QUALITY ASSURANCE PRINCIPLES AND GUIDELINES FOR WATER QUALITY SAMPLING

WATER QUALITY BRANCH
INLAND WATERS & LANDS
CONSERVATION & PROTECTION
ENVIRONMENT CANADA
HULL/OTTAWA

James E. Gaskin

02/88

PREFACE

A fundamental consideration in the reliability of any analytical measurement is that of sample quality. Sample quality may be appraised on the basis of the quality of the resulting chemical, physical and biological measurement data.

Assurance of acceptable data quality requires a system which ensures that all activities associated with the sampling program be well defined and supported by accepted and standardized practices.

This manual is written to provide guidance for the development of a comprehensive and workable field quality assurance program within the Water Quality Branch. Section 1 serves as an 'Introduction' and looks at the need for a field QA/QC program, and the objectives of such a program. Section 2 discusses different aspects of the 'Design of a Water Quality Monitoring Program', beginning at the sampling design stage, progressing through considerations for sample analysis, right through to data quality objectives. Section 3 points out the need and usefulness of a 'Field Personnel Training Program', with suggestions and recommendations on the directions that program should take. In section 4 the focus is on 'Field Trip Preparation', 'Selection of Sampling Equipment and Sample Containers'. Section 5 deals with the 'Accessibility to Sampling Sites' and is complemented by Section 6 which describes a number of general QA features for water quality sampling at the chosen sites. 'Sampling for Specific parameters in Specific Matrices' (E.g. toxic chemicals in water) is given special attention in Section 7, followed by Section 8 which describes a specific type of QA sampling program, namely, 'Sequential Triplicate Sampling'.

QA approaches to 'Sample Handling, Preservation, Storage and Transportation' are outlined in Section 9. Section 10 lists the 'Maintenance and Calibration' procedures that must be undertaken before 'Field Testing' of samples is begun (Section 11), while 'Data Collection' is addressed in Section 12, with emphasis being placed on the gathering of 'Support Data'. 'Chain of Custody'protocols that relate to the protection, validity and integrity of samples and data are outlined in Section 13, followed by 'Safety Guidelines' in Section 14. The safety recommendations are based on a number of established health and safety regulations which have been issued by a number of government departments.

The 'Field Audit Program' is one of the main vehicles used to ensure that the Field QA Program is working efficiently and effectively, and a number of recommendations are cited in Section 15 for establishing and running such a program. One of the groups that assists in the coordination of the Audit Program is the Technical and Advisory Committee. The functions of this committee are spelled out in Section 16.

The four remaining portions of the manual highlight a glossary section, references, a flowchart depicting the various QA activities that go to make up the sampling QA Program, and finally an index section that facilitates the location of various QA related topics.

Many sections relating to "Sampling for Specific Parameters in Specific Matrices" and "Sequential Triplicate Sampling" are based on the work done by the Atlantic Region (WQB) and have been reported in the 'Water Quality Branch Atlantic Region Field Quality Assurance/Quality Control Program Version 2', by R. Arseneault and G. Howell. This work has been freely quoted.

ACKNOWLEDGEMENT

We acknowledge the valuable contribution made by R. Arseneault and G. Howell to a number of sections in the Manual. The effort made by E. Watt in an earlier version of a "Field Sampling QA Manual" also contributed significantly to various portions of the text.

We are also appreciative of the constructive comments and suggestions made in the review process by the following Water Quality Branch personnel: H. Agemian, R. Arseneault, P. Brooksbank, L. Désilets, R. John, F. Philbert, C. Thorpe, H. Vaughan and D. Warry. The patience and efforts demonstrated by Mrs. Francine Goulet in the typing and re-typing of the manuscript are also greatly appreciated.

TABLE OF CONTENTS

Page

PREFACE .... (i)
ACKNOWLEDGEMENT .... (iii)
TABLE OF CONTENTS .... (iv)
LIST OF TABLES .... (v)
LIST OF FIGURES .... (v)

1.0 INTRODUCTION 1
  1.1 The need for a Field QA/QC Program 1
  1.2 The Objectives of the Field QA/QC Program 1
  1.3 QA/QC Documentation 2

2.0 DESIGNING A WATER QUALITY MONITORING PLAN 7
  2.1 Sampling Program 7
  2.2 Site Selection 10
    2.2.1 Selection of River Sampling Stations 13
    2.2.2 Selection of Lake Sampling Stations 14
    2.2.3 Selection of Stream Sampling Stations 15
    2.2.4 General Considerations for Station Location 16
  2.3 Site Documentation 17
  2.4 Establishing the H_0 and H_a Hypotheses 19
  2.5 Sampling Frequency and Sample Size 20
  2.6 Field and Laboratory Analytical Practices 25
  2.7 Data Quality Objectives 26
  2.8 The Use of Statistical Analysis 27
  2.9 Cost Considerations 28

3.0 TRAINING OF FIELD PERSONNEL 32

4.0 FIELD TRIP PREPARATION 35
  4.1 Selection of Sampling Equipment 36
  4.2 Sample Bottles 37

5.0 ACCESSIBILITY TO SAMPLING SITES 41

6.0 WATER QUALITY SAMPLING 43
  6.1 Sample Representativeness 43
  6.2 Automatic Sampling 45
  6.3 Sampling in Winter Conditions 47

7.0 SAMPLING FOR SPECIFIC PARAMETERS IN SPECIFIC MATRICES 49
  7.1 Toxic Chemicals in Water 49
    7.1.1 Toxic Organic Chemicals 49
    7.1.2 Liquid-Liquid Extraction Techniques 54
    7.1.3 Column Extraction 55
  7.2 Toxic Chemicals in Bottom Sediment 56
  7.3 Toxic Chemicals in Biota 61
  7.4 Toxic Chemicals in Packed Snow 65
  7.5 Bacterial Sample Collection 67
  7.6 Sampling For Radioactive Parameters 69

8.0 SEQUENTIAL TRIPLICATE SAMPLING.................................... 70

9.0 SAMPLE HANDLING, PRESERVATION, STORAGE AND TRANSPORTATION..... 74

10.0 MAINTENANCE AND CALIBRATION OF INSTRUMENTATION................ 78
  10.1 General Maintenance and Calibration........................ 78
  10.2 Maintenance of Specific Instrumentation.................... 81

11.0 FIELD TESTING.. 84
  11.1 Quantitative Analysis...................................... 84
    11.1.1 Application and Scope.................................. 84
    11.1.2 Preparation of Standards, Blanks, Reagents and Sample Solutions.......................... 84
    11.1.3 Calibration and Measurements........................... 85
    11.1.4 Standard Addition Technique............................ 86
  11.2 Precision and Accuracy..................................... 87
  11.3 Measurement Comparisons.................................... 94

12.0 DATA COLLECTION.. 95
  12.1 Recording Field Data....................................... 95
  12.2 Support Data... 97

13.0 CHAIN OF CUSTODY... 100

14.0 FIELD SATEFY... 102

15.0 FIELD AUDIT PROGRAM.. 106

16.0 TECHNICAL AND ADVISORY COMMITTEES............................. 107

17.0 REFERENCES... 110

GLOSSARY.. 117

APPENDIX 1.. 130

INDEX... 131

LIST OF TABLES

Page

TABLE 2.1 Total Quality Cost Summary.............................. 30

TABLE 4.1 Recommended Containers and Washing Procedures for Selected Water Quality Parameters................. 38

TABLE 7.1 Procedures Used for the Preservation of Water Samples Collected for Toxic Chemical Analyses................. 51

TABLE 8.1 Partial Results of Sequential Triplicate Sampling of Selected Stations Included in the Nova Scotia LRTAP Lakes Monitoring Program (1984-85).............. 73

TABLE 11.1 Specific Conductance Results Obtained in the Field...... 91

TABLE 11.3 Precision and Accuracy Statistics Associated with Field and Laboratory Measurements of Specific Conductance... 93

LIST OF FIGURES

FIGURE 2.1 Related Activities in a Water Quality Pilot Sampling Survey.................................... 11

FIGURE 11.1 Example of Standard-addition Method...................... 88

FIGURE 12.1 General Format for a Field Sampling Sheet............... 98

1.0 INTRODUCTION

1.1 The Need for a Field QA/QC Program

A quality assurance/quality control program will ensure the integrity and representativeness of the samples taken from Canadian Inland Waters.

If non-representative samples are collected, and if sampling and preservation techniques are inadequate, the quantitative results will be invalid. In the past, QA/QC principles and protocols were mainly applied to laboratory analysis, and very little QA/QC activity was devoted to the sampling program. Emphasis is now being placed not only on the collection of samples that are appropriately representative of the aquatic source from which they are taken, but also on the appropriate preservation, transportation and handling procedures that are used in the life of each sample in its journey between the collection site and the laboratory.

Collective practices in the sampling and preservation activities need checks and balances to foster confidence in the resulting data. These checks and balances are the QA/QC protocols used to create the climate of data integrity and data acceptability.

1.2 Objectives of the Field QA/QC Program

One of the primary objectives of the field QA/QC program is concerned with the Branch's ability to collect and deliver appropriately representative water quality samples to the laboratory.

A second equally important objective is to produce data of known quality, sufficient to meet the needs of the network and its data users. There are six major characteristics of data quality, namely: accuracy, precision, completeness, representativeness, data comparability and data compatibility. Under ideal conditions it is desirable to specify at the outset of the monitoring program, acceptable levels of these characteristics. The quality assurance/quality control program should then be designed to ensure that these levels are met.

1.3 QA/QC Documentation

For a field sampling QA/QC program, there are three documents that are required (Stanley and Verner, 1983). The first is the QA 'Program Plan', which commits management to a QA policy and sets forth the requirements for data needed to support program objectives. The program plan describes the overall policies, organization, objectives, and functional responsibilities for achieving data quality goals. The five major functions of the plan are:

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

- A description of how QA implementation will be evaluated.

The second document is the 'QA Project Plan', a technical document that specifies the QA and QC requirements for each project. The plan specifies any QA/QC activities required to achieve the data quality goals of the project. It 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 must address the following items in sufficient detail to permit unambiguous evaluation of project results:

- 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.

- 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 action.

- Quality assurance reports to management.

To satisfy the requirements for quality data, the project plan must describe the following activities:

- 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.
- Sample custody.

The field sampling QA/QC manual is also a component of the QA Project Plan and must provide guidance on policy and procedures. This manual will contribute to the quality of the data generated, by:

- 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 safety practices in sampling and field testing operations;
- providing accepted procedures designed to control and define errors associated with field measurements;
- defining statistical techniques for assessing the experimental data; and,
- ensuring that the collected data have met the measurement program objectives.

The third document that is needed, is a 'Program Implementation Plan'. A number of mechanisms 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). The management committee directing the cooperative water quality arrangements, will coordinate the monitoring and survey programs to ensure that data of known and acceptable quality are produced. Resource levels, schedules, turnaround times, responsibility centres, performance indicators, milestones, risk factors, implications, emerging issues, etc., must all be given attention, if the programs are to succeed.

2.0 DESIGNING A WATER QUALITY MONITORING PLAN

2.1 Sampling Program

The field QA/QC strategy includes a sampling plan which serves as the central element for directing the various operational activities. To produce a truly effective sampling plan, an interdisciplinary approach is necessary. The inter-disciplinary contributions assure the development of a plan that is specific and has all the requirements for successful sampling operations.

The sampling plan must concern itself with the 'why', 'what', 'where', 'when' and 'how' questions. The 'why' question must address the broad objective(s) of the monitoring program, and the data quality objectives associated with the various specified projects. The rationale for each project should include an estimation of the project's utility and cost-effectiveness. The 'why' question can be influenced by considerations such as: prevailing environmental concerns and problems; a combination of socio-economic, socio-political and environmental issues; the need for continuing and/or expanding existing projects or programs; and the need to capture baseline data at new specific sites.

The 'what to sample' should be a logical fallout from the answer to the 'why to sample' question. Specific water quality parameters may be issue-oriented, or may result from water quality objectives arising from negotiated water quality monitoring agreements between Federal and Provincial agencies.

The choice on 'where to sample' may be controlled by the decisions taken on 'why to sample' and 'what to sample for'. However, once a river basin, lake or stream (macro-level choice) has been agreed upon, selecting sampling stations (micro-level choices) is an exercise controlled by a number of exogenous and endogenous factors. These factors include: hydrologic data (flow rates, sediment discharges, etc.) for various sections of the aquatic body; topography of the macro-site; geographical location with regards to interjuristictional boundaries; ease of access to sampling sites; run-offs and material infusions (sediment, water, sludge, sewage, etc.) from eternal sources; mixing currents; water depth; and anthropogenic activity.

The 'when to sample' choice is influenced by, for example, (a) objectives of the study; (b) available resources; (c) seasonality, including spring run-off, heavy snow fall and heavy rain fall; (d) required estimated sampling frequency; (e) high or low flow rates within the sampling cross-section of the aquatic body; (f) unusual environmental and ecological occurrences such as flooding and chemical spills; (g) intentional or unintentional toxic waste discharges; (h) anthropogenic activities which may be deleterious to the aquatic body; and, (i) the density of air-borne and non-point source pollutants.

The appropriateness of 'how to sample' can be addressed by consideration of nine principles (Green, 1979):

(1) Preliminary sampling such as a pilot survey, should be conducted in order to provide a basis for an evaluation of the sampling design and the statistical options.

(2) Replicate samples should be taken within each combination of time, location, and any other controlled variable. Differences 'among' can only be demonstrated by comparison to differences 'within'.

(3) An equal number of randomly allocated replicate samples should be collected for each combination of controlled variables. Collecting samples from 'representative' or 'typical' places is not random sampling.

(4) Verification should be made, that the sampling method is correct for the range of sampling conditions to be encountered. Note that variation in efficiency of sampling can bias 'among-area' comparisons.

(5) If the area sampled has a large-scale environmental pattern, it should be broken up into relatively homogeneous sub-areas, and sample collections should be proportioned to the size of each sub-area.

(6) The sample size should be verified as appropriate to the quantity and spatial distribution of the parameter. An estimate should then be made of the number of replicate samples required to obtain the necessary precision.

(7) To test whether a condition has an effect, samples should be collected both where the condition is present and absent, but all else is the same. An effect can only be demonstrated by comparison with a control.

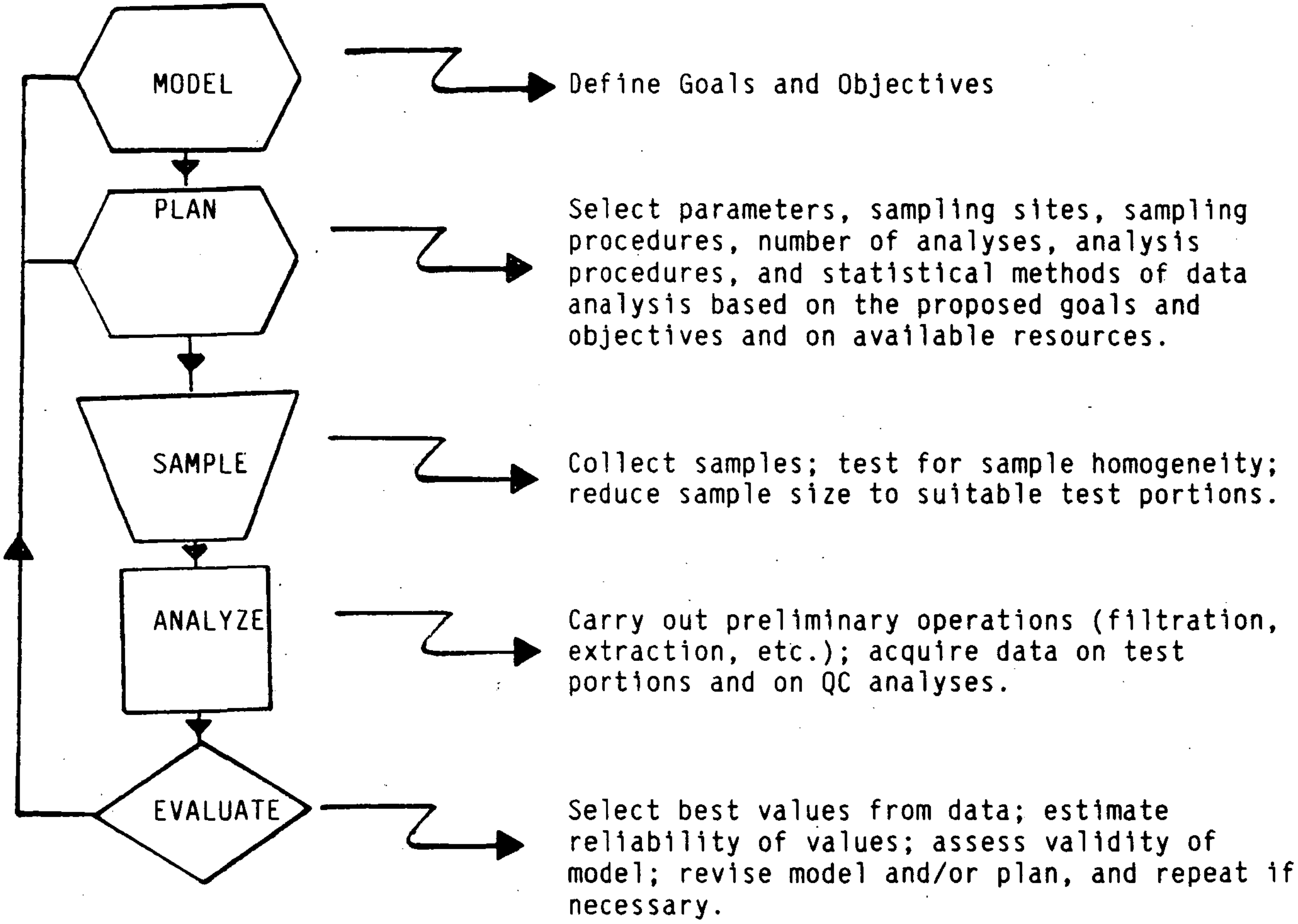
(8) On-going site evaluations for parameters such as pH, conductivity, turbidity and dissolved oxygen should be incorporated into the sampling plan, with some consideration given to the possible need for more extensive studies at sites where specific problems have been identified.

