of 10% sodium thiosulfate per gallon and cool to 4°C. Soil/Sediment & Sludges: Use an 8 oz. widemouth glass with a screw-top Teflon lined cover. Pre-wash with detergent, rinse with distilled water and methanol (or isopropanol). Flush glassware immediately before use with some of the same solvent that will be used in the analysis. Cool samples to 4°C.	Store all samples except fish and adipuse tissue samples at 4°C in the dark. Samples must be extracted within 30 days and extracts analyzed within 45 days of collection.

Table 11B. Sample Collection, Preservation and Storage for Inorganics

Method No./Type	Sampling and Preservation	Storage
EPA-340.2 Fluoride (Potentiometric Ion Selective Electrode)	No special requirements.	No special requirements.
SM-3111B AA (Flame-AIR)	Use sample containers made of polypropylene or linear polyethylene with a polyethylene cap. Store samples for determination of silver in light-absorbing containers. Use only containers and filters that have been acid rinsed. Preserve samples immediately after collection by acidifying with concentrated HNO_3 to pH <2. Filter samples for dissolved metals before preserving.	After acidifying sample, store at approximately 4°C to prevent change in volume due to evaporation. Samples with metal concentrations of several milligrams per liter are stable for up to six months. For microgram per liter metal levels analyze samples as soon as possible after collection.
SM-3111D AA (Flame-N_2O)	Use sample containers made of polypropylene or linear polyethylene with a polyethylene cap. Store samples for determination of silver in light-absorbing containers. Use only containers and filters that have been acid rinsed. Preserve samples immediately after collection by acidifying with concentrated HNO_3 to pH <2. Filter samples for dissolved metals before preserving.	After acidifying sample, store at approximately 4°C to prevent change in volume due to evaporation. Samples with metal concentrations of several milligrams per liter are stable for up to six months. For microgram per liter metal levels analyze samples as soon as possible after collection.
SM-3112B AA (Hg)	Use sample containers made of polypropylene or linear polyethylene with a polyethylene cap. Store samples for determination of silver in light-absorbing containers. Use only containers and filters that have been acid rinsed. Preserve samples immediately after collection by acidifying with concentrated HNO_3 to pH <2. Filter samples for dissolved metals before preserving.	After acidifying sample, store at approximately 4°C to prevent change in volume due to evaporation. Samples with metal concentrations of several milligrams per liter are stable for up to six months. For microgram per liter metal levels analyze samples as soon as possible after collection.
SM-3113B AA (electrothermal)	Use sample containers made of polypropylene or linear polyethylene with a polyethylene cap. Store samples for determination of silver in light-absorbing containers. Use only containers and filters that have been acid rinsed. Preserve samples immediately after collection by acidifying with concentrated HNO_3 to pH <2. Filter samples for dissolved metals before preserving.	After acidifying sample, store at approximately 4°C to prevent change in volume due to evaporation. Samples with metal concentrations of several milligrams per liter are stable for up to six months. For microgram per liter metal levels analyze samples as soon as possible after collection.

Table 11B - Continued

Method No./Type	Sampling and Preservation	Storage
SM-3114B AA (Hydride-As,Se)	Use sample containers made of polypropylene or linear polyethylene with a polyethylene cap. Store samples for determination of silver in light-absorbing containers. Use only containers and filters that have been acid rinsed. Preserve samples immediately after collection by acidifying with concentrated HNO_3 to pH <2. Filter samples for dissolved metals before preserving.	After acidifying sample, store at approximately 4°C to prevent change in volume due to evaporation. Samples with metal concentrations of several milligrams per liter are stable for up to six months. For microgram per liter metal levels analyze samples as soon as possible after collection.
SM-3120B ICP	Use sample containers made of polypropylene or linear polyethylene with a polyethylene cap. Store samples for determination of silver in light-absorbing containers. Use only containers and filters that have been acid rinsed. Preserve samples immediately after collection by acidifying with concentrated HNO_3 to pH <2. Filter samples for dissolved metals before preserving.	After acidifying sample, store at approximately 4°C to prevent change in volume due to evaporation. Samples with metal concentrations of several milligrams per liter are stable for up to six months. For microgram per liter metal levels analyze samples as soon as possible after collection.
EPA-6010, Rev. 0 ICP	Samples should be collected in borosilicate glass, linear polyethylene, polypropylene, or Teflon bottles that have been pre-washed with detergent and tap water, and rinsed with 1:1 nitric acid and tap water or 1:1 hydrochloric acid and tap water. The appropriate collection volume and preservative is shown in Table 11C.	The maximum holding times from time of collection to time of extraction is shown in Table 11C for each type of analyte.
EPA-7196, Rev. 0 Colorimetric	Collect samples in 500 mL or 1 liter glass or plastic bottles previously washed with detergent, rinsed with tap water, 1:1 hydrochloric acid, tap water and Type II water. Cool to 4°C.	To retard the chemical activity of Cr VI, the samples and extracts should be stored at 4°C. The maximum holding time prior to analysis is 24 hours.
EPA-7470A, Rev. 1 Liquid Waste Vapor Technique-Hg	All sample containers must be prewashed with detergents, acids, and reagent water. Plastic and glass containers are both suitable. Aqueous samples must be acidified to a pH <2 with HNO_3. Non-aqueous samples should be refrigerated, when possible.	Store non-aqueous samples at 4°C when possible, and analyze as soon as possible. The suggested maximum hold times for mercury is 28 days.
EPA-7471A, Rev. 1 Solid/Semi-Solid Vapor Technique-Hg	All sample containers must be prewashed with detergents, acid, and reagent water. Plastic and glass containers are both suitable. Aqueous samples must be acidified to a pH <2 with nitric acid. Nonaqueous samples must be refrigerated, when possible.	Store non-aqueous samples at 4°C, when possible, and analyze as soon as possible. The suggested maximum hold times for mercury is 28 days.

Table 11B - Continued

Method No./Type	Sampling and Preservation	Storage
EPA-7870, Rev. 0 AA/AD	Liquid Samples: Collect samples in 1 liter glass or plastic bottles (previously washed with detergent, rinsed with tap water, 1:1 nitric acid, tap water, 1:1 hydrochloric acid, tap water and Type II water). Add HNO_3 to pH < 2. Cool to 4°C. Soils/Sediments: Collect in same type bottles as liquid samples. Solid samples usually require no preservation, do not adjust pH.	Store samples at 4°C for a maximum of 6 months.
EPA-9012, Rev. 0 Colorimetric, Automated UV	Collect samples in 1 liter or larger, plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed to remove soluble materials. Oxidizing agents such as chlorine decompose most cyanides. To determine whether oxidizing agents are present, test a drop of the sample with acidified potassium iodide (KI) - starch test paper at the time of collection; a blue color indicates the need for treatment. Add ascorbic acid a few crystals at a time until a drop of sample produces no color on the indicator. Then, add an additional 0.6 g of ascorbic acid for each liter of water. Samples must be preserved by adding 10N sodium hydroxide until sample pH is greater than or equal to 12 at time of collection.	Samples should be stored at 4°C and analyzed as soon as possible.
EPA-9040A, Rev. 1 pH Electrometric Measurement	Not listed.	Not listed.
EPA-9050A, Rev. 1 Spec. Conductance	Not listed.	Not listed.

Table 11C. Method 6010 Sample Holding Times, Required Digestion Volumes, and Recommended Collection Volumes for Metal Determinations

Measurement	Digestion* Volume (mL)	Collection Volume (mL)	Preservative	Holding Times
Metals (except Cr 6 and Hg)				
Total Recoverable	100	600	HNO_3 to pH < 2	6 months
Dissolved	100	600	Filter on site HNO_3 to pH < 2	6 months
Suspended	100	600	Filter on site	6 months
Total	100	600	HNO_3 to pH < 2	6 months
Chromium VI	100	400	Cool to 4 °C	24 hours
Mercury				
Total	100	400	HNO_3 to pH < 2	28 days
Dissolved	100	400	Filter; HNO_3 to pH <2	28 days

* Solid samples should be at least 200 g and usually require no preservation other than storing at 4° C.

Chapter 3 - Laboratory Analyses

Importance of QA/QC Protocols

A laboratory QA/QC program is an essential part of a sound management system. It should be used to prevent, detect, and correct problems in the measurement process and/or demonstrate attainment of statistical control through quality control samples. The objective of QA/QC programs is to control analytical measurement errors at levels acceptable to the data user and to assure that the analytical results have a high probability of acceptable quality.

The data quality is ordinarily evaluated on the basis of its uncertainty when compared with end-use requirements. If the data are consistent and the uncertainty is adequate for the intended use, the data are considered to be of adequate quality. When analytical results are excessively variable or the level of uncertainty exceeds the needs, the data may be of low or inadequate quality. The evaluation of data quality is thus a relative determination. What is high quality in one situation could be unacceptable in another.[39]

Definitions of QA and QC

Quality Assurance (QA) has been described as a system of activities that assures the producer or user of a product or a service that defined standards of quality with a stated level of confidence are met. *Quality Control* (QC) differs in that it is an overall system of activities that controls the quality of a product or service so that it meets the needs of users.[39] In other words, QC consists of the internal (technical), day-to-day activities, such as use of QC check samples, spikes, etc., to control and assess the quality of the measurements, while QA is the management system that ensures an effective QC system is in place and working as intended.

The objectives of a comprehensive QA program[6] are to:

- Establish policies and protocols on laboratory quality control;
- Document QA methodology;
- Standardize data quality control;
- Provide guidelines for good laboratory practices;
- Establish a quantitative approach to determine single/multiple operator and overall precision and confidence intervals of analytical results;
- Make available data quality information documents for clients and data users;
- Implement a mechanism for auditing laboratory operations;
- Establish a framework for high calibre analytical practices; and
- Provide QC statements to support analytical practices.

Selection of an Analytical Method

There are usually at least several methods available for most environmental analytes of interest. Some analytes may have almost a dozen methods to select from. On the other hand, some analytes (including a few on the list that are of interest to the National Contaminated Sites Remediation Program) have none. In the latter case, this usually means that some of the specific isomers that were selected as representative compounds for environmental pollution have not been verified to perform acceptably with any of the commonly used methods.

Often initial analyses may be performed with a variety of field methods that are used for screening. The purpose of using initial field screening methods is to decide if the level of pollution at a site is high enough to warrant more expensive (and more specific and accurate) laboratory analyses. Methods which screen for a wide range of compounds, even if determined as groups or homologues, are useful because they allow more samples to be measured faster and more inexpensively than with conventional laboratory analyses.

In general, these less specific screening methods have not been included in these guidelines because of the preliminary nature of the data obtained from them. However, some of the methods included in this manual are also applicable to field screening methods. For example, the gas chromatographic methods with flame ionization detectors (i.e., SM-6410B), or electron capture detectors (i.e., SM-6420B and EPA-505) or other selective detectors can be used with portable instruments or with laboratory type instruments installed in mobile laboratories. Under these conditions analyses are conducted on site and thus also qualify as field screening methods but their accuracy can be equivalent to that obtained in a conventional remote laboratory.

When there are multiple methods from which to select, the principal considerations used to select the most suitable one for the situation at hand include:

- Availability of instrumentation;
- Confidence level needed;
- Sensitivity desired;
- Potential interferences, and
- Applicability of the method for the matrix.

This listing does not imply a priority because priorities of the above considerations will vary depending on each specific situation.

Certainly one of the first considerations must be availability of instrumentation. If, for example, the method selected requires a mass spectrometer for analysis and the laboratory does not have that instrument, then clearly either another method or another laboratory must be selected. In another example, specific gas chromatographic columns may be required and, if they are not available, then the choice becomes one of delaying the analyses until the required column can be obtained or using

another column on hand and verifying that all the analytes of interest separate from each other and from any sample interferences.

Another early consideration involves the matrix for which the method has been designed. Some methods are designed for aqueous matrices and others for solid matrices (soils or sediments). Aqueous matrices usually are subdivided into drinking water, raw source water for drinking water, and industrial wastewaters. The National Contaminated Sites Remediation Program is specifically interested in surface water (rivers, lakes, streams) and groundwater samples. Both surface waters and groundwaters are sources for drinking water so all methods that mention raw source waters should be applicable for either of these water types. In actuality, most methods differ in the application for various matrices in sample preparation. Once a sample has been prepared correctly according to matrix requirements, the instrumental analytical protocols should be able to be used, with proper verification of precision and bias from most other related methods.

For example, dieldrin has methods that are applicable for water samples but not for soils or sediments. If soil or sediment samples were prepared for analysis according to the sample extraction steps in EPA Method 8270B, then the extracts could be analyzed using the instrumental conditions (GC column and mass spectrometric ions) in Standard Method 6410B. However, precision and bias (from sample preparation recovery and method interferences) would have to be documented using appropriate quality control samples before the environmental samples could be analyzed.[7]

The selectivity of some methods is better than others and this will affect the degree of confidence in the identification of specific analytes as well as the possibility of false positive detections. Note that there is an important difference between detection and identification. Detection involves determining whether a signal produced by using a specific method is from the sample instead of being an artifact from instrumental noise, background contamination or other types of interferences. A signal that meets detection criteria and that has the characteristics of the analyte of interest (for example, a peak in a gas

chromatogram at the correct retention time for that analyte) is often assumed to also identify that analyte. This is not necessarily true; multiple identification characteristics are required for an identification to be valid. In the example above, repeating the analyses using a different GC column so that a second and different retention time of the analyte can be compared to a standard of it, is one way to verify an identification. Another way to verify an identification would be to check for the presence of characteristic ions, and their ratios to one another, if a mass spectrometer was used as a detector.

