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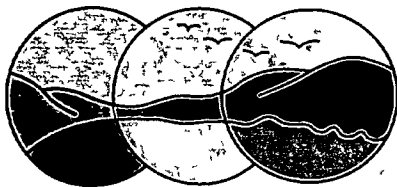
Guidance Manual on Sampling, Analysis, and Data Management for Contaminated Sites

Volume I: Main Report

December 1993

PN 1101

The National
Contaminated Sites
Remediation Program



Reprinted May 1998

**Guidance Manual on Sampling,
Analysis, and Data Management for
Contaminated Sites**

Volume I: Main Report

**Winnipeg, Manitoba
December 1993**

The Canadian Council of Ministers of the Environment (CCME) is the major intergovernmental forum in Canada for discussion and joint action on environmental issues of national, international and global concern. The 13 member governments work as partners in developing nationally consistent environmental standards, practices and legislation.

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Printed on paper that contains recovered waste

Published by authority of
the Minister of the Environment

ISBN 0-919074-21-9

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Abstract

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

- to provide guidance for sampling and analyzing complex environmental matrices, such that the data obtained will be representative and of known quality
- 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 consistent and comparable

The manual stresses the significance of quality assurance (QA)/quality control (QC) and planning, and emphasizes the interdependence of sampling, analysis, and data management objectives in the planning and execution of tasks within each of these three areas. It focuses on the specific analytes identified in the CCME's Interim Environmental Quality Criteria for Contaminated Sites, which was published in September 1991.

In Volume I, Main Report, Chapter 1 introduces the subject matter covered in this manual. Chapter 2 is devoted to the principles and problems involved with obtaining representative samples from the four matrices: soils, sediments, surface waters, and groundwater. Topics include problems unique to each matrix and 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. Chapter 4 describes the criteria for selecting analytical methods. Chapter 5 discusses data management, including such topics as data recording and documentation, data custody and transfer, and data validation, completeness, comparability, compatibility, review, verification, handling, and transmission. A final section addresses data reporting by laboratories and data presentation in final reports.

A glossary of scientific terms used is included at the end.

Volume II, Analytical Method Summaries, provides method summaries for the analytes in a consistent format that identifies all the information needed to decide whether to use that method in preference to another, and if so, what major analytical instrumentation would be required. A method summary includes sample preparation, potential interferences, QC requirements, comments on use, and, where applicable, comparison with other methods. For detailed information, however, users are advised to look up the original references. A list of unpublished analytical methods that are used by various federal, provincial, and commercial laboratories is provided in an appendix. Volume II is available in hard copy format or on a computer diskette.

Résumé

Le présent document fait partie d'une série de guides techniques préparés dans le cadre du Programme national d'assainissement des lieux contaminés du Conseil canadien des ministres de l'environnement. Cet ouvrage permettra d'harmoniser à l'échelle nationale l'échantillonnage, l'analyse des échantillons et la gestion des données. Ses deux principaux objectifs sont les suivants

- constituer un guide pour l'échantillonnage et l'analyse de matrices environnementales complexes de manière à ce que les données obtenues soient représentatives et de qualité reconnue,
- choisir les meilleures méthodes parmi celles qui existent de manière à ce que les données analytiques fournies par les laboratoires participants soient plus cohérentes et comparables

Dans tout le document, on insiste sur l'importance de l'assurance de la qualité (AQ) et du contrôle de la qualité (CQ). Par ailleurs, on insiste sur l'interdépendance des objectifs de l'échantillonnage, de l'analyse des échantillons et de la gestion des données en ce qui a trait à la planification et à l'exécution des tâches dans chacun de ces trois domaines. Le document porte particulièrement sur les substances mentionnées dans les Critères provisoires canadiens de qualité environnementale pour les lieux contaminés qui ont été publiés en septembre 1991.

Dans le Volume I, Rapport principal, le Chapitre 1 présente le sujet de manière générale. Le Chapitre 2 est consacré aux principes et aux problèmes relatifs au prélèvement d'échantillons représentatifs à partir de quatre matrices, en l'occurrence des sols, des sédiments, des eaux superficielles et des eaux souterraines. Les thèmes traités sont entre autres les

sujets suivants : problèmes particuliers liés à chaque matrice, considérations relatives à l'obtention d'échantillons représentatifs, sélection des points de prélèvement et de l'équipement et conservation des échantillons après le prélèvement.

Le Chapitre 3 expose brièvement les critères qui sont importants dans le choix de méthodes d'analyse appropriées. Dans le Chapitre 4, on décrit les critères de sélection des méthodes d'analyse. Le Chapitre 5 porte sur la gestion des données. On y traite entre autres de la présentation des données et de la documentation, de la garde et du transfert des données, de la validation des données, de l'intégralité des données, de leur compatibilité, de leur révision, de leur vérification, de leur traitement et de leur transmission. Une dernière section porte sur les données fournies par les laboratoires et sur la présentation des données dans les rapports finaux.

Un glossaire des termes scientifiques employés est inclus en appendice à la fin du manuel.

Dans le Volume II, on présente les sommaires des méthodes applicables aux substances spécifiées, de manière à fournir toute l'information nécessaire pour choisir une méthode de préférence à une autre et pour connaître les principaux appareils d'analyse requis. Un sommaire de la méthode comprend la préparation des échantillons, les interférences potentielles, les exigences relatives au contrôle de la qualité, des remarques sur l'utilisation et, le cas échéant, des comparaisons avec d'autres méthodes. On recommande toutefois aux utilisateurs de consulter les références originales pour plus de détails. Une liste des méthodes d'analyse inédites qui sont utilisées par divers laboratoires fédéraux, provinciaux et commerciaux se trouve dans une annexe. Le Volume II existe sous forme imprimée ou sur disquette.

Acknowledgements

This guidance manual was prepared under contract to Radian Canada Inc , Dr Lawrence H Keith acted as group leader During its preparation, this document was extensively reviewed by members of the CCME's Contaminated Sites Advisory Committee, selected Environment Canada scientific personnel, and a number of commercial laboratories The reviewers who devoted their valuable time and expertise are gratefully acknowledged Special thanks are due to Anar S Baweja and T W Foote of Environment Canada, Dr Baweja acted as scientific authority and Mr Foote provided general guidance

Introduction

BACKGROUND AND OBJECTIVES

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

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

The program operates on a cost-shared, five-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 high-risk orphan contaminated sites, and \$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: the development of a National Classification System and the development of Interim Environmental Quality Criteria. Both provide information that is important to the organization of this manual, particularly the latter, upon which the analytical groupings of contaminants are based (Table 1).

