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MANUAL ON WATER-QUALITY MONITORING

PLANNING AND IMPLEMENTATION OF SAMPLING AND FIELD TESTING

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NOTE

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FOREWORD

In the context of its present-day definition, the assessment of water resources requires that due consideration be given to both the quantitative and qualitative aspects. However, while attention to water quantity dates as far back as man's interest in its storage and utilization, focus on water-quality issues has been a comparatively recent development. Its importance is nevertheless gaining recognition in view of the growing global concern for protection of the environment.

The WMO Commission for Hydrology (CHy) recognized the need for operational guidance material in the field of water-quality monitoring. Thus, in 1972 the Commission embarked on a project to initiate the preparation of this much-needed guidance material. In subsequent years valuable contributions to the project in the form of technical notes were made by Mr J. Picard (France, 1972-1976), Mr H.R.S. Page (UK, 1976-1980) and Dr E. Rosenthal (Israel, 1980-1984).

At its seventh session (Geneva, August/September 1984) the Commission requested the Secretary-General to arrange for the preparation of a manual on the subject on the basis of the material and publications, including those of other UN organizations, that had recently become available. This manual, which is a culmination of the CHy project, has been prepared with the assistance of Prof. Paul M. Laughton (Canada) and Dr Adrian Demayo (Canada), whose services were arranged through the kind collaboration of the Inland Waters Directorate of Environment Canada.

This manual is intended as a practical handbook for those who plan water-quality sampling programmes, for those who do the actual field work and for the training of personnel on the subject of water-quality data collection.

I am pleased to express to all who have contributed time and effort to this project and, in particular, to the preparation of this manual, the sincere appreciation of the World Meteorological Organization. It is hoped that this publication will assist national hydrological agencies responsible for operational hydrology in the development and operation of their water-quality monitoring programmes.

G.O.P. Obasi
(Secretary-General)

SUMMARY

This publication discusses the monitoring of the quality of inland waters, i.e. lakes, rivers, reservoirs, groundwater and precipitation, and describes in detail the planning, field activities and methods used in carrying out a water-quality monitoring programme. Chapter 1 contains a brief discussion on water-quality management, the objectives of water-quality monitoring programmes and the planning of water-quality measurement networks. Under general considerations in Chapter 2 details are provided on the location of monitoring stations, representativesness of samples, frequency of sampling, classification of water-quality parameters and the use of statistics in selecting sampling frequencies. Chapter 3 covers collection of surface-water samples with some discussion on the type of samples and a detailed description of equipment and sampling techniques.

Chapters 4 to 6 are concerned with field activities: *in situ* measurement of parameters, recording of field data and filtration and preservation procedures. Sampling for radioactivity measurements and biological analysis are discussed in Chapters 7 and 8 respectively .

The procedures for monitoring the quality of precipitation, sediment and groundwater and the shipment of samples are described in Chapters 9 to 12. Chapters 13 and 14, provide some discussion of safety precautions in the field and of personnel training in water-quality monitoring.

A glossary and a bibliography respectively constitute the final two sections, Chapters 15 and 16.

RÉSUMÉ

Cette publication traite de la surveillance de la qualité des eaux intérieures, c'est-à-dire lacs, rivières, réservoirs, eaux souterraines et précipitations, et décrit en détail la planification, les activités sur le terrain et les méthodes utilisées pour exécuter des programmes de surveillance de la qualité de l'eau. Le chapitre 1 donne un bref examen de la gestion de la qualité de l'eau, des objectifs des programmes de surveillance de la qualité de l'eau et de la planification des réseaux de mesure de la qualité de l'eau. Dans les considérations générales du chapitre 2, on trouvera des détails relatifs à l'emplacement des stations de surveillance, à la représentativité des échantillons, à la fréquence des prélèvements, au classement des paramètres concernant la qualité de l'eau et à l'utilisation de statistiques pour le choix des fréquences de prélèvement. Le chapitre 3 porte sur le prélèvement d'échantillons d'eau de surface; il aborde la question des types d'échantillons et donne une description détaillée du matériel et des techniques de prélèvement.

Les chapitres 4 et 6 concernent les activités sur le terrain: mesure *in situ* des paramètres, enregistrement des données sur le terrain et procédés de filtration et de conservation. Le prélèvement d'échantillons aux fins de mesures de la radioactivité et l'analyse biologique font l'objet des chapitres 7 et 8 respectivement.