Sensitivity can be an important consideration when concentration levels of the analytes of interest are likely to be very low. Sensitivity will vary among methods for most of the analytes. Therefore, detector selection is important for organic compounds and instrument selection (e.g., ICP versus direct aspiration atomic absorption or electrothermal atomic absorption instruments) is important for metals. In the case of detectors for organic compound analyses, sensitivity and selectivity characteristics must be weighed versus one another. An expert system called the *GC Advisor*[7] has been written based on rules deduced from knowledge of the characteristics of various detectors and the American Chemical Society *Principles of Environmental Analysis*.[40] The expert system provides advice on which detectors to select, based on answers to questions about the user's needs and it also summarizes major advantages and disadvantages of each of the candidate detectors.

Selection of an Analytical Laboratory

Environment Canada specifies the use of laboratories certified by the Canadian Association for Environmental Analytical Laboratories (CAEAL). This non-profit organization was formed in 1989 on the initiative of a number of laboratories in government and industry with the overall goal of improving the quality of laboratory information necessary for legislators and decision-makers to develop effective policies and regulations to protect Canada's environment.

The three general objectives of CAEAL are:

- To raise and continually improve the quality of laboratory analyses in Canada;
- To provide a national forum for communication and dialogue between laboratories; and
- To provide a variety of services to help the industry in upgrading its product and competitiveness.

Services offered by CAEAL include the provision of QA/QC programs leading to certification/accreditation for member laboratories. Certification is the formal recognition by the Association of the proficiency of an environmental analytical laboratory to carry out specific tests. Formal recognition is based on a screening of laboratory capability and an evaluation of laboratory performance. Under this program participating laboratories are sent test samples at six month intervals for analyses. Results are submitted to CAEAL for evaluation.

Although current performance evaluation (PE) samples are limited, they are being expanded to include additional pollutants in water, and will eventually include other important matrices.

CAEAL is also expanding its program to include not only the provision of test samples but also site visits to observe the actual operations of laboratories. Protocols are being developed to conduct site visits by qualified assessors. Laboratories which successfully meet the national standards associated with site inspections and analyses of test samples will be granted accreditation which will replace the certification currently offered.

Membership in CAEAL is open to individuals, institutions, user groups, consultants, industrial organizations, regulatory agencies, standard materials and laboratory equipment suppliers, and others interested in the work being carried out in environmental analytical laboratories. Information on CAEAL may be obtained from:

Canadian Association for Environmental
Analytical Laboratories, Inc.
Suite 532, 1 Nicholas Street
Ottawa, Ontario
K1N 7B7
Telephone: (613) 562-2200
Fax: (613) 562-2203

A *Practical Guide for Laboratory Analysis of Environmental Samples* is being prepared for CAEAL and the Ontario Ministry of the Environment in support of the Municipal/Industrial Strategy for Abatement (MISA) Program. Later in 1992 the guide will be available from CAEAL. Member laboratories will be encouraged to adhere to the guidelines specified therein.

The Importance of Communication Between Laboratory and Field Personnel

In the previous chapter the relationship between the methods that will be used for analysis of the samples, the amount of sample to be collected and requirements for preservation and storage were discussed. The importance of this communication between sampling and laboratory personnel becomes obvious when the many different method summaries in Volume Two are reviewed. If the samples are not collected, preserved and stored correctly before they are analyzed, then the analytical data may be compromised because of uncertainties as to their validity. If sufficient sample amounts are not collected then the sensitivity documented in the method will not be achieved. Usually the laboratory that is responsible for conducting the analysis is also responsible for providing sample bottles, preservation materials, and explicit sample collection instructions because of the complexity of gathering many different "fractions" of a sample that is to be analyzed for a potentially large variety of analytes.

Chapter 4 - Analytical Method Summaries

Recommended Analytical Methods

There are usually multiple analytical methods for most of the analytes of interest to the National Contaminated Sites Remediation Program (Table 12). However, there are also some analytes for which there are no known methods; these sometimes involve isomers of similar compounds for which there are verified methods.

In selecting methods for recommendation to the National Contaminated Sites Remediation Program the following criteria were used:

General Criteria

In order for the recommended analytical methods to be widely used by multiple laboratories they must be scientifically validated by peer review and published so that they can be located easily by the user for further details. Although many unpublished methods are in use, they are not readily available in published formats and may lack some of the important characteristics such as QC requirements, MDLs, and expected accuracy and precision. These methods and their sources are listed in Appendix 2.

Methods for Organic Compounds

- Methods with highly selective detectors (eg. mass spectrometers) were chosen in preference to those with less selective detectors (electron capture, photoionization, etc);
- Some non-mass spectrometric methods were selected to provide lower cost analyses that are appropriate for monitoring situations;
- Methods that used capillary GC columns were generally selected over those that used packed GC columns because of the higher chromatographic resolution that capillary columns have;

Table 12. Analytes Covered by the National Contaminated Sites Remediation Program

General Parameters
pH
conductivity
sodium adsorption ratio

Inorganic Parameters
antimony
arsenic
barium
beryllium
boron (hot water soluble)
cadmium
chromium (+6)
chromium (total)
cobalt
copper
cyanide (free)
cyanide (total)
fluoride (total)
lead
mercury
molybdenum
nickel
selenium
silver
sulphur (elemental)
thallium
tin
vanadium
zinc

Monocyclic Aromatic Hydrocarbons
benzene
chlorobenzene
ethylbenzene
1,2-dichlorobenzene
1,3-dichlorobenzene
1,4-dichlorobenzene
styrene
toluene
xylene (unspecified mixture)
- o-xylene
- m-xylene
- p-xylene

Polycyclic Aromatic Hydrocarbons (PAHs)
benzo(a)anthracene
benzo(a)pryene
benzo(b)fluoranthene
benzo(k)fluoranthene
dibenz(a,h)anthracene
indeno(1,2,3,-c,d)pyrene
naphthalene
phenanthrene
pyrene

Phenolic Compounds
2,4-dimethylphenol
2,4-dinitrophenol
2-methyl-4,6-dinitrophenol
2-nitrophenol
4-nitrophenol
phenol
cresol (unspecified mixture)
- 2-cresol
- 3-cresol
- 4-cresol

2-chlorophenol
3-chlorophenol
4-chlorophenol
2,3-dichlorophenol
2,4-dichlorophenol
2,5-dichlorophenol
2,6-dichlorophenol
3,4-dichlorophenol
3,5-dichlorophenol
2,3,4-trichlorophenol
2,3,5-trichlorophenol
2,3,6-trichlorophenol
2,4,5-trichlorophenol
2,4,6-trichlorophenol
3,4,5-trichlorophenol
2,3,4,5-tetrachlorophenol
2,3,4,6-tetrachlorophenol
2,3,5,6-tetrachlorophenol
pentachlorophenol

Miscellaneous organic parameters
non-chlorinated aliphatics (each)
phthalic acid esters (each)
- n-butyl benzyl phthalate
- di-n-butyl phthalate
- diethyl phthalate
- bis(2-Ethylhexyl) phthalate
- dimethyl phthalate
- di-n-octyl phthalate

quinoline
thiophene

Pesticides
aldrin and dieldrin
chlordane
DDT
endrin
heptachlor (+metabolites)
lindane
methoxychlor
carbaryl
carbofuran
2,4-D
diazinon
parathion
diquat
paraquat

Chlorinated Hydrocarbons
chloroform
1,1-dichloroethane
1,2-dichloroethane
1,1-dichloroethene
cis-1,2-dichloroethene
trans-1,2-dichloroethene
dichloromethane
1,2-dichloropropane
cis-1,2-dichloropropene
trans-1,2-dichloropropene
1,1,2,2-tetrachloroethane
tetrachloroethene
carbon tetrachloride
1,1,1-trichloroethane
1,1,2-trichloroethane
trichloroethene
1,2,3-trichlorobenzene
1,2,4-trichlorobenzene
1,2,5-trichlorobenzene
1,3,5-trichlorobenzene
1,2,3,4-tetrachlorobenzene
1,2,3,5-tetrachlorobenzene
1,2,4,6-tetrachlorobenzene
pentachlorobenzene
hexachlorobenzene
hexachlorocyclohexane
Aroclor 1242
Aroclor 1248
Aroclor 1254
Aroclor 1260
2,3,7,8-T_4CDD
1,2,3,7,8-P_5CDD
1,2,3,4,7,8-H_6CDD
1,2,3,7,8,9-H_6CDD
1,2,3,6,7,8-H_6CDD
1,2,3,4,6,7,8-H_7CDD
O_8CDD
2,3,7,8-T_4CDF
2,3,4,7,8-P_5CDF
1,2,3,7,8-P_5CDF
1,2,3,4,7,8-H_6CDF
1,2,3,7,8,9-H_6CDF
1,2,3,6,7,8-H_6CDF
2,3,4,6,7,8-H_6CDF
1,2,3,4,6,7,8-H_7CDF
1,2,3,4,7,8,9-H_7CDF
O_8CDF

- Methods that cover both solid and aqueous matrices were selected over those that covered one or the other; and
- Methods that cover both soils and sediments or that cover both surface waters and groundwaters were selected over those that covered only one when there was a choice between methods that covered solid matrices and others that covered liquid matrices.

Methods for Metals

- Methods for both atomic absorption (AA) and argon plasma emission (ICP) spectrophotometric techniques were selected when available; and
- Methods from the *Standard Methods for the Examination of Water and Wastewater* book were selected over U.S. EPA methods when they were comparable because the book is a more convenient source of the full methods.

Major Analyte Groups

The analytes of interest to the National Contaminated Sites Remediation Program are divided into 8 major groups. The arrangement of the analytes within these groups does not always correspond to logical groupings from an analytical viewpoint; thus in the discussions below some redundancy is necessary in order to keep discussions within the government's pre-established framework for these analytes.

The eight major analyte groups are:

- General Variables;
- Inorganic Variables;
- Monocyclic Aromatic Hydrocarbons;
- Phenolic Compounds;
- Polycyclic Aromatic Hydrocarbons;

- Chlorinated Hydrocarbons;
- Miscellaneous Organic Parameters; and
- Pesticides.

Each of these groups are discussed below with general comments on the applicability of the methods selected for recommendation and any problems to be noted in using them.

General Variables

This group consists not of individual analytes but, rather, of water quality parameters or physical property attributes.

Two instrumental methods were selected for pH measurements: EPA-9040A for aqueous samples and EPA-9045A for soils and waste. The latter should also be satisfactory for sediment analysis although sediments are not specifically mentioned as a suitable matrix.

One conductivity method, EPA-9050A, was selected for aqueous samples. There are no methods for specific conductance in soil and sediment samples since the technique only has application to water samples.

Inorganic Variables

Method EPA-6010A, an ICP (argon plasma emission) method is considered to be the most generally useful method in that it covers 16 of the 24 analytes in this group (Table 12) and, furthermore, is useful for both liquid and solid samples. Some methods from *Standard Methods for the Examination of Water and Wastewater* were selected for

metals analyses in water; these have the prefix SM in front of the method number in following discussions.

SM-3111B is a direct aspiration atomic absorption (AA) method commonly used for many of the metals in water samples and SM-3113B is a complimentary method that uses a thermoelectric (graphite furnace) source of energy instead of a flame.

SM-3120B is an ICP method that is analogous to the EPA-6010A method described above except that, unlike the EPA method, SM-3120B is limited to aqueous samples.

Two other variations on the atomic absorption technique involve methods SM-3111D and SM-3114B. These methods are used for AA analysis of metals not covered by the more widely applicable AA methods described above (SM-3111B and SM-3113B). Barium, beryllium, molybdenum and vanadium in water are analyzed by SM-3111D while arsenic and selenium in water are analyzed by SM-3114B. Three cold vapour methods are summarized for the analysis of mercury: SM-3112B for mercury in surface or groundwater, EPA-7470A for mercury in groundwater, and EPA 7471A for mercury in soils and sediments. Although surface waters are not mentioned as a matrix for EPA-7470A, it should perform just as well for lakes, rivers and stream samples as for groundwater samples if the same sample preparation steps are followed.

Total and amenable cyanides can be measured in aqueous samples (including soil or waste leachates) using EPA-9012. This is a colormetric determination that can be performed manually or automated. Fluoride analytes in aqueous samples may be made using EPA-340.2 which is a potentiometric method using ion selective electrodes.

Monocyclic Aromatic Hydrocarbons

EPA-8240B and EPA-8260A are the most generally applicable methods for this group of compounds because they cover all of them (Table 12) in the four matrices of interest (surface water, groundwater, soils and sediments). Both use purge-and-trap GC/MS techniques, the primary difference being that EPA-8240B employs a packed GC column for separation of the compounds while EPA-8260A uses a high resolution capillary column. EPA-8240B is the only method that analyzes specifically for xylenes as an unspecified mixture because they are poorly resolved using a packed column. All of the other recommended methods (EPA-524.2, EPA-502.2, and EPA-8260A) use capillary columns whose superior resolution separates all three xylene isomers.

EPA-524.2 mentioned above will also provide good analytical data using GC/MS with a capillary column and low resolution mass spectrometry. Although it is limited to aqueous samples, it may be the method of choice over EPA-8260A when only water samples are involved.

EPA-502.2 is recommended as a less expensive, but also less specific method, that can be used for monitoring situations, i.e., the identity and presence of the analytes of interest will already have been established using one of the mass spectrometric methods above and their continuing presence over time can be monitored using less expensive analyses. The method uses a photoionization detector (PID) in series with an electroconductivity detector (ELCD) and a high resolution capillary GC column for compound separation. The PID is used for detection of all the monocyclic aromatic hydrocarbons of interest to the National Contaminated Sites Remediation Program. As with the other two mass spectrometric methods that use capillary columns, the three xylene isomers are measured individually so if data on only the total xylenes in an unspecified mixture are needed, it can be obtained by summation of the concentrations of the individual xylene isomers. Additional applicable methods for this group, discussed below, include SM-6410B and EPA-8260.