The CCME's 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 as high risk when site contamination 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 cleanup.

Interim Canadian Environmental Quality Criteria for Contaminated Sites (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 primary objectives of this manual are as follows:

- to provide guidance for sampling and analyzing complex environmental matrices, such that the data obtained will be representative and of known quality
- 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 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 data processing and reporting. They 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

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

General Parameters	Monocyclic Aromatic Hydrocarbons	Chlorinated Hydrocarbons
pH	benzene	chlorinated aliphatics ³
conductivity	chlorobenzene	(each)
sodium adsorption ratio	ethylbenzene	chlorobenzenes ⁴ (each)
Inorganic Parameters	1,2-dichlorobenzene	hexachlorobenzene
antimony	1,3-dichlorobenzene	hexachlorocyclohexane
arsenic	1,4-dichlorobenzene	PCBs ⁵
barium	styrene	PCDDs and PCDFs ⁶
beryllium	toluene	Pesticides
boron (hot water soluble)	xylene	aldrin and dieldrin
cadmium	Phenolic Compounds	chlordane
chromium (+6)	nonchlorinated ¹ (each)	DDT
chromium (total)	chlorophenols ² (each)	endrin
cobalt	Polycyclic Aromatic Hydrocarbons (PAHs)	heptachlor (+metabolites)
copper	benzo(a)anthracene	lindane
cyanide (free)	benzo(a)pyrene	methoxychlor
cyanide (total)	benzo(b)fluoranthene	carbaryl
fluoride (total)	benzo(k)fluoranthene	carbofuran
lead	dibenz(a,h)anthracene	2,4-D
mercury	indeno(1,2,3-c,d)pyrene	diazinon
molybdenum	naphthalene	parathion
nickel	phenanthrene	diquat
selenium	pyrene	paraquat
silver		
sulphur (elemental)		
thallium		
tin		
vanadium		
zinc		

¹ Nonchlorinated phenolic compounds include 2,4-dimethylphenol, 2,4-dinitrophenol, 2-methyl-4,6-dinitrophenol, nitrophenol (2, 4-), phenol, and 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) and 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-) and trichloroethene

⁴ Chlorobenzenes include all trichlorobenzene isomers, all tetrachlorobenzene isomers, and pentachlorobenzene

⁵ PCBs includes mixtures 1242, 1248, 1254, and 1260

⁶ PCDDs and PCDFs

2,3,7,8-T ₄ CDD	2,3,7,8-T ₄ CDF
1,2,3,7,8-P ₅ CDD	2,3,4,7,8-P ₅ CDF
1,2,3,4,7,8-H ₆ CDD	1,2,3,7,8-P ₃ CDF
1,2,3,7,8,9-H ₆ CDD	1,2,3,4,7,8-H ₆ CDF
1,2,3,6,7,8-H ₆ CDD	1,2,3,7,8,9-H ₆ CDF
1,2,3,4,6,7,8-H ₇ CDD	1,2,3,6,7,8-H ₆ CDF
O ₂ CDD	2,3,4,6,7,8-H ₆ CDF
	1,2,3,4,6,7,8-H ₇ CDF
	1,2,3,4,7,8,9-H ₇ CDF
	O ₂ CDF

sampling and analysis plan, and are achieved by using detailed sampling and analysis protocols. Data quality objectives differ from measurement quality objectives (MQOs) (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 DQOs must be balanced against the cost of sampling and analysis, and more realistic objectives must be established with the concurrence of the data users. Three factors that most influence the cost of sampling are site location and accessibility to sampling points, the number, kind, complexity, and size of samples to be collected, and 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. Data quality objectives are developed using a process that encourages the sequential consideration of relevant issues. Table 2 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 following:

- 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
- the uncertainty constraints

Table 2. Steps in the Data Quality Objectives Process

-
- State the problem to be resolved
 - Identify the decision to be made
 - Identify inputs to the decision
 - Narrow the boundaries of the study
 - Develop a decision rule
 - Develop uncertainty constraints
 - Optimize design for obtaining data
-

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
- Data quality objectives 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.
- The DQO process facilitates communication among data users, data collectors, managers, and other technical staff before time and money 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. This process, however, 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.

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 non-representative samples are sometimes needed, e.g., a particular spot at a contaminated site that appears to be discoloured. Samples taken at that spot, however, 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.

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 QA guidelines and principles that cover every aspect of data collection (3). Table 3 provides a convenient checklist of the subjects that should be considered when planning for sampling contaminated sites (4). Table 4 lists the minimum documentation needed for sampling activities (4).

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 performs a certain specific function. Some are used to estimate bias and others to estimate precision. Some are useful for determining different sources of sampling errors, and others for 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., the data 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. 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 complement sampling and analysis processes for the production of known quality data (7).

The bottom line of the importance of QA and QC to sampling is that if samples are not representative of the contaminated site being investigated, it does not 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 5 are the minimum requirements for documenting laboratory work (6).

After analyses are completed, the third phase, data handling and reporting, begins. Data handling and data management QA programs focus on production of data that are accurate, precise, complete, and representative (3). The processes involved are summarized in Table 6 and are discussed in detail in Chapter 4.

Measurement results must be reported with clear SI units of measurement such as micrograms per litre (mg/L) (for water and liquids) or micrograms per kilogram (mg/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 not recommended for use.

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 6 are followed. However, there are many unmeasurable factors (Table 7) that can severely bias data and that are not necessarily readily identified even by good data-handling and data management procedures (8).

When good QA/QC procedures have been used in the total monitoring process, 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.

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 involved within each of these activities. Each of these activities is often planned independently, but sampling, analysis, and data management are all inter-related, 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

Table 3. 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 and 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%
-

Table 4. 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)
-

Table 5. Minimum Requirements for Documenting Laboratory Work

-
- Method of analysis
 - Date of analysis
 - Analyst's name and laboratory
 - Calibration charts and other measurement charts (e.g., spectral)
 - Method detection levels (or limits)
 - Confidence limits
 - Records of calculations
 - Actual analytical results
-

Table 6. 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
-

Table 7. 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
 - Not recognizing matrix-specific interferences
 - Using the wrong method for analysis
-

performed and 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 and concentration 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 (e.g., wastewater pipes, drainage ditches, and roads). In addition to transport mechanisms, physical and biological influences may also affect migration of pollutants. Physical influences include topographical features (e.g., valleys, mountains, slopes, lakes, and rivers) and geological features (e.g., aquifers, soil composition, and mineral composition). These physical influences can either aid or impede pollutant 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).