Les chapitres 9 et 12 portent sur les méthodes de surveillance de la qualité des précipitations, des sédiments et des eaux souterraines ainsi que sur l'expédition d'échantillons. Les chapitres 13 et 14 traitent des mesures de précaution à prendre sur le terrain et de la formation du personnel responsable de la surveillance de la qualité de l'eau.

Les deux derniers chapitres (chapitres 15 et 16) contiennent respectivement un glossaire et une bibliographie.

РЕЗЮМЕ

В публикации рассматриваются вопросы мониторинга качества внутренних вод, то есть озер, рек, водохранилищ, грунтовых вод и осадков и подробно обсуждаются планирование, полевые работы и методы, используемые для проведения программы мониторинга качества воды. В главе 1 содержится краткое описание управления качеством воды, целей программ мониторинга и планирования сетей для измерения качества воды. В главе 2 приведены детали, касающиеся местоположения станций мониторинга, репрезентативности проб, частоты отбора проб, классификации параметров качества воды и использования статистики при выборе частоты отбора проб. В главе 3 представлен материал, касающийся сбора проб поверхностных вод, типа проб, и дается подробное описание оборудования и методов отбора проб.

В главах 4-6 рассматриваются вопросы полевых работ: измерение параметров in situ, регистрация полевых данных и процедуры фильтрации и сохранения проб. Отбор проб для измерения радиоактивности и проведения биологического анализа изложен соответственно в главах 7 и 8.

Процедуры мониторинга качества атмосферных осадков, отложений и грунтовых вод и отправка проб описаны в главах 9-12. В главах 13 и 14 обсуждаются меры безопасности работы в полевых условиях и обучение персонала для работы, связанной с мониторингом качества воды.

В последних двух разделах, то есть в главах 15 и 16, приведен глоссарий и библиография.

RESUMEN

La presente publicación trata del control de la calidad de las aguas interiores, por ejemplo de los lagos, de los ríos, de los embalses, de las aguas subterráneas y de la precipitación, y describe detalladamente la planificación, las actividades sobre el terreno y los métodos utilizados para poner en práctica el programa de control de la calidad del agua. En el Capítulo 1 se describe brevemente la gestión de la calidad del agua, se habla de los objetivos de los programas de control de la calidad del agua y de la planificación de las redes de medida de la calidad del agua. En el Capítulo 2, bajo aspectos generales, se facilitan detalles sobre el emplazamiento de las estaciones de control, la representatividad de las muestras, la frecuencia del muestreo, la clasificación de los parámetros sobre calidad del agua y la utilización de estadísticas para seleccionar las frecuencias de muestreo. El Capítulo 3 trata de la concentración de muestras del agua de superficie y presenta algunos tipos de muestras, describiendo detalladamente el equipo y las técnicas de muestreo.

Los Capítulos 4 a 6 tratan de las actividades sobre el terreno: medidas *in situ* de los parámetros, registro de los datos sobre el terreno, procedimientos de filtración y preservación. El muestreo de las medidas de la radioactividad y el análisis biológico se describen en los Capítulos 7 y 8, respectivamente.

Los procedimientos para el control de la calidad de la precipitación, de los sedimentos y de las aguas subterráneas y la expedición de las muestras se describen en los Capítulos 9 a 12. Los Capítulos 13 y 14 tratan de las precauciones de seguridad que se toman sobre el terreno y de la formación del personal que se ocupa del control de la calidad del agua.

En las últimas secciones, los Capítulos 15 y 16, figuran un glosario y una bibliografía, respectivamente.

CHAPTER 1

INTRODUCTION

For the purposes of this manual, it is assumed that adequate hydrological information about the watersheds to be monitored is available for planning the networks. Some hints are provided about how to estimate flow rates in cases where local information is inadequate and no great precision is necessary.

To select appropriate containers and methods of preservation, field workers need to know what parameters will be analysed in the laboratory. However, they do not need to be conversant with all the details of the laboratory analytical procedures. Thus, no discussion is included in this manual of what happens after the samples have been prepared for delivery to the laboratory, i.e. the methods of laboratory analysis.

Water-quality managers, on the other hand, do need to be informed about analytical methods in order to plan their work. They face a very difficult problem in keeping up with the rapid development of increasingly sophisticated instrumentation. Their task is not made easier by the proliferation of new toxic compounds and the need to detect lower and lower concentrations of pollutants. To keep this manual to a manageable size, it was decided to confine the information here to the sample-handling requirements for the compounds currently being measured.