Phenolic Compounds

The phenolic compounds are divided into two groups: non-chlorinated (each) and chlorophenols (each). There are 9 non-chlorinated phenols and 19 chlorophenols specified as analytes of interest (Table 12). The chlorophenols specify all of the isomers for chlorophenol, dichlorophenol, trichlorophenol and tetrachlorophenol plus the single pentachlorophenol isomer. The problem encountered during surveys of the methods being used for these compounds with environmental samples is that several of the chlorophenol isomers and cresol are not usually analyzed; so there are no specific data in any of the methods that involve them. The specific chlorophenol isomers for which methodology is lacking are:

- 3-chlorophenol;
- 4-chlorophenol;
- 2,3-dichlorophenol;
- 2,5-dichlorophenol;
- 3,4-dichlorophenol;
- 3,5-dichlorophenol;
- 2,3,4-trichlorophenol;
- 2,3,5-trichlorophenol;
- 2,3,6-trichlorophenol;
- 2,4,5-trichlorophenol;
- 3,4,5-trichlorophenol;
- 2,3,4,5-tetrachlorophenol; and
- 2,3,5,6-tetrachlorophenol.

Each of the methods described below is likely to be acceptable for the analysis of the above chlorophenols and also the cresols. However, these methods must be validated for analysis of these phenols and cresols.

The most generally useful method for phenolic compounds is EPA-8270B because it is applicable to both aqueous and solid (soil/sediment) samples. Groundwater is listed specifically as an applicable matrix in this method and, although surface waters are not specifically listed, they will be equally applicable in every respect with no exceptions. The method uses high resolution GC capillary columns and low resolution mass spectrometry. It should be noted that this is the only generally applicable method that is recommended for use with soils and sediments.

There are two additional methods that are recommended for use with aqueous samples: SM-6410B and SM-6420B. In many ways SM-6410B is similar to EPA-8270B but it is more limited in that it uses a packed GC column (with lower separation resolution) and it only covers aqueous matrices. For monitoring purposes, SM-6420B may sometimes be useful. It also uses a packed column and is limited to water samples. The detectors may be either flame ionization (FID) or electron capture (ECD). Both are very nonselective detectors and the data will be subject to false positive interferences if the water samples have many compounds in them. However, if they are relatively non-complex samples, this method can provide economical monitoring data. The same caveat as discussed above also applies even more strongly to the use of either of these less selective methods for the phenolic compounds for which there is no information, i.e. complete method validation will be required for each method before it can be used with these compounds.

Cresol is a mixture of three isomers: 2-cresol, 3-cresol, and 4-cresol. It is not specified whether total cresol determinations are desired or whether analysis of each of the isomers is necessary.

Polycyclic Aromatic Hydrocarbons

The National Contaminated Sites Remediation Program includes nine specific compounds in this group (Table 12). EPA-8270B, discussed above, is the most generally applicable method because it covers all of the listed compounds in both solid (soils/sediments) and aqueous matrices. SM-6410B, discussed above, also covers all of these compounds but is more limited in that it uses a packed GC column and only applies to water samples. Although SM-6410B was developed for industrial wastewater analyses, it will be entirely applicable to surface water and groundwater samples from contaminated sites.

One of the compounds, naphthalene, may be analyzed using any of the following methods also: EPA-524.2, EPA-502.2, SM-6210D or EPA-8260.

Chlorinated Hydrocarbons

The largest group of compounds consists of 47 chlorinated hydrocarbons (Table 12). This is a diverse group that consists of chlorinated aliphatics, chlorobenzenes, PCBs, and chlorinated dioxins and furans. Because of the diverse nature of these compounds, no single method is applicable to all of them.

EPA-524.2 and EPA-502.2 discussed above, are applicable to many of the volatile chlorinated hydrocarbons in water. Likewise, EPA-8240B and EPA-8260 are applicable to many of these same compounds in water, soils, and sediment samples. EPA-8270B is applicable to some of the less volatile chlorinated hydrocarbons and also the selected PCBs (Aroclors 1242-1260) in both aqueous and solid matrices. Also, SM-6410B is applicable to the PCBs, 1,2,4-trichlorobenzene, and hexachlorobenzene. However, it should be noted that only EPA-524.2 and EPA-502.2 are applicable to cis-1,2-dichloroethene so no validated method exists for analysis of this compound in soils and sediments. Also, only EPA-8240B is applicable for analysis of cis- and trans-1,2-dichloropropene in soils and

sediments; EPA-524.2 and EPA-502.2 may be used for water samples but not for soils or sediments.

The chlorinated dioxins and furans can all be analyzed for in water, soil, and sediment samples using EPA-8290. This method uses high resolution capillary GC columns and high resolution mass spectrometry. Thus, it is very sensitive, very selective, very good and also more expensive than the other methods. An alternative method EPA-8280 may be used. This method uses high resolution capillary GC columns with low resolution mass spectrometry so it is less expensive; and, therefore more laboratories may have the required instrumentation available. However, one hexachloro-p-dioxin and five of the chlorinated furan isomers are not covered by this method. Therefore, EPA-8280 would have to be validated for the analysis of these compounds.

In addition to the problems mentioned above, there are six chlorinated compounds that none of the above methods cover. These are:

- 1,2,5 - trichlorobenzene;
- 1,3,5 - trichlorobenzene;
- 1,2,3,4 - tetrachlorobenzene;
- 1,2,3,5 - tetrachlorobenzene;
- 1,2,4,6 - tetrachlorobenzene; and
- hexachlorocyclohexane.

Although not specifically listed, the five chlorinated benzenes come about from the designations "all trichlorobenzene isomers, all tetrachlorobenzene isomers, and all pentachlorobenzene isomers." There is only one pentachlorobenzene isomer and EPA-8270B covers it in both liquid and solid matrices. However, the five chlorinated benzene isomers and hexachlorocyclohexane will have to be deleted from the list of analytes or else they will have to be validated by whatever methods are used (e.g. EPA-8270B, EPA-524.2,

EPA-502.2 and/or SM-6410B). Hexachlorocyclohexane has 22 isomers and one of them (lindane) is also covered in the pesticide group. Therefore, if coverage of hexachlorocyclohexane can be considered to be acceptable using lindane (the most common and commercially used isomer), then a separate listing for hexachlorocyclohexane in this group will not be necessary.

Pesticides

The pesticides (Table 12) are another diverse group of compounds from a molecular, and therefore from an analytical point of view. Five of them may be analyzed (in water samples only) using SM-6410B which was discussed above. Nine of the pesticides may be analyzed from either water, soil or sediment samples using EPA-8270B. A number of the pesticide methods only cover a few pesticides at a time and only in a water matrix (e.g., EPA-505, EPA-507, EPA-515.1, EPA-531.1, etc.).

Miscellaneous Organic Parameters

This group consists of non-chlorinated aliphatics (each), phthalic acid esters (each), quinoline and thiophene. The last two are individual compounds. However, there are hundreds of phthalic acid esters and thousands of non-chlorinated aliphatics.

Since the phthalate esters were not specified, six representative compounds were selected for which methods exist and which also are commonly found in environmental samples. These are:

- dimethyl phthalate;
- diethyl phthalate;
- di-n-butyl phthalate;
- di-n-octyl phthalate;

- bis(2-ethylhexyl) phthalate; and
- n-butyl benzyl phthalate.

All of these compounds may be analyzed using EPA-8270B with both water, soil and sediment samples or using SM-6410B with both surface water and groundwater samples.

The analysis of "non-chlorinated aliphatics (each)" is a more difficult problem because of the vagueness of its definition. A clearer definition must be made as to specific representative compounds (e.g. pentane, hexane, heptane, octane, etc.), or to a nonspecific group of compounds such as total petroleum hydrocarbons before analytical methods can be recommended.

Summary

The recommended methods in this guidance manual should not be viewed as restrictive but rather as preferable suggestions in the absence of reasons to perform analyses in a different way. Certainly the purpose is to narrow the field of selected methods that laboratories use from many to a few so that the resulting information will be more comparable. However, there may be mitigating circumstances which lead a laboratory or a project director to select different methods. For example:

- Exploratory or field screening analyses may be desired which are faster and cheaper than many of the recommended methods in this document. These may be appropriate when lower confidence levels in the qualitative and/or quantitative data are acceptable for DQOs.
- New advances are being made in the areas of sample preparation and analysis which may be more efficient and cost effective under certain cases than those used in the methods referenced here.
    - Microwave extraction techniques are being evaluated for some metals analyses and, in some matrices such as soils and

sediments, may soon be the preferred technique for some sample preparations.

- Microextraction techniques for some hydrophobic organic compounds (especially volatile organics) may sometimes be preferable to the conventional purge and trap techniques.

Thus, users of this guidance manual should consider the recommended methods herein as preferential methods unless there are reasons to use others. When other methods or modifications are used, if both the reasoning for a change and a clear documentation of the method(s) used are recorded, then the data produced from that study will hopefully be able to be compared in terms of confidence levels and DQOs to data from other studies.

Summaries of each of the selected methods are described in Volume 2. This Volume is available in hard copy format, or on a computer diskette.

Chapter 5 - Data Management

Quality Assurance Practices

Quality assurance practices in Data Management involve a number of systematic processes and protocols that are designed to provide a framework for providing quality environmental measurements with a high degree of credibility. In the previous chapters, requirements for the collection and analysis of samples from various environmental matrices in order to obtain good quality data are discussed. When these operations have been successfully carried out, then the final step involves the overall management of the data.

From the beginning of the sampling operation to this stage where the collected data undergo analysis, evaluation and interpretation, there must be clear and precise documentation encompassing QA/QC guidelines and principles which cover every aspect of data collection.[3]

An appropriately designed and comprehensive data quality assurance program can assist not only in the evaluation of project-related data, but also in the evaluation of the projects themselves, such as the National Contaminated Sites Remediation Program. The elements of data management involve the following:

- Data Recording and Documentation, which also includes data custody and records involving transfer of data;
- Data Validation, which also includes completeness and representativeness in addition to its "correctness";
- Data Verification, which includes checking that all the data are present and correct;
- Data Handling, which also includes data rounding and treatment of significant figures;
- Data Transmission, including electronic transmission; and

- Data Evaluation, which includes interpretation, reporting by laboratories, and presentation in reports.

Data Recording and Documentation

Data documentation should include the processes used in the calculations and computations of the data; corrections required; adjustment to standard conditions; normalization of data; computer programs; statistical procedures used to report data; method for evaluating limits of uncertainty; corrections for systematic errors; and the source of all constants used in calculations.[3]

Data in the form of charts, instrument recordings, and printouts should be given suitable identification numbers and maintained in a manner consistent with good record-keeping practices. Laboratory record books must refer to the location and identification of such records. In addition, all calibrations and standardizations should be fully documented, and the data should provide clear traceability to the calibrations/standardizations to which they relate.[3]

Systematic inspection and periodic review of notebooks and similar primary records will ensure the general quality of their contents. Changes or revisions of notebooks entries must be justified and documented. Any changes should be made by crossing out the original entry and substituting the new value. The person making the change should initial the entry and state why the change was made. No erasures of records or data should be permitted.[3]

Records of equipment maintenance also must be documented. Routine maintenance may be indicated by labels on the equipment. Maintenance which results in modification of equipment must be described in sufficient detail and recorded in the operation manual for the particular equipment. Likewise, field and laboratory records should be retained in permanent files and bound notebooks are much preferred to looseleaf-type notebooks.[3]

Collecting supporting information (auxiliary data) during all phases of the measurement program is an excellent practice because it may become necessary to use this information during the data interpretation process.

The following information may be considered as auxiliary data:

- Data charts and printouts;
- Equipment performance records;
- Calibration records;
- Operation logs;
- Environmental conditions prior to and during sampling;
- Measurement comparison records;
- Quality control and system audit records; and
- Records of corrective actions.

Auxiliary data should be collected throughout the measurement program and reviewed periodically. They are important in determining the validity of the measurement program data. For example, auxiliary or support data could be used in deciding whether or not an outlier is a valid value or an artifact.[3] Unusual conditions should always be recorded on the field data reports.

Data Custody and Transfer

Data custody and transfer involve two distinct forms today; physical written or typed forms that may carry signatures and be stored in file cabinets, and electronic forms and data will constitute elements of database records and computerized files.

The QA objectives for data custody are to ensure that data handling operations follow well-organized data management principles and procedures, and that all relevant information appears in any files and/or databases that involve QC studies.

QA procedures for data custody should include:

- Development of a chain-of-custody system for acquired data, including electronic data communication links;
- Use of simple and explicit sample and laboratory tracking forms;
- Implementing a procedure for authorizing changes to QC databases where corrections and data changes are warranted; and
- Implementing checks to ensure that the QC databases are always complete.

QA procedures for data transfer should include:

- A mechanism and schedule for data transfer in order to ensure that the respective formats for data reports and data tapes are suitable;
- Documentation of data transfer procedures and schedules in a QC operational manual;
- Use of data recording forms and good data entry procedures to ensure that correct and complete data are recorded and transmitted through all stages of the QC program;
- Complete and accurate transfer of data from and through all stages of the sampling and analysis QC programs; and
- Establishing procedures and protocols to ensure and facilitate the transfer of data including a data traceability mechanism for pinpointing the location of any specific piece or block of data at any given time.

Additional QC procedures for handling electronic transmission of data are discussed later in the section entitled, "Data Handling and Transmission".