An important objective of a contaminated site study will often 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.

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 is discussed in Chapter 5.

Decisions involving the presence or absence of pollutants are very important when their concentrations are near method detection levels (MDLs). 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 II 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 II) 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, 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 must also make clear which results, if any, have been corrected for blank and recovery measurements. If a published methodology (such as those in Volume II) is used, it must be cited, and any modifications made must be fully documented.

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 interpretation 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 their 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 DQOs 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
- 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 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, documenting, verifying, validating, handling, and transmitting data. Key sections also include discussions on reporting data involving low-level concentrations of pollutants and data presentation in final reports.

The manual concludes with a list of all references and a glossary of common terms used in the manual.

A summary of each of the recommended methods is provided in Volume II. 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. This volume also lists unpublished analytical methods that are used by various federal, provincial, and commercial laboratories in Canada.

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) and monitoring (assessment) goals (4). Exploratory sampling is designed to provide preliminary information about the site or material being analyzed. Monitoring is usually 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 is usually more effective if it is preceded by exploratory sampling or if there are 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 that 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 that are collected must be representative of the entity being sampled, but not necessarily representative of the entire area of which it 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. 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, are critical to defining data quality and quantity requirements (4).

The choice of a data analysis method is an important decision that should also 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). There are also 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 centre of the spaces defined by a grid, or randomly within the spaces defined by a grid. Table 8 summarizes the differences among the three basic approaches.

A combination of judgmental, systematic, or random sampling is often 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, 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 the following:

- 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 nonhalogenated, 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 nonpolluted 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 will not 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.

Table 8. Basic Sampling Approaches

Approach	Relative number 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

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?
- What are the available funds versus estimated (real) cost of sampling?

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

no of control samples = No of matrices at the sample sites

no of QC samples = % of test samples or a statistically calculated number

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 that 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 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 (J.J. van Ee, 1993, pers. com.). 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

Exploratory sampling (screening) is often 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) is also 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 (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 from the sampling site
- when possible, local control site samples should be taken first to avoid contamination from the sampling site
- travel between local control sites and sampling areas should be minimized because of potential contamination caused 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, because 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. The disadvantages of large samples, however, include additional costs for storage space, materials, and disposal.

Each analytical method summary selected for inclusion in Volume II contains specific sample size requirements or guidance on collecting an appropriately

sized sample. However, a single sample may often 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 ensure that they are compatible with such a plan. A sufficient amount of the 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 above, 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 II have a section entitled Quality Control Requirements. In this section, specific types of QC samples are listed for each method. These QC samples, however, 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; it 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 that 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 II. When this occurs, they are found in the section 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, then 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 useful only 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 several grab samples may often be taken at the same spot over a period of time when information relating to changes in concentrations of analytes with time is desired (e.g., with flowing streams or with air samples).

There are two types of grab samples that are used for sampling water matrices: discrete and depth-integrated. 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 collect and combine a series of grab samples automatically or to sample the environmental matrix and combine the samples continuously.

Using the same water matrix as an example, there are two main types of composite samples: sequential or time and flow proportional. 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 that 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. If possible, half of the individual samples should be saved before compositing.
- 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, health and 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 apparatus, gloves, and hazardous materials suits, if 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 eight 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 data bases have been published that allow rapid searches to be conducted using personal computers either at the sampling site or at an office/laboratory facility (15, 16, 17).

DOCUMENTING SAMPLING PROTOCOLS

Sampling protocols are written descriptions of the detailed procedures to be followed in collecting, packaging, labeling, preserving, transporting, storing, and documenting samples. The more specific a sampling protocol is, the less chance there will be for errors or erroneous assumptions. Table 9 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). It should also identify those physical, meteorological, and hydrological variables that should be recorded or

Table 9. 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, transporting, and storing been included?

Have instructions for chain of custody procedures been included?

Have safety plans been included?

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 that commits management to a specific QA policy and sets forth the requirements for data needed to support program objectives The QA 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 as follows (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 that require QA project plans
- a description of how QA implementation will be evaluated

The second document, a QA project plan, is a technical document that details specific QA and QC requirements for a project The QA project 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
- quality assurance reports to management

To satisfy the requirements for quality data, a QA project plan must describe the following activities (21)

- sampling 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
- 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 the following (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 calibrating and maintaining equipment
- providing information on health and 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
- 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 centres, 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 tend to 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. Another 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, they are 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 that 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 that 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 may 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 human-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 that 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 unique to soil sampling (and 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)

Reviewing 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
- 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 that 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.

- **Human-made pathways** A site located in an urban and/or rural setting will have a number of human-made pathways that affect contaminant migration. These include storm and sanitary sewers, drainage culverts, sump 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. Leaching of dissolved constituents into groundwater is also possible.

- **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. Wind can also disperse contaminants that exist in air through volatilization.
- **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) that may be utilized to narrow the possible groups or classes of chemicals to support the selection of analytical parameters. Field screening can evaluate a large number of samples cost effectively 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 that 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 reflect 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 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. Contaminants that have been deposited by liquid spills or by long-term deposition of water-soluble materials, however, may be found at depths up to several metres. 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. It is often impossible 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. 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 soils, 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 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 sampling approach has been selected, the next step is to select sampling locations. For statistical (nonjudgmental) 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 that 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, aerial coordinates of the sampling points are plotted on a map and the actual sampling points marked for future reference. Where the sampling design demands a greater degree of precision, each sampling point should be located by means of a survey. After field sample collection, each sampling 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: scooping, coring, or augering devices.

Two major considerations must be addressed when selecting a specific sampling tool: 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 10 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. These tools are also 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 made of stainless steel for soils contaminated with organics and of high density polyethylene for soils contaminated with inorganic species (4).