(9) The data from the pilot survey(s) should be tested and analyzed in order to determine whether the error variation is homogeneous, normally distributed and independent of the mean. If this is not the case (a situation which is highly probable with biological parameters), then the data could be appropriately transformed, or distribution free (non-parametric) procedures could be used.

Figure 2.1 illustrates the inter-connection between a number of water quality sampling activities in a pilot survey. See Appendix 1 for a complete flowchart of activities and sub-activities connected with the sampling operation.

2.2 Site Selection

Site selection must be given detailed consideration during the development of the 'Sampling Program Plan', since sampling techniques to be used in a given situation will depend not only on the data needs, but also on the nature of the flow and other conditions.



Define Goals and Objectives

Select parameters, sampling sites, sampling procedures, number of analyses, analysis procedures, and statistical methods of data analysis based on the proposed goals and objectives and on available resources.

Collect samples; test for sample homogeneity; reduce sample size to suitable test portions.

Carry out preliminary operations (filtration, extraction, etc.); acquire data on test portions and on QC analyses.

Select best values from data; estimate reliability of values; assess validity of model; revise model and/or plan, and repeat if necessary.

FIGURE 2.1 - RELATED ACTIVITIES IN A WATER QUALITY PILOT SAMPLING SURVEY

Appropriate siting is critical to the success of the monitoring network. Poor siting could result in low quality unrepresentative data. It is therefore important that comprehensive quality assurance/quality control procedures be developed to address network siting. These procedures should be designed to meet a specific set of quality assurance objectives, namely:

- to assure that the geographical distribution of sampling locations meets network objectives.

- to ensure that the sampling sites (micro-locations) that are chosen, are appropriately representative of the existing aquatic characteristics of the given water body.

- to ensure that site documentation is sufficient for data users to assess the suitability of the sites for the required purposes.

Meeting these three QA/QC objectives requires the implementation of the following procedures:

- Conducting a preliminary site assessment, followed by a report prepared within the first six months of operations, so that obvious problems are detected early, and the site can be changed before a large data set is obtained.

- Routine reporting of significant changes in data obtained from the site during period to period sampling.

- Proper documentation of sampling sites during program operations.

- Independent quality assurance audits of sampling sites. This should be conducted in order to (a) independently assess the accuracy and completeness of current site documentation, and (b) to assess the represenativeness of each site with respect to its monitoring objectives. Site representativeness could be checked by looking at data for a number of physical parameters (turbidity, pH, conductivity and dissolved oxygen).

Apart from using objectives to allocate sampling stations, other factors such as basin size and available resources must enter the selection scheme so that a reasonable degree of optimization can be achieved. Resources may be allocated on the basis of basin size, sampling frequency, number of sampling sites within a macro-location, site accessibility, cost-shared arrangements between monitoring agencies and distance of site(s) from the office which is coordinating or conducting the sampling operations.

2.2.1. Selection of River Sampling Stations

Three approaches have been defined for selecting the sampling macrolocation within a river basin (Désilets, 1986): (a) the 'global Approach', the 'Sub-basin Approach' and the 'River Stretch Approach'.

The global approach is designed to assess a river basin's hydrochemical balance; the sub-basin approach is aimed at assessing water quality impairments induced by diffused sources such as agricultural lands and forestry areas; and, the river stretch approach is structured towards assessing the importance of one or various point sources of pollutants and their impact on downstream aquatic environmental quality. Point sources to consider, include major cities (wastewaters), hydroelectric dams, industrial sites, landfills, construction sites, commercial fishing areas and recreational areas.

2.2.2 Selection of Lake Sampling Stations

It has been observed that lake water sampling often show less temporal variance (but greater spatial variance) than river sampling. This observation favours the use of lakes for long-term trend assessments, as the monitoring costs are potentially reduced. The following criteria have been suggested (Désilets, 1986) to assist in the selection of headwater lakes for inclusion in the monitoring network:

(a) Headwater lakes measure the effects of atmospheric deposition and therefore should be located on the most elevated sites of the basin, away from agricultural lands and urban areas, to avoid local climatic effects.

(b) Selected lakes should be easily accessible.

(c) Lake depth should be at least ten metres, for stable thermal conditions.

(d) Dystrophic or bog lakes should be avoided.

(e) Lakes that are fed by large inlets should be avoided because of the possible dominance of stream characteristics.

(f) As a general rule, water and sediment sampling stations should be located near the centre of the lake, at the greatest depth, to avoid shoreline effects.

2.2.3 Selection of Stream Sampling Stations

Many factors are involved in the proper selection of sampling stations for streams (Kittrell, 1969). The factors include:

(a) Objectives of the stream study.
(b) Water uses.
(c) Access to desirable sampling points.
(d) Entrance and mixing of wastes and tributaries.
(e) Flow velocities an times of water travel.
(f) Marked changes in characteristics of the stream channel.
(g) Types of stream bed, depth and turbulence.
(h) Artificial and physical structures such as dams, weirs and wingwalls.
(i) Resources available for the study.

The ideal sampling station would be a cross-section of a stream at which samples from all points on the cross-section would yield the same values (e.g. concentrations) for respective constituents, and sequentially taken samples at a given point in time would yield the same values. The former situation should occur when vertical and lateral mixing of any upstream wastes or tributaries are complete at the sampling station. The latter situation should occur only if there is no variation in upstream waste discharges or there is complete mixing longitudinally of any variable waste discharge, and if there are no upstream variations in stream flow, time-of-water travel, temperature, biological activity or other factors that contribute to variation in water quality.

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

2.2.4 General Considerations for Station Location

As a general rule, past or present monitored sites should be taken into account when locating a water quality sampling station, to ensure a long-term continuity in data set or to identify seasonal cycles. Water quality monitoring stations should be located close to water quantity stations when these already exist, in order to facilitate the study of water quality-quantity relationships. The distance between the collection site and a gauge recorder should not be more than a few hundred feet, unless it has been ascertained that there is no appreciable inflow between sites. If there is no gauging station at or near the sampling site, a discharge measurement should be made at the time of sampling (Kister et al. 1983).

When locating a sampling station within a given jurisdiction (Province, territory, international border), cooperation between the respective water quality agencies is essential.

2.3 Site Documentation

Documentation of each site should include the following:

(a) Name of lake, river or stream, county and township, province or territory.

(b) Boundaries of segment sampled, basin and sub-basin (using NAQUADAT codes).

(c) Universal Transverse Mercator or latitude - longitude coordinates of site.

(d) Elevation of site above sea level.

(e) Area of watershed.

(f) Morphometric measurements for lakes (area, volume, mean depth and maximum depth).

(g) Topographic map showing site location.

(h) For streams and rivers, location of nearest flow recorder; also stream classification.

(i) Exact location of sampling point (distance from bank; whether mid-stream, location in lake, etc.).

(j) Distance of sampling site from point source discharges.

(k) A general description of the area including land use practices upstream of sampling locations, and ease of access.

(l) Water quality objectives.

(m) Availability of sediment surveys.

(n) Data from other agencies (federal, provincial, territorial, interjurisdictional, international and private).

(o) Hydrologic data.

(p) Major issues and concerns.

2.4 Establishing the H_o and H_a Hypotheses

Having decided on the 'why', 'what', 'where',, 'when' and 'how' to sample, the next step is to formulate a hypothesis that is simple, rational and consistent with the information gathered from a pilot study or survey regarding the aquatic system which is to be monitored.

All models for testing statistical hypotheses provide a set of decision rules which specify the conditions under which the hypothesis will be rejected or accepted. Often the statistical hypothesis is stated in null form (e.g., "there is no association between variables X and Y"). Hypotheses such as this are referred to as null hypotheses (H_o).

The formulation of hypotheses establishes a bridge between the objectives of the water quality project and the studied phenomenon. It can also help to reduce the scope of the project, and collect only the pertinent information needed.

In establishing the null hypothesis (H_o), the alternative hypothesis (H_a) must also be considered, and the assembly of both hypotheses is a prerequisite to the later application of statistical tests to the experimental data.

The sampling design should reflect the H_o model as closely as possible. If for example, H_o is given as, "An impact (resulting from the presence of increased total cyanide concentration) has not led to fish kill effects", contrasts with an H_a, that it has, then the sampling study should be designed so that as many as possible of the environmental variables unrelated to impact, are controlled; perhaps this can be achieved by choosing control and impact areas that are similar except for the fact that one will be impacted and the other will not.

To assist in the acceptance or rejection of the null hypothesis, at a given significant level, careful thought must also be given to the choice of predictor and criterion variables: examples of predictor variables would be spatial and temporal patterns, and criterion variables could be: sample representability, precision measurements, and data completeness.

2.5 Sampling Frequency and Sample Size

Most water quality sampling for the WQB is conducted monthly, but the day of the month and the time of day may vary randomly. In many cases, sampling frequency is related to the estimated variance in the measurements of the water quality constituents of concern.

The simplest design case on a single station-single variable basis, would be to select the sampling frequency which results in the desired confidence interval width about the annual mean (or geometric mean) for the specified water quality variable at the specified site (Sanders et al, 1983). If the estimate of the variance (obtained from historical data or a pilot program) is assumed to be the population variance, σ^2, then the number of samples N (per period) required to obtain a given degree of confidence in estimating a mean value for the parameter of interest, can be derived from the following equation:

$$N \geq \frac{Z^2_{\alpha/2} \cdot \sigma^2}{E^2} \qquad (2.1)$$

where: $Z_{\alpha/2}$ is the standard normal deviate corresponding to a probability of $\alpha/2$; E is the error term, and is given by μ-x.

If s is used instead of σ, $t_{\alpha/2}$ (Student's t) is used in place of $Z_{\alpha/2}$, and N is given as:

$$N \geq \frac{t^2_{\alpha/2} \cdot S^2}{E^2} \qquad (2.2)$$

Sanders et al (1983) have provided a very comprehensive outline on methods for determining sampling frequencies for 'single station-single variable'; 'single station-multiple variables'; 'multiple station-multiple water quality variables'.

The following is an example of the use of Equation 2.1.

"The samples to be measured for a given parameter are expected to have a mean annual concentration of approximately 0.1 ppm, with standard deviation of 0.05 ppm, and the tolerable error in the stated value of the mean at the 95% confidence level (Z=1.96) is not to exceed 20% (0.02 ppm). If it can be assumed that the measurement error is small in comparison with the measured values, find the number of samples required per year to estimate future annual means for the given parameter".

With the above values, the number of samples required will be:

$$N = \frac{(1.96)^2 \cdot (0.05)^2}{(0.02)^2}$$

$$= 24 \text{ samples per year, or 2 samples per month.}$$

The appropriate size of samples to be collected for any given parameter will depend on the estimated natural concentration level of that parameter within the aquatic source. The smaller the existing analyte concentration, the larger the volume necessary for obtaining a reasonable measurement (a measurement equal to or greater than the limit of quantitation, subsequent to volume reduction).

For organics, samples of 100 litres or more are collected for solvent extraction. New field in-situ solvent extraction techniques are now providing alternatives to handling large liquid volumes. However, for a number of diverse parameters, there is still a need for estimating the sample volumes required to measure levels of interest. A number of empirical and semi-empirical methods have been developed for determining sample sizes so as not to exceed a predetermined level of sample uncertainty. One approach (Ingamells, 1973) is based on the knowledge that the between-sample standard deviation decreases as the sample size increases.

A modified form of the Ingamells' Equation can be adopted to determine the sample volume that is required for an estimated standard deviation and a predicted sampling uncertainty. The equation is of the form:

$$VR^2 = M_s \tag{2.3}$$

where: V is the volume of sample analyzed; R is the relative standard deviation (in percent) of sample analyte; and M_s is the sampling constant, corresponding to the volume of sample required to limit the sampling uncertainty to a chosen percentage value (e.g. 1%) with a proposed level of confidence (e.g. 68%).

The magnitude of M_s can be determined by estimating the between sample standard deviation S_s from a series of measurements of samples of volume V.

Once M_s is evaluated for a given sample, the minimum volume V required for a maximum relative standard deviation of R percent can be calculated.

An example of the use of M_s is as follows:

"Estimate the volume of sample to be collected for the analytical measurement of a given parameter, when the values of M_s and R are given as 100 ml and 20% respectively".

Inserting the values of M_s and R in Equation 2.3, V is calculated as:

$$V = \frac{100 \text{ ml}}{(0.2)^2} = 2.5 \text{ litres}$$

When a reduction of the original volume (via solvent extraction, distillation, evaporation, etc.) is required before analysis, back-calculations must be carried out to determine the original volume that must be collected to give the desired measurable level of the parameter. For example, if V_1, is the volume calculated from the use of M_s and R, then the required original volume V_o is obtained from the product of V_1 and the volume reduction factor. For a volume reduction of 100, V_o would be $100V_1$.

The Ingamells' Equation:

$$WR^2 = K_s \qquad (2.4)$$

can be applied to measurements involving bottom sediment samples. W represents the weight of the sample analyzed, R has the same meaning as in Equation 2.3, while K_s replaces M_s in the same equation.

Whether volumes or weights are being considered, every effort should be made to assure homogeneity in the sample matrix before any sub-sampling is carried out.

2.6 Field and Laboratory Analytical Practices

The sampling plan must consider the role of good field and laboratory analytical practices. The basic QA/QC field testing and laboratory analytical protocols that will be adopted, must be spelled out in the sampling plan. For the laboratory, the scope of both the intra- and inter-laboratory QA/QC programs should be referenced, and should be consistent with the size of available resources.

The sensitivity of each analytical method is an important characteristic, and must be known. The precision and accuracy of measurements must reflect the level of confidence placed on the measurements.

The accuracy required from the measuring system should be determined by the objectives of the sampling program, and by the use of the data. The measurement system should avoid superfluous and expensive accuracy and precision determinations if there is a failure in the monitoring program to meet the stipulated objectives. The analytical measurements must also be rugged and complete.

2.7 Data Quality Objectives

Data generated from the sampling program must possess a number of quality factors if they are to be used objectively in judging the water quality, and if correct and unbiased management decisions are to be made.

All data used in examining and diagnosing water quality should be accompanied by the following characteristics:

(a) accuracy;
(b) precision;
(c) completeness;
(d) method detection limit (MDL);
(e) representativeness;
(f) traceability;

and should be suitable to meet network objectives. Accuracy, precision, completeness and the Method Detection Limit are established through accepted statistical principles, and are distinguishable from other quality characteristics by their quantifiability.

Another aspect of data quality, relates to data comparability and compatibility among similar data sets from agencies involved in water quality monitoring. To achieve data comparability and compatibility, a number of steps must be taken. These include:

(a) employing techniques and practices that can be duplicated at different locations and times, and by different agencies;

(b) providing results that can be understood and tested on a comparative basis;

(c) reducing systematic errors and increasing comparability between measurements by additional interlaboratory sample testing exercises; and,

(d) using certified reference materials, and/or carefully selected natural areas as common reference sites, especially when there is a need to compare the results from different existing measurements.

The achievement of data quality objectives can often be difficult. Limitations of resources, methodologies, equipment and technical expertise may reduce the quality and amount of data collected. However, any consideration of the limitations associated with the data collection process should lead to the establishment of objectives that adequately satisfy the goals of the project.

2.8 The Use of Statistical Analysis

One of the basic aims of the Water Quality Branch's monitoring program is to provide representative water quality data that can be understood and tested on a statistical or comparative basis. The most appropriate statistical techniques must be employed to produce comprehensive analyses and interpretations (Gaskin, 1988).

The choice of appropriate statistical analyses should flow logically from the objective(s) of the sampling or monitoring study, the null hypothesis, and the sampling plan. The hypothesis model should determine the statistical model.

An efficient statistical analysis method should be as conservative, powerful and robust as possible (Green, 1979). If it is conservative, it will have a low probability α of making the Type I-Error. If the statistical method is powerful, it will have a low probability β of making the Type II-Error. If the method is robust, the stipulated error levels will not be seriously affected by the kinds of data commonly encountered in environmental studies.