Data Validation

Data validation is an essential element of data quality assurance. It provides for reviewing a body of data against a set of criteria, so that assurance can be made that the

data of interest are adequate for their intended use. The validation process includes not only the identification or flagging of questionable data, but also the investigation of apparent anomalies. Several of the more important steps for data validation are briefly summarized below. These are comprehensively covered in a recent Environment Canada report.[3] Validation checks for the data from a contaminated site should include:

- Data identification

  This includes data entries such as dates of sampling and/or analysis, location, laboratory identification, sample code numbers, analytical method identifications, etc. The latter should also include the identification of QC samples that were analyzed with a set of environmental samples, the presence of method detection limits and data uncertainty intervals (+ or - values bracketing the analytical data values).

- Unusual events

  This includes both sampling information (such as inclement weather, oil slicks on the water being sampled, etc.) and analytical information (such as noting deterioration in GC peak resolution, a dirty ion source in the mass spectrometer, etc.).

- Transmittal errors

  For paperwork systems, simple checks should be made to assure that the data have not been incorrectly transferred from one paper (medium) to another. With electronic and computer data handling, and with telemetry of data, checks could be made to assure that the data have not been changed in the transmission or transfer process.[3]

- Temporal continuity

  This includes checks for continuity with respect to time, such as looking for breaks, discontinuities or gaps, etc.

- Flagged or rejected data

  This includes a scheme for flagging questionable data. The basis for any data rejection should be centered around several criteria, which include numerical errors, round-off errors, anomalous values, ionic imbalances, mass imbalances, etc.

- Checks for errors in automatic data processing

  These include internal, historical, and parallel data consistency checks, plus routines that are peculiar to data processing. Processing errors are usually caused by deficiencies in the computer programs which manipulate the data files, perform mathematical calculations and computations, and format the output results. A standard method of checking for processing errors is to make up a small but typical data set, perform the appropriate data manipulations and calculations by hand, and compare these results with the results from the data processing system.[3]

- Control charts

  These must be maintained in a real-time mode to the greatest extent possible if they are to be most effective in data validation. This will allow responsive corrective actions to be taken as soon as problems are detected, and will also provide the possibility for minimization of anomalous data arising from out-of-control operations.[3]

- Sample consistency checks

  These will help to determine the validity of a given sample by investigating the relationships between the individual chemical species in the sample. They make use of the relationships between measured and calculated parameters associated with solution chemistry.[3]

- Ion balances

  In any given sample, the theoretical sum of the anions must equal that of the cations, when both are similarly expressed in milliequivalents per liter. In practice, however, the sums are seldom equal because of variations in analysis. This inequality increases as the ionic concentration increases.[3] Another source of error in the ionic balance

equation may arise because only the traditional major ions are considered. Unless all ions are measured (which is rarely done), there will be errors in the values used for comparison.

Completeness and Representativeness

Completeness is also a measure of valid data. It measures the amount of valid data obtained from a measurement system, and is expressed as a percentage of the number of valid measurements that were planned. An additional, complimentary measure is representativeness of data. Data representativeness compares how closely the measured results reflect the actual concentration of analyte distribution in the media sampled. Thus a study could have 100% data completeness (all samples planned to be collected were actually collected and found to be valid), but the results do not accurately reflect the analyte concentration actually present. For example, the method might be biased or the sampling points might not be representative of the average distribution in the media.[3]

Data Comparability and Compatibility

Data Comparability is based on the measure of confidence with which one data set can be compared with another while data compatibility among data sets relies on the likeness and consistency with which the data sets being compared are acquired (similar sampling, analyses, data procedures and treatments; similar QA/QC protocols; similar reporting data units; etc.).

Data Review and Evaluation

Review and evaluation of the data is one of the final key activities that are important to data validation. Review and evaluation of data should be centered around a number of performance indicators such as the accuracy and precision with which the data were gathered, and the representativeness, and completeness of the assembled database or data package. Data review and evaluation operations should be structured to address

aspects of accuracy, precision, etc., and also to link performance indicators to the data quality objectives of the project.[3]

Data Verification

Verification controls are required for data originating from sampling, field testing and laboratory analysis. Data verification checks must be conducted by field and laboratory personnel before the data are sent out for storage and ultimately, to data users. Any discrepancies or errors found must be corrected prior to storage, and the data must also be checked again upon its merger into an existing database. The merging of field data with laboratory data provides an additional quality assurance check. Any mismatch will indicate a sample loss or data loss as a result of shipping or data transmittal inefficiencies.[3]

In selecting laboratories to perform analyses, check to be sure that the laboratory data system is designed to incorporate comment codes into the results reported for individual analyses. For example, codes must be available to indicate reasons for missing parameters (e.g., insufficient sample volume), results invalidated at the laboratory (e.g., calibration problems), missing samples, non-preserved samples, and data reported at the detection limit of the analytical system. It is important that numerical values below the method detection limit be reported with a flag rather than simply as, "less than the detection limit", in order to facilitate data manipulation routines.[3]

When all the laboratory analyses (physical, chemical, biological, and computational) have been completed and the laboratory data have been subjected to data validation procedures, further data verification checks should be made before the data leave the laboratory. These checks consist of:[3]

- Verifying that a result is reported for each sample;
- Checking for transcription errors by reviewing all transcribed data;
- Spot checking the laboratory data printout against original field sheets;

- Ensuring that all laboratory checks of field QA/QC are reported (e.g., shipping temperature, sample volumes, preservation, etc.); and,
- Ensuring that any missing or invalid results are explained (i.e., with comment codes).

The laboratory also should be responsible for performing a number of QC checks on the field portion of the monitoring program. These checks consist of:[3]

- Verifying sample labelling and matching field sheets with samples;
- Ensuring that samples were submitted as recorded in the sample log book (or computer sample registry); monitoring sample shipping (time, temperature, mode of shipping), sample condition (leaks, contaminants), and sample volume (independent measurement of sample volume); and,
- Reporting any other comments that may be important on the Sample Submission Form.

In the final verification step, the technical project director is responsible for reviewing (and editing if necessary) all data connected to a specific project or program before those data are released or entered into the final database for subsequent data reporting and analysis. This review should consist of an investigation of all data points that were flagged as a result of the gross sample checks, data screening and data validation checks, as well as an overall evaluation of the data set. In general, data should be rejected only in clear cases of non-representative or contaminated samples. Comparison of the suspect data points to related historical data could aid in the acceptance or rejection decision process.[3]

Personnel involved in the verification, evaluation, or validation of data should also have the opportunity to enter a set of comment codes (related to the sample validity) to the database to reflect the results of both the data validation and data verification processes.[3]

Data Handling

In performing mathematical operations or calculations, the preferred protocol is for measured or observed data to be recorded with as many numbers as possible; rounding numbers should be deferred until all calculations have been made and their statistical significance has been evaluated. The number of significant figures is the number of digits remaining when the data are so rounded. The last digit, or at most the last two digits, are expected to be the only ones that would be subject to change on further experimentation. Thus, for a measured value of 21.5, only the 5, and at most the 1.5, would be expected to be subject to change. Such data would be described as having three significant figures. In counting significant figures, any zeros used to locate a decimal point are not considered as significant. Thus, 0.0025 contains only two significant figures. Any zeros to the right of the digits are considered significant; thus, 2500 and 2501 each have four significant figures. Only those that have significance should be retained. Zeros should not be added to the right of significant digits to define the magnitude of a value unless they are significant, since this would confuse the significance of the value. For example, it is not good practice to report a value as 2500 ng, but rather 2.5 μg if the data are reliable to two significant figures. The use of exponential notation, e.g., 3.5×10^3 is an acceptable way to express both the number of significant figures and the magnitude of a result.[39]

If possible, and within the scope of desired results, a number of measurements sufficient for statistical treatment should be made. Three measurements, as a minimum, are recommended to calculate standard deviations. When no statistical treatment is made, an explanation is necessary, including complete details of the treatment of the data.

Since laboratories generate data for their clients (users of the data), they are not the final step in the data use process; therefore, rounding performed by the laboratory should attempt to preserve measurement variability. A good rule is for a laboratory to retain at least one significant figure beyond that known with reasonable certainty. Also, the laboratory should not attempt to convey measurement uncertainty through use of significant

figures -- this information should be provided in accompanying statements of precision and accuracy. The data user provides the final step in presenting and working with data sets so this is the point at which rounding of data should occur.[4]

The following rules for rounding data, consistent with its significance, are recommended:[39]

- When the digit immediately after the one to be retained is less than five, the retained figure is kept unchanged. For example: 2.541 becomes 2.5 to two significant figures.
- When the digit immediately after the one to be retained is greater than five, the retained figure is increased by one. For example: 2.453 becomes 2.5 to two significant figures.
- When the digit immediately after the one to be retained is exactly five and the retained digit is even, it is left unchanged but when it is exactly five and the retained digit is odd the retained digit is increased by one. For example: 3.450 becomes 3.4, but 3.550 becomes 3.6 to two significant figures.
- When two or more figures are to the right of the last figure to be retained, they are considered as a group in rounding decision. Thus in 2.4(501), the group (501) is considered to be greater than 5, while for 2.5(499), (499) is considered to be less than 5.

Data Transmission

Electronic data handling, data reduction and data storage systems are important parts of many analytical systems. They greatly facilitate data management and control of errors due to misreading, faulty transcription or miscalculations. However, the performance of the data system in any participating laboratory should be tested regularly to ensure that it is working properly and correctly. This should be done periodically by using known data that have already been analyzed. These tests must have sufficient accuracy and precision to provide a reliable examination of the data handling system.[41]

The principal result of transmission errors is the loss or alteration of data. A simple way to check for transmission errors is to transmit the data a second time, and then compare the two data streams. Gaps and alterations will immediately become apparent, unless the transmission error is systematic.[3] However, there is a second type of transmission error that can only be found by comparing transmitted data to the original data. This involves the deletion during transmission of certain non-common alpha-numeric characters which serve as notations and "flags" in data reports.[4] Examples of these symbols include >, <, *, ‡ , #, etc.

The loss of these symbols during transmission of data can be very significant. For example, < 100 μg/L can become 100 μg/L.

Data Evaluation for Interpretation

The end of this long process is the evaluation and interpretation of all the data and, finally, presenting it in a cohesive report so that others can not only understand the conclusions as stated, but can also make interpretative evaluations of their own. Part of a reader's interpretative evaluation will certainly include:

- A comparison between the data quality objectives and goals and the findings presented;
- An evaluation of the QA/QC data or summary information with the data and supporting information presented; and
- An extrapolation of the information presented to some form which will ultimately be useful for their own purposes.

Bear in mind that few people read technical reports for the fun of it. Invariably, they will be searching for one or more parts of it that will be useful in some way to their own personal goals. Also bear in mind that people with exactly opposite goals will probably read most environmentally-related technical reports and attempt to find information useful for their own purposes. Therefore, it is the responsibility of the people who are involved in

evaluating, interpreting and presenting the information to do so as clearly and unambiguously as possible, bearing in mind the constraints of time and reasonable size of reports. Although it is not necessary to exhaustively provide all the data used in a report, it is very necessary to be thorough in its description and use in drawing the conclusions presented in a report. If someone needs additional information (such as portions of the raw data or portions of a database) it can be requested of the author later.

Data Reporting by Laboratories

Laboratory reports must contain sufficient data and information so that users of the conclusions (even years later) can understand the interpretations from raw data, without having to make their own. Unless this objective is achieved, the samplers and analysts have not done their jobs properly. Laboratory reports also must clarify which results, if any, have been corrected for blank and recovery measurements. Generally, corrections for recovery are not made, but percent recovery should always be reported where it is involved. Any other limitations should also be noted.[4]

Raw data for each sample, along with data from reagent blanks, controls, spiked samples, and all other quality control samples, should be suitably identified if included in laboratory reports. If average values are reported, an expression of the precision, including the number of measurements, must be included. Details of the analytical results should be written with the standard deviation and the mean. They should show that the averaging process accounts for sample heterogeneity as well as observed imprecision among replicate measurements of homogenized samples.[4]

Laboratories generate and perform QC checks on individual measurements; they are reported as individual analytical results and associated QC data. However, users usually compile these individual measurements into sets of data, and reports and conclusions are generally made from these sets of data. Therefore, a laboratory is responsible for producing individual test measurements with analytical systems that are in statistical control

and reporting that data with a statement of its uncertainty interval. This means providing appropriate rounded or truncated data that have a specified uncertainty interval (+ or - some percentage). Uncertainty intervals may be quoted for an individual analyte, or more often, for a specific method. Laboratories have the responsibility to provide this information with every analytical report.[4]

The data user should request these uncertainty intervals from the laboratory if they are not provided, because the responsibility for using and presenting final data belongs with the user and not the laboratory. The user should seek help from the laboratory or another source to determine what data to present in a report, but the laboratory is not responsible for deciding whether or not to give the user censored reports; the user should request censored reports if these are desired.[4]

Many environmental analytical laboratories today subscribe to the practice of not reporting data less than the Method Detection Limit (MDL) or the Limit Of Detection (LOD) because data below these levels have very poor statistical confidence.[40] The National Water Quality Laboratory (NWQL) takes the opposite position that a laboratory is responsible for reporting all detectable analyte concentrations, provided they are well defined with appropriate levels of statistical confidence. The NWQL feels that a laboratory that takes the initiative to censor and eliminate a certain amount of detected data, is doing an injustice to data users because these data, irrespective of their level of statistical confidence, may contain valuable environmental information. This same position is held by both the American Society for Testing and Materials[42] and the American Chemical Society.[4]

There is an active movement to revise the definition of MDL and to change the name from Method Detection Limit to Method Detection Level. Furthermore, proposed new definitions of a Reliable Detection Level (RDL) and a Reliable Quantitation Level (RQL) would directly be derived from the Method Detection Level. The RDL would

be equal to twice the Method Detection Level and the RQL would be four times the Method Detection Level (i.e., twice the RDL).