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 laboratory 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 30 cm requires different techniques and devices. Trenching can obtain analyte profiles, however, it usually costs more than other techniques. Trenches should be excavated

Table 10. 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 two or more equipment operators, can be difficult to decontaminate, requires gasoline-powered engine (potential for cross-contamination)

approximately 30 cm 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 nonpowered, are also useful in obtaining solid samples from depths greater

than about 30 cm. Augers come in different sizes, and samples may be obtained directly from the auger cuttings. This technique, however, can introduce cross-contamination between soil layers, contamination from drilling material, nonreproducibility 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 core samples or large portions of them should be shipped to a laboratory wrapped in solvent-washed and dried aluminum foil or sealed in glass bottles. Half-litre, 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). Air drying, however, 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 under water. Additional sampling problems occur when wintertime sampling requires that holes be cut 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 in the 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)

Reviewing 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 the following:

- 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
- 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 information that are relevant to project planning for sediments include the following (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 or 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
- 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 for the following

- 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)
- quality of data (based on reported limits of detection and precision compared to precision now required) (24)

Site Reconnaissance

An important aspect that 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 the 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. The first 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 practices, and methods for sediment analyses. The results will show variations that 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 second 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 collecting sediments for determining 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 centre of the sampler. Plastic liners and core barrels used with gravity corers may be a source of contamination with various organic compounds. No data are available, however, 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 position of sampling stations needs to be carefully designed. There is no one formula for designing a sediment sampling pattern that 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

- purpose of sampling
- study objectives
- historical data and other available information
- bottom dynamics at the sampling area
- size of the sampling area
- available funds versus estimated (real) cost of the project

Generally, the reasons for bottom sediment sampling can be divided into the following categories (24)

- geochemical survey

- environmental assessment of contaminants in sediments
- evaluation of sediment for a dredging/disposal permit
- 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 sediments to be dredged from a channel within the same estuary. Although both workers will collect samples to characterize the sediments, 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 should be 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 that 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 usually need to be located 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 backwater 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. Attention must also 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. It is also 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 and suspended. In addition, bottom sediments contain two primary zones of sediment 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. For most purposes, however, 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
- 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 that 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: grab samplers, corers, and 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: (a) 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 that can disperse fine-grained sediment or flocs at the sediment-water interface), (b) loss of material, especially fine-grained sediments, during recovery of the sampler through the water column (washout), (c) the efficiency of the grab sampler for collecting sediments of varying textures (e.g., grain size, degree of induration), and (d) 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 are usually 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: gravity corers, piston corers, and 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 that 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 that 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 because of 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 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 are 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: integrating samplers, which accumulate a water-sediment mixture over time, instantaneous samplers, which trap a volume of whole water by sealing the ends of a flow-through chamber, and 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 or technique deals simultaneously with both cross-sectional (spatial) 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 for 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 should always be precleaned, thoroughly washed, dried, and sealed before being transported to the sampling site.

Sediment samples should be filtered as soon as possible after collection. The filtrate can then be used for measuring the dissolved constituents. Preservation 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, requiring different sampling equipment, but 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 be sampled infrequently, 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, 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 will also 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 will sink to the bottom (4) The chemical composition of lakes and ponds may also 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 5 m, 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, and 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)

Reviewing 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 nonhomogeneous 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 preventing 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, and 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 de-slushing 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 subzero 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 at 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 meltwater immediately under the ice, which is not representative of the water chemistry of the system. Care must therefore 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).

Sample handling is another problem associated with winter sampling. It is essential that water samples not be 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. It is necessary, therefore, 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 three to ten 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 must also be prevented. Contaminant leaching from sampling devices and containers is very complex and requires serious attention. Table 11 shows the types of contaminants caused by materials used in sampling devices and well construction monitoring. Tin and lead are also 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).

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 should usually include equipment, field, and background blanks. Selections should be made by considering all likely sources of contamination for the specific situation.

Table 11. 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

Analyte sorption is also a common problem. Polyvinyl chloride 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 pre-rinse 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).

Polyvinyl chloride 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, and 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. Various sampling situations occur in the field that 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 as to be prepared for any situation (14).

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

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

Although sampling from bridges has some obvious advantages, there are also some possible contamination problems. Because most of these structures are made of metals, concrete, or creosoted timber, caution must be exercised to avoid heavy metal, major ion, and organic contamination, respectively. In addition, because many of these structures are subject to heavy vehicular traffic, 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 form concrete dust 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. Histories and knowledge of any chemical usage in or near wells can also 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. When dealing with hazardous waste disposal sites, it is not recommended that drilling be carried out into the waste material itself because of the possibility of encountering unknown and potentially dangerous situations. A grid similar to that used for sampling soils may also be employed to gather geostatistical samples at a site. More detailed information on groundwater sampling can be found in the National Contaminated 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 centre, at the greatest depth, to avoid shoreline effects. Lake depth should be at least 10 m for stable thermal conditions, and dystrophic or bog lakes should be avoided. Lakes that are fed by large inlets should also be avoided because of the possible dominance of stream characteristics

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

Samples from lakes are often collected from stations that 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, 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 that have poor accessibility, it may be necessary to use a helicopter, however, this increases the risk of contaminating 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 (rinse) blanks are very important. Usually double- or triple-distilled water is used to rinse sampling equipment prior to use.

Medical grade silicone rubber in peristaltic pumps avoids sample contamination by the organic peroxides used in the manufacturing of conventional grade silicone rubber, 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.), 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, 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, 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 the following (4):

- intake velocity
- watertightness
- electrical or insulation quality
- explosion-proof quality
- 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 (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 are 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. A few of the most commonly 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 that 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

A sampling iron is a device made of iron and painted with a rust inhibitor. Typically, it uses a 2-L sample bottle, but smaller bottles may also 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

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.

The Van Dorn bottle is designed for sampling at depth of 2 m or greater. The sampler is available in both PVC 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, 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, the water sample is transferred from the Van Dorn bottle to individual sample containers via the drain valve

The Kemmerer 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 PVC and acrylic plastic with silicone rubber seals. Both metal and plastic samplers are available in volumes ranging from 0.5 to 8 L. The operation of the Kemmerer sampler is the same as that for the Van Dorn bottle.

Three types of pumps are available to collect samples from specified depths: diaphragm, peristaltic, and rotary. In general, diaphragm pumps are hand-operated, the peristaltic and rotary pumps require a power source and, consequently, 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

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 that 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 of time 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.

Maximum holding times 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 (3).