The other very important aspects of water-quality monitoring not dealt with in this manual are data management, data analysis and interpretation, and report writing. All are essential components of a well-planned monitoring programme. If any of these aspects are missing much of the work done in the monitoring programme will go to waste.

The planning and sampling methods described are confined to the monitoring of natural bodies of fresh water. Several of the documents listed in the Bibliography (Chapter 16) discuss methods of studying other types of water such as municipal and industrial waste waters and agricultural runoffs.

This manual is based on the useful and practical publication, "Sampling for Water Quality", of the Water Quality Branch, Inland Waters Directorate of Environment Canada (code SWQ). A number of other national and international publications have also been scanned, resulting in revisions and enlargements in most of the chapters.

Publications from which quotations or facts have been cited are listed in the Bibliography. A number of these were kindly made available in draft form and may now have been published. Attributions to the sources are made, using the three-letter codes given in the Bibliography, whenever extensive passages, tables or figures are quoted.

1.1 Why should water quality be monitored?

As the power of mankind to damage the environment has increased, it has been realized around the globe that effective protection of the environment requires accurate and detailed knowledge of existing environmental conditions, and the ability to detect and measure environmental changes quickly.

Natural water sources have always been regarded as a vital part of our environment, and water-quantity management has been common since prehistoric times. The recognition that some water sources were better to drink than others has also been a normal part of our culture but water-quality management is a more recent development. Through urbanization and population growth we have disturbed or destroyed the natural, healthy quality of water bodies in many regions. These water bodies have become unsuitable for many beneficial uses for which they were earlier utilized. Furthermore, there is a world-wide increase in demand for good quality water. Few, if any, places in the world are so fortunate as to have unlimited supplies of good quality water sufficient for rising populations and growing industrial needs.

1.2 Water-quality management

Water quality is a term used to comprise all the chemical, physical and biological properties of water.

Thus, water-quality management may be defined as the effort by society to control the physical, chemical and biological characteristics of water (DNM, p. 1). The efforts are directed at controlling the impacts of society upon the quality of water. Water quality in the environment is the result of two primary causes: (1) the activities of society and (2) the natural hydrologic cycle. Modification of the former is feasible; change in the latter presents a challenge for the future.

1.3 General considerations

The monitoring of water quality to give reliable and usable data involves many distinct activities (see Table 1.1 and Figure 1.1) and is expensive; care therefore must be taken to ensure that the resources are employed to the best advantage. The first step in planning a water monitoring system should therefore be to define the objectives of the monitoring, i.e. what is to be accomplished. With these objectives one can then decide what data are needed and how they will be used. Sampling locations and frequencies are then chosen with a view to obtaining the required information with a minimum of effort and cost.

In establishing monitoring objectives, the intended uses of the water are particularly important. Aquatic life, drinking-water sources and bathing areas require high quality, while navigation and water for cooling of industrial processes have lesser quality requirements. Livestock watering, irrigation, boiler water, fisheries — each demands its own standard of quality and has its own relative economic importance.

Since the processes, natural and societal, which affect water quality have random features, water-quality monitoring in many instances has been treated as a statistical sampling procedure. This is a large subject in itself, and in what follows the reader will be directed, where appropriate, to more detailed treatments. It is not possible to monitor continuously all possible adverse changes; compromises are necessary and statistical methods can help the planner to stay within a budget yet reduce the probability of missing an important fluctuation.

TABLE 1.1 Activities of a water-quality monitoring programme

MONITORING OBJECTIVES
1. Legislation
2. Mandate
3. Resources
4. Programmes

NETWORK DESIGN
1. Station location
2. Parameter selection
3. Sampling frequency

SAMPLE COLLECTION
1. Sampling technique
2. Field measurements
3. Sampling preservation
4. Sampling point
5. Sample transport

LABORATORY ANALYSIS
1. Analysis techniques
2. Operational procedures
3. Quality control
4. Data recording

DATA HANDLING
1. Data reception
   a. laboratory b. outside sources
2. Screening and verification
3. Storage and retrieval
4. Reporting
5. Dissemination

DATA ANALYSIS
1. Basic summary statistics
2. Regression analysis
3. Water-quality indices
4. "Quality-control" interpretation
5. Time series analysis
6. Water-quality models

INFORMATION UTILIZATION
1. Obtain other data and information, e.g. land use, water use, socio-economic data, aquatic life information past, present or planned
2. Water-quality objectives
3. Impact assessment