Over-complicated statistical approaches should be avoided as much as possible, and results of the statistical analysis should always be reported in a form that is understandable by the data users.

2.9 Cost Considerations

Quality costs for environmental monitoring systems have been treated by Rhodes and Hochheiser (1971), and by Strong et al (1980). Table 2.1 is an example of how quality costs can be itemized by category, group and activity.

Program managers involved with water quality monitoring programs must be concerned with program cost-effectiveness. The operation of a quality cost system would help to minimize the cost of operational activities which are directed toward controlling data quality. The basic concept of the quality cost system is to minimize total quality costs through proper allocation of planned expenditures for the quality assurance and quality control efforts, while maintaining an acceptable level of data quality.

The quality cost system structure provides a means of identification of quality-related activities and for organization of these activities into prevention, appraisal, and failure cost categories. These categories are defined as follows:

- Prevention Costs are associated with planned activities whose purpose is to ensure the collection of data of acceptable quality and to prevent the generation of data of unacceptable quality.

- Appraisal Costs are associated with measurement and evaluation of data quality. This includes the measurement and evaluation of materials, equipment, and processes used to obtain quality data.

- Failure Costs are incurred directly by the monitoring agency or organization producing the failure (unacceptable data).

TABLE 2.1

TOTAL QUALITY COST SUMMARY

COST GROUP	1st QUARTER	2nd QUARTER	3rd QUARTER	4th QUARTER
	$	$	$	$
PREVENTION				
Planning & Documentation				
Procurement				
Training				
Preventive Maintenance				
System Calibration & Operation				
TOTAL PREVENTION COSTS				
APPRAISAL				
QC Measures				
Audits				
Data Validation				
QA Assessment & Reporting				
TOTAL APPRAISAL COSTS				
FAILURE				
Problem Investigation				
Corrective Action				
Lost Data (Unacquired Data)				
TOTAL FAILURE COSTS				
TOTAL QUALITY COSTS				

There is no pre-set formula for determining the optimum mode of operation. Rather, the cost effectiveness of quality costs is optimized through an iterative process requiring a continuing analysis and evaluation effort. Maximum benefits are realized when the system is applied to a specific measurement method in a stable long-term monitoring program. For example, a monitoring program with a fixed number of monitoring sites, scheduled to operate for more than one year, would be a desirable candidate for a quality cost system.

The size and diversity of a water quality monitoring operation is an important determining factor in decisions related to formalization of the QA program. Operations concerned with defined programs of work may be more easily adaptable to formal QA activities, and the program costs can be easily justified. For operations involving numerous repetitive measurements as in the case of WQB monitoring activities, a formal quality assurance program is a necessity, and the time and effort devoted to its development should be compensated by cost-effective reliable analytical data. The overall cost of the activities should not exceed 10-15% of the total operational effort, and 'repeats' and lost data should be minimized.

3.0 TRAINING OF FIELD PERSONNEL

All personnel involved in sample collection, field analysis, data reduction, and quality control procedures must be adequately trained. They must be made aware of the importance of obtaining data of known quality, must become familiar with the quality assurance program, and must be knowledgeable of the various ways of achieving and maintaining good quality data.

Training personnel for field operations will involve a broad range of disciplines, because of the diversified requirements (mechanical, physical, chemical, biological, hydrological, etc.).

Personnel training must start before operations begin, and must continue during operations, with periodic reviews and retaining when indicated.

In order to maintain and foster consistency in the quality of collected data, all field personnel (particularly new employees) should become familiar with project objectives, sampling protocols, station location, equipment operation, and safety rules prior to the commencement of field work.

Lay sampling personnel (i.e. persons engaged in water quality sampling for the WQB but are not employees of the Branch) should be strictly supervised until it is fully demonstrated that they can conduct the required operations in the desired manner. In cases where provincial staff are involved in water quality sampling activities (e.g. Federal-Provincial Water Quality Monitoring Agreement Programs), proper training should be given by WQB personnel. Training may take the form of a course on 'Water Quality Sampling' with hands-on participation. Station micro-locations and initial sampling runs should be conducted as a collaborative effort between personnel of the two agencies, in order to ensure compatibility between provincial and federal procedures.

Suggestions for general on-the-job training for sampling and field testing personnel, include:

(a) Studying operation manuals and the sampling program plan.

(b) Observing a trained and experienced operator perform the various tasks in the data collection process.

(c) Performing field operations under the direct supervision of a trained and experienced person, and then independently performing operations related to instruments, sample collection, sample analysis, and data handling.

(d) Attending and participating in in-house seminars which are directed towards problem solving and confidence building.

(e) Gaining experience and acquiring new skills and technical information through interchange programs between the various regions, in cases where the interchange becomes a beneficial exercise.

(f) Announced and un-announced periodic proficiency testing of operational personnel to determine the need for additional training.

4.0 FIELD TRIP PREPARATION

Before starting out on a water quality data collection trip, field personnel should determine the types of samples that are to be collected and the field measurements required in order to assemble the proper sampling and testing equipment. field personnel should also determine that the equipment being transported to the field is in good working order and that there are spares available for those pieces of equipment which are hard to replace once out in the field. The present WQB field manual ('Sampling for Water Quality', 1983) gives a detailed outline of necessary preparation for field trips. The preparation deals with:

(a) obtaining specific instructions on sampling procedures;

(b) preparation of an itinerary according to the sampling schedule;

(c) preparation of lists of required equipment, supplies and materials;

(d) ensuring that all sample bottles and bottle covers have been cleaned in accordance with standard procedures, and that they are safely packed;

(e) ensuring that the laboratory has prepared the chemical reagents and standards needed for trip; and,

(f) preparation of checklist (including road maps, station location descriptions, field sampling sheets, labels, equipment manuals, tool box, etc.).

An additional pre-sampling preparation that is necessary for some regions, is the consultation of the project flow chart or project description manual (Program outline) in order to determine which sites are to be sampled in sequential triplicate (as part of the field quality control program) on a particular sampling trip.

4.1 Selection of Sampling Equipment

The collection of water samples requires the use of a variety of sampling equipment depending on the station, the medium to be sampled and the parameter list. Generally, the Water Quality Branch has used sampling irons, discrete samplers such as the Kemmerer sampler and the Van Dorn bottle, multiple samplers, dissolved oxygen samplers, and sediment grab samplers. The choice of sampler type must be closely related to the parameter list in order to avoid sample contamination. Past experience with the PVC Kemmerer-Plus has indicated contamination of 'heavy metal' samples (Arseneault and Howell, 1987). In addition to being parameter and station specific, samplers must be such that they provide suitable sample volumes, and are suitable for use in a wide variety of environmental conditions.

4.2 Sample Bottles

Sample bottles are generally provided by the analytical laboratory. The selected bottles (including the liners and caps) must be free of contamination and suitable for the water quality parameters to be analyzed. Table 3.1 gives a description of the recommended containers for specific parameters, and also outlines the bottle washing and preparation procedures used for ensuring the cleanliness of the sample bottles. the volume of sample required depends on the type and number of parameters to be analyzed, the analytical method, and the expected concentrations of the parameters in the water.

Recommended sample containers, washing and preparation procedures associated with the collection of suspended sediment and bottom sediment samples, are outlined in the document, 'Sampling for Water Quality' (Environment Canada, 1983).

Prior to sampling, every bottle (or sample container) should be rinsed twice with the water to be sampled. During the rinsing process, bottle caps should be put on loosely to ensure adequate rinsing of the cap, liner and bottle threads. If replicate samples are taken, every set of bottles should be rinsed twice and then filled, one set after the other (i.e. sequentially).

Proper labelling of the sample bottle is necessary to avoid possible mistakes and confusion when the sample arrives at the laboratory.

TABLE 4.1

RECOMMENDED CONTAINERS AND WASHING PROCEDURES FOR SELECTED WATER QUALITY PARAMETERS

PARAMETER(S) TO BE ANALYZED	RECOMMENDED CONTAINER	WASHING PROCEDURE
Physical Parameters Major Ions Nitrogen: NO_2/NO_3 Nitrogen: NH_3 Nitrogen Total Dissolved Organic Carbon Dissolved Inorganic Carbon	1 L Polyethylene Bottle	Rinse 3 times with tap water, once with chromic acid, 3 times with tap water, once with 1:1 nitric acid, and then 3 times with distilled water in the given order.
Suspended Solids	2 L Polyethylene Bottle	Same as for physical parameters.
Phosphorus, Total	0.5 L Glass (Sovirel) Bottle	Rinse 3 times with tap water, once with chromic acid, 3 times with tap water, once with 1:1 nitric acid and then 3 times with ultra-pure distilled water, in the given order.

PARAMETER(S) TO BE ANALYZED	RECOMMENDED CONTAINER	WASHING PROCEDURE
Metals, Extractable	0.5 Polyethylene Bottle	Rinse 3 times with tap water, once with chromic acid, 3 times with tap water, once with 1:1 nitric acid and then 3 times with ultra-pure distilled water, in the given order.
Chromium, Extractable	0.25 L Polyethylene Bottle	Same as for metals but chromic acid is not used.
Mercury	0.125 L Glass (Sovirel) Bottle	Rinse 3 times with tap water, once with chromic acid, 3 times with tap water, once with 1:1 nitric acid and then 3 times with ultra-pure distilled water, in the given order.

PARAMETER(S) TO BE ANALYZED	RECOMMENDED CONTAINER	WASHING PROCEDURE
Organic Toxic Chemicals	1L or 4L Glass (Amber) Bottles with Teflon-Lined Cap	Rinse 3 times with tap water, once with chromic acid, 3 times with organic free water, twice with washing acetone, twice with pesticide grade hexane, and dry the uncapped bottle in a hot air oven at 360°C for at least 1 hour.
UREA	1 L Glass (Amber) Bottle	Same as for organic toxic chemicals.

All sample and sub-sample containers must be affixed with a strip of vinyl labelling tape when the containers are warm and dry. The NAQUADAT station number, sampling date and time, parameter(s) to be analyzed, and the program submitter identification (Sub. I.D.) must be clearly printed on each container with a water-proof fine tipped nylon marker. Blank bottles should be similarly identified using a special NAQUADAT number that has been reserved for the identification of field blank samples.

5.0 ACCESSIBILITY TO SAMPLING SITES

Ready accessibility to some sampling stations which extend across the width of a water body, can sometimes be difficult, and it is therefore customary to find a number of WQB stations located on bridges. The main station is generally located at the mid-point, and additional stations are established when spatial discontinuities are expected. All stations are located by permanent identification marks on the bridge structures.

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

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

Some WQB stations require that samples be collected from the shore, which also results in QA/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.

Some samples are collected from stations which require the use of aluminum boats, rubber rafts and occasionally, helicopters. Use of these means of transport must be project specific with particular emphasis placed on the parameter list. Thus if heavy metals are the major concern, the rubber boat should be used, while the aluminum boat is more suitable for the toxic organics program.

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.

For lakes which have poor accessibility, it is often necessary to use a helicopter, and this increases the risk of contamination of samples for toxic organic chemicals with fuel and kerosene fumes. Thus the data obtained from helicopter sampling of toxic organic chemicals must be viewed with extreme caution (Arseneault and Howell, 1987).

6.0 WATER QUALITY SAMPLING

6.1 Sample Representativeness

For new sampling programs, pilot projects should be conducted to resolve logistic problems and implement procedures that would support the objectives for reaching the program goals. This should include an evaluation of each collection site by investigating temporal and spatial homogeneity. Also, the collection frequency for priority variables, sample size, preservation effectiveness, shipping efficiency, and minimization of contamination risks could be determined or checked at this stage. In addition, proper sampling techniques must be used to insure that a sample is representative of the flow in the sampled cross-section.

The number of verticals to be samples in a cross-section should relate primarily to the collection of a representative sample and secondarily to the volume of the sample required (Kister et al., 1983). If field measurements of specific conductance, temperature, pH and dissolved oxygen show the water to be well mixed, then a sample obtained at a single vertical near the centroid of the flow may be assumed to be representative of the total flow.

In situ measurements of pH, temperature, specific conductance and dissolved oxygen should be taken before actual water samples are collected, in order to minimize water column disturbance caused by the lowering and raising of the sampling apparatus. This is particularly important in the case of residence time waterbodies, and during periods of ice cover when the vertical distribution of many parameters may be highly variable. Once the in situ measurements are conducted, water samples may be collected, starting at the surface and proceeding down through the water column if applicable. Collection of sediment samples should be performed after all water column samples have been taken.

Samples that are to be collected for suspended sediment, or samples to be analysed for total constituents should be collected by using approved and properly treated water-sediment depth-integrating samplers. Suggested instances (Kister et al., 1983) where use of these samplers are not required are as follows:

(a) Extreme low flow where use of the sediment sampler is impractical. Samples may be collected by immersing the bottle by hand.

(b) Flood conditions when velocity of flow is so great that the sampler cannot be lowered.

(c) Samples collected for dissolved chemical constituents that are well mixed within the sampled cross-section.

(d) The necessity for aseptic collection techniques for bacteriological samples. Consequently, these samples can be collected at a single vertical near the centroid of flow, or by immersing the sample bottle by hand (when the water source is shallow).

In sampling for suspended sediment, cross-section samples should be obtained at every opportunity, using either the 'Equal Discharge Increment' (EDI) or 'Equal Width Increment' method to obtain cross-section coefficients to apply to the point samples obtained by the sampler (Guy et al., 1970).

6.2 Automatic Sampling

In many instances, particularly in accessible remote areas, automatic samplers are used very effectively. In comparison to manual sampling, automatic sampling can be more cost effective at remote sites than manual sampling. The cost-effectiveness is closely linked to the instrument's reliability, improved capabilities and greater sampling frequency ability.

For the efficient and effective use of an automatic water quality sampler, flow data should be available at every sampling station where the sampler is used. Flow data can provide a sound basis for interpretation of water quality results.

Unfortunately, automatic samplers are limited in their application. The sample handling procedures required in quantitative measurements for a wide range of water quality parameters (nutrients, major ions, total metals, toxic organics, etc.), make it virtually impossible to use automatic sampling for detecting and measuring parameters other than: dissolved oxygen (DO), pH, specific conductance, temperature, colour and turbidity.

Samples collected at remote sites by automatic samplers should be retrieved at the earliest possible time. Samples collected in this manner should be analyzed only for constituents that do not require on-site preparation and could be assumed to be representative of the associated flow event.

High concentrations of suspended solids and floating materials can limit the performance of automatic samplers and reduce the accuracy of the measurements made. Suspended sediment samples collected by automatic samplers should be analyzed individually, and the specific conductance should be measured for each sample. This helps to determine the sample representativeness of the individual samples.

Periodic manual sampling should be conducted to verify the accuracy and representativeness of results obtained from automatic samplers, and in selecting these instruments for limited water quality monitoring, attention must be paid to such factors as:

- The range of intended use.
- The level of accuracy desired.
- The skill level required for installing and servicing the automatic sampler.
- Mechanical reliability of the sampler.
- Adaptability of the sampler to varying weather patterns and flow regimes.
- Cost of the sampler.

6.3 Sampling in Winter Conditions

The Water Quality Branch conducts its monitoring program throughout the entire year, and must deal with a number of QA/QC problems during winter sampling, where ice conditions and low temperatures have considerable influence on sampling protocols (Arseneault and Howell, 1987). Heavy ice conditions at many sites require the use of power ice augers and thus contamination of toxic organic chemical samples by gasolines and oils must be considered.

During thaw periods, there is often a layer of melt water immediately under the ice, and this water is not representative of the water chemistry of the system. Thus care must be taken to ensure that samples are collected from a stratum that is below the ice-water interface.

The in-situ measurement of pH, specific conductance, temperature and dissolved oxygen during winter conditions, must be carefully scrutinized, since some of the measurement meters (e.g. pH meters) do not function well in cold temperatures. Conductivity meters such as the Hydro TC-2 may give erroneous results (usually biased low) if slush or ice is allowed to build up around the thermistor or in the conductivity cell (Arseneault and Howell, 1987). Similarly, dissolved oxygen probes can also suffer from build up of ice and slush around the membrane. Therefore, in these winter conditions it may be necessary to determine dissolved oxygen concentrations by the Winkler method, even though BOD bottle breakage and DO sampler freeze-up can also cause difficulties.

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

7.0 SAMPLING FOR SPECIFIC PARAMETERS IN SPECIFIC MATRICES

7.1 Toxic Chemicals in Water

Many pesticides and heavy metals are toxic to aquatic life even when these parameters are in low concentrations. The toxicity of a particular substance is dependent to a large extent on other water quality characteristics such as temperature, pH, alkalinity and dissolved oxygen. The complex nature of toxic chemicals (particularly trace organic toxic chemicals) demands the application of a number of QA/QC efforts which are additional to those generally used for less complex substances.

Although this section will focus on trace organic toxic chemical sampling, preservation and analysis, the protocols and procedures that are outlined can be applied (with less complexity) to trace inorganic toxic chemicals (metals).

In the toxic chemical monitoring programs, water, bottom sediments, fish (forage and predator) and other biota samples are collected and analyzed.