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, chlorophenols, 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 the addition of sodium bisulfite 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 may also 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. The addition of sodium hydroxide or sulfuric acid, however, 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. A check must also be made to ensure that all samples bottles recorded on the field sampling sheets have been placed in a given carton before

shipping. 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 II also have instructions for collecting, preserving, and storing samples. A summary of these requirements for each of those methods is provided in Tables 12, 13, and 14. 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 12. Sample Collection, Preservation, and Storage for Organics

Method number/type	Sampling and preservation	Storage
EPA-502.2, Rev 2 Cap GC/PID/ELCD (VOA)	Use a 40- to 120-mL screw cap vial (prewashed 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 (or 3 mg of sodium thiosulfate) to each vial before collection of bubble-free samples. Add hydrochloric acid (1 l) until a pH of <2 is achieved. Seal bottles with PTFE faced down and shake vigorously for 1 min. Immediately cool samples to about 4°C.	The maximum holding time is 14 d 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 2 GC	Fill a 40-mL screw cap vial (prewashed with detergent, rinsed with distilled water, and oven-dried at 400°C for 1 h) 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 ⁻¹) 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 d from the date of collection. If heptachlor is to be determined, the maximum holding time should be 7 d.
EPA-507, Rev 2 GC/NPD	Collect grab samples in 1-L glass sample bottles (prewashed with detergent and hot tap water, rinsed with reagent water, and oven-dried at 400°C for 1 h) with screw caps lined with PTFE-fluorocarbon. Add mercuric chloride to the sample bottle in amounts to produce a concentration of 10 mg L ⁻¹ . If residual chlorine is present, add 80 mg of sodium thiosulfate per litre of sample to the sample bottle prior to collection. After collection, seal bottle and shake vigorously for 1 min. 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 d under these conditions during preservation studies, however, carboxin, EPTC, fluridone, metolachlor, naptiopamide, tebutburon, and terbacil exhibited recoveries of less than 60% after 14 d during preservation studies. Extracts should be stored at 4°C in the dark for a maximum of 14 d.

Table 12. (Cont.)

Method number/type	Sampling and preservation	Storage
EPA-515 1, Rev 4 GC/ECD	Collect grab samples in 1-L glass sample bottles (prewashed with detergent and hot tap water, rinsed with reagent water, and oven-dried at 400°C for 1 h) with screw caps lined with PTFE-fluorocarbon. Add mercuric chloride to the sample bottle in amounts to produce a concentration of 10 mg L ⁻¹ . If residual chlorine is present, add 80 mg of sodium thiosulfate per litre of sample to the sample bottle prior to collection. After collection, seal bottle and shake vigorously for 1 min. Cool sample to 4°C immediately.	Store samples at 4°C in the dark until extraction. Maximum holding times are 14 d for samples and 28 d for extracts.
EPA-524 2, Rev 3 Cap GC/MS (VOA)	Use a 60- to 120-ml screw cap vial (prewashed 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 d 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	Collect grab samples in 60-ml glass vials (prewashed with detergent and hot tap water, rinsed with reagent water, and oven-dried at 450°C for 1 h) 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 litre of sample to the sample bottle prior to collection. After collection, seal bottle and shake vigorously for 1 min. 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 holding time for samples is 28 d when adjusted to pH 3 and stored at -10°C.

Table 12. (Cont.)

Method number/type	Sampling and preservation	Storage
SM-6220C GC/PID-Purge & Trap	Use a 25- or 40-mL vial (prewashed with detergent, rinsed with distilled water, and oven-dried at 105°C for 1 h) 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 d 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 litre of sample and mix well.	Cool samples to 4°C and keep refrigerated from time of collection to extraction. Extract samples within 7 d of collection and analyze completely within 40 d of extraction.

Table 12. (Cont.)

Method number/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 litre 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 d of collection and analyze completely within 40 d of extraction.
EPA-8080B, Rev 2 GC	Liquid samples Use a 1- or 2½-gal amber glass with a screw-top Teflon®-lined cover. Prewash with detergent and 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.	Liquid samples must be extracted within 7 d and extracts analyzed within 40 d. Soil/sediments may be stored for a maximum of 14 d prior to extraction. All extracts and samples should be stored under refrigeration away from the presence of exhaust fumes.
	Soil/sediments and sludges Use an 8 oz widemouthed glass with a screw-top Teflon®-lined cover. Prewash 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.	

Table 12. (Cont.)

Method number/type	Sampling and preservation	Storage
2LPA-8240B, Rev 2 Cap GC/MS (VOA)	<p>Liquid samples Use a 40-mL glass screw-cap VOA vial with Teflon®-faced silicone septum (prewashed with detergent, rinsed with distilled deionized water, and oven-dried at 105°C for 1 h) If residual chlorine is present, collect sample in a 40 oz soil VOA container that 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</p>	<p>The two vials/glasses from each sampling should be sealed in separate plastic bags and stored at 4°C for a maximum of 14 d from date of collection</p>
EPA-8260A, Rev 1 GC/MS Cap	<p>Soil/sediments and sludges Use an 8 oz widemouthed glass with Teflon®-faced silicone septum (prewashed with detergent, rinsed with distilled deionized water, and oven-dried at 105°C for 1 h) Tap slightly to eliminate free air space Collect in duplicate and cool to 4°C</p>	<p>The two vials/glasses from each sampling should be sealed in separate plastic bags and stored at 4°C for a maximum of 14 d from date of collection</p>
	<p>Liquid samples Use a 40-mL glass screw-cap VOA vial with Teflon®-faced silicone septum (prewashed with detergent, rinsed with distilled deionized water, and oven-dried at 105°C for 1 h) If residual chlorine is present, collect sample in a 4 oz soil VOA container that 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</p>	
	<p>Soil/sediments and sludges Use an 8 oz widemouthed glass with Teflon®-faced silicone septum (prewashed with detergent, rinsed with distilled deionized water, and oven-dried at 105°C for 1 h) Do not heat septum for more than 1 h Tap slightly to eliminate free air space Collect in duplicate and cool to 4°C</p>	

Table 12. (Cont.)