The purpose of the proposed RDL is to deal with the statistical probability of failing to detect an analyte when it is present (i.e., having an acceptably small percentage of false negatives). At the MDL, there is a 50% chance of a false negative determination assuming a Gaussian distribution around an MDL selected at 3σ above zero or a blank analyte concentration. However, at twice the MDL the probability of false negatives is about equally as low as the risk of false positives at the MDL. This is a much more reliable detection level and statisticians have given it various names in the past. "Reliable Detection Level" is recommended as an unambiguous name that is recognizable by non-statisticians for this concept by the ACS Subcommittee on Environmental Monitoring and Analysis.[4]

The current commonly used definition of Method Detection Limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyte concentration is greater than zero.[43] As such, it does not take into account the situation when there is a statistically significant background concentration of an analyte. The latter situation is accommodated by the ACS term, "Limit of Detection" (LOD) which is the minimum concentration of a substance that can be determined to be statistically different from a blank at a specified level of confidence.[40] These two definitions (MDL and LOD) are essentially the same except one (MDL) uses zero as a reference point and the other (LOD) uses a background signal as a reference point. The proposed revised definition is a single definition that accommodates both situations.

Another serious problem with the current commonly used definition of MDL is that the Method Detection Limit does not take matrix effects into consideration. Yet, most MDLs are dependent on the sample matrix in addition to the method itself (and corresponding influences such as instrument and/or operator variability). The result is an unrealistic use of MDLs that often causes large analytical and regulatory problems. These evolve from published MDLs where the measurements are performed using reagent water

but where regulatory decisions are based on real environmental samples. Because of matrix and other effects the MDLs in environment samples are often many times higher than the published MDLs (sometimes 10,000 times higher). To accommodate this problem an arbitrary set of multiplication factors has been promulgated for regulators. An MDL when multiplied by one of these arbitrary factors produces a PQL (Practical Quantitation Limit). PQLs have been severely criticized as having very little technical basis for their selection. However, PQLs were created to try to accommodate the use of MDLs which were incorrectly defined in the first place by omitting matrix effects.

The following proposed draft definition of MDL has attempted to correct each of the above deficiencies. The rewording of MDL will:

- replace the word "limit" with "level;"
- accommodate either zero or background signals of an analyte as a reference point;
- reflect statistically variable confidence levels that may be used as a basis for estimating the probability of eliminating false positive detections; and
- take a representative matrix into consideration when making analytical measurements.

These proposed definitions, if widely adopted by the scientific community, will affect the way that laboratories report data from future analyses. The proposed definitions are provided below.

METHOD DETECTION LEVEL (MDL) - The lowest concentration at which individual measurement results for a specific analyte are statistically different from a blank (that may be zero) with a specified confidence level for a given method and representative matrix. An *intra-laboratory* MDL estimate represents the average detection capability of a single laboratory for a specific analyte, method and matrix at a given point in time. An *inter-laboratory* MDL

estimate represents the method detection capability, for a specific analyte and specific matrix, determined in more than one laboratory.

RELIABLE DETECTION LEVEL (RDL) - For a given MDL, method, and representative matrix, a single analysis should consistently detect analytes present at concentrations equal to or greater than the RDL. When sufficient data are available, the RDL is the experimentally determined concentration at which false negative and false positive rates are specified. Otherwise, the RDL is the concentration which is twice that of the Method Detection Level (RDL = 2 x MDL). The RDL is the recommended lowest level for qualitative decisions based on individual measurements, and it provides a much lower statistical probability of false negative determinations than the MDL.

RELIABLE QUANTITATION LEVEL (RQL) - The RQL is the recommended lowest level for quantitative decisions based on individual measurements for a given method and representative matrix. The RQL is the concentration which is two times the Reliable Detection Level (RQL = 2 x RDL). This recognizes that the RDL estimates produced at different times by different operators for different representative matrices will not often exceed the RQL.

Data Presentation

Laboratories report data they generate from analyses to users. Data users interpret these data and present them with discussion and/or interpretation in documents, reports, summaries, etc. Guidelines for reporting data by laboratories (based on these distinctions) are given in Table 13. In using the table, remember that the concentration levels indicated refer to interpretation of single measurements. Users typically work with data sets composed of several or many such individual measurements.[4]

Table 13. Guidelines for Laboratories Reporting Data

Analyte Concentration in Units of σ	Regions of Relative Reliability	Report As
"Zero"	No observed signal	ND (MDL = X)
$< 3\sigma$	Region of high uncertainty (<MDL)	Y* (MDL = X)
$> 3\sigma$	Method detection level (MDL) and above	Y (MDL = X)

"Zero" may be a negative value or no discernable detector response.
Y = Reported sample concentration.
X = Calculated MDL
* = Data below the MDL should be flagged. The flag notation varies and is not important, but the key to all notations must always be included.

The symbols "T" or "tr" for amounts and the term "trace" and similar statements of relative concentration should be avoided because of the relative nature of such terminology, the confusion surrounding it, and the danger of its misuse.[40]

It must be emphasized that the MDL, RDL, and RQL are not intrinsic constraints of the analytical methodology. They depend upon the precision attainable by a specific laboratory, working with a specific matrix, when using that methodology. Thus, MDLs, RDLs, and RQLs can be very diverse. Unfortunately, this basic fact generally is not considered when evaluating environmental analytical data. Many users of analytical data are unaware of this caveat. Published values of MDLs must be considered only typical. Each laboratory reporting data must evaluate its own precision and estimate its own MDL, RDL, and RQL values for analytes of interest, for each type of matrix it analyzes. A common and acceptable alternative, when method-specified limits are available (for example with many EPA methods), is to verify that each instrument can meet or exceed these published limits. If a method has any possible sensitivity to operator variability, the instrument and method verification should be performed by each person who will use it.

Method sensitivity in this context is defined as the rate of change in instrument response to the change in analyte concentration (i.e., the slope of the calibration curve).[4]

There are also upper levels of reliable measurements. These vary from method to method and are a function of a particular instrument's detector response to each specific analyte. At high concentration levels (a term that is relative to each analyte and detector considered) measurements will become nonlinear with increasing concentration. This is called the *limit of linearity* (LOL) and is usually caused by the analyte chemically or physically saturating the detector.[4]

The analytical chemist is responsible for fully describing and interpreting the data and reporting them in an appropriate manner. It must be remembered that all users of those data will depend (perhaps years later) on how clearly and thoroughly the data were recorded and described. Measurement results also should be expressed so that their meaning is not distorted by the reporting process. The public at large is not able to recognize that 10,000 ng/kg and 10 μg/kg are the same. In general, μg/kg (parts per billion) are commonly employed with most ambient environmental samples; ng/kg (parts per trillion) are sometimes employed with very low level analytes in potable (drinking) water and human samples. Since parts per million, billion, trillion, etc., are less definitive than specific units of measurement such as mg/L, μg/cm^3, ng/kg, etc., the use of these more specific units for expression of concentration is recommended.[4]

Generally, analytical values from a laboratory should be reported as measured (uncorrected for recovery) with full and complete supporting data involving recovery experiments. If the measurements are reported as "recovery-corrected," all calculations and experimental data should be documented so that the original uncorrected values can be derived if desired. In carrying out recovery studies, the analyst should recognize that an analyte added to a blank sample may behave differently (typically, showing higher recovery) than that analyte in a test sample. In such cases, the method of standard addition tends to lead to erroneously low values.[40]

Finally, if published methodology is used, it always must be cited. Any modifications, as well as any new methodology techniques, new approaches in making test sample measurements, or interpretations of results, must be described in detail, including test results and details of their validation.

Chapter 6 - References

1. CMME (Canadian Council of Ministers of the Environment). 1992. National Classification System for Contaminated Sites. Canadian Council of Ministers of the Environment, Winnipeg, Manitoba.

2. CMME (Canadian Council of Ministers of the Environment). 1991. Interim Canadian Environmental Quality Criteria for Contaminated Sites. Canadian Council of Ministers of the Environment, Winnipeg, Manitoba.

3. Gaskin, J.E. 1988. Quality Assurance Guidelines and Principles for the Handling and Management of Water Quality Data. Water Quality Branch, Inland Waters & Lands Conservation and Protection. Environment Canada. Hull/Ottawa, Quebec/Ontario.

4. Keith, L.H. 1991. Environmental Sampling and Analysis - A Practical Guide. Lewis Publishers, 2000 Corporate Blvd., Boca Raton, FL, 33431, USA.

5. U.S. EPA. 1992. Characterizing Heterogeneous Wastes: Methods and Recommendations. U.S. Environmental Protection Agency, P.O. Box 93478, Las Vegas, NV 89193-3478. EPA/600/R-92/033.

6. Agemian, H. 1988. Quality Assurance in the National Water Quality Laboratory. 3rd Edition. Canada Centre for Inland Waters, 867 Lakeshore Road, P.O. Box 5050, Burlington, Ontario L7R4A6.

7. Keith, L.H. 1991. Quality Control and GC Advisor. Lewis Publishers, 2000 Corporate Blvd., Boca Raton, FL 33431, USA.

8. Maney, J.P. and A. Dallas. 1991. The Important of Measurement Integrity. Environ. Lab. 23 pp.

9. Rogers, L.B., et al. 1982. Chem. Eng. News. 60(23): 44 pp.

10. Keith, L.H. 1991. Report Results Right - Part 1. Chemtech 21: 352-356 pp.

11. Grakin, J.E., et al. 1990. Analysts 1990. Vol. 115: 507-510.

12. Keith, L.H. 1991. Report Results Right - Part 2. Chemtech 21: 486-489.

13. Keith, L.H. 1988. Principles of Environmental Sampling. American Chemical Society, 1155 16th St., N.W., Washington, DC, 20046.

14. Water Quality Branch. 1983. Sampling for Water Quality. Inland Waters Directorate. Environment Canada, Ottawa, Ontario. 5-9 pp.

15. Forsberg, K.F. 1992. Chemical Protective Clothing Degradation and Permeation Database - IBM Compatible Version. Lewis Publishers, 2000 Corporate Blvd., Boca Raton, FL 33431, USA.

16. Forsberg, K.F. and M. Blotzer. 1992. Chemical Protective Clothing Degradation and Permeation Database - Macintosh Version. Lewis Publishers, 2000 Corporate Blvd., Boca Raton, FL 33431, USA.

17. Keith, L.H., et al. 1992. The National Toxicology Program's GlovES+. Lewis Publishers, 2000 Corporate Blvd., Boca Raton, FL 33431, USA.

18. Bone, L.T. 1988. Preservation Techniques for Samples of Solids, Sludges and Non-aqueous Liquids. *IN* Principles of Environmental Sampling. L.H. Keith, ed. American Chemical Society, 1155 16th St., N.W. Washington, D.C. 20046. pp 409.

19. Barcelona, M.J. 1988. Overview of the Sampling Process. *IN* Principles of Environmental Sampling. L.H. Keith, Ed. American Chemical Society, 1155 16th St., N.W., Washington, D.C., 20046. 3 pp.

20. Taylor, J.K. 1988. Defining the Accuracy, Precision and Confidence Limits of Sample Data. *IN* Principles of Environmental Sampling. L.H. Keith, Ed. American Chemical Society, 1155 16th St., N.W., Washington, D.C., 20460. 101 pp.

21. Gaskin, J.E. 1988. Quality Assurance Principles and Guidelines for Water Quality Sampling. Water Quality Branch, Inland Waters and Lands Conservation and Protection. Environment Canada, Ottawa, Ontario. 2-6 pp.

22. Petersen, R.G. and L.D. Calvin. 1986. Sampling. *IN* Methods of Soil Analysis, Part 1. 2nd Edition. A. Klute, Ed. American Association of Agronomy Inc., Soil Science Society of America, Inc., Madison, WI. 34-45 pp.

23. van Ee, J.J., L.J. Blume and T.H. Starks. 1989. A Rationale for the Assessment of Errors in the Sampling of Soils. U.S. EPA, EMSL-Las Vegas, P.O. Box 93478, Las Vegas, NV, 89193-3478. EPA-600-8-89-203. 5-6 pp.

24. Mudrock, A. and S.D. MacKnight. 1991. Handbook of Techniques for Aquatic Sediments Sampling. CRC Press, Inc., 2000 Corporate Blvd., Boca Raton, FL 33431, USA. 6-95 pp.

25. Water Quality Branch. 1983. Sampling for Water Quality. Inland Waters Directorate, Environment Canada, Ottawa, Ontario.

26. Horowitz, A.J. 1991. A Primer on Sediment-Trace Element Chemistry, 2nd Edition. Lewis Publishers, 2000 Corporate Blvd., Boca Raton, FL 33431, USA,. 94-100 pp.

27. Newburn, L.H. 1988. Modern Sampling Equipment: Design and Application. *IN* Principles of Environmental Sampling. L.H. Keith, Ed. American Chemical Society, 1155 16th St. N.W., Washington, D.C., 20046, USA. 209 pp.

28. Cargill, U.M. 1988. Sampling Waters: The Impact of Sample Variability on Planning and Confidence Levels. *IN* Principles of Environmental Sampling. L.H. Keith, Ed. American Chemical Society, 1155 16th St., N.W., Washington, D.C., USA, 20046. 171 pp.

29. Smith, J.J., et al. 1988. Groundwater Sampling. *IN* Principles of Environmental Sampling. , L.H. Keith, Ed. American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20046, USA. 255 pp.