DECISION MAKING

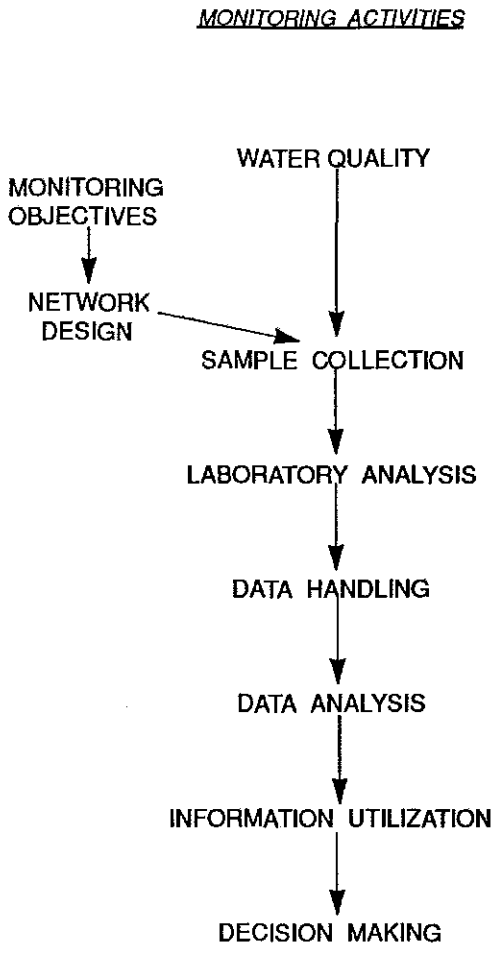


Figure 1.1 The water-quality monitoring system *(adapted from DNM)*

1.4 Objectives for water-quality monitoring programmes

The establishment of objectives for a water-quality programme is a combination of a scientific task and a political process which requires a critical assessment of national priorities (WQS, p. 33). It is based on economic considerations, population trends, present and future water uses, forecasts regarding industrial and agricultural development, and many other socio-economic factors. The development of programme objectives is also based on risk-benefit and cost-benefit evaluations for each specific situation. Experience has shown that the development of compatible national and regional goals is highly desirable. This permits a consistent and co-ordinated

approach toward water-quality management. For example, detrimental pollution effects can be prevented by early establishment of water-quality objectives and goals and land-use plans. Then the location of new industrial sites, for example, can be carried out in a manner which optimizes the use of available land and water resources, thus avoiding completely or keeping to a minimum any detrimental environmental effects.

While the details and emphases in the selection of objectives vary with circumstances, the fundamental long-range objectives of any water-quality monitoring system are to (TNW, p. 1):

(a) Increase knowledge of existing water-quality conditions and understanding of the aquatic environment, both under natural and man-affected conditions;

(b) Determine the amount of water available to meet future needs requiring a given quality; a quantity-quality inventory of water resources;

(c) Provide information on the past, present and future effects of significant natural and anthropogenic activities on the aquatic environment including water projects such as dams, diversions, stream enlargements, massive irrigation projects and aquifer flooding, and industrial, agricultural and urban developments;

(d) Assess the effectiveness of pollution-control measures;

(e) Assess the effects of water quality on human and aquatic ecosystem health and well-being;

(f) Monitor polluting systems such as industrial complexes, urban areas, mineralized water and sea-water to safeguard water supplies;

(g) Detect trends in water quality and provide an early-warning system.

Some of the more specific short-term objectives to implement the above long-range plans are (primarily TNW, p. 2):

(a) Provision of information on current water quality and its trends;

(b) Identification of areas in need of improvement and establishment of priorities;

(c) Monitoring trends to warn of changes that may be damaging to the aquatic environment;

(d) Establishment of early-warning systems for sudden changes;

(e) Identification of sources of pollutants and their loads;

(f) Identification of precautions to be taken to avoid spills of toxic substances and, when accidental spills happen, the best cleanup procedures to reduce the environmental impact;

(g) Determination of the suitability of natural waters for an intended use;

(h) Determination of compliance with regulations and standards;

(i) Determination of water quality where international frontiers are crossed;

(j) Identification of gaps in knowledge requiring research or special studies.