Method number/type	Sampling and preservation	Storage
FPA-8270B, Rev 2 Cap GC/MS (B/N/A)	Liquid samples. Use a 1- or 2½-gal amber glass bottle with a screw-top Teflon®-lined cover. Prewash with detergent and 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.	Liquid samples must be extracted within 7 d and extracts analyzed within 40 d. Soil/sediments and sludges may be stored for a maximum of 14 d. Do not store in the presence of exhaust fumes.
Soil/sediments and sludges	Use an 8 oz widemouthed glass with a screw-top Teflon®-lined cover. Prewash with detergent and 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.	
FPA-8280, Rev 0 Cap GC/MS (PCDD/PCDF)	Grab and composite samples must be collected in 1-l or 1-qt 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 d, and analyzed within 45 d of collection.

Table 12. (Cont)

Method number/type	Sampling and preservation	Storage
EPA-8290, Rev 0 HRGC-HRMS	<p>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.</p> <p>Liquid samples Use a 1- or 2½-gal amber glass bottle with a screw-top Teflon®-lined cover. Prewash with detergent and 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.</p> <p>Soil/sediment and sludges Use an 8 oz widemouthed glass with a screw-top Teflon®-lined cover. Prewash with detergent and 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.</p>	<p>Store all samples except fish and adipose tissue samples at 4°C in the dark. Samples must be extracted within 30 d and extracts analyzed within 45 d of collection.</p>

*polytetrafluoroethylene

Table 13 Sample Collection, Preservation, and Storage for Inorganics

Method number/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 litre are stable for up to 6 months. For microgram-per-litre metal levels, analyze samples as soon as possible after collection.
SM-3111D AA (Flame-N ₂ O)	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 litre are stable for up to 6 months. For microgram-per-litre 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 litre are stable for up to 6 months. For microgram-per-litre metal levels, analyze samples as soon as possible after collection.

Table 13. (Cont.)

Method number/type	Sampling and preservation	Storage
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 litre are stable for up to 6 months. For microgram-per-litre metal levels, analyze samples as soon as possible after collection.
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 litre are stable for up to 6 months. For microgram-per-litre 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 litre are stable for up to 6 months. For microgram-per-litre metal levels, analyze samples as soon as possible after collection.
I PA-6010, Rev 0 ICP	Samples should be collected in borosilicate glass, linear polyethylene, polypropylene, or Teflon® bottles that have been prewashed with detergent and tap water and rinsed with 1 l nitric acid and tap water or 1 l hydrochloric acid and tap water. The appropriate collection volume and preservative is shown in Table 14.	The maximum holding times from time of collection to time of extraction is shown in Table 14 for each type of analyte.

Table 13. (Cont.)

Method number/type	Sampling and preservation	Storage
EPA-7196, Rev 0 Colorimetric	Collect samples in 500-ml or 1-L glass or plastic bottles previously washed with detergent and rinsed with tap water, 1 l 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 h
EPA-7470A, Rev 1 Liquid Waste Vapor Technique-Hg	Prewash all sample containers 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 . Nonaqueous samples should be refrigerated, when possible.	Store nonaqueous samples at 4°C, when possible, and analyze as soon as possible. The suggested maximum holding time for mercury is 28 d
EPA-7471A, Rev 1 Solid/Semi-Solid Vapor Technique-Hg	Prewash all sample containers 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 nonaqueous samples at 4°C, when possible, and analyze as soon as possible. The suggested maximum holding time for mercury is 28 d
EPA-7870, Rev 0 AA/AD	Liquid samples: Collect samples in 1-L glass or plastic bottles (previously washed with detergent and rinsed with tap water, 1 l nitric acid, tap water, 1 l 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

Table 13. (Cont.)

Method number/type	Sampling and preservation	Storage
EPA-9012, Rev 0 Colorimetric, Automated UV	Collect samples in 1-L 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 colour on the indicator Then, add an additional 0.6 g of ascorbic acid for each litre of water	Samples should be stored at 4°C and analyzed as soon as possible
EPA-9040A, Rev 1 pH Electrometric Measurement	Samples must be preserved by adding 10N sodium hydroxide until sample pH is ≥ 12 at time of collection	Not listed
EPA-9050A, Rev 1 Spec Conductance	Not listed	Not listed

Table 14. 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 mo
Dissolved	100	600	Filter on site HNO ₃ to pH <2	6 mo
Suspended	100	600	Filter on site	6 mo
Total	100	600	HNO ₃ to pH <2	6 mo
Chromium VI	100	400	Cool to 4°C	24 h
Mercury				
Total	100	400	HNO ₃ to pH <2	28 d
Dissolved	100	400	Filter, HNO ₃ to pH <2	28 d

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

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 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 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
- provide QC statements to support analytical practices

SELECTION OF AN ANALYTICAL METHOD

Usually there are 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 that 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 the following:

- availability of instrumentation
- confidence level needed
- sensitivity desired
- potential interferences
- 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, and 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. 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 (e.g., 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 against 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 users' needs, it also summarizes major advantages and disadvantages of each of the candidate detectors.

SELECTION OF AN ANALYTICAL LABORATORY

Environment Canada recommends the use of laboratories certified by the Canadian Association for Environmental Analytical Laboratories (CAEAL). This nonprofit 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 as follows:

- to raise and continually improve the quality of laboratory analyses in Canada
- to provide a national forum for communication and dialogue between laboratories
- 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 that successfully meet the national standards associated with site inspections and analyses of test samples will be granted accreditation that 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. The guide will be available from CAEAL. Member laboratories will be encouraged to adhere to the guidelines specified therein.

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 II are reviewed. If the samples are not collected, preserved, and stored correctly before they are analyzed, the analytical data may be compromised because of uncertainties as to their validity. If sufficient sample amounts are not collected, the sensitivity documented in the method will not be achieved. Usually the laboratory 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.

Analytical Method Summaries

RECOMMENDED ANALYTICAL METHODS

Usually there are multiple analytical methods for most of the analytes of interest to the National Contaminated Sites Remediation Program (Table 15). 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 Volume II.

Methods for Organic Compounds

Methods with highly selective detectors (e.g., 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. Methods that cover both solid and aqueous matrices were selected over those that covered one or the other. 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. Methods from the Standard Methods for the Examination of Water and Wastewater were selected over U.S. EPA methods when they were comparable because it is a more convenient source for the full methods.