7.1.1 Toxic Organic Chemicals

Sampling for toxic organic chemicals in water is conducted in a manner similar to any other type of water sample collection. Customarily, 4L amber glass bottles with teflon-lined caps are used, and rinsing of these bottles in the field is not required. Sample preservation is carried out using the procedures listed in Table 7.1.

Recently, a number of improved field QA/QC procedures have been instituted by the Water Quality Branch, Atlantic Region (Arseneault and Howell, 1987) with regards to toxic chemical survey projects. These procedures include the following:

- preparation of field blanks;
- preparation of spiked field blanks;
- preparation of spiked field samples (often in replicates);
- sequential replicate sampling; and,
- preservation of spiked blanks and samples a few hours after spiking, to permit prolonged interaction between sample matrix and spiking solution.

In the preparation of a field blank, distilled deionized water is first added to a sample bottle prior to the field trip. The appropriate preservative is then added to the water blank in the field at the same time the collected samples are being preserved. The resulting blank is called a field blank. The field blank is used to check on:

(a) the cleanliness of sample containers;
(b) random field contamination; and,
(c) the purity of added preservatives.

In addition, solvent blanks are also run during the analytical determinations in the laboratory.

Prior to its use in the blanks' preparation, the distilled or deionized water should be checked for its purity in the laboratory. It is possible that the water may require some treatment (solvent extraction, filtering through XAD type resin columns, etc.) before it is suitable for the required use.

Preparation of spiked field blanks is also required to check on the recovery of a spiked analyte of interest in a 'clean' matrix. Spiking solutions are prepared by laboratory personnel prior to field trips. Preparation of spiked field blanks also serves to monitor the stability of the spiking solution in a 'clean' matrix, and to check the accuracy of its preparation. The analytical results of the spiked field blanks and the spiked field samples (which are prepared at the same time in the field) are compared to see if the analytical measurement process is indicating analyte recovery at the same level in a natural sample (matrix effects) as in a blank (no matrix effects).

Spikes are prepared by using an appropriate micro-syringe (which has been previously rinsed with solvent) to add a precise volume (generally 100 to 200 µL) of a spiking solution (of known concentration) into blanks and/or regular samples. All field personnel involved in the preparation of spikes should be trained in the correct use of a micro-syringe. Larger volumes of less concentrated spiking solutions may be appropriate for the preparation of spikes. This could minimize possible manipulation errors when a spiking solution is added to a sample.

TABLE 7.1
PROCEDURES USED FOR THE PRESERVATION* OF WATER SAMPLES COLLECTED FOR TOXIC CHEMICAL ANALYSES

PARAMETER	PRESERVATION
PESTICIDES - Organochlorine - Organophosphorous POLYAROMATIC HYDROCARBONS POLYCHLORINATED BIPHENYLS	Add 200 ml of hexane per 4 L sample (in a 4.5 L amber glass bottle), shake well and deliver to the laboratory as soon as possible. Place a piece of aluminum foil over the mouth of the bottle before screwing on the cover (except when they are teflon liners in the cap).
CHLOROPHENOLS	Adjust to pH 4 with 25% H_2SO_4
CARBAMATES	Adjust to pH 3 with 25% H_2SO_4
CHLOROBENZENES sample	Add 50 ml of hexane per 1 L and shake.
TRIAZINES	Adjust to pH 8 with 0.1N NaOH solution, add 200 ml of methylene chloride per 4.5 L sample and shake.

*All samples are kept as cool as possible in the field.

Spiked samples are generally prepared in duplicate or triplicate in the field, to verify the reproducibility of spike recoveries, and to gain a better understanding of the spiking process (matrix effects, systematic errors, etc.). Replication of spikes on all occasions is recommended. Based on resource availability, duplication of spikes could be an acceptable minimum, although triplication would possibly provide more information.

The addition of preservative to spiked blanks and spiked samples should be carried out a few hours after spiking; this time delay permits physical interaction between the sample matrix and the spiking solution.

In reporting the analytical results on thes spikes, both the absolute concentrations and the percent recoveries should be reported by the laboratory.

The frequency with which this set of field QA/QC samples, namely, blanks, spiked blanks, spiked samples (in replicate) should be prepared, would be dictated by the water quality study or project and available resources.

Random 'Sequential Replicate Sampling' (See Section 8.0) should also be conducted regularly in addition to the above activities. Conducting sequential replicate sampling for 10-15% of all samples collected, may be an adequate level of operation for the toxic chemicals QA/QC program. This sampling replication provides a means of monitoring the short-term variability of the parameters of interest. Additionally, the replication program in concert with information obtained from other field QA/QC samples, may permit the discernment of contamination problems and/or contamination sources.

7.1.2 Liquid-Liquid Extraction Techniques

The use of liquid-liquid extraction techniques by the National Water Research Institute (NWRI) in collaboration with the WQB has permitted the detection of very low concentration (sub-ppt) of organic contaminants (Fox, 1985; Environment Canada, 1987). In the extraction process, large quantities of solvent are needed for 40 litre samples, and the purity of the solvent must be assured. When the 40L sample is filtered by the extractor (e.g. CRAB APLE Extractor), the suspended solids retained on the filter can also be kept for analyses.

The CRAB APLE Extractor is relatively inexpensive and readily available. Water collection, filtration and extraction of both phases can be accomplished in less than an hour. Fox (1985) presented some data on recoveries of organochlorines in spiked organic free water and natural Lake Ontario water. In general, recoveries were very good. However, this was limited to organochlorine contaminants, and thorough testing of this extractor is being conducted for other contaminants of interest.

Future studies involving the CRAB APLE and other extractors should address a number of QA/QC aspects such as the preparation of field blanks and field spikes, to verify the recoveries attained by the extraction techniques, and to investigate any possible contamination originating from the use of the extractor.

Another positive aspect associated with the CRAB APLE extraction system, is its capacity for filtering the water and retaining the suspended solids on a filter for analyses. It could be used routinely for this purpose only.

7.1.3 Column Extraction

In the past, use has been made of Amberlite XAD-4 resin columns in the field for sample extraction of fenitrothion and aminocarb in rain water (WQB-Atlantic Region). The rain water was collected and extracted with the aid of a special sampling (collection) device equipped with Amberlite XAD-4 columns. The sample columns were replaced each week by fresh ones and the spent oneswere brought to the laboratory and eluted with an appropriate solvent for the parameters of interest. The parameters were then identified and quantified analytically. After elution, the columns were regenerated with specific solvents, wrapped in clean aluminum foil and returned to the field. It is possible that these types of extraction columns could have some field application in the extraction of large volumes of surface water for the determination of specific organic contaminants (Woodrow et al., 1986; Leenheer and Noyes, 1984). However, one drawback associated with resin columns, is the requirement of exhaustive cleaning with various solvents to remove all trace contaminants. Preparation of blanks, spiked blanks, spiked samples (in replicate) and sequential replicate sampling should be included as part of the specific QA/QC procedures that are needed, if these Amberlite XAD-4 resin columns (or others) are used more extensively in the future.

The inclusion of QA/QC procedures would assist in routinely checking the purity of the resin column(s), the cleanliness of the apparatus, the recoveries attained by the extraction and elution processes, the reproducibility of the extraction and elution efficiencies, and the representativeness of the water samples.

7.2 Toxic Chemicals in Bottom Sediment

The general procedures employed by the Water Quality Branch for obtaining bottom sediment samples, involve:

(a) The use of a 15x15 cm or 30x30 cm Ekman Grab sampler as the collection device.

(b) Transferring the sample to a pyrex tray.

(c) Removing the top 2.0 cm of sediments for toxic organic chemical analysis. The selection of this sample portion is carried out using an aluminum scoop.

(d) Obtaining a sample for heavy metal determinations, using a plastic scoop. The sub-sample is taken from the centre of the grab sample to avoid sediments which have been in direct contact with the dredge.

In addition to the first grab, three or more grabs are taken, and the top 2.0 cm of sediments of each grab are put in a large plastic or stainless steel bowl (depending on the type of analyses required). The three or more portions are mixed together, using an appropriate scoop to obtain a well homegenized sample. Sub-samples (often triplicate splits) are then placed in individual aluminum containers or in the case of samples to be analyzed for metals, they are placed in whirl pak polyethylene bags and frozen until they are used for analysis (Arseneault and Howell, 1987).

All apparatus and containers involved in the collection and storage of sediment samples for organics are pre-washed and rinsed with acetone and hexane.

In addition to the determination of the concentrations of the selected parameters, each bottom sediment sample is characterised by measuring water content and percent organic carbon (CHN analysis). This information is essential for the interpretation of results from the toxic chemicals' analysis. In some studies, samples are also characterized through particle size analyses. 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. This approach obviously places a bias on the sampling site selection, but adherence to the criterion (for the specific sediment constituents) must be encouraged (Arseneault and Howell, 1987).

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 parameters 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.

As is the case with the water matrix, spiking of bottom sediment subsamples with organic contaminant standard solutions is carried out regularly in the field. About 20.0 gm of bottom sediments are weighed in a pre-washed aluminum sample container. Then 100 or 200 µL of spiking solution are added and thoroughly mixed with the sample. Following this, the container is closed and stored in a freezer (Arseneault and Howell, 1987).

It is felt that the present containers used for holding the 20 gm of spiked samples should be replaced with smaller ones, in an effort to prevent or reduce th risk of volatilization of some of the spiked contaminants. The WQB-Atlantic Region has made a switch to 50 ml pre-washed sovirel bottles for the preparation of spiked bottom sediment samples. The sovirel containers appear to be better suited than the aluminum containers for housing the bottom sediment samples, where toxic organic chemicals are the parameters of interest (Arseneault et al., 1987).

At present there is no 'bona fide' body of reference samples of bottom sediments that can be used to prepare spiked field blanks, and it is proposed that a bank of reference material be prepared for this purpose. As is the case for water, blanks and spiked blanks are needed to check on contamination caused by containers, and on accuracy, reproducibility, stability and recovery efficiency of the spiking process.

The reference bottom sediment bank could consist of a large bottom sediment sample which would be previously approved by NWRI and NWQL through subsample analyses and spiked subsample recoveries. The banked sample would have to be sterilized and kept this way in order to eliminate any biological activity that could have an effect on the integrity of the added spiking solutions, when the spiked field blanks are prepared. For storing and handling purposes, it may be better to dry the bottom sediment sample, and re-humidify portions of it as needed. With the use of the prepared standard reference material, comparisons can be made between spiked sample and spiked blank recoveries. This approach could permit a better interpretation of the analytical results.

Some QA/QC testing of the storing procedure presently used for bottom sediments is recommended. As previously noted, bottom sediment samples are frozen after collection, then brought to the laboratory where they are kept frozen until analysis. Samples are then thawed, so that an aliquot can be obtained for the analysis of specific parameters. After aliquot extraction(s), the samples are refrozen. Before taking an aliquot, samples are homogenized as best as possible in the container.

As additional aliquots are taken within a few days (or weeks) for analyses of the same or other parameters, the same bottom sediment sample will be re-thawed and refrozen successively. This procedure will be repeated until all analyses and rechecks are completed.

The effect which this multiple thawing and freezing has on the contaminants of interest in a sample, is unknown (Arseneault and Howell, 1987). Also, when the bottom sediment sample undergoes thawing, a water layer is very often observed in the container; the size of the water layer seems to depend on the type of bottom sediments collected. It is uncertain what role the water layer plays in its interaction with the solid sediment component during the thawing period. Perhaps some of the chemicals of interest may be released into the water by the sediment particles. This possibility could be determined by conducting the required analyses on the water component.

Another cause for concern would be the ineffective mixing of the water with the rest of the bottom sediment sample during the re-homogenizing process, should there be some of the chemicals of interest in the water as a result of the thawing action. Some laboratory analysts have also indicated that it is very difficult to properly homogenize thawed bottom sediment samples in the aluminum containers that are presently in use, and that a move to more appropriate containers may be justified.

7.3 Toxic Chemicals in Biota

The collection and interpretation of biological data present more difficulty than in the parallel cases with water and bottom sediment. Many of the organisms collected are mobile, and thus it is difficult to class them as representative of the site from which they are taken. Some water quality investigations involving biological parameters require monitoring or surveillance of an aquatic area over a long period of time. Such systematic re-sampling usually employs either a 'transverse' or a 'longitudinal transect' system, or a 'grid' or 'quadrant' system.

In a stream, transect sampling consists of collecting samples either along a section of its length or along a line across the stream. In a lake or a reservoir, it consists of collecting samples along a line which may be delineated by buoys. Samples may be collected at uniform intervals along the transect line or at random location selected with the help of a table of random numbers.

A sampling grid or quadrant consists of an imaginary or physical rectangular arrangement of lines, covering all or part of a given habitat. For example, assume that a riffle measuring 10x30 square metres is to be sampled for benthic organisms. If a 1 m^2 sampling device is used, there are potentially 300 sampling units, each of which could be assigned a number. If 15 sampling units are to be sampled, they may be selected by numbers taken from a table of random numbers (Snedecor, 1956; Snedecor and Cochran, 1967), or in some other randomized fashion. A grid or quadrant sampling scheme should, as with the transect scheme, give equal consideration to the various habitat types.

Regardless of the type or purpose of the biological sampling study, sample collection should be designed on a meaningful basis. A large number of samples collected at the wrong time or place have less value than a few samples carefully selected as to time and place of collection. The frequency of sample collection will depend on the variability of environmental and biological factors and on the study objectives. The greater the habitat variability, the more intensive the sampling program must be. Life history events of the organisms also must be considered in the design of a sampling program. Some organisms have two or more generations a year; others have but one. Moreover, many aquatic insects spend only the juvenile period of their lives in water, emerging just prior to the adult transformation. In lakes and reservoirs, phytoplankton and zooplankton succeed one another in a somewhat rhythmic fashion; one may be abundant while the other is scarce. Vertical and horizontal movements of phytoplankton and zooplankton also are common in lakes and reservoirs. These facts, plus many others, increase the variability of the results of biological investigations.

In spite of the temporal and spatial variability of aquatic populations, statistical techniques are available for the design of sampling programs and for the evaluation of biological data. References on the subject of statistical sampling an analysis are Snedecor (1956), Steel and Torrie (1960), Stanley (1963), and Snedecor and Cochran (1967). Specific work on sampling statistics in aquatic biology has been reported by Needham and Usinger (1956), Ricker (1958, 1971), Elliot (1971) and Chutter (1972).

A number of biological sampling activities of the Water Quality Branch is centred around the collection of fish, with occasional sampling of freshwater clams, macrophytes, phytoplankton and zooplankton. Fish are collected by gill and seine netting, depending on the species required. For toxic organic and inorganic chemical analyses, small size fish species (forage fish) are pooled in order to provide adequate sample volumes while large fish are dissected, and the egg mass, livers and muscle are analyzed separately. Care must be taken during dissection to avoid cross-contamination of samples. Samples are stored in aluminum containers or aluminum foil (for toxic organic chemical analyses) or plastic bags (for metals' analyses) and frozen until analysis.

In the quality assurance program for biota sampling, attempts must be made at maintaining statistically significant sample sizes for each site. In addition, where appropriate, factors such as population size, size of habitat, feeding habits, weight, sex, lipid content and geographical disposition of habitat (relative to industrial sites, agricultural lands and developments, waste dumps and sewage inputs) should be determined to help in data interpretation.

Selection of discrete samples of the aquatic biota should be random, and the mean of five or more measurements on individual samples should be determined in order to give representative values of the parameters of interest during the laboratory analysis stage.

All dissecting equipment and sample containers must be pre-washed appropriately, and dissection of fish by WQB personnel should be carried out preferably at the collection site in order to reduce the risk of contamination from avoidable extraneous sources.

In the shallow littoral zone, freshwater clams may be collected by hand, and in deeper regions by a benthic drag. The clams may be shucked and pooled to provide adequate sample volumes, and then stored in a manner similar to the storage of fish tissue.

Information on Species' identification, sex, shell length, total weight and body weights should be gathered. As in the case of fish species, this information could prove useful for data interpretation during consideration of toxic organic and/or inorganic chemicals' concentrations.

The infrequency in the sampling of macrophytes, phytoplanktons and zooplanktons has resulted in a lack of established standardized QA procedures for treating the collection and preservation of these entities, and has made it necessary at the present time to treat these classes of aquatic biota in a similar fashion to fish and freshwater clams.

Field spiking of biota should be attempted in those cases where a sample processor (grinder, homogenizer) of some type is available to prepare and mix samples with spiking solutions. Precaution against field contamination would be required during the extra manipulations of cutting, grinding (homogenizing) and extraction of the homogenate. Wherever possible, the laboratory should regularly prepare spiked samples, in order to verify the efficiency of the employed analytical process (Arseneault and Howell, 1987).

7.4 Toxic Chemicals in Packed Snow

Sample collection in packed snow can be accomplished by excavating a pit to the full depth of the annual snow pack, such that a clean cross-section is available for sampling. The pit should be dugged with a clean acetone rinsed metallic shovel or teflon coated aluminum shovel; the shovel should be subsequently cleaned in nearby snow (Sandberg et al., 1986). The bags in which the snow is placed, should either be sealed air-tight at the snow pit site or should be folded close and sealed air-tight at the first possible opportunity.