1.5 Planning of water-quality measurement networks

In addition to defining its objectives, the major elements in planning a water quality monitoring system are:

(a) Choosing the location of sampling stations;

(b) Deciding the frequency of sampling;

(c) Selecting the water-quality parameters to be measured and in which medium, i.e. water, bottom or suspended sediment and/or biota;

(d) Selecting the sampling methods;

(e) Selecting the field and laboratory analytical methods;

(f) Selecting the methods for data storage and retrieval;

(g) Establishing the appropriate quality-assurance programme;

(h) Choosing the methods for analysing and interpreting the data collected;

(i) Reporting on the findings.

Only the first four items and part of the fifth, i.e. the field methods, are discussed in this manual.

1.5.1 Location of sampling stations

Monitoring of water quality can be accomplished through operation of a network of strategically located long-term stations. A second approach makes use of repeated short-term surveys, each providing limited spatial coverage. A third and the most common approach is a combination of the two (SAQ). Location of stations in either case should take into account the following factors (WQS, p. 27):

(a) Existing problems and conditions;

(b) Potential growth centres (industrial and municipal);

(c) Population trends;

(d) Climate, geography and geology;

(e) Accessibility of station locations;

(f) Available manpower, funding and field, laboratory and data-handling facilities;

(g) Degree of interjurisdictional co-operation;

(h) Travel time to the laboratory (for deteriorating samples);

(i) Safety of the site.

For reasons of efficiency, the goal of network planning and design is to accomplish the objectives of the water-quality programme in a given area with the minimum of effort and expense.

1.5.2 Methods of sampling

Methods of sampling are determined by a number of factors: the type of material being sampled — ground- or surface water, precipitation, bottom or suspended sediment; the type of sample — grab, composite or integrated; the quality parameter being analysed which in turn determines the kind of container; the amount of sample; whether the sample is analysed on the spot or sent back to a laboratory; and the method of preservation.

1.5.3 Frequency of sampling

The processes, natural and societal, which affect water quality have random features superimposed on the hydrologic, climatic and possibly other cyclic factors. The sampling schedule should permit the adequate evaluation of the contribution of each of these factors to the water quality at a given location. The common approach in establishing the frequency of sampling is statistical. Frequency of sampling is established based on the variability of the data, the concentrations to be measured and the changes to be detected. In the absence of sufficient background data, some arbitrary frequency is chosen, based on some knowledge of local conditions. After sufficient data have been collected to evaluate the variability, the frequency is adjusted to reflect this (section 2.4.1). The frequency is also influenced by the relative importance of the station and whether or not the concentrations approach critical levels for some of substances measured.

1.5.4 Water-quality parameters

The parameters (also called determinands) selected for evaluation at a station will be determined largely by the objectives of the monitoring programme. To minimize the cost of the operation, the selection must also consider known characteristics of the water resource and of the polluting sources. For example, samples may not always be analysed for all selected parameters; choices can be based on their pattern of use, concentration and fate in the environment.

1.5.5 Data-handling

The usefulness of the data will in large measure depend on agreement among participating agencies to standardize the methods used and information collected: the description of sample locations, the methods of sampling and preservation, and the analytical procedures and data recorded.

Only the recording of the field data is discussed in this manual. Additional information on water-quality data handling can be found in WQS.

1.5.6 Costs

One of the important elements which must be considered in planning a water-quality monitoring network is the cost of operating the programme. Its major components are sampling, analysis, data handling, quality assurance, data interpretation and reporting costs.

Often, the projected cost of what is considered to be the best monitoring programme may be too high for the agency planning to carry out the monitoring.

When faced by such a situation, some of the possible solutions are:

- Look for additional sources of funding, e.g. other agencies interested in the data collected and information provided;
- Re-examine the objectives of the programme, deleting some of the less important and/or relaxing some of the conditions, e.g. changes to be detected;
- Re-examine the proposed sampling locations deleting some of the less important sites, e.g. locations at which water quality can be inferred from data already existing or from data collected at other points in the system;
- Re-examine the proposed list of parameters to be analysed deleting the less important ones, e.g. those that can be predicted from other measurements or those that have a small or no environmental significance at a given site;
- Re-examine the frequency of sampling, especially when the objectives of the monitoring have been changed.

1.5.7 DOCUMENTATION

In any monitoring programme it is essential that full documentation be compiled. Every step of the planning process should be recorded, starting with the monitoring objectives through the choosing of sampling locations; determination of frequency of sampling; field, laboratory, data handling and analysis, and quality-assurance methodology; to the reporting of results and findings.

The documentation should also include the distribution of resources (person/years and money) between the various activities of the monitoring programme as well as the provisions made for its implementation and evaluation.