MAJOR ANALYTE GROUPS

The analytes of interest to the National Contaminated Sites Remediation Program are divided into eight 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 as follows:

- general variables
- inorganic variables
- monocyclic aromatic hydrocarbons
- phenolic compounds
- polycyclic aromatic hydrocarbons
- chlorinated hydrocarbons
- pesticides
- miscellaneous organic parameters

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

Table 15 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)pyrene		
	benzo(b)fluoranthene	bis(2-ethylhexyl) phthalate
	benzo(k)fluoranthene	dimethyl phthalate
	dibenz(a,h)anthracene	di-n-octyl phthalate
	indeno(1,2,3,-c,d)pyrene	quinoline
	naphthalene	thiophene
	phenanthrene	
	pyrene	Pesticides
		aldrin and dieldrin
	Phenolic compounds	chlordane
	2,4-dimethylphenol	DDT
	2,4-dinitrophenol	endrin
	2-methyl-4,6-dinitrophenol	heptachlor (+metabolites)
	2-nitrophenol	lindane
	4-nitrophenol	methoxychlor
	phenol	carbaryl
	cresol (unspecified mixture)	carbofuran
	2-cresol	2,4-D diazimon
	3-cresol	parathion
	4-cresol	diquat
	2-chlorophenol	paraquat
	3-chlorophenol	
	4-chlorophenol	Chlorinated hydrocarbons
	2,3-dichlorophenol	chloroform
	2,4-dichlorophenol	1,1-dichloroethane
	2,5-dichlorophenol	1,2-dichloroethane
	2,6-dichlorophenol	1,1-dichloroethene
	3,4-dichlorophenol	cis-1,2-dichloroethene
	3,5-dichlorophenol	trans-1,2-dichloroethene
	2,3,4-trichlorophenol	dichloromethane
	2,3,5-trichlorophenol	1,2-dichloropropane
	2,3,6-trichlorophenol	cis-1,2-dichloropropene
	2,4,5-trichlorophenol	trans-1,2-dichloropropene
	2,4,6-trichlorophenol	1,1,2,2-tetrachloroethane
	3,4,5-trichlorophenol	tetrachloroethene
	2,3,4,5-tetrachlorophenol	carbon tetrachloride
	2,3,4,6-tetrachlorophenol	1,1,1-trichloroethane
	2,3,5,6-tetrachlorophenol	1,1,2-trichloroethane
	pentachlorophenol	trichloroethene
		1,2,3-trichlorobenzene
	Miscellaneous organic parameters	1,2,4-trichlorobenzene
	nonchlorinated aliphatics (each)	1,2,5-trichlorobenzene
	phthalic acid esters (each)	1,3,5-trichlorobenzene
	n-butyl benzyl phthalate	1,2,3,4-tetrachlorobenzene
	di-n-butyl phthalate	1,2,3,5-tetrachlorobenzene
	diethyl phthalate	1,2,4,6-tetrachlorobenzene
		pentachlorobenzene
		hexachlorobenzene
		hexachlorocyclohexane
		Aroclor 1242
		Aroclor 1248

Table 15 (Cont.)

Aroclor 1254	1,2,3,4,6,7,8-H ₇ CDD	1,2,3,6,7,8-H ₆ CDF
Aroclor 1260	O ₈ CDD	2,3,4,6,7,8-H ₆ CDF
2,3,7,8-T ₁ CDD	2,3,7,8-T ₁ CDF	1,2,3,4,6,7,8-H ₇ CDF
1,2,3,7,8-P ₁ CDD	2,3,4,7,8-P ₁ CDF	1,2,3,4,7,8,9-H ₇ CDF
1,2,3,4,7,8-H ₆ CDD	1,2,3,7,8-P ₂ CDF	O ₈ CDF
1,2,3,7,8,9-H ₆ CDD	1,2,3,4,7,8-H ₇ CDF	
1,2,3,6,7,8-H ₆ CDD	1,2,3,7,8,9-H ₇ CDF	

General Variables

This group consists, not of individual analytes, but 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 has application only 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 15) 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 the following discussions.

SM-3111B is a direct aspiration atomic absorption (AA) method commonly used for many of the metals in water samples. It 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 lake, river, 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 colorimetric determination that can be performed manually or be 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 monocyclic aromatic hydrocarbons because they cover all of them (Table 15) 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, they 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: nonchlorinated (each) and chlorophenols (each). There are 9 nonchlorinated phenols and 19 chlorophenols specified as analytes of interest (Table 15). 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. Methodology is lacking for the following specific chlorophenol isomers:

- 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
- 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 covers only 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. If the samples are relatively noncomplex, however, 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 the polycyclic aromatic hydrocarbon group (Table 15). 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 also be analyzed using any of the following methods: EPA-524 2, EPA-502 2, SM-6210D, or EPA-8260.

Chlorinated Hydrocarbons

The largest group of compounds consists of 47 chlorinated hydrocarbons (Table 15). 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. It should be noted, however, 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. Because this method uses high resolution capillary GC columns with low resolution mass spectrometry, it is less expensive and 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, six chlorinated compounds are not covered by the above methods:

- 1,2,5-trichlorobenzene
- 1,3,5-trichlorobenzene
- 1,2,3,4-tetrachlorobenzene
- 1,2,3,5-tetrachlorobenzene
- 1,2,4,6-tetrachlorobenzene
- 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, 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 15) 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 cover only 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 nonchlorinated 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 nonchlorinated aliphatics

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

- dimethyl phthalate
- diethyl phthalate
- di-n-butyl phthalate
- di-n-octyl phthalate
- bis(2-ethylhexyl) phthalate
- n-butyl benzyl phthalate

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

The analysis of nonchlorinated 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. There may, however, be mitigating circumstances that lead a laboratory or a project director to select different methods. For example,

- Exploratory or field screening analyses may be desired that are faster and cheaper than many of the recommended methods in this manual. 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 that 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 methods used are recorded, then the data produced from that study will, it is hoped, 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 II, which is available in hard copy format or on a computer diskette

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, the final step is 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 covering 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 include data custody and records involving transfer of data
- data validation, which includes completeness and representativeness in addition to correctness
- data verification, which includes checking that all the data are present and correct
- data handling, which includes data rounding and treatment of significant figures
- data transmission, including electronic transmission
- 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 notebook 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 must also be documented. Routine maintenance may be indicated by labels on the equipment. Maintenance that 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; bound notebooks are much preferred to looseleaf 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
- 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: written or typed forms that may carry signatures and be stored in file cabinets, and electronic forms and data that will constitute elements of data base 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 data bases that involve QC studies.