30. Kent, R.T. and K.E. Payne. Sampling Groundwater Monitoring Wells: Special Quality Assurance and Quality Control Procedures. *IN* Principles of Environmental Sampling. L.H. Keith, Ed. American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20046, USA. 231 pp.

31. CCME (Canadian Council of Ministers of the Environment). Handbook on Subsurface Assessment for Contaminated Sites. Winnipeg, Manitoba (in preparation).

32. Ho. J.S.Y. 1983. Effects of Sampling Variables on Recovery of Volatile Organics in Water. J. Am Water Works Assoc. 583-586 pp.

33. Parr, J.D. et al. 1988. Preservation Techniques for Organic and Inorganic Compounds in Water Samples. *IN* Principles of Environmental Sampling. L.H. Keith, Ed. American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20046, USA. 221 pp.

34. Maskarinec, M.P. et al. 1990. Stability of Volatile Organic Compounds in Environmental Water Samples During Transport and Storage. ES&T 24: 1665-1670 pp.

35. Lewis, R.G. 1986. Problems Associated With Sampling for Semivolatile Organic Chemicals in Air. Proceedings of the 1986 EPA/APCA Symposium on Measurements of Toxic Air Pollutants. APCA Special Publication VIP-7. Air and Waste Management Association. 134-145 pp.

36. Clemments, J.B. and R.B. Lewis. 1988. Sampling for Organic Compounds. *IN* Principles of Environmental Sampling. L.H. Keith, Ed. American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20046, USA. 287 pp.

37. Hicks, B.B., et al. 1988. Aerometric Measurement Requirements for Quantifying Dry Deposition. IN Principles of Environmental Sampling. L.H. Keith, Ed. American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20046, USA. 297 pp.

38. Devitt, D.A., et al. 1987. Soil Gas Sensing for Detection and Mapping of Volatile Organics. National Water Well Association, 5375 Riverside Dr., Dublin, OH, 43017. 11-14 pp.

39. Taylor, J.K. 1987. Quality Assurance of Chemical Measurements. Lewis Publishers, 2000 Corporate Blvd., Boca Raton, FL 33431, USA.

40. Keith, L.H., et al. 1983. Principles of Environmental Analysis Anal. Chem. 55: 2210-2218 pp.

41. Gaskin, J.E. 1991. Principles and Guidelines for Interlaboratory QC Studies. Quality Assurance Work Group. Federal-B.C. Water Quality Monitoring Agreement. Environment Canada, Ottawa, Ontario. 28-50 pp.

42. ASTM. 1983. Standard Practice for Interlaboratory Quality Control Procedures and a Discussion on Reporting Low-Level Data. ASTM, D4110-81. Philadelphia, PA.

43. U.S. EPA. Federal Register, Part VIII. 1984. Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act: Final Rule and Proposed Rule. 40 CFR Part 136.

APPENDIX 1

GLOSSARY

GLOSSARY

AA - atomic absorption spectrophotometry.

Accreditation - the formal recognition of the competence of an Environmental Analytical Laboratory to carry out specified tests. Formal recognition is based on an evaluation of laboratory capability and performance; site inspections are utilized in the evaluation of capability.

Accuracy - the agreement between the measured value and the accepted or "true" value.

Adsorption - the surface retention of solid, liquid or gas molecules, atoms or ions by a solid or liquid surface.

Aliquot - a representative sample from a larger quantity of sample.

Analyte - the specific component or element measured in a chemical analysis.

Analytical batch (set) - the basic unit for analytical quality control is the analytical batch or set. The analytical batch is defined as samples which are analyzed together with the same method sequence and the same lots of reagents and with the manipulations common to each sample within the same time period or in continuous sequential time periods. Samples in each batch should be of similar composition.

Analytical Data Set - data from an analytical batch which includes environmental test samples and the associated QC samples. An analytical data set stands on its own merits; if the QC samples are unacceptable then all the samples in the analytical batch must be reanalyzed.

Analytical grade - a chemical with a level of purity high enough to permit its use in precise analytical determinations.

Aquifer - a geological formation that contains enough saturated permeable material to be capable of yielding significant quantities of water to wells or springs.

Area Control Sites - background (control) sites that are farther away from the test sample sites than local control sites. When sampling problems preclude taking background samples from local control sites than they should be as close as possible to the area where test samples are taken, for example, in the same city.

Arithmetic mean - the sum of observations divided by their number; also called 'average'.

Atomic Absorption Spectrophotometry - an analysis technique that uses the absorption spectra of isolated atoms to determine elemental concentrations.

Background Samples - matrices minus the analytes of interest that are carried through all steps of the analytical procedure. They are used to provide a reference for determining whether environmental test sample results are significantly higher than "unpolluted" samples which contain "zero," low or acceptable levels of the analytes of interest. They are needed in order to attribute the presence of analytes of interest to pollution rather than to a natural occurrence or to a previous occurrence of the analytes of interest in the environmental matrix. All matrices, reagents, glassware, preparations, and instrumental analyses are included in the analysis of background samples.

Bed material - the sediment mixture of which the bed of the water body is composed.

Between-day Precision - a measure of variability among replicate analyses of a single sample, all performed on different days, under identical conditions.

Between-Laboratory Precision - the variability between results obtained on the same material in different laboratories in interlaboratory analyses.

Bias - a systematic displacement of all the observations on a sample from the true or accepted value; or a systematic and constant error in test results.

Biodegradation - the process of destruction or mineralization of either natural or synthetic materials by the microorganisms of soils, waters or wastewater treatment systems.

Blank - the measured value obtained when a specified component of a sample is not present.

Blind samples - analysis conducted on specified control samples where the expected values are unknown to the analyst.

Blue ice - a synthetic glycol packaged in plastic bags and frozen prior to sampling in order to provide a convenient coolant for shipment of environmental samples. It is effective for maintaining cold temperatures but not for cooling samples from ambient temperatures to preservation temperatures.

Bottom sediment - those sediments which make-up the bed of a body of running or still water.

Calibration - comparison of a measurement standard or instrument with another standard or instrument in order to report or eliminate by adjustment, any variation (deviation) in the accuracy of the item being compared.

Calibration check - verification of the efficacy of the calibration process by analysis of a check sample of known composition. Calibration check solutions are made from a stock solution which is different from the stock used to prepare standards.

Calibration Standards - solutions containing analytes of interest at known and measurable concentrations. Many methods are multipoint calibration where standards at 3 to 5 different concentrations are used to bracket the analyte concentrations in the environmental samples.

Certification - the formal recognition by the Canadian Association for Environmental Analytical Laboratories of the proficiency of an Environmental Analytical Laboratory to carry out specified tests. Formal recognition is based on a screening of laboratory capability and an evaluation of laboratory performance.

Coefficient of Variation (Relative Standard Deviations) - a measure of precision that is calculated as the standard deviation of a set of values divided by the average and usually multiplied by 100 to be expressed as a percentage.

Collocated samples - independent samples collected in such a manner that they are equally representative of the variable(s) of interest at a given point in space and time.

Composite sample - a sample obtained by mixing several discrete samples, or representative portions thereof, into one bottle.

Concentration - a measure of the amount of a substance present per unit volume or per unit weight of material.

Confidence limit (interval) - that range of values, calculated from an estimate of the mean and the standard deviation, which is expected to include the population mean with a stated level of confidence. Confidence limits in the same context may also be calculated for standard deviations, lines, slopes and points.

Confirmation - an experimental process to assure that the analytes in question have been detected and measured acceptably and reliably.

Contamination - a foreign or unwanted material which renders a sample unfit for meaningful analyses.

Control Samples - an environmental sample or simulated samples designed to help control the analytical process by checking the acceptability of some quality characteristic. These are often used synonymously with QC check samples.

Correlation coefficient (r) - a measurement used to express the degree of association between the independent variable and the dependent variable(s). The square of the correlation coefficient is called the "Coefficient of Determination."

Data Audits - randomly selected data sets that are checked for accurate and complete performance. They are commonly checked for documentation, correct data entry, calculations, calibration, data transcription, report format, and chain of custody.

Data Quality Objectives (DQO) - those desired outcomes in which the collected data are accompanied with the best achievable and optimum data quality parameters such as precision, accuracy, data completeness and confidence limit values that can be extracted from the monitoring system.

Density - mass per unit volume.

Depth-integrated sample - a sample which represents the water-suspended sediment mixture throughout the water column so that the contribution to the sample from each point is proportional to the stream velocity at that point.

Desorption - the release of ions, molecules, or atoms from the surface of a solid.

Detection limit - the smallest concentration of a substance which can be reported as present with a specified degree of precision and accuracy by a specific analytical method.

Deterioration - a decline in the quality of a sample over a period of time due to improper preservation techniques.

Dispersion - mixing of solutes at the interface between two aqueous solutions.

Duplicate measurement - a second measurement made on the same (or identical) sample of material to assist in the evaluation of measurement variance.

Duplicate sample - a second sample randomly selected from a population of interest to assist in the evaluation of sample variance.

Electrolytic Conductivity Detector - a very sensitive detector that can be made to be selective to either halogen-, sulfur-, or nitrogen-containing compounds by modifying the detector. It has a good linear range, but it is complex, destroys the analytes, and may be affected by acids, bases or water in the samples analyzed. This detector is also commonly called the "Hall detector," so named after Dr. Randy Hall.

Electron Capture Detector - a very sensitive but nonselective detector for pollutants that contain halogens or some hetero atoms. This detector is not affected by presence of moisture and it is nondestructive. However, it has a relatively small linear range, responses are not usually predictable from molecular structure, and a radioactive license is required.

Element - a chemical substance that cannot be separated into substances of other kinds. All atoms of a chemical element have the same atomic number.

Environmental Analytical Laboratory - a laboratory engaged in the physical, chemical or biological measurements of either the receiving environment or discharges to the receiving environment.

Environmental Sample - a representative sample of any environmental material (aqueous, nonaqueous, or multimedia) collected from any source for determination of composition or contamination.

Equipment Blanks - samples of analyte-free media that have been used to rinse the sampling equipment. They are used to document adequate decontamination of sampling equipment after its use.

Error - difference between the true or expected value and the measured value or quantity of parameter.

Exploratory Samples - initial surveillance samples used to determine preliminary information about a test site before the main sampling effort is started. Often these may be 10 to 15 percent of the total samples collected and analyzed.

External Standards - reference material analyzed separately from the environmental test samples. Usually external standards are analyzed before, after, and often in between a set of environmental test samples.

False Negative - a "type II error" where the incorrect decision is made that an analyte is not present (not detected) when, in fact, it is present. False positive - see Type I error.

False Positive - a "type I error" where the incorrect decision is made that an analyte is present (is detected) when, in fact, it is not present.

Field Blanks - samples of analyte-free media similar to the sample matrix that are transferred from one vessel to another or exposed to the sampling environment at the sampling site. They are used to measure incidental or accidental contamination of a sample during the whole process (sampling, transport, sample preparation, and analysis).

Flame Ionization Detector - a sensitive general purpose detector for most organic compounds. It has as excellent linear range and low maintenance but it has poor sensitivity for halogenated

compounds and those that lack hydrocarbon characteristics (for example, carbon monoxide, carbon dioxide, and phosgene).

Flame Photometric Detector - a detector that is selective and sensitive for compounds containing sulfur or phosphorus atoms. However, it has rather poor linearity, destroys the analytes, and is relatively complex to operate and maintain.

Flow proportional composite sample - a sample obtained by (1) continuous pumping at a rate proportional to the flow; (2) mixing equal volumes of water collected at time intervals which are inversely proportional to the volume of flow: (3) mixing volumes of water proportional to the flow collected during or at regular time intervals. This sample will indicate a "flow" average water quality condition over the period of time of compositing.

Fluvial characteristics - of or pertaining to a river(s); existing, growing or living in or about a stream of river; produced by the action of a stream or river.

Gas chromatography - an analytical technique that employs separation of components of a gas phase mixture by passing the mixture through a column.

Grab sample - a sample taken at a selected location, depth and time.

Groundwater - all subsurface water that occurs beneath the water table in rocks and geologic formations that are fully saturated.

Heterogeneity - the condition in which a property of a material is different at different locations within a specified volume of space.

Homogeneity - the degree to which a property or substance is randomly and uniformly distributed throughout a material.

ICPES or ICP - inductively coupled plasma emission spectroscopy.

Imprecision - random error in data.

Inductively Coupled Plasma Emission Spectrometry - a chemical analysis technique that uses element-specific atomic line emission spectra produced by a radio-frequency inductively coupled plasma to measure elemental concentrations.

Infiltration - the entry into an aquifer of water available at the ground surface.

Instrument Blanks - solvent or reagent blanks used to measure interference or contamination from an analytical instrument by cycling matrices containing materials that are normal to the analysis (but minus the analytes of interest) through the instrument.

Instrument Detection Limit - the smallest analyte signal above background noises that an instrument can detect. It does not take into consideration matrix or laboratory blank interferences.

Interlaboratory Variability - the portion of the total imprecision in measurement of data which is attributable to between-laboratory variability. It is often quantitated through interlaboratory collaborative testing or "round robin" studies.

Intralaboratory Variability - that portion of the total imprecision in measurement of data which is attributable to within-laboratory variability. It is often quantitated by measuring a common sample repeatedly.

Internal Standards - reference material that is added to environmental test samples before their preparation and analysis. Internal standards are subjected to the same laboratory procedures and conditions as the analytes of interest in the samples.

Judgmental Sampling - samples collected on the basis of prior history, visual assessment or technical judgement so that they will provide the best probability for meeting a specific objective.

Kemmerer samples - a messenger-operated vertical point sampler for water-suspended sediment.