CHAPTER 2

GENERAL WATER-SAMPLING CONSIDERATIONS

2.1 Introduction

This chapter reviews some factors to be considered in choosing sampling locations, determining sampling frequency, obtaining a representative sample and selecting the procedures for field quality assurance.

2.2 Location of water-quality sampling sites

The location of the sampling sites follows directly from the objectives of the water-quality monitoring programme. If this is not so, e.g. the objectives are too vague or confusing, then these objectives should be reviewed before attempting to select any locations. Sometimes the objectives will define fairly precisely the best locations for sampling in a river or lake system. For example, if it is desired to determine the effect of an effluent discharge on a receiving stream, sampling locations upstream and downstream of the discharge would be required. In other cases, both location and frequency of sampling will be determined by anti-pollution laws or by a requirement of quality for a specific use of a water body. For example, a permit to discharge to surface waters may spell out details of self-monitoring, such as location, number of samples, frequency and parameters to analyse, as well as the details of compliance monitoring usually carried out by the regulatory agencies.

2.2.1 Varieties of water bodies

Given a specific objective, sampling strategies are quite different for different kinds of water bodies and for different types of samples to be collected, e.g. water, sediment or biota. River water flows longitudinally and reaches mixing homogeneity within distances ranging from a few to a few hundred kilometres of any addition. Lakes may be vertically stratified because of the temperature or because of inflows of high-density saline water. Groundwater tends to flow, often very slowly but with no surface indication of the changes in its solutes taking place down below. Precipitation sampling has its own requirements.

2.2.2 River basins

Efforts have been made to design networks for river basins in a systematic and objective manner. Various mathematical approaches using, for example, centroids of numbers of tributaries, number of outfalls, biological oxygen demand, "running-water mass" or water momentum units have been proposed (DNM, Chap.4; SPS). However, the design resulting from the application of any of these methods must be reviewed and modified, if necessary, to ensure that the objectives of the water-quality study are met. If the objective is, for example, to study the impact of human activities on the water quality of a given river basin, then the basin can be separated for study into natural regions and regions altered by human activity or "impacted regions". The latter can be further subdivided into regions in which the impact is constant or stationary over periods longer than, for example, 10 years, and those in which the impact is variable such as agricultural, residential and industrial zones (TNW, p. 5). In acid deposition studies an important factor to consider in locating sampling sites is the terrain sensitivity to this deposition (LTM, section 3.1).

The next step in locating sampling locations is to collect all relevant information about the region to be monitored (QMS, p. 3; DNM, p. 251). Much of the information will be in the form of published and unpublished papers and reports. To obtain additional information or to update what exists, interviews and questionnaires can be used. The information sought includes geological, hydrological and demographic aspects as well as items such as numbers of lakes and streams, sizes and locations of aquifers, location of existing water-quality or stream-gauging stations, flow rates, climatic conditions in the catchment area, historical developments, present and potential municipal and industrial centres, current water intakes and waste outlets, natural salt springs, mine drainage, irrigation schedules, flow regulation (dams), present and planned water uses, stream or lake water-quality objectives or standards, accessibility of potential sampling sites (land ownership, roads, airstrips), availability of services such as electricity and existing water-quality data.