Several centimetres (in depth) of snow should be left undisturbed at the bottom of the pit so as to minimize incorporation of terrestrial material other than that which is incorporated within the profile through wind action. Additional samples could be taken in wide mouth 500 ml polyethylene containers for the purpose of determining snow density. The polyethylene containers should be filled in such a way as to represent the entire section (as density varies with layers), thereby providing a composite density measurement. Whenever possible, replication should be effected.

Once the sample (consisting of a number of boxes of snow per site) is melted, the water can be extracted using a continuous flow liquid/liquid extractor (Gregor, 1987). Dichloromethane is the solvent employed for the extraction, and this solvent should be kept sealed until its use is required at the extraction site. The dichloromethane should be pretested for impurities prior to use, and DCM blanks must be submitted to the laboratory with the samples.

The bottles used to hold the samples along with the cap-liners must be previously washed, rinsed with pesticide grade acetone and hexane, then baked for eight hours prior to being sealed and shipped to the sampling or operational site. The bottles with their contents are sealed and stored frozen until shipped to the laboratory.

Samples for metals and trace elements should be placed in 250 ml teflon bottles which are previously washed in accordance to WQB bottle washing procedures (Environment Canada, 1983) and double rinsed with sample water. Preservation should be carried out using 1 ml of 50% HNO_3 with subsequent refrigeration until delivery to the laboratory.

Major ion samples should be stored in 1 L polyethylene bottles which are pre-washed and subsequently double rinsed with sample water. These samples are then refrigerated until delivery to the laboratory.

The in-field liquid phase continuous flow extraction technique is useful for the extraction of organic compounds, and provides detection of the ultra-trace concentrations expected in the snow. In addition, the extraction technique helps to minimize the possibility of sample contamination and simplifies the logistics and expense of shipping large quantities of samples from the snow pack region (e.g. the Arctic Region) to a laboratory which is thousands of miles away.

Refined QA/QC protocols for snow pack sampling will evolve as the frequency of this type of sampling increases.

An abridged description of precipitation sampling including QA/QC general procedures for site selection, sample collection and handling, is outlined in 'Sampling for Water Quality' (Environment Canada, 1983). A more detailed account of this sampling activity can be found in the CANSAP Manual, the Canadian Network for Sampling Precipitation (Atmospheric Research Directorate, 1980).

Effective QA/QC procedures in the area of toxic organic chemical investigations related to aquatic sources are steadily evolving, and greater statistical confidence is being attached to both field and laboratory measurements. However, there is still a long way to go before the point is reached where specific QA/QC practices and protocols for toxic organic chemicals in various matrices (water, bottom sediment, biota) are comparable in effectiveness to those employed in the area of inorganic parameters in water.

7.5 Bacterial Sample Collection

Samples for bacteriological examination must be collected in bottles that have been carefully cleaned and autoclaved for approximately 20 minutes at 121°C at 15 psi. Also, glassware, except when in metal containers, may be sterilized in an hot-air oven for not less than 1 hour at a temperature of 170°C. Glassware in metal containers may be sterilized at 170°C for not less than 2 hours (USGS, 1977).

Samples from shallow streams should be collected from a single vertical near the centroid of flow by wading. When collecting the sample, field personnel should face upstream, holding the collection bottle near its base, and immersing the bottle with its mouth directed towards the current.

Samples from deep streams can be collected from a bridge or cableway with a weighted bottle by immersing the sampler at a single vertical near the centroid of flow. The empty sampler should be immersed in the stream before the sample bottle is inserted in order to avoid the possibility of contamination of the sample. When the sample is collected, air space should be left in the bottle to facilitate mixing of the sample.

Bacteriological determinations should be commenced as soon as possible after sample collection, preferably within 1 hour and not more than 6 hours after sample collection. Samples must be chilled in ice during the time between collection and filtration. However, samples must not be subjected to freezing.

Residual chlorine in a water sample will destroy the biological population and may prevent an accurate determination of bacteria in the sample, unless the chlorine is destroyed at the time of sample collection. Therefore, if a sample from a haligenated water supply is taken, 1.0 ml of 10 percent solution of sodium thiosulphate should be added to the 1-litre sample bottle, before sterilization in the field service unit. This reagent should neutralize about 15 mg/L of residual chlorine in the sample, and should show no effect upon variability or growth (Kister and Garrett, 1983).

7.6 Sampling for Radioactive Parameters

Limited QA/QC directives are outlined for the 'Sampling of Radioactive Parameters' in the manual on Sampling for Water Quality (Environment Canada, 1983). Additional principles and guidelines will evolve in this area as more specific sampling operations are conducted in aquatic systems which receive their radioactive pollutants from the major sources of radioactivity (e.g. uranium mining, nuclear power industries, nuclear weapons testing, and the peaceful applications of nuclear materials and devices).

8.0 SEQUENTIAL TRIPLICATE SAMPLING

The 'Sequential Triplicate Sampling' program is designed to assess the efficiency and effectiveness of the overall water quality monitoring program. The program serves to evaluate whether the water sampling performed is representative; it aids in discerning contamination and/or analytical problems; and, reveals problems associated with water quality data management. Overall, the sequential triplicate sampling program covers the entire quality assurance picture by providing some information on the combination of field, laboratory, and data management components. When a problem is revealed through the use of sequential triplicate sampling, other quality control measures (field and/or laboratory) can be used to elucidate and correct that problem (Arseneault and Howell, 1987).

Sequential triplicate sampling may not define the exact source(s) of a problem, but can be used as an aid in determining the cause(s) of the problem.

Triplicate sampling is more effective than duplicate sampling; the use of three replicates delivers more statistical information than the use of two replicates. Higher replication (quadruplicates, quintuplicates, etc.) would be more statistically significant, but the increase cost could possibly outweigh the benefit of the potential additional information. In cases where there are very specific problems (re: sampling, preservation, contamination, storage, analysis, etc.), increase repeat sampling may be deemed necessary in order to provide conclusive experimental and statistical evidence relating to the source(s) of the problems.

In order to conduct a comprehensive evaluation of the triplicate results, it is essential to first define the acceptable degree of reproducibility between triplicate samples. One accepted rule-of-thumb is to set the maximum variation between triplicate results at a level of 10% (Arseneault and Howell, 1985). The arbitrary limit depends to some extent on the complexity of any or all of the stages within the monitoring program for any given parameter or suite of parameters. In the case of toxic organic chemicals, the maximum limit could possibly be extended from 10% to 20% for results at sub-ppm and sub-ppt levels or 50% or greater near the detection limit. However, upper parameter based limits of variation should not be chosen in an ad hoc fashion, but should be consistent not only with valid and documented triplication data, but also with parameter associated operational complexities.

The frequency of sequential triplication sampling in a number of WQB regions is presently running at a level of 15-20% of all collected samples. This commitment should remain the same until rigorous data assessments are made of the results collected in the past five to ten years. For those projects which have a small number of stations, one triplicate sample may be collected for each sampling trip, and thus in practice, replication may occur in the range of 20 to 25%.

In order to ensure equal weighting within designated projects, stations to be replicated should be selected from a pre-determined rotational schedule. This approach overcomes the possibility of field technician bias towards easily accessible stations.

Currently, only the median value originating from the three replicate results for each parameter per site, is recorded in the NAQUADAT system. However, it is possible that in the future, more information from the triplication program will be included in the system.

Table 8.1 presents a partial record of the results from a sequential triplicate sampling program conducted by the Water Quality Branch (Atlantic Region) in the period 1984 to 1985.

Over 80% of the variations from the median values were less than 10%, indicating the possibility for achieving substantial success with the program.

The usefulness of a sequential triplicate sampling program and its ultimate success will rest heavily, not only on the efforts that are directed towards the evaluation and interpretation of the collected data, but also on the use of the results from these two data processes.

TABLE 8.1
PARTIAL RESULTS OF SEQUENTIAL TRIPLICATE SAMPLING OF SELECTED STATIONS INCLUDED IN THE NOVA SCOTIA LRTAP LAKES MONITORING PROGRAM (1984-1985)

NAQUADAT DIFFERENCE #	SAMPLE DATE	ALUMINUM (AL) EXTRACTABLE ACTUAL VALUES (MG/L)	ALUMINUM (AL) EXTRACTABLE |%| DIFFERENCE FROM MEDIAN	MANGANESE (MN) EXTRACTABLE ACTUAL VALUES (MG/L)	MANGANESE (MN) EXTRACTABLE |%| FROM MEDIAN
01NS01DA0004	02/05/84	0.110	0	0.02	0
01NS01DA0004	02/05/84	0.110*	-	0.02*	-
01NS01DA0004	02/05/84	0.110	0	0.02	0
01NS01DA0006	02/05/84	0.087*	-	0.02	50.00
01NS01DA0006	02/05/84	0.100	14.94	0.01*	-
01NS01DA0006	02/05/84	0.085	2.30	0.01	0
01NS01DA0007	02/05/84	0.210*	-	0.02	0
01NS01DA0007	02/05/84	0.200	4.76	0.01	50.00
01NS01DA0007	02/05/84	0.220	4.76	0.02*	-
01NS01EA0010	02/05/84	0.100	0	0.02	0
01NS01EA0010	02/05/84	0.100*	-	0.02*	-
01NS01EA0010	02/05/84	0.110	10.00	0.02	0
01NS01ED0013	02/05/84	0.170*	-	0.01	0
01NS01ED0013	02/05/84	0.160	5.88	0.01*	-
01NS01ED0013	02/05/84	0.170	0	0.01	0
01NS01ED0021	02/05/84	0.210	5.00	0.01	0
01NS01ED0021	02/05/84	0.200*	-	0.01*	-
01NS01ED0021	02/05/84	0.200	0	0.01	0
01NS01DA0003	16/10/84	0.014	0	0.01	0
01NS01DA0003	16/10/84	0.014*	-	0.01*	-
01NS01DA0003	16/10/84	0.018	28.57	0.01	0
01NS01EA0002	16/10/84	0.022	0	0.02	0
01NS01EA0002	16/10/84	0.022*	-	0.02*	-
01NS01EA0002	16/10/84	0.022	0	0.02	0
01NS01ED0006	17/10/84	0.043	4.44	0.05	0
01NS01ED0006	17/10/84	0.045*	-	0.05*	-
01NS01ED0006	17/10/84	0.045	0	0.05	0
01NS01ED0008	17/10/84	0.210	8.70	0.01	0
01NS01ED0008	17/10/84	0.240	4.35	0.01*	-
01NS01ED0008	17/10/84	0.230*	-	0.01	0
01NS01ED0010	17/10/84	0.280	9.68	0.01	0
01NS01ED0010	17/10/84	0.320	3.23	0.01*	-
01NS01ED0010	17/10/84	0.310*	-	0.01	0
01NS01ED0013	17/10/84	0.090	3.44	0.01	0
01NS01ED0013	17/10/84	0.065	25.29	0.01*	-
01NS01ED0013	17/10/84	0.087*	-	0.01	0
01NS01ED0017	17/10/84	0.100	0	0.01	0
01NS01ED0017	17/10/84	0.100*	-	0.02	50.00
01NS01ED0017	17/10/84	0.100	0	0.01*	-

* Median Value

9.0 SAMPLE HANDLING, PRESERVATION, STORAGE AND TRANSPORTATION

Efforts must be made to minimize errors that can be introduced as a result of collecting and handling the sample. The objective is to provide the laboratory with a set of samples which closely represent the aquatic environment from which they are taken.

To ensure consistency and efficiency, sample handling (filtration, decantation, centrifugation, sample splitting, etc.) preservation, storage and transportation procedures must be properly and accurately documented, and adhered to by field personnel.

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. Previously, in some regions, large carboys of ultra-pure distilled water were taken on each trip to be used as rinse water and for blank preparation. However, as this water was kept in the containers for varying lengths of time, it was felt that contamination by leaching of materials (e.g. metals) from the walls of the vessel was a possibility.

It is necessary to pass the water sample through a filter of specified porosity, type and quality when a determination of the concentration of dissolved inorganic constituents has to be made. Some filters and filtration apparatus may require laboratory pre-treatment and must also be rinsed with a portion of the collected sample (subsequent to rinsing with ultra-pure water) before the filtrate is collected. The filtrate should be preserved (if required) by adding the proper preservative. The glassware utilized should be specific to the parameter that is to be analyzed. The filtering apparatus should be placed in transportation cases that permit proper storage and provide protection against shock and dirt. The transportation case can also be used as stable work platforms for filtration.

Filtration should be performed at the end of the day, to ensure the same conditions for all samples. A filtration blank for each parameter or suite of parameters should be prepared from ultra-pure distilled water using the same procedure as that used for the sample. At the end of a set of filtration runs, the glassware must be rinsed with an appropriate solution (e.g. diluted acid solution for phosphorous and metal parameters) and afterwards with ultra-pure distilled water. All glassware should be rinsed with ultra-pure distilled water prior to filtration and between filtration of individual samples. The glassware and filter should be rinsed by filtering the excess water, and the sample bottle used for collecting the filtrate rinsed twice with filtrate.

In order to prevent chemical transformation due to photo-oxidative processes and/or biologically mediated reactions, bottles containing samples should be stored in coolers during transportation. Refrigeration at 4°C should be employed for the maintenance of the quality of both preserved and unpreserved water samples. When cooler space is limited, priority should be given to the housing of unpresreved samples in the mobile laboratory's refrigerator. In the absence of a refrigeration unit, 'koolatrons' should be used to keep the samples cooled during transportation.

If a WQB mobile laboratory is not equipped with a refrigerator, field activities and transportation schedules must be planned in such a manner, that it is possible to ensure expedient return of samples to the laboratory.

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 be made to ensure that all samples bottles recorded on the field sampling sheets have been placed in a given carton, before shipping is effected. The shipping date and mode of transport must be indicated on the field sampling sheet.

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

Additional QA/QC information on sample handling, preservation, storage and transportation is given in the WQB manual on "Sampling for Water Quality" (Environment Canada, 1983).

10.0 MAINTENANCE AND CALIBRATION OF INSTRUMENTATION

10.1 General Maintenance and Calibration

The performance of an instrument must be checked out and appraised by a qualified person before being transported to the field. This involves a visual inspection and verification of its operation including the zero and full-scale calibration.

Documents on standardization, calibration, maintenance, equipment safety, and spare parts should accompany each instrument.

Specially designed brief cases should be used to pack and protect each instrument and equipment during transportation. Conductivity meters, pH meters, dissolved oxygen meters, turbidity meters and thermometers should be encased in robust and shock resistant housings, and the electrically operated meters should be open to as little electrostatic and electromagnetic interference as possible. In addition, caution notices for the protection of the equipment during transportation, should be visible, and packing instructions indicating environmental tolerance limits (e.g. in relation to temperature and humidity) should be included in order to prevent the exposure of equipment to conditions that could affect performance.

The standardization of instruments should be performed using reference standards when these are available, or against certified standard instruments. This must be done before the instrument is transported to the field, or in some cases the reference instrument could be transported to the field and employed under actual field conditions. Laboratory standardized instruments should be rechecked upon arrival in the field.

Calibrations must be conducted under the same instrumental and chemical conditions as those that will exist during the measurement process. The frequency of calibration will depend on the accuracy requirements of the investigation and the stability of the instruments. Daily calibration checks are recommended when the instrument is in daily use, or immediately prior to a series of measurments, at other times. For unstable instruments, the calibration should be checked prior to each series of measurements, in-between measurements, and after the last measurement.

The calibration process is vital to all measurement programs and should be governed by a calibration plan. Such a plan should provide for:

(a) Calibration procedures and record forms.

(b) Stated calibrated frequencies.

(c) Appropriate sources for obtaining certified and high quality standards, or the best means of producing accurate in-house standards.

(d) A list of all calibration standards (including nomenclature and assigned identification numbers).

(e) Specifications of environmental conditions.

(f) Intended range of validity.

Calibration procedures should include information on the following:

(i) The specific equipment or groups of equipment to which the procedure is applicable.

(ii) A brief description of the scope, principle, or theory of the calibration method. An example and a reference may also be included.

(iii) Calibration specifications, such as number of calibration points, environmental requirements, precision and accuracy requirements.

(iv) A list of the calibration standards and accessory equipment needed to perform an effective calibration; manufacturer's name and instrument model number.

(v) A complete, clear and concise, step-by-step written calibration procedure.

(vi) Specifications for calibration facilities, equipment, temperature and humidity; and also physical protection for calibration standards.

(vii) Specific instructions for obtaining and recording the test data. Data forms should also be furnished.

Pre- and post-shipping checks may verify the performance of an instrument during its operation, and could reveal the occurrence of measurement drift.

10.2 Maintenance of Specific Instrumentation

The precision thermistor temperature sensor of the Hydrolab Model TC-2 should be checked at least every 6 months against an ASTM Certified Mercury Thermometer in the laboratory at controlled temperatures which span the range of temperatures encountered in the field.