Laboratory Blanks - analyte-free matrices used to measure laboratory sources of contamination (bias) in environmental analyses. There are four common types of laboratory blanks: solvent blanks, reagent blanks, glassware blanks, and instrument (system) blanks.

Limit of Detection - the lowest concentration that can be determined to be statistically different from a blank at a specified level of confidence. Usually

the limit of detection is recommended to be 3 standard deviations above the average level of a well characterized blank sample.

Limit of Linearity - the upper concentration level of reliable measurements of analytes. The LOL is usually reached when a detector becomes nonlinear with increase amounts of analytes being measured.

Low Level Bias - systematic error from artifacts or low level contamination commonly found in environmental samples where analyses are conducted near detection limits of modern methods.

Material Blanks - samples of construction materials that are exposed to analyte-free water or solvents. They are used to document decontamination (or measure artifacts) from use of these materials in wells and other types of construction where environmental samples being gathered can be contaminated with artifacts.

Matrix Effects - systematic errors caused by the matrix; these include interferences with the analytes of interest (these may result in false positives or false negatives), incomplete recovery of analytes during sample preparation (these may result in false negatives), instability of analytes (these may result in false negatives), biased blank correction (these may result in false positives or negatives) and unrepresentative sampling (these may result in false positives or negatives).

Matrix Spikes - samples to which predetermined quantities of selected analytes are added prior to sample preparation (extraction, digestion) and analysis. Samples are split into duplicates, spiked and analyzed. Percent recoveries are calculated for each of the analytes detected. The difference between the samples is calculated and used to assess analytical accuracy in terms of recovery.

MDL - Method Detection Limit or Method Detection Level.

Measurement Quality Objectives - limits for the uncertainty of specific measurements.

Method Detection Level (proposed) - the lowest concentration at which individual measurement results for a specific analyte are statistically different from a blank (that may be zero) with a specified confidence level for a given method and representative matrix.

Method Validation - an experimental process involving external collaboration by other laboratories (internal or external to an organization), methods, or reference materials to independently verify the suitability of a method.

Method Verification - an experimental process used to decide whether a method is producing accurate and reliable data. It involves internal collaboration by the person or laboratory using a method. It essentially means that a method has been used with a known sample and has provided data of acceptable quality and quantity.

Multiple sampler - an instrument permitting the collection of several water-suspended sediment samples of equal or different volumes at each site, simultaneously.

Nitrogen/Phosphorus Detector - a detector selective and sensitive for compounds containing nitrogen or phosphorus. It destroys the analytes and may have large analytical variations with sensitivity.

Non-point waste source - a general, unconfined waste discharge.

Normal Level Bias - systematic error measured at "normal" working concentrations of analyses with a given method; it is usually caused by systematic operational errors and/or errors caused by the analytical method protocols.

Performance Audits - audits that use performance evaluation samples to quantitatively measure data quality. These may indirectly evaluate ability to meet DQOs by assessing accuracy of data measurements.

Performance Evaluation (PE) Sample - samples that have been well characterized with respect to known or expected quantitative measurement results. They are used to measure the accuracy with which a laboratory can perform analyses using very specific methods and criteria.

pH - the negative $\log_0$ of the hydrogen ion activity in solution. Water with pH values between 0 and 7 is acidic, with pH value of 7 is neutral, and with pH values between 7 and 14 is alkaline.

Photoionization Detector - a detector that is selective for and very sensitive to aromatic and unsaturated organic compounds. It has low maintenance, excellent linear range, and does not destroy the analytes. However, it responds to a relatively limited number of compounds and it is difficult to predict responses from molecular structures.

Point wastes source - any discernible, confined and discrete conveyance such as any pipe, ditch, channel, tunnel or conduit from which pollutants are discharged.

Pollution - the condition caused by the presence of substances of such character and in such quantities that the quality of the environment is impaired.

Population - a generic term denoting any finite or infinite collection of individual things, objects or events in the broadest concept.

Porous - containing interstices, voids, pores, and other openings that may or may not interconnect.

Precipitate - solids that form from a gas or an aqueous solution as the result of a chemical reaction.

Precipitation - the process of forming a solid from an aqueous solution or a gas.

Precision - denotes the agreement between the numerical values of two or more measurements on the same homogeneous sample made under the same conditions. The term is used to describe the reproducibility of the measurement or method. It can be expressed by the standard deviation.

Preservative - a substance added to the sample in order to maintain given component(s) in a particular state, i.e., to maintain the original integrity of the sample.

Probability - the likelihood of the occurrence of any particular form of an event, estimated as the ratio of the number of ways or times that the event may occur in that form, to the total number of ways that it could occur in any form.

Procedure - a set of systematic instructions for using a method of measurement or of sampling or of the steps or operations associated with sampling and analyses.

Protocol - a procedure specified to be used when performing a measurement or related operations, as a condition to obtain results that could be acceptable to the specifier.

QC Check Samples - certified standards, usually supplied by a source independent from the laboratory that is using them. They consist of a blank that has been spiked with the analyte(s) from an independent source in order to monitor the execution of an analytical method.

Quality Assurance - relates to a system of activities whose purpose is to provide the producer or user of a product (e.g., data) or a service, the assurance that the product (service) meets defined standards of quality. It consists of two separate but related activities, quality control and quality assessment. The quality assurance process includes documentation of procedures, identification of critical points within the data collection activities which require monitoring by quality control procedures, the level of quality achieved, problems encountered, and corrective actions undertaken.

Quality Assessment - the overall system of activities whose purpose is to provide assurance that the quality control activities are being carried out effectively. It involves a continuing evaluation of performance of the data producing systems and the quality of the data produced.

Quality Control - the overall system of activities whose purpose is to control the quality of a product (e.g., data) or service so that it meets the needs of users. The aim is to provide quality that is satisfactory, adequate, dependable, and economic.

Random error - errors due to chance or uncontrollable situations. Examples are variation in reagent addition, instrument response, and inadvertent contamination of samples.

Random sample - a sample selected from a population, using a randomization process.

Random sampling - selecting a sample from a population in such a manner that each sample has an equal chance of being selected.

Range - the difference between the lowest and highest values in a set of data.

RDL - Reliable Detection Level

Reagent Blank - aliquots of the analyte-free reagents used to prepare test samples.

Recovery - a measure of the amount of an analyte of interest that has been added to an environmental test sample and, after sample preparation, then analyzed. Recovery is usually expressed in terms of percent. Recovery is influenced by: the analyte's concentration, sample matrix, and time of sample storage before analysis.

Reference material (RM) - a material or substance possessing one or more properties which are sufficiently well established to be used for the calibration of an apparatus or the assessment of a measurement method, or for the assignment of values to materials.

Region of Certain Detection - the region above the Reliable Detection Level.

Region of Certain Quantitation - the region from the Reliable Quantitation Level to the limit of linearity of a detector.

Region of High Uncertainty - the region from zero or the average well characterized signal from a matrix or method blank to the Method Detection Level.

Region of Less Certain Detection - the region between the Method Detection Level and the Reliable Detection Level.

Region of Less Certain Quantitation - the region between the Reliable Quantitation Level and the Reliable Detection Level.

Relative Standard Deviation - a value obtained by multiplying the coefficient of variation times 100%.

Reliable Detection Level (Proposed) - when sufficient data are available, the RDL is the experimentally determined concentration at which false negative and false positive rates are specified. Otherwise, the RDL is the concentration which is twice that of the Method Detection Level (RDL - 2 x MDL). The RDL is the recommended lowest level for qualitative decisions based on individual measurements, and it provides a much lower statistical probability of false negative determinations than the MDL.

Reliable Quantitation Level (proposed) - the RQL is the concentration which is two times the Reliable Detection Level (RQL = 2 x RDL). The RQL is the recommended lowest level for quantitative decisions based on individual measurements for a given method and representative matrix.

Repeatability - the precision, usually expressed as a standard deviation, that measures the variability among results of measurements at different times on the same sample at the same laboratory.

Replicate analyses - identical analyses carried out on the same sample multiple times. They measure only within-laboratory precision.

Replicate samples - samples that are identical, or very similar, which are collected and analyzed exactly the same way. Often, replicate samples are prepared by dividing a sample into two or more separate aliquots. Duplicate samples are considered to be two replicates, triplicate samples are three replicates, etc. Replicate samples are used to measure the overall precision of the sampling and analytical methods used.

Replicates - repeated but independent determination on the same sample by the same analyst at essentially the same time and under the same conditions.

Representative sample - a subset or group of objects, quantities, or parts selected from a larger set designated as a lot or population, so that each selected subset has the defined characteristics of the whole population.

Reproducibility - the precision, usually expressed as a standard deviation, that measures the variability among results of measurements of the same sample at different laboratories.

Residue - material that remains after gases, liquids and some solids have been removed, usually by heating up the sample at a specified temperature for a specified period of time.

RQL - Reliable Quantitation Level

Safety - a quality of being devoid of whatever exposes one to danger or harm; freedom from danger or hazards.

Sediment - soil fragmental material that originates from weathering of rocks and is transported or deposited by air, water or ice, or that accumulates by other processes, such as chemical precipitation from solution or secretion by organisms. The term is usually applied to material held in suspension in water or recently deposited from suspension and to all kinds of deposits, essentially of unconsolidated materials.

Sediment sample - a quantity of water-sediment mixture or deposited sediment collected to characterize its properties.

Sensitivity - the ability of an analytical method to detect small quantities of the measured component (it has no numerical value). Alternatively, sensitivity can be regarded as the change in measured value resulting from a concentration change of one unit.

Sequential composite sample - a sample obtained either by continuous, constant pumping of water or by mixing equal volumes of water collected at regular time intervals. This sample will indicate an average water quality condition over the period of time of compositing.

Solvent Blanks - blanks consisting only of the solvent used to dilute or extract a sample. They are used to identify and/or correct for signals produced by the solvent or by impurities in the solvent.

Species - a chemical entity such as an ion, a molecule, an atom, or an uncharged ion pair.

Specific Gravity - the ratio of the density of a material to the density of water at a stated temperature.

Spectrophotometry - a chemical analysis technique that involves measuring the relative intensities of light within narrowly defined wavelength bands.

Spiked Field Blanks - field blanks fortified with known amounts of the analytes of interest. They are used to estimate bias that both sampling and the sample matrix may introduce. The most common bias caused by the sample matrix is incomplete recovery of analytes of interest during sample preparation.

Spiked Laboratory Blanks - laboratory blanks fortified with known amounts of the analytes of interest. They are used to estimate bias from all laboratory sources including glassware, solvents, reagents, calibration standards, instruments, etc.

Spiked Test Samples - fortified test samples used to measure effects that the sample matrix may have on the analytical methods (usually analyte recovery).

Split sample - a single sample separated into two or more parts such that each part is representative of the original sample.

Standard - A substance or material, the properties of which are believed to be known with sufficient accuracy to permit its use to evaluate the same property of another. In chemical measurements, it often describes a solution or substance, commonly prepared by the analyst, to establish a calibration curve, or the analytical response function of the instrument.

Standard addition - a procedure where different known amounts of analytes are added to an environmental test samples after it has been first analyzed without such addition. Reanalysis of the test sample is conducted after one or more standard additions are performed.

Standard curve - a plot of multiple concentrations of a known analyte standard versus an instrument response to that analyte.

Standard deviation - a measurement of the dispersion or spread of data points around the mean value of the data set obtained by repetitive testing of a homogeneous sample under specified conditions. It is calculated from the square root of the variance of a set of values.

Standard method - a method (or procedure) of testing developed by a standards-writing organization, based on consensus opinion or other criteria, and often evaluated for its reliability by a collaborative testing procedure.

Statistical control - when the variability of a measurement system is due only to chance causes.

Statistics - the process of collecting numerical information (data), analyzing it, and making meaningful decisions based on the results of those analyses.

Sub-sample - a portion taken from a sample. A laboratory sample may be a sub-sample of a gross sample; similarly, a test portion may be a sub-sample of a laboratory sample.

Surface water - natural water bodies, such as rivers, streams, brooks and lakes as well as artificial water courses, such as irrigation,industrial and navigational canals in direct contact with the atmosphere.

Surrogate - organic compounds which are similar to analytes of interest in chemical composition, extraction, and/or chromatography properties, but which are not normally found in environmental samples. These compounds are spiked into all blanks, standards, samples and spiked samples prior to analysis. Percent recoveries are calculated for each surrogate.

Suspended sediment - those constituents of an unacidified water sample that are retained by a 0.45 μm membrane filter. It can impart a cloudy appearance to a sample.

System Audits - qualitative reviews to assess whether all prescribed methods and procedures in sampling and analysis plans are being used appropriately and as planned.

Systematic errors - errors which can, at least in principle, be ascribed to definite causes and which contribute a constant error or bias to results.

Systematic sampling - samples collected on the basis of a consistent grid or pattern over a selected sampling area.

Technique - a physical or chemical principle utilized separately or in combination with other techniques to determine the composition (analysis) of materials.

Teflon® - a man-made plastic material inert to all chemical reagents except molten alkali metals. It is use for laboratory and field equipment.

Traceability - the ability to trace the source of uncertainty of a measurement or a measured value or of a source of an analytical standard.

Trip Blanks - samples of analyte-free media taken from the laboratory to the sampling site and returned to the laboratory unopened. They are used to measure cross-contamination from the container and preservative during transport, field handling, and storage.

Type I Error - rejecting a true or null hypothesis in favour of the alternative hypothesis. This is also called alpha (α) error or false positive.

Type II Error - Failure to reject the null hypothesis in favour of the alternative hypothesis. This is also called beta (β) error or false negative.

UV - ultraviolet.