The QA procedures for data custody should include the following:

- 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
- implementation of a procedure for authorizing changes to QC data bases where corrections and data changes are warranted

- implementation of checks to ensure that the QC data bases are always complete

The QA procedures for data transfer should include the following:

- 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
- establishment of 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 sections entitled Data Handling and Data 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

Validation checks for the data from a contaminated site should include:

- data identification
- unusual events

- transmittal errors
- temporal continuity
- flagged or rejected data
- checks for errors in automatic data processing
- control charts
- sample consistency checks
- ion balances

Data Identification

Data identification includes such data entries 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

Unusual events include 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

Checks for continuity with respect to time, such as looking for breaks, discontinuities, or gaps, etc., should be made

Flagged or Rejected Data

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

Checks for Errors in Automatic Data Processing

These checks 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 that 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

Control charts 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

Sample consistency checks 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 litre. 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 are the final key activities of data validation. Review and evaluation of data should be centred on 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 data base 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 before storage, and the data must also be checked again when merged into an existing data base. 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, nonpreserved 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 the following (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.)
- ensuring that any missing or invalid results are explained (i.e., with comment codes)

The laboratory should also be responsible for performing a number of QC checks on the field portion of the monitoring program. These checks consist of the following (3)

- verifying sample labeling and matching field sheets with samples
- ensuring that samples were submitted as recorded in the sample log book (or computer sample registry) and monitoring sample shipping (time, temperature, mode of shipping), sample condition (leaks, contaminants), and sample volume (independent measurement of sample volume)
- 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 data base 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 nonrepresentative 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 data base 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 mg 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 5, 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 5, the retained figure is increased by 1. For example, 2.463 becomes 2.5 to two significant figures.
- When the digit immediately after the one to be retained is exactly 5 and the retained digit is even, it is left unchanged, but when it is exactly 5 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 2.4501, the group 501 is considered to be greater than 5, while for 2.5499, the group 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). There is a second type of transmission error, however, which can be found only by comparing transmitted data to the original data. This involves the deletion during

transmission of certain noncommon alpha-numeric characters that 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 the presentation of them in a cohesive report so that others cannot 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 the following

- 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
- an extrapolation of the information presented to some form that will ultimately be useful

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, considering 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 their description and use in drawing up the conclusions presented in a report If someone needs additional information (such as portions of the raw data or portions of a data base), 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 must also 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 their uncertainty interval This means providing appropriate rounded or truncated data that have a specified uncertainty interval (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 (4) 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 view is held by both the American Society for Testing and Materials (42) and the American Chemical Society (4).

Proposed Definitions

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 MDL and the RQL would be four times the MDL (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 3% 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. When multiplied by one of these arbitrary factors, an MDL produces a practical quantitation limit (PQL). Practical quantitation limits 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 that 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
- 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.

Method Detection Level (MDL)

The MDL is 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 intralaboratory 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 interlaboratory 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 that is twice that of the method detection level ($RDL = 2 \times MDL$). The RDL is the lowest recommended 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 lowest recommended level for quantitative decisions based on individual measurements for a given method and representative matrix. The RQL is the concentration that is two times the reliable detection level ($RQL = 2 \times RDL$). 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

Table 16. 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)

Note "Zero" may be a negative value or no discernable detector response
 σ = Standard deviation
 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.

reporting data by laboratories (based on these distinctions) are given in Table 16. 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).

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 should also 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 $\mu\text{g}/\text{kg}$ are the same. In general, $\mu\text{g}/\text{kg}$ (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, $\mu\text{g}/\text{cm}^3$, 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 must always 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.

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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. The analytical batch is defined as samples that 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 that 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 re-analyzed

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, they should be as close as possible to the area where test samples are taken, e.g., 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 that 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 that 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 three to five 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 deviation) - 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 that 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 that 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. 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 that 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 that 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 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 non-selective detector for pollutants that contain halogens or some hetero atoms. This detector is not affected by the presence of moisture and is nondestructive. However, it has a relatively small linear range, its responses are not usually predictable from molecular structure, and its use may require a license.

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 - 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 an excellent linear range and low maintenance, but poor sensitivity for halogenated compounds and those that lack hydrocarbon characteristics (e.g., carbon monoxide, carbon dioxide, and phosphene)

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 (a) pumping continuously at a rate proportional to the flow, (b) mixing equal volumes of water collected at time intervals that are inversely proportional to the volume of flow, or (c) 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 or rivers, existing, growing, or living in or about a stream or 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

imprecision - random error in data

inductively coupled plasma emission spectrometry (ICPES or ICP) - 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 that is attributable to between-laboratory variability. It is often quantitated through interlaboratory collaborative testing or "round robin" studies

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

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

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 sampler - 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 three standard deviations above the average level of a well-characterized blank sample

limit of linearity (LOL) - the upper concentration level of reliable measurements of analytes. The LOL is usually reached when a detector becomes non-linear 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 and 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

measurement quality objectives (MQOs) - limits for the uncertainty of specific measurements

method detection level (MDL) (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

nonpoint 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 the 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_{10} 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 its responses are difficult to predict from molecular structures

point waste 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 a given component or components 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 sampling, 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 using them, consisting of a blank spiked with the analyte(s) from an independent source, in order to monitor the execution of an analytical method

quality assurance (QA) - 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 or 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 that 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 (QC) - 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 economical

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

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, 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 that are sufficiently well established to be used for the calibration of an apparatus, the assessment of a measurement method, or 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 by 100%

reliable detection level (RDL) (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 that is twice that of the method detection level ($RDL = 2 \times MDL$). 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) (proposed) - the concentration that is two times the reliable detection level ($RQL = 2 \times RDL$). 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

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

replicate samples - samples that are identical or very similar and 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

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

safety - a quality of being devoid of whatever exposes one to danger or harm, freedom from danger or hazards

sediment - fragmental soil 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 continuously pumping 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 sample after it has been first analyzed without such addition. Re-analysis 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

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

surrogates - organic compounds that are similar to analytes of interest in chemical composition, extraction, and/or chromatographic 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 - constituents of an unacidified water sample retained by a 0.45- μm membrane filter, can impart a cloudy appearance to a sample

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

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 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 tech-

niques to determine the composition (analysis) of materials

Teflon® - a human-made plastic material inert to all chemical reagents except molten alkali metals. It is used 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 an 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 a beta (β) error or false negative

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

UV - ultraviolet

validation - the process by which a sample, measurement method, or 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)