The four-electrode configured specific conductance cell of the Hydrolab Model TC-2 should be ckecked before the commencement of each field trip. The check should be performed against the specific conductance of two freshly prepared standards at the 74µs/cm and 177µs/cm levels. Calibration can be routinely carried out at each sampling site by switching to the provided internal standards.

The combination glass electrode should be calibrated daily in the field at pH values of 7.0 and 4.0 using commercially prepared buffers that are kept at a temperature difference of ±1.0°C from the sampling temperature. If the temperature of the pH buffers is not ±1.0°C from that of the sample(s), it is adjusted by placing the buffer bottles in a colder or hotter water bath or in cold air (during winter), whichever is applicable.

Calibration curves should be prepared for each range of the turbidity meter by using appropriate standards that have a range of 0 to 1000 nephelometric turbidity units (NTU's). The standards are generally supplied by the manufacturer, but can be prepared from stock standard turbidity suspensions. Tests should be conducted on at least one standard in each range to be used.

The YSI (Yellow Springs Instrument) Dissolved Oxygen probe should be visually examined prior to a field trip, to check the condition of the membrane. Defective membranes must be replaced. The instrument should be tested each day at the first site by using the 'Azide Modification of the Standard Iodiometric Method' (with freshly prepared reagents) on two samples. The resulting values should be averaged, and the meter then set (with the calibration knob) to read the average value of the samples. On the same day, only air calibrations need be performed at the other sites. Calibration of the meter can also be accomplished using a calibration chamber, in which the Dissolved Oxygen probe is placed, and then immersing the chamber in the stream or lake to carry out the measurement. The latter approach provides an adequate environment for proper calibration.

All equipment must be kept clean and in good working condition, using the techniques described by the manufacturer and/or by those techniques set out in the Field Methods Manual.

Each instrument should have a log book detailing its operational history, and all data originating from checks, calibrations and standardizations should be recorded in the log book as support data.

11.0 FIELD TESTING

11.1 Quantitative Analysis

11.1.1 Application and Scope

This practice is applicable to: field analyses involving the use of automated measurements for the determination of pH, specific conductance, dissolved oxygen, and turbidity.

11.1.2 Preparation of Standards, Blanks, Reagents and Sample Solutions

Stock standard solutions should be prepared in the laboratory before the sampling trip is undertaken. The stock solutions should be well preserved according to the directions in the analytical method outline (for the particular parameter to be determined).

The intermediate standards must be freshly prepared in the field by the method of serial dilution, just before the commencement of calibration and measurement exercises. A minimum of five to six working level standards spaced evenly over the analytical range should be acceptable.

The blanks must of necessity be composed of the same matrix (deionized water or ultra-pure distilled water) with which the samples, standards and reagent solutions are constituted.

Reagents should preferably be fresh or kept preserved as set out in the Analytical Methods Manual. Note that some reagents will deteriorate with age, or on continuous exposure to such agents as U.V., light and heat.

Whenever possible, modification of the original sample solutions should be avoided, except in cases where operations such as decantation filtration or dilution are deemed necessary.

Accurate volumetric measurement of sample aliquots cannot be overstressed.

11.1.3 Calibration and Measurements

The apparatus should be set up as specified in the appropriate analytical procedure, and the proper analytical working conditions should be selected.

The analytical procedure for calibrating the instrument should be followed, and a complete set of standards (minimum of 5 or 6) should be run. By using blanks at the beginning and end of a calibration run, changes in instrument behaviour may be detected.

When the calibration curve has been satisfactorily constructed, a number of appropriate sample solutions should be chosen, and the values of the parameter of interest should be determined using the calibration curve.

11.1.4 Standard Addition Technique

The method of Standard-Addition (TWRI, 1982) is used to compensate for known matrix effects or analytical interferences which can cause inaccuracies in analyte determinations. This technique is only useful if the measured analytical response is linear with respect to the added quantity of the parameter being determined, and if the observable interference is independent of the same quantity.

Since both samples and standards are affected equally, it is not necessary to prepare matrix water that is comparable to the unknown sample in order to correct the analyses.

In practice a preliminary analysis is made for the water quality parameter of interest, and a blank and three standards containing different amounts (generally multiples of each other) of the parameter to be analyzed are prepared. Equal volumes of the sample are then added to the blank and three standards. The analytical responses are plotted on the vertical axis while the horizontal axis is used for plotting the known quantities of the parameter prior to the addition of the sample. The horizontal axis is extented to the left of the vertical axis and is scaled backwards from the zero (blank) quantity of the analyte of interest.

A line is drawn through the plotted points (Figure 11.1) and then extrapolated to the zero analytical response. The value at the intercept is recorded as the quantity of the parameter in the sample.

11.2 Precision and Accuracy Estimates

For replicate analyses involving precision and accuracy measurements, a value which conveniently lies at a position of either 1/2 or 3/4 of the calibration range is chosen for the parameter of interest. For the 'total precision' estimate (involving collection, handling and analytical processes), measurements must be made on samples collected in replicates, and for the precision estimate related to the collection and handling processes, measurements must be made on sample splits (replicates from a single water sample).

Ideally, for good estimates of both types of precision, no less than 10 repeat measurements should be performed. Five to six replicated measurements may be adequate in situations of time constraints and/or shortfalls in sample volumes or sample collections.

From the determinations of both the total precision (CV_T) and the analytical precision (CV_L), the field sampling and sample handling precision (CV_F) can be calculated with the use of the approximate Equation 11.1.

$$\underset{(CV_F)}{\text{FIELD PRECISION}} = \underset{(CV_T)}{\text{TOTAL PRECISION}} - \underset{(CV_L)}{\text{ANALYTICAL PRECISION}} \qquad (11.1)$$

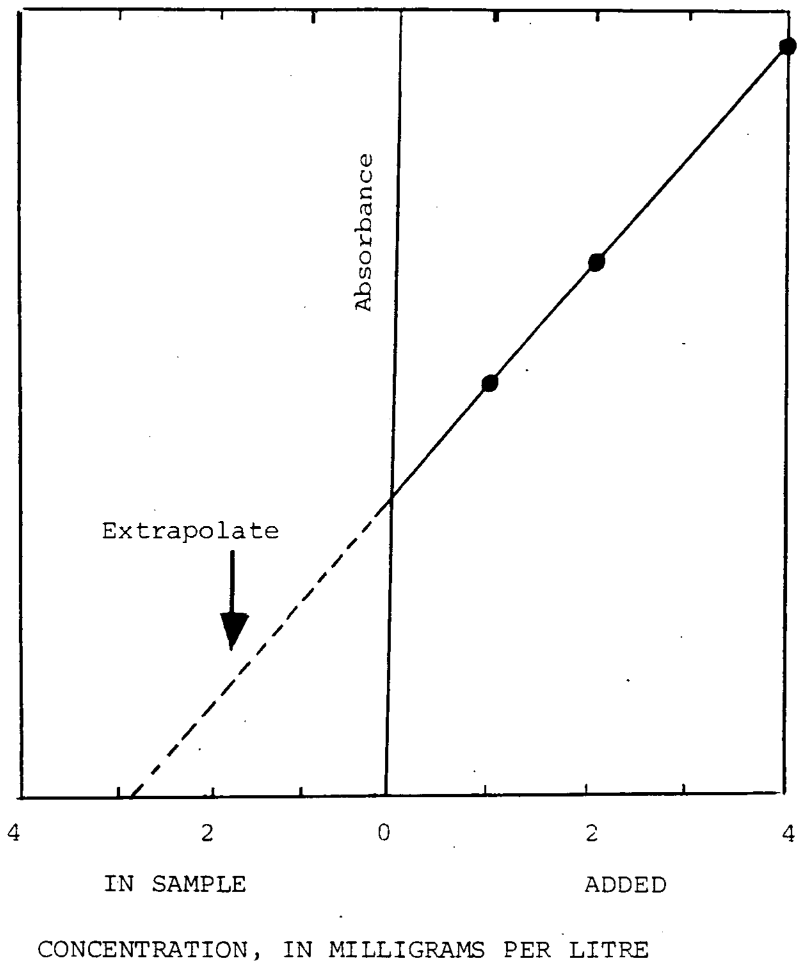


FIGURE 11.1 - Example of Standard-addition Method (from Skougstad et al., 1979).

The coefficient of Variation (CV) otherwise called the Relative Standard Deviation (RSD) is generally used to represent the precision of a set of replicate measurements, and is defined as follows:

$$CV(\%) = \left(\frac{S}{\bar{X}}\right) .100 \qquad (11.2)$$

where for N replicate measurements,

$$\bar{X} = \frac{1}{N} \sum_{i=1}^{N} X_i \qquad (11.3)$$

$$\text{and, } S = \sqrt{\frac{\Sigma (X_i - \bar{X})^2}{N - 1}} \qquad (11.4)$$

If standard reference materials (SRM's) are available, the accuracy of the field analytical measurements can be determined. The accuracy of the determination can be expressed as a percentage error according to Equation 11.5.

$$\% \text{ Error} = \left(\frac{\bar{X} - X_{SRM}}{X_{SRM}}\right) .100 \qquad (11.5)$$

Where: $\bar{X}$ is the mean value of replicate determinations of a standard reference material.

X_{SRM} is the certified value of standard reference material.

In the absence of SRM's it is possible to estimate the accuracy by determining the 'spike recovery' of a given parameter (Agemian et al., 1986). Recovery is calculated on a percentage basis as follows:

$$\% \text{ Recovery} = \left(\frac{C_F - \bar{C}_B}{C_A}\right) .100 \qquad (11.6)$$

Where: C_F is the measured concentration in the sample;

$\bar{C}_B$ is the average concentration of the blank; and,

C_A is the known concentration added to the sample.

The following example outlines the determination of precision and accuracy statistics in field analytical measurements for samples taken from a given site.

EXAMPLE

Field and laboratory analytical measurements (Table 11.1 and 11.2) were analysed for precision and accuracy values, and a comparison was made between field and laboratory results.

TABLE 11.1

SPECIFIC CONDUCTANCE (µs/cm) RESULTS OBTAINED IN THE FIELD

DATA FOR INDIVIDUAL SAMPLES (REPLICATES)		DATA FOR SAMPLE SPLITS		SPIKED AND UNSPIKED BLANKS	
(1)	306.1	(1)	305.0	(1)	0.3 (BLANK)
(2)	305.2	(2)	305.0	(2)	706.2 (SPIKED)
(3)	306.2	(3)	304.4	(3)	706.0 (ADDED)
(4)	307.1	(4)	305.0		
(5)	305.3	(5)	305.2		
(6)	304.5	(6)	305.0		
(7)	305.4	(7)	305.0		
(8)	306.2	(8)	305.0		
(9)	307.0	(9)	305.0		
(10)	308.0	(10)	304.4		

TABLE 11.2

SPECIFIC CONDUCTANCE (µs/cm) RESULTS OBTAINED IN THE LABORATORY

DATA FOR INDIVIDUAL SAMPLES (REPLICATES)		DATA FOR SAMPLE SPLITS		SPIKED AND UNSPIKED BLANKS	
(1)	307.0	(1)	305.0	(1)	0.2 (BLANK)
(2)	306.1	(2)	305.0	(2)	706.4 (SPIKED)
(3)	307.0	(3)	305.2	(3)	706.0 (ADDED)
(4)	306.3	(4)	305.1		
(5)	304.8	(5)	305.0		
(6)	305.2	(6)	305.1		
(7)	305.4	(7)	305.2		
(8)	308.0	(8)	305.1		
(9)	306.2	(9)	304.3		
(10)	306.0	(10)	305.0		

The use of Equation 11.1 permits the calculation of precision values associated with field sampling and sample handling. These precision values (Table 11.3) are larger than the corresponding values obtained for the analytical operation. The higher the numerical value of the precision statistic, the lower the measurement precision.

Precised data for analytical operations can be acquired from measurements which are under statistical control, and should therefore show less variability (greater precision) than the corresponding field sampling and sample handling activities.

Table 11.3 also reveals that the precision and accuracy values which were determined in the laboratory, show only small differences from the corresponding values obtained in the field measurements. This suggests that the samples did not undergo any significant change in constitution during the preservation, storage and transportation phases.

The comparison of field and laboratory statistics pertaining to the same sample(s), can generally serve as an indicator of sample contamination or sample change during the sample handling process; if the difference of the 'Means' (M_d) for the corresponding field and laboratory analytical results is compared with the average standard deviation (S_a), for the same two sets, and,

$$\frac{M_d}{S_a} > 4 \qquad (11.7)$$

TABLE 11.3

PRECISION AND ACCURACY STATISTICS ASSOCIATED WITH FIELD AND LABORATORY MEASUREMENTS OF SPECIFIC CONDUCTANCE

	STATISTIC	FIELD VALUE (%)	REGIONAL LABORATORY VALUE (%)
(1)	TOTAL PRECISION = CV_T (INDIVIDUAL SAMPLES)	$\frac{0.940}{306.1} \times 100$ $= 0.307$	$\frac{0.953}{306.2} \times 100$ $= 0.311$
(2)	ANALYTICAL PRECISION $=CV_L$ (SUBSAMPLES)	$\frac{0.260}{304.9} \times 100$ $= 0.085$	$\frac{0.258}{305.0} \times 100$ $= 0.085$
(3)	PRECISION FOR FIELD SAMPLING AND SAMPLE HANDLING $=CV_F$ ($CV_F=CV_T-CV_L$)	0.222	0.226
(4)	ACCURACY	99.99	100.03

then there exists the possibility that contamination, deterioration or some change has occurred within the sample. In the present example, the application of the criterion gives favourable results.

For example:

$$\frac{306.2 - 306.1}{0.309} = 0.32 \qquad < 4$$

and, $$\frac{305.0 - 304.9}{0.085} = 1.18 \qquad < 4$$

The criterion in Equation (11.7) is arbitrary and only serves as an 'Empirical Test Error' (Taylor, 1984; Gaskin, 1986).

11.3 Measurement Comparisons

Intercomparison programs could be used appropriately to evaluate the performance and variability (bias, precision and accuracy) of any or all of the measurement system. The intercomparison exercises could consist of on-site comparison of different instruments measuring the same parameter. Standard solutions should be used in the measurements.

Unsatisfactory results from intercomparison tests should lead to the reassessment of equipment calibration procedures, frequencies of instrumental checks and calibrations, and operating procedures. Errors in operator performance may also be pinpointed during assessment of the tests results.

12.0 DATA COLLECTION

12.1 Recording Field Data

Accurate and reliable records must be kept of all field data. Detailed accounts of the station and sampling locations must include distances related to specific reference points. Descriptions of the water body should include the banks on either side, the bed material, irregularities in morphology that affect flow or water quality, seasonal conditions, and natural or man-made conditions which may have a bearing on water quality. Wherever and whenever possible, a detailed sketch should be made of the location of the station. A combination of a map which locates the sampling station on a larger scale with respect to roads, highways and towns, and the sketch of station location, should provide complete location information.

The 'station data' form must be completed so that the recorded information can be subsequently stored in NAQUADAT. The information required to complete this form is outlined in the 'NAQUADAT Guide to Interactive Retrieval' (Whitlow and Lamb, 1982), and refers to:

(a) The station number.
(b) Location, as Latitude and Longitude or UTM (Universal Transverse Mercator) coordinates.
(c) Narrative description.
(d) Reference station.
(e) Station parameters.

A number of recordings must be made on the Field Sheets that are issued to the sampling personnel. Records must be made of such items as:

(i) Experimental observations.
(ii) Sampling date.
(iii) Time.
(iv) Location.
(v) Weather patterns.
(vi) Excessive Algae growth.
(vii) Deadfish or debris.
(viii) Grease or oil slicks on the water surface.
(ix) Unusual colour or odour of the water.
(x) A preponderance of leaves and detritus.
(xi) Other phenomena.

An example of a systematic format for recording field analyses and observations, is provided in Figure 12.1.

Particular attention must be paid to quality control requirements for the sampling operation and the field measurements. In addition, records must be kept of the sampling techniques employed (depth-integrated, grab, sequential replication, spatial or temporal sampling), and the data obtained from field analytical determinations must be accurately recorded.

Details regarding either the erratic behaviour or the less than expected performance of any piece of equipment or apparatus must be recorded. These details may later help to explain any anomalies in the experimental data.

12.2 Support Data

Support data are information collected during the measurement program, and their use could play a valuable role during the interpretation process. Support data must be easily available via EDP capability or field and laboratory books. A variety of information may be considered as support data: data charts and printouts, equipment performance records, calibration records, operation logs, environmental conditions (weather patterns, tides, precipitation, etc.) prior to and during sampling, measurement comparison records, quality control and system audit records and records of corrective actions.

Support data are important in determining the validity of the measurement program data, and should be used, for example, in deciding on whether or not an outlier is valid or an artifact.

Ideally, unusual conditions should be recorded on the field data report sheets. Failure to report such circumstances can lead to rejection or misinterpretation of valuable data.