Uncertainty - the range of values within which the true value is estimated to lie. It is a best estimate of possible inaccuracy due to both random and systematic errors.

Validation - the process by which a sample, measurement method, or a piece of data is deemed to be useful for a specified purpose.

Van Dorn sampler - a messenger-operated water-suspended sediment point sampler used to collect samples at a specified depth. The long axis of the cylinder can be lowered either horizontally or vertically.

Variance - standard deviation squared. Variance is useful in estimating sampling imprecision; a numerical estimate of sampling imprecision is obtained by subtracting variance of the measurements from laboratory sources from variance of the measurements from overall sources (both sampling and analytical components).

VOA - volatile organic analysis (or analyzer or analyte).

VOC - volatile organic compound.

Volatile constituents - components of a sample which are readily lost by evaporation. They include dissolved gases as well as substances with low boiling points.

Water quality criteria - scientific information, e.g., concentration-effect data, used to recommend water quality objectives.

Within Day Precision - a measure of variability among replicate analyses of a single sample (or multiple similar samples) all performed on the same day, under identical conditions.

Within Laboratory Precision - the variability between replicate results obtained on the same material within a single laboratory (intralaboratory analyses). It is sometimes also referred to as 'repeatability.'

Working Standards - those prepared by the laboratory analyst for daily or frequent use. They are usually calibrated against certified laboratory QC check standards.

APPENDIX 2

Unpublished Methods in Use

Unpublished Analytical Methods

The references in this Appendix are a list of unpublished methods used by various federal, provincial and commercial laboratories.

Environment Canada Conservation and Protection. 1991. Chlorinated Phenols. Gas Chromatographic - Diazomethane Derivative. Laboratories Pacific & Yukon Region.

Environment Canada Conservation and Protection. 1990. Substituted Phenols. Gas Chromatographic/Mass Spectrometric. Laboratories Pacific & Yukon Region.

Environment Canada Conservation and Protection. 1990. Polychlorinated Biphenyls. Gas Chromatographic. Laboratories Pacific & Yukon Region.

Environment Canada Conservation and Protection. 1988. Fluoride. Specific Ion Electrode - Combined. Laboratories Pacific & Yukon Region.

Environment Canada Conservation and Protection. 1990. Metals in Sediment. Laboratories Pacific & Yukon Region.

Environment Canada Conservation and Protection. 1984. Cyanide. Tetracyanonickelate (II) - UV - Colorimetric. Laboratories Pacific & Yukon Region.

Environment Canada Conservation and Protection. 1988. pH. Version 1.1. Laboratories Pacific & Yukon Region.

Environment Canada Conservation and Protection. 1990. Conductivity. Version 2.0. Laboratories Pacific & Yukon Region.

Environment Canada Conservation and Protection. 1987. Mercury in Water. Version 2.0. Laboratories Pacific & Yukon Region.

Environment Canada Conservation and Protection. 1990. Metals in Water. Laboratories Pacific & Yukon Region.

Wastewater Technology Centre. 1989. The Determination of Organophosphorus Pesticides (OP) in Drinking Water by GC-AFID. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Organochlorine Pesticides (OC) and Polychlorinated Biphenyls (PCB) in Water by GC-ECD/MSD. Ontario Ministry of Environment.

Wastewater Technology Centre. 1990. The Determination of Polychlorinated Biphenyls (PCB), Organochlorines (OC), and Chlorobenzenes (CB) in Soils and Sediments by GLC-ECD. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of CDD and CDF in Ground Water and Aqueous Effluents by GC-MS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of CDD and CDF in Drinking Water by GC-MS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of 2,3,7,8-TCDD in Groundwater and Aqueous Effluents by GC-MS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of PCDD and PCDF in Drinking Water, Effluents, Incineration Fly Ash, Biological Samples, Soil and Sediments by HRGC-HRMS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Purgeable Organic Compounds in Potable and Surface Waters by GC-FID and ECD. Ontario Ministry of Environment.

Wastewater Technology Centre. 1990. The Determination of Volatile Organohalides and Hydrocarbons in Sediments, Sludges and Kiln Dust by Headspace Capillary GC. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Polynuclear Aromatic Hydrocarbons in Surface Water, Drinking Water and Ground Water by HPLC. Ontario Ministry of Environment.

Wastewater Technology Centre. 1990. The Determination of Chlorophenols (CP) and Phenoxyacid Herbicides (PA) in Soils and Sediments by GC-ECD. Ontario Ministry of Environment.

Wastewater Technology Centre. 1990. The Determination of Chlorophenols and Phenoxyacid Herbicides in Water by Using Solid Phase Extraction and GC-ECD. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Extractable Organics in Water, Aqueous Effluent, Sediment and Soil by GC/MS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Conductivity, pH, and Alkalinity in Water and Effluents. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Conductivity in Soils and Sediments by Conductance Meter. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of pH in Soil and Sediment by Potentiometry. Ontario Ministry of Environment.

Wastewater Technology Centre. 1990. The Determination of Free Cyanide in Aqueous Samples by Colourimetry. Ontario Ministry of Environment.

Wastewater Technology Centre. 1990. The Determination of Total Cyanide in Solid Samples by Colourimetry. Ontario Ministry of Environment.

Wastewater Technology Centre. 1990. The Determination of Free Cyanide in Solid Samples by Colourimetry. Ontario Ministry of Environment.

Wastewater Technology Centre. 1990. The Determination of Total Cyanide in Aqueous Samples by Colourimetry. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Trace Metals in Potable Waters by ICP-MS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Mercury in Water by AAS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1988. The Determination of Hexavalent Chromium in Waters, Landfill Leachates and Effluents by Colourimetry. Ontario Ministry of Environment.

Wastewater Technology Centre. 1988. The Determination of Arsenic, Selenium and Antimony in Water by HYD-FAAS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1988. The Determination of Boron in Water by ICP-OES. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Trace Metals in Surface Waters by ICP AES. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Silver in Water by AAS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Fluoride in Water, Leachates, Effluents by Colourimetry. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Heavy Metals in Soils by AAS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1991. The Determination of Trace Metals in Soil by Sequential ICP-AES. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Fluoride in Soil, Sediments and Mossbag Samples by Ion Selective Electrode (I.S.E.). Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Trace Metals in Soil by ICP-AES. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Mercury in Soils, Sediments and Vegetation by AAS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1990. The Determination of Arsenic, Selenium and Antimony in Vegetation, Soils and Sediments by HYD-FAS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Heavy Metals in Sediments by AAS. Ontario Ministry of Environment.

Wastewater Technology Centre. 1989. The Determination of Trace Metals in Sediments by ICP-AES. Ontario Ministry of Environment.

Ministere de l'Environment. 1989. Eaux - Determination des Byphenyles Polychlores. Extraction avec de l'Hexane et Purification avec Florisil. Dosage par Chromatographic en Phase Gazeuse. Gouvernment du Quebec.

Ministere de l'Environment. 1988. Eaux - Determination des Cyanures Totaux. Methode Colorimetrique Automatisee avec La Pyridene et l'Acide Barbitureque. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Eaux - Determination du Diquat et du paraquat. Extraction et Purification avec C-18 Dosage par Chromatographic en Phase Liquide. Gouvernment du Quebec.

Ministere de l'Environment. 1987. Eaux - Determination des Fluorures. Methode Colorimetrique Automatisee A l'Alizarin. Gouvernment du Quebec.

Ministere de l'Environment. 1990. Eaux - Determination des Hydrocarbures Aromatiques Polycycliques. Extraction et Purification avec C-18 et Si. Dosage par Chromatographic en Phase Liquide. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Eaux - Determination des Pesticides de Type Carbomates. Dosage par Chromatographic en Phase Liquide avec Derivation Post-Colonne. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Eaux - Determination des Pesticides de Type Carbamates. Extraction et Purification avec C-18. Dosage par Chromatographic en Phase Liquide avec Derivation Post-Colonne. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Eaux - Determination de Pesticides de Type Organochlores. Extraction avec de l'Hexane et Purification avec Fluorisil. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Eaux - Determination des Pesticides Euivants: Deethyle Atrazine, Deethyl Simazine, Atrazine, Simazine, Fonofos, Dimethoate et Carbofuran. Extraction avec C-18. Dosage par Chromatographic en Phase Gazense. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Eaux - Determination des Pesticides Suivants: Azinophos-Methyl, Carbaryl, Carbofuran, Chlorothalonil, Chlorpyrifos, Chloroxuron, Cyanazine, Diazinon, Fenithrothion, Linuron, Malathion, Methyl-Parathion, Metribuzine, Parathion, Phosalone, Phosmet et Tebuthiuron. Extraction Liquide-Solide. Dosage Par Chromatogrpahic en Phase Gazeuse. Gouvernment du Quebec.

Ministere de l'Environment. 1987. Eaux - Determination du pH. Methode Electrometrique. Gouvernment du Quebec.

Ministere de l'Environment. 1987. Eaux - Determination du pH. Methode Electrometrique Automatisee. Gouvernment du Quebec.

Ministere de l'Environment. 1988. Eaux - Determination des Cyanures Disponibles. Methode Colorimetrique Automatisse avec La Pyridine et l'Acide Barbiturique. Distillation Manuelle. Gouvernment du Quebec.

Ministere de l'Environment. 1988. Eaux - Determination des Cyanures Totaux. Methode Colorimetrique Automatisee avec La Pyridine et l'Acid Barbiturique. Distillation Manuelle. Gouvernment du Quebec.

Ministere de l'Environment. 1990. Eaux - Determination des Fluorures. Methode Electrometrique. Gouvernment du Quebec.

Ministere de l'Environment. 1990. Eaux - Determination de l'Arsenic. Methode Automatisee par Spectrophotometric. d'Absorption Atomique. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Eaux - Determination du Mercure. Methode par Spectrophotometric d'Absorption Atomique. Generation de Vapour. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Eaux - Determination des Metaux Extractibles. Methode par Spectrophotometric d'Emission Au Plasma d'Argon. Gouvernment du Quebec.

Ministere de l'Environment. 1990. Eaux - Determination du Selenium. Methode Automatisce par Spectrophotometric d'Absorption Atomique. Apres Digestion et Generation d'Hydrues. Gouvernment du Quebec.

Ministere de l'Environment. 1990. Eaux - Determination des Hydrocarbures Aromatiques Polycycliques. Extraction et Purification avec C-18 et Si. Dosage par Chromatographic en Phase Liquide. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Eaux - Determination des Pesticides de Type Carbamates. Extraction et Purification avec C-18. Dosage par Chromatographic en Phase Liquide avec Derivation Post-Colonne. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Sediments - Determination des Biphenyles Polychlores. Extraction Liquide-Solide et Purification avec C-18, Si, Cu. Dosage par Chromatographic en Phase Gazeuse. Gouvernment du Quebec.

Ministere de l'Environment. 1990. Sediments - Determination des Hydrocarbures Aromatiques Polycycliques. Extraction et Purification avec C-18 et Si. Dosage par Chromatographic en Phase Liquide. Gouvernment du Quebec.

Ministere de l'Environment. 1990. Sols - Determination de l'Arsenic. Methode Automatisee par Spectrophotometric d'Absorption Atomique. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Sols - Determination des Biphenyles Polychlores. Extraction avec de l'Hexane et Purification avec Florisil. Dosage par Chromatographic en Phase Gazeuse. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Sols - Determination des Biphenyles Polychlores. Extraction Liquide-Solide et Purification avec C-18, Si, Cu. Dosage par Chromatographic en Phase Gazeuse. Gouvernment du Quebec.

Ministere de l'Environment. 1990. Sols - Determination des Hydrocarbures Aromatiques Polycycliques. Extraction et Purification avec C-18 et Si. Dosage par Chromatographic en Phase Liquide. Gouvernment du Quebec.

Ministere de l'Environment. 1990. Sols - Determination des Metaux. Methode Par Spectrometric d'Emissino Au Plasma d'Argon. Met. 1.2. Gouvernment du Quebec.

Ministere de l'Environment. 1990. Sols - Determination des Metaux. Methode Par Spectrometric d'Emission Au Plasma d'Argon. Met. 1.3. Gouvernment du Quebec.

Ministere de l'Environment. 1989. Sols - Determination de Pesticides de Type Organochlores. Extraction avec de l'Hexane et Purification avec Florisil. Dosage par Chromatographic en Phase Gazeuse. Gouvernment du Quebec.

Ministere de l'Environment. 1990. Sols - Determination du Selenium. Methode Automatisee par Spectrophotometric d'Absorption Atomique. Gouvernment du Quebec.

Ministere de l'Environment du Quebec. 1990. Guide Methodes de Conservation et d'Analyses des Enchantillons d'Eau et de Sol. Direction des Laboratories.

Novak, N. 1990. Optimization of Organic Contaminant and Toxicity Testing Analytical Procedures for Estimating the Characteristics and Environmental Significance of Natural Gas Processing Plant Waste Sludges. Canadian Petroleum Association.

Environment Canada. 1992. Gas Plant Sludge Characterization Study. Summary and Presentation of Characterization Protocol. Canadian Petroleum Association.

Monenco Consultants. 1985. Information Review and Development of a Methodology for Determining the Characteristics and Environmental Significance of Natural Gas Processing Plant Waste Sludges. Conservation and Protection. Environment Canada. Ottawa, Ontario.

Enviro-Test. 1992. Analysis of Volatile Organics for Low Detection Limits of Landfill Prohibition by Headspace Using GC/MSD in Scan Mode. Edmonton, Alberta.

Enviro-Test. 1992. Analyses of Volatile Organics for Landfill Prohibition by Headspace Using GC/MSD in Scan Mode. Edmonton, Alberta.