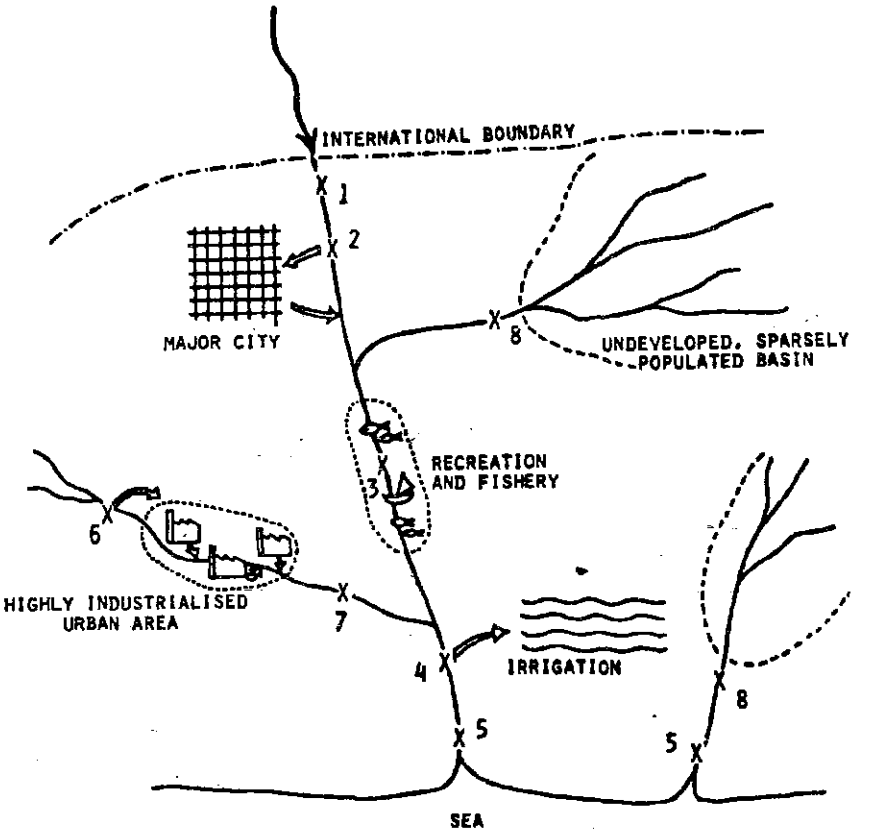
As an example of how stations could be located to meet specific objectives, Figure 2.1 displays a hypothetical river network system (GEM, Chap. 1, p. 6). Not shown in this diagram is the possibility that some of the stations may be designated as "long term" and some "temporary" for special studies.

More detailed information about river networks may be found in DNM, Chaps. 4 and 7 and SRS, section 6. Some discussion is given in FSN, section 4, on a national river and groundwater network created by adding urban and industrial area-monitoring capability to the US National Stream Quality Accounting Network.

2.2.3 Lakes

Unlike the case for rivers, water circulation in lakes is significantly modified by wind. The energy of such movements decreases with depth. Hence, sediment

distribution is predictable because finer-particle-size sediment will be deposited in the deeper offshore regions of the lake while sand and gravel will settle around the periphery (WQS, p. 295). This distribution will, of course, be disturbed where major river input occurs or where nearshore slopes give rise to turbidity currents.



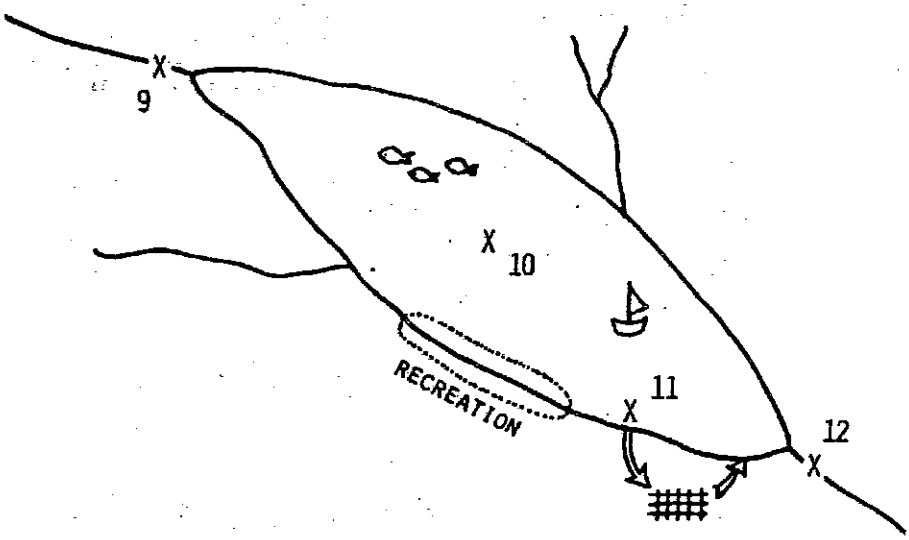
Station	Criteria
1	Immediately downstream of an international boundary
2	Abstraction for public supply of large town
3	Important fishing, recreation and amenity zone
4	Abstraction for large-scale agricultural irrigation
5	Fresh water tidal limit of major river
6	Abstraction for large industrial supply
7	Downstream of industrial effluent discharges and important tributary influencing main river
8	Base line station, water in natural state

Figure 2.1 Monitoring site selection — rivers

In deeper lakes, photosynthetic activity will lead to changes in the composition of the surface layer while bottom water is modified by contact with nutrient-rich fine sediment. Inshore zones also require attention, particularly around river mouths and in regions where upwelling occurs under certain weather conditions.