STATION NO. ______________________

DESCRIPTION: ______________________

____

DATE OF SAMPLING DY __________ MO __________ YR __________

TIME OF SAMPLING HR __________ MI __________ TIME ZONE __________

SAMPLED BY ______________________

FIELD MEASURED PARAMETERS

Water Temp. °C __________ Air Temp. °C __________

pH ______ Specific Cond. ______ Diss. Oxygen ______ Turb. ______

Depth of Water __________ Depth at which Sample Taken __________

Ice Thickness ______________________

Other ______________________

Remarks ______________________

____

INSTRUMENT CALIBRATION

Diss. Oxygen Meter Model __________ Winkler Calibration __________ mg/L

Meter Reading before Adjustment __________

Conductivity Meter Model ______________________

pH Meter Model __________ Calibration Buffers Used __________

Remarks ______________________

____

WATER QUANTITY MEASUREMENT DATA

Location Description ______________________

____

Description of Gauge ______________________

Stage Height ______________________

Time ______________________

FIGURE 12.1 General format for a Field sampling sheet.

SAMPLING APPARATUS USED AND PROCEDURES

SAMPLE SPECIFICS

	Container Material	Vol. Collected	Preparation	Quality Control
Major Ions				
Metals				
Organics				
Pesticides & Herbicides				
Mercury				
Phenols				
Nutrients				
BOD & COD				
BACTI				
OTHERS				

QUALITY CONTROL REMARKS

GENERAL REMARKS

MODE OF TRANSPORT

SHIPPING DATE

Figure 12.1. General format for a field sampling sheet (cont'd)

13.0 CHAIN OF CUSTODY

Complete records must be kept of every transfer of data or samples to an individual, laboratory, or a storage facility. Such records will permit an investigator to determine who had custody of the material and where it was, at any given time. Custody documentation is part of the support data, and should be available for review by an independent auditor.

Transfer documents must be updated and maintained at a central location such as in the office of the program or project manager. These records are of great importance in establishing the validity of any questionable data.

Chain of custody procedures must assure that:

(a) Only authorized personnel handle the sample.
(b) Only the field sampling techniques specified for the measurement program are used.
(c) A record tag is attached to the sample immediately after collection, and the tag should include the following information: program or project identification; sample field number; location; depth; collection date; time; and collector.

(d) Blank samples with and without added chemicals (preservatives) are interspersed with the actual samples.

(e) All record forms are completed.

(f) The transfer of samples is documented.

(g) Transfer procedures provide for proper protection and preservation. For example, if samples are mailed, they should be sent by certified mail with a request for an acknowledgement of receipt.

14.0 FIELD SAFETY

Safety procedures and guidelines affecting every phase of the sampling operation must not only be documented, but must be enforced if accidents and hazardous conditions are to be avoided.

All field personnel must have the 'Field Safety Manual' which gives the procedures and precautions to be observed during the collection of water samples, and personnel must be provided with the appropriate safety equipment (protection hat, boots, float-jackets, security belt, etc.). A knowledge of the provisions of the Canada Labour Code, Part IV as it applies to safety during field operations, is very important.

Brochures, documents and books relating to Field Safety, Laboratory Safety, Occupational Health and Safety, Hazardous chemicals, and Transportation of dangerous goods should be made readily accessible and available to all field personnel. A copy of each document should be kept in the sampling vehicle or the mobile laboratory.

The following are some of the precautionary measures that must be taken during sampling.

- When sampling from bridges, and traffic interference presents a safety hazard, the use of a circular flasher is advised.

- Areas where power lines are strung close to bridges should be avoided.

- Ice thickness should be tested before the commencement of sampling in order to avoid falling through the ice.

- When wading in streams in which unexpected large holes and swift currents may be encountered, and footing becomes unsafe, the use of a wading rod, and attaching the investigator to a rope that is safely enchored, would be useful safety precautions.

- All field personnel should be able to swim as a safeguard against drowning. Life jackets are necessary equipment.

- Boats should be given a thorough servicing prior to the sampling trip. When sampling for an extended period of time in remote areas, an extra motor and emergency rations should be taken along.

- Light airplanes used for transportation to remote areas, and helicopters from which sampling is conducted should also be subject to thorough servicing and evaluations for safety before the commencement of a sampling trip.

- The handling of chemicals requires care. Inhalation of chemical vapours, or chemicals coming into direct contact with the skin, eyes and clothing must always be avoided. Acid and base preservatives or organic extractants must always be carefully stored when not in use. Any spillage of acids or bases should be cleaned up immediately either by dilution with large quantities of water, neutralization, or by careful mopping of the chemical solution followed by disposal of the contaminated material. Spilled organic solvents like n-hexane and dichlonomethane (methylene dichloride) should be sucked up with a mechanical or automatic suction pump, and the waste stored for disposal.

- Rubber gloves, safety eye glasses (goggles) and face masks should be worn by personnel involved in clean-up operations related to chemical spills. Contact of chemicals with skin or eyes should be remedied immediately by washing affected areas with plenty of water, followed by an application of a neutralizing solution (in the case of an accident with a base or acid). Eye or skin injuries should be subsequently treated by a physician.

- Oral pipetting of solutions is forbidden.

- Routine care must be taken to prevent glassware breakage during sampling, packing, unpacking and storage in sub-zero weather.

- Clothing should be appropriate to the season and weather conditions. Survival kits and rations should be taken along on a sampling trip, especially on extended trips, and trips in remote areas. The manual on 'Sampling for Water Quality' (Environment Canada, 1983) gives a list of some of the items and articles that would comprise a survival kit and rations.

- A first aid kit should always be included among the supplies and equipment that are taken on the sampling trip. The Canada Labour Code, Part IV gives a list of items that the first aid kit should contain for various types of field work.

- At least two persons should travel together to collect samples during periods involving either long sampling trips, sampling in wilderness and remote areas, and sampling in hazardous winter and flood conditions.

In addition to the Health and Safety Regulations that are issued by the Treasury Board Secretariat (1982), Labour Canada (1986), Transport Canada (1980) and Consumer and Corporate Affairs Canada (1981), a number of informational texts on Health and Safety Practices in the work-place (field and laboratory) can also be obtained from provincial and territorial agencies.

15.0 FIELD AUDIT PROGRAM

Performance and systems audits must be instituted and should become stable and continuing features in the field quality assurance/quality control program.

The systems audit should consist of a review of the total data production process, which includes on-site reviews of the field's operational systems, the physical facilities for sampling, sample handling, storage and transportation, and the measurement protocols.

The audit system should be used as one of the channels for detecting, flagging and correcting errors or defects at any point in the field QA/QC process.

Guidelines in the audit program should specify who will conduct the audit, what protocols and procedures will be used, and to whom the audit reports will go. Garfield (1984) and Freeberg (1980) have proposed a number of procedures for conducting an audit program for laboratory operations. These procedures and guidelines are easily adaptable to the field sampling and testing operations, since there is a similarity in the mechanics of both types of program (e.g. constructing the audit team; planning prior to the audit; developing audit methods; subjective and objective measurement procedures; evaluating and assessing the audit fundings; and using the audit report to effect change).

16.0 TECHNICAL AND ADVISORY COMMITTEES

Technical and Advisory QA/QC Committees should be established for water quality monitoring programs. The technical and advisory support functions should fall into four broad categories.

(1) Assisting the monitoring program with the most appropriate, up-to-date and effective technical advice, to aid in the production of reliable data.

(2) Developing and implementing a system for continually evaluating the performance of field sampling and testing, laboratory analysis and data management operations, and evaluating the personnel who are involved in these operations.

(3) Regularly evaluating the adequacy of operational methods, instruments and equipment being used.

(4) Enhancing the overall capability and performance of sampling and laboratory analytical activities through corrective actions and training.

On a more definitive basis, the activities of the Technical and Advisory Committee may be associated with the following Terms of Reference:

- To advise on, and recommend measures to ensure the fulfillment of the Quality Assurance/Quality Control objectives of Water Quality Monitoring Programs.

- To assist in improving regional QA/QC programs, by identifying quality defects in procedures and methodologies through the Audit Program, and by suggesting/recommending appropriate corrective actions.

- To ensure that personnel within the Water Quality Branch are properly trained and able to carry out their QA/QC responsibilities.

- To ensure that documentation of QA/QC guidelines, principles and protocols is effected and implemented by all participating groups.

- To provide information, advice and recommendations to operational managers within the Water Quality Branch, concerning all aspects of the WQB QA/QC programs.

- To provide technical assistance and coordination in communicating the WQB QA/QC protocols to collaborating provincial and U.S. agencies, and assist them in implementing identical or compatible methodologies, so that the groundwork for the generation of comparable and compatible data can be established.

- To assist in the implementation and monitoring of the performance of QA/QC programs, so that collected data meet established standards of precision, accuracy, and completeness.

- To organize periodic QA/QC workshops and advanced seminars for WQB personnel, and identify suitable training courses in interdisciplinary areas of water quality monitoring and water quality technology.

Finally, the Technical and Advisory Committee should be responsible for ensuring that the guidance and services provided, are used effectively in all measurement activities.

17.0 REFERENCES

1. Arseneault, R. and G. Howell, 1985. "Field Quality Control/Quality Assurance Program Results of 1984/85 Sequential Triplicate Sampling". Water Quality Branch, Environment Canada, Moncton,, N.B.

2. Arseneault, R. and G. Howell, 1987. "The Water Quality Branch Atlantic Region Field Quality Assurance/Quality Control Program". Version 2, Water Quality Branch, Environment Canada, Moncton, N.B.

3. Atmospheric Research Directorate, 1980. CANSAP Manual, "The Canadian Network for Sampling Precipitation". Atmospheric Environment Service, Environment Canada, Toronto, Ontario.

4. Chutter, F.M., 1972. "A Reappraisal of Needham and Usinger's Data on the Variability of a Stream Fauna when Sampled with a Surber Sampler". Limnology and Oceanography, Vol. 17, No. 1, p. 139-141.

5. Consumer and Corporate Affairs Canada, 1981. "Hazardous Products Act and Regulations". Ottawa, Ontario.

6. Désilets, L., 1986. "Water Quality Branch Strategy for Assessments of Aquatic Environmental Quality, and Criteria for Basin Selection and Sampling Station Macrolocation". Water Quality Branch, Environment Canada, Ottawa-Hull.

7. Elliot, J.M., 1971. "Some Methods for the Statistical Analysis of Samples of Benthic Invertebrates". Freshwater Biol. Assoc. Sci. Pub. 25, 144 p.

8. Environment Canada, 1983. "Sampling for Water Quality". Water Quality Branch, Environment Canada, Ottawa.

9. Environment Canada, 1987. Proceedings: "Workshop on Preconcentration of Trace Organic Compounds from Large Volumes of Water". WQB & NWRI, Canada Centre for Inland Waters, Burlington, Ontario.

10. Fox, M.E., 1985. "A Practical Sampling and Extraction System for the Quantitative Analysis of Sub ng/L of Organochlorine Contaminants in Filtered Water and Suspended Solids". National Water Research Institute, Canada Center for Inland Waters, Environment Canada, Burlington.

11. Freeberg, F.E., 1980. "Optimizing Chemical Laboratory Performance through the Application of Quality Assurance Principles". Garfield, F.M. et al. (Ed.), Association of Official Analytical Chemists, Arlington, Va.; "Meaningful Quality Assurance Program for the Chemical Laboratory", pp. 13-23.

12. Garfield, F.M., 1984. "Quality Assurance Principles for Analytical Laboratories". Association of Official Analytical Chemists, Arlington, Va. 22209, U.S.A.

13. Gaskin, J.E., 1986. "Procedures for the Acquisition of Precision and Accuracy Data in Field Sampling and Field Testing". Water Quality Branch, Environment Canada, Western & Northern Region, Regina, Saskatchewan.

14. Gaskin, J.E., 1988. "Quality Assurance Principles and Guidelines for Water Quality Data Management". Water Quality Branch, Environment Canada, Ottawa.

15. Green, R.H., 1979. "Sampling Design and Statistical Methods for Environmental Biologists; Wiley - Interscience Publication, John Wiley & Sons, New York, Toronto.

16. Gregor, D.J., 1987. "Evidence of Atmospheric Transport and Deposition of Toxic Substances in Canadian Arctic Snow". WQB, Environment Canada, Western & Northern Region, Regina, Saskatchewan.

17. Guy, H.P., and V.W. Norman, 1970. "Field Methods for Measurement of Fluvial Sediments"; Techniques of Water Resources Investigations of the United States Geological Survey, Book 3, U.S. Government Print. Off., Washington, D.C.

18. Ingamells, C.O. and P. Switzer, 1973. Talanta, Vol. 20, p. 547.

19. Kister, L.R. and W.B. Garrett, 1983. "Field Guidelines for Collection, Treatment and Analysis of Water Samples". Arizona District, Arizona.

20. Kittrell, F.W., 1969. "A Practical Guide to Water Quality Studies of Streams". U.S. Department of the Interior; Federal Water Pollution Control Administration, CWR-5. Washington, D.C. 20402.

21. Labour Canada, 1986. "Canada Occupational Safety and Health Regulations", SOR/86/304; Canada Gazette Part II, p. 1105.

22. Leenheer, J.A. and T.I. Noyes, 1984. "A Filtration and Column Adsorption System for On-site Concentration and Fractionation of Organic Substances from Large Volumes of water. U.S. Geological Survey Water-Supply Paper 2230, Washington.

23. Needham, P.R. and R.L. Usinger, 1956. "Variability in the macrofauna of a single riffle in Prosser Creek, California, as indicated by the Surber Sampler: Hilgardia, V. 24, No. 14, p. 383-409.

24. Rhodes, R.C. and S. Hochheiser, 1971. "Quality Costs for Environmental Monitoring Systems". American Society for Quality Control, Technical Conference, Vol. 77, p. 151.

25. Ricker, W.E., 1958. "Handbook of Computations for Biological Statistics of Fish Populations: Ottawa, Fisheries Research Board, Canada Bull., 119, 300 p.

26. Ricket, W.E., etc., 1971. "Methods for Assessment of Fish Production in Freshwaters (2nd ed.): Internat. Biol. Programme Hand. 3, 326 p.; Oxford and Edingburgh, Blackwell Sci. Pubs.

27. Sandberg, D.K., N.R. McQuaker, R.J. Vet and H.A. Weibe, 1986. "Snowpack: Recommended Methods for Sampling and Site Selection". Federal/Provincial Research and Monitoring Coordinating Committee, Quality Assurance Subgroup, Downsview, Ontario, Canada.

28. Sanders, T.G., R.C. Ward, J.C. Loftis, T.D. Steele, D.D. Adrian and V. Yevjevich, 1983. "Design of Networks for Monitoring Water Quality". Water Resources Publications, Littleton, Colorado 80161, U.S.A.

29. Skougstad, M.W., M.J. Fishman, L.C. Friedman, D.E. Erdman and S.S. Duncan, eds., 1979. "Methods for the Analysis of Inorganic Substances in Water and Fluvial Sediment". U.S. Geological Survey Techniques of Water Resources Investigations, Book 5, Chapter Al, p. 32.

30. Snedecor, G.W., 1956. "Statistical Methods Applied to Experiments in Agriculture" (5th ed.). Iowa State Univ. Press, 534 p.

31. Snedecor, G.W. and W.G. Cochran, 1967. "Statistical Methods (6th ed.). Iowa State Univ. Press, 593 p.

32. Stanley, J., 1963. "The Essence of Biometry". Montreal, McGill Univ. Press, 147 p.

33. Stanley, T.W. and .S. Verner, (1985). "The U.S. Environmental Protection Agency's Quality Assurance Program"; Quality Assurance for Environmental Measurements, ASTM STP 867, J.K. Taylor and T.W. Stanley, Eds., American Society for Testing and Materials, Philadelphia.

34. Steel, R.G.D. and J.H. Torrie, 1960. "Principles and Procedures of Statistics". New York, McGraw-Hill Book Co., Inc., 481 p.

35. Strong, R.B., J.H. White and F. Smith, 1980. "Guidelines for the Development and Implementation of a Quality Cost System for Air Pollution Measurement Programs". Research Triangle Institute, Research Triangle Park, North Carolina; EPA Contract No. 68-02-2722.

36. Taylor, J.K., 1984. "Quality Assurance of Chemical Measurements". Center for Analytical Chemistry, National Bureau of Standards, Gaithersburg, MD 20899.

37. Transport Canada, 1980. "Transportation of Dangerous Goods Act and Regulations". Ottawa, Ontario.

38. Treasury Board Secretariat, 1982. "Personnel Management Manual". Personnel Policy Branch, BT-32-19-1/1982, Vol. 12.

39. TWRI (Techniques of Water-Resources Investigations of the United States Geological Survey), 1977. "Methods for Collection and Analysis of Aquatic Biological and Microbiological Samples". Book 5, Laboratory Analysis Chapter A4; USGS, U.S.A.

40. Whitlow, S. and M. Lamb, 1983. "NAQUADAT Guide to Interactive Retrieval". Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa, Canada.

41. Woodrow, J.E., M.S. Majewski and J.N. Seiber, 1986. Environ. Sci. Health, B21(2):143.

18.0 GLOSSARY

ACCURACY -	The nearness, of a result or the mean of a set of results, to the true or accepted value.
ALTERNATIVE HYPOTHESIS -	A statement which provides an alternative or opposite claim to that made in the Null Hypothesis.
ANALYTE -	The specific component measured in a chemical analysis; also called 'analate'.
ARITHMETIC MEAN -	The sum of observations divided by their number; also called 'average'.
BIAS -	A system displacement of all the observations in a sample from the true or accepted value; or a systematic and consistent error in test results.

BLANK -	The measured value obtained when a specified component of a sample is not present during the measurement. In such a case, the measured value/signal for the component is believed to be due to artifacts, hence should be deducted from a measured value to give a new value due to the component in a sample. The blank measurement must be made so that the correction process is valid.
CALIBRATION -	Comparison of a measurement standard of instrument with another standard or instrument to report or eliminate by adjustment, any variation (deviation) in the accuracy of the item being compared.
CERTIFIED REFERENCE MATERIAL (CRM) -	A reference material, one or more of whose property values are certified by a technically valid procedure, accompanied by or traceable to a certificate, or other documentation which is issued by a certifying body.

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.
CONFIDENCE INTERVAL -	That range of values, calculated from an estimate of the mean and the standard deviation, which is expected to include the population mean with a stated level of confidence. Confidence intervals in the same context also may be calculated for standard deviations, lines, slopes and points.
COMPOSITE SAMPLE -	A sample composed of two or more increments selected to represent a population of interest.
DEPTH-INTEGRATED SAMPLE -	A sample which represents the water suspended sediment mixture throughout the water column so that the contribution to the sample from each point is proportional to the flow velocity at that point.

DETECTION LIMIT -	The smallest concentration or value of measurement that can be determined with a specified degree of precision and accuracy, utilizing a specific analytical method.
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.
ERROR -	Difference between the true or expected value and the measured value of quantity or parameter.
FORAGE FISH -	Small fish which reproduce prolifically and are used as prey by predatory fishes. Forage fish are used to monitor the water quality in rivers.
GOAL -	This is a short term, planned measurable result, to be achieved within a given time frame (usually not more than one year) and contributes to the overall attainment of objectives. Well-defined goals are stated in terms of the result or output.

HOMOGENEITY -	The degree to which a property or substance is randomly and uniformly distributed throughout a material. Homegeneity depends on the size of the sub-sample under consideration. Thus a mixture of two minerals may be non-homogeneous (heterogeneous) at the molecular or atomic level but homogeneous at the particulate level.
LITTORAL -	Pertaining to the shore line; either as existing, taking place upon, or adjacent to the shore.
METHOD -	An assemblage of measurement techniques and the order in which they are used.
NETWORK DESIGN -	The term 'Network Design' can be defined as the activity involved in determining the placement of sampling points, the calculation of sampling frequencies, and the selection of water quality variables to measure in a hydrologically and statistically sound manner.
NULL HYPOTHESIS -	A statement made in support of a proposal or claim prior to the use of experimentation to test the claim.

OBJECTIVE -	This is a statement of intended output to be achieved in a time of 3 to 5 years. The objective should express, in concrete terms, the quantity and quality of results expected and the period in which they are to be achieved.
PARAMETER -	The word 'parameter' as used in Water Quality Monitoring, denotes any physical, chemical or biological entity that can be determined qualitatively and/or quantitatively. In other scientific fields (besides water pollution) the term 'variable' is used in place of parameter.
POPULATION -	A generic term denoting any finite or infinite collection of individual things, objects, or events; in the broadest sense, it is an aggregate determined by some property that distinguishes between things that do and do not belong.
PRECISION -	The degree of mutual agreement characteristic of independent measurements as the result of repeated application of the process under specified conditions. It is concerned with the closeness between the replicated measurements.

PREVENTIVE MAINTENANCE -	An orderly program of positive actions for preventing failure of equipment and ensuring, in so far as possible, that the equipment is operating with the reliability required for quality results.
PROBABILITY -	The likelihood of the occurrence of any particular form of an event, estimated as the ratio of the number of ways or times that the event may occur in that form, to the total number of ways that it could occur in any form.
PROCEDURE -	A set of systematic instructions for using a method of measurement or of sampling or of the steps or operations associated with such.
PROTOCOL -	A procedure specified to be used when performing a measurement or related operation, as a condition to obtain results that could be acceptable to the specifier.
QUALITY -	An estimation of acceptability or suitability for a given purpose of an object, item, tangible or intangible thing.

QUALITY ASSESSMENT -	The overall system of activities whose purpose is to provide assurance that the quality control activities are being done effectively. It involves a continuing evaluation of performance of the production system and the quality of the products produced.
QUALITY ASSURANCE -	A system of activities whose purpose is to provide to the producer or user of a product or a service the assurance that it meets defined standards of quality. It consists of two separate but related activities, quality control and quality assessment.
QUALITY ASSURANCE MANUAL -	A written document that identifies the policies, organization, objectives, functional activities, and specific quality assurance activities designed to achieve the quality goal that is desired for the operation of a given program.
QUALITY CONTROL -	The overall system of activities whose purpose is to control the quality of a product or service so that it meets the needs of users. The aim is to provide quality that is satisfactory, adequate, dependable and economic.

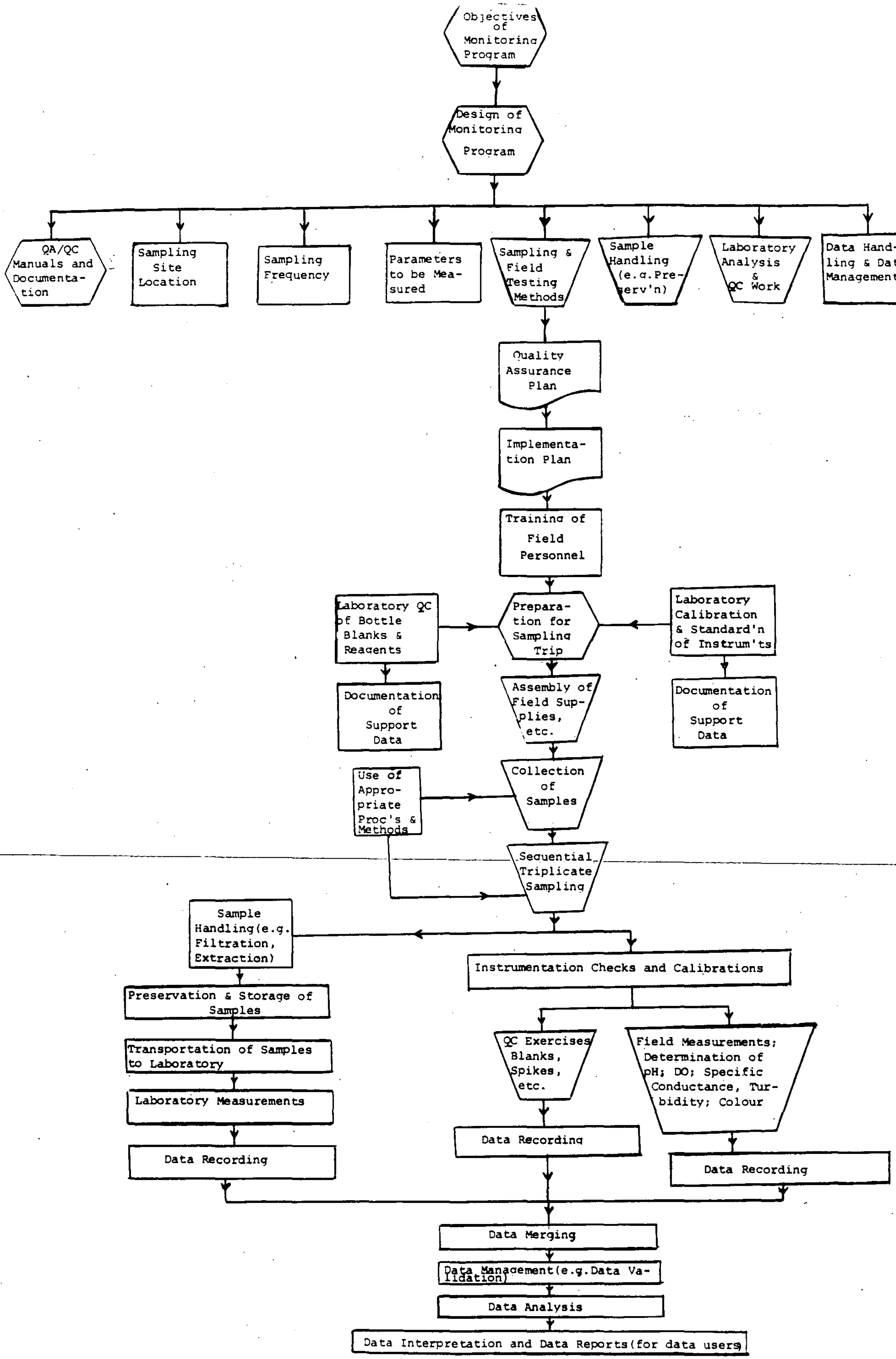
RANDOM SAMPLE -	A sample selected from a population, using a randomization process.
RANDOM SAMPLING -	Selecting a sample from a population in such a manner that each sample has an equal chance of being selected.
REFERENCE MATERIAL (RM) -	A material or substance possessing one or more properties which are sufficiently well established to be used for the calibration of an apparatus or the assessment of a measurement method, or for the assignment of values to materials.
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.
REPLICATES -	Repeated but independent determinations on the same sample by the same analyst at essentially the same time and under the same conditions. The term also applies to repeated and independent choices made on the same population at the same time (or in sequence, in a limited prescribed time period) and under the same conditions.

REPRESENTATIVE SAMPLE -	A subset or group of objects or things selected from a larger set designated as a 'lot' or population, so that each selected subset has the defined characteristics of the 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.
RUGGEDNESS TESTS -	A series of tests performed to empirically determine the sensitivity of the measurement system to variations of certain factors that are suspected to affect the method.
SAFETY -	A quality of being devoid of whatever exposes one to danger or harm; freedom from danger or hazards.
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 DEVIATION -	The square root of the variance of a set of values.
STANDARDIZATION -	The process whereby the value of a potential standard is fixed by measurement with respect to a standard of known value.
STANDARD METHOD -	A method (or procedure) of test developed by a standards-writing organization, based on concensus opinion or other criteria, and often evaluated for its reliability by a collaborative testing procedure.
STANDARD OPERATIONS PROCEDURE (SOP) -	A procedure adopted for repetitive use when performing a specific measurement or sampling operation. It may be a standard method or one developed by the user.
STANDARD REFERENCE MATERIAL (SRM) -	A reference material distributed and certified by the National Bureau of Standards or any such body or agency.
STATISTICS -	The term 'Statistics' as used by the mathematician, involves collecting numerical information called 'data', analyzing it, and making meaningful decisions based upon the data.

SUB-SAMPLE -	A portion taken from a sample. A laboratory sample may be a sub-sample of a gross sample; similarly, a test portion may be a sub-sample of a laboratory sample.
SYSTEMATIC ERRORS -	Errors which can, at least in principle, be ascribed to definite causes, are termed 'determinate' or 'systematic' errors.
TECHNIQUE -	A physical or chemical principle utilized separately or in combination with other techniques to determine the composition (analysis) of materials.
TEST PORTION -	(Sometimes called specimen, test unit or aliquot) is that quantity of a material of proper size for measurement of the property of interest. Test portions may be taken from the gross sample directly, but often preliminary operations, such as mixing or further reduction in particle size, are necessary.
TRACEABILITY	The ability to trace the source of uncertainty of a measurement or a measured value.

TRAINING -	Formal or informal instruction designed to provide competence of a specific nature.
TYPE I ERROR -	Rejecting a true or Null Hypothesis in favour of the alternative Hypothesis, is called a TYPE I - ERROR.
TYPE II ERROR -	Failure to reject the Null Hypothesis in favour of the Alternative Hypothesis is called a TYPE II - ERROR.
UNCERTAINTY -	The range of values within which the true value is estimated to lie. It is a best estimate of possible inaccuracy due to both random and systematic errors.
VALIDATION -	The process by which a sample, measurement method, or a piece of data is deemed to be useful for a specified purpose.
VARIANCE -	Mathematically, this is the sum of the squares of the difference between the individual values of a set and the arithmetic mean of the set, divided by one less than the number of values.



APPENDIX 1 : FLOW CHART OF QA/QC ACTIVITIES FOR WATER QUALITY SAMPLING
(the arrows only serve to outline the general sequential steps)

INDEX

A

Accessibility to Sampling
  Sites 15, 41
Accuracy 2, 3, 26, 89
Analyses
  CHN 57
  Field 90, 92
  Laboratory 90, 92
  Replicate 87
Appraisal Costs 29
Audit
  Operation 106
  Systems 106
Automatic Sampling 45

B

Bacterial Sampling
  Collection 67
Bacteriological
  Examination 67
Blanks
  Field 50
  Spiked Field 50, 51

C

Calibration 85
Chain of Custody 100
Column Extraction 55
Confidence
  Interval 20
  Level 22
Contamination Problems 43
Cost Considerations 28
Crab APLE Extractor 54
Cross-sectional Sampling 42

D

Data
  Collection 95
  Collection Activities 3
  Comparability 2, 3, 26
  Compatibility 2, 3, 26
  Completeness 2, 3, 26
  Quality Objectives 26
  Recording 95
  Reduction 4
  Reporting 4
  Validation 4
  Verification 4
Discharge Measurement 17

E

Error
  Type I 28
  Type II 28
Estimates
  Accuracy 89
  Precision 87
Extraction
  Column 55
  Liquid/Liquid 54, 66

F

Failure Costs 29
Field
  Audit Program 106
  Practices 25
  Sheet 98
  Testing 84
  Trip Preparation 35
First Aid 105

G

Gauging Station 16, 17

H

Health and Safety Regulations 105
Hydro-Lab 81
Hypotheses
  Acceptance of 19
  Alternative (H_a) 19
  Null (H_0) 19

I

Interpretive Reports 28

L

Labelling 76
Laboratory Analytical Practices 25
Lateral and Vertical Mixing 16
Littoral Zone 64
Locations
  Macro 8, 13
  Micro 8, 12
Log Book 83

M

Maintenance and Calibration
  General 78
  Preventive 5
  Remedial 5
  Specfic 81
Management
  Committee 6
  Documents 2, 6
Materials
  Standard Reference 59, 89
  Certified Standard
  Reference 59
Matrix Effects 51
Measurement Comparisons 94
Method Detection Limit 26

N

Network Design 4
Number
  Identification 40
  NAQUADAT 40
  Station 40

O

Outliers 97

P

Performance Indicators 6
Pilot Survey 8, 10, 11
Power Ice Augers 47
Precision
  Analytical 87
  Field 87
  Total 87
Precipitation Sampling 67
Prevention Costs 29
Procedures
  Interlaboratory QC 5
  Preservation 52
Proficiency Testing 5
Program Implementation Plan 6
Project
  Description 3
  Identification 2

Q

Quality Assurance
  Implementation Plan 3
  Manual 5
  Plan 2
  Project Plan 3, 5
  Reports 4
QA/QC
  Documentation 2, 13
  Principles and
  Procedures 1, 12
  Strategy 7
Quality Control
  Checks 4
  Internal 4
Quality Cost 29

R

Radioactive Parameters 69
Replicate
  Sampling 5
  Samples 9
  Analyses 5
Representativeness 1, 5
Representative Sample
Responsibility
  Centres 6
  Designated 5
Risk Factors 6
River Stretch Approach 13
Ruggedness 3

S

Sample
  Bottles 37
  Containers 37
  Contamination 70, 92
  Custody 5
  Filtration 75
  Handling
  Preservation
  Representativeness 43
  Size 9, 20
  Storage 74
  Transportation 77
Samplers
  Automatic 36
  Discrete 36
  Multiple 36

Samples
  Bottom Sediment 37
  Major Ions 66
  Metals 66
  Spiked Field 50
  Suspended Sediment 37
  Trace Elements 66
Sampling
  Automatic 45
  Date 96
  Design 19
  For Radioactive Parameters 69
  For Specific Parameters 49
  Frequency 20
  Grid 61
  In Winter Conditions 47
  Procedures 3
  Program Plan 10
  Sites 4
  Time 96
Selection
  of Lake Sampling Stations 14
  of River Sampling Stations 13
  of Sampling Equipment 36
  of Stream Sampling Stations 15
Sequential Triplicate Sampling 70
Site
  Documentation 13, 17
  Evaluation 10
  Selection 10
Spikes 51, 53, 64
Standard Addition Technique 86
Standard Normal Deviate 21
Station
  Data Form 95
  Multiple 21
  Single 20, 21
Statistical Analysis 27
Statistical Techniques 62
Support Data 97

T

Technical and Advisory Committee 107
Toxic Chemicals
  In Water 49
  In Biota 61
  In Bottom Sediments 56
  In Packed Snow 65
Toxic Organic Chemicals 49
Training 32
Transportation of Samples 76
Triplicate Sampling 70
Turnaround Times 6

V

Variables
  Criteria 20
  Predictor 20
Variance
  Temporal 14
  Spatial 14
Van Dorn Bottle 36

X

XAD Columns 55