A sampling network for a hypothetical lake is shown in Figure 2.2 (GEM, Chap. 1, p. 7). Further information about lake sampling may be found in GEM, Chap. 1, section 6 and in SLN.

Depth sampling based on bathymetry (temperature profiles) is touched on in section 2.3.2.



Station	Criteria
9	Principal feeder tributary
10	General water quality of lake
11	Water supply for major city
12	Water leaving lake

Figure 2.2 Monitoring site selection — lakes

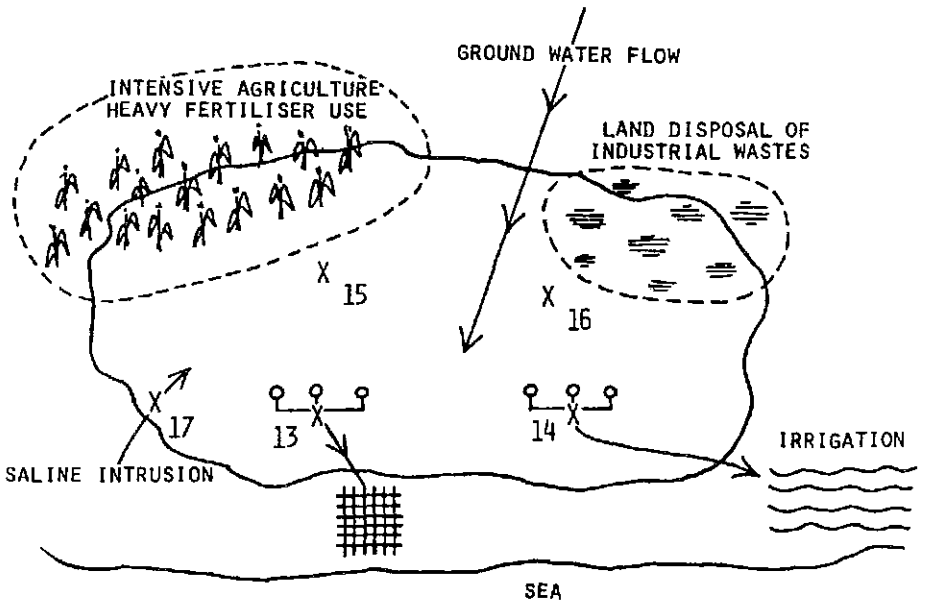
2.2.4 GROUNDWATER

A great deal of hydrogeological information may be necessary to plan the sampling strategy for aquifers. Water levels, hydraulic gradients, velocity and direction of water movements should be known. An inventory of wells, boreholes and

springs fed by the aquifer should be drawn up and details of land use should be recorded. Table 2.1 (GEM, Chap. 1, p. 21) is a guide to obtaining the latter information.

Groundwater samples are taken from drainage water, open wells and drilled wells. Wells should be sampled only after they have been pumped long enough to ensure that a fresh sample has been obtained (WQS, pp. 143-144). This is particularly necessary where a well has a lining subject to corrosion.

Figure 2.3 (GEM, Chap. 1, p. 8) shows a hypothetical groundwater sampling network. Further information may be found in GEM (Chap. 1, section 7) and in DNM (pp. 134-149).



Station	Criteria
13	Water supply to large town threatened by fertilizer residues and saline intrusion
14	Water for large-scale irrigation threatened by leachate from waste tips
15)	
16)	Boreholes for advanced impact monitoring
17)	

Figure 2.3 Monitoring site selection — groundwater

TABLE 2.1 Artificial sources of underground pollution

	Point sources	Distributed sources
Domestic sewage	Cesspool and septic tank soakaways	Artificial recharge with treated sewage
	Leakage from sewerage systems	Excessive distribution of sewage sludge on farm land
	Infiltration from stabilization ponds	
Domestic waste	Leachate from garbage tips and sanitary land fill	
Agricultural waste	Soakage from animal feed areas	Rainwater and irrigation water and the solution of fertilizers and biocides
	Leaching from dung heaps	
Industrial wastes	Leaching from tipped industrial waste	Disposal of induistrial wastes by land irrigation
	Disposal of industrial wastes, including cooling water, by discharge into boreholes	
	Accidental spillages during use, storage or transport	
	Leakages from tanks and pipe lines	
General		Artificial recharge with surface water
		Natural recharge by polluted river or lake water
		Intrusion of saline water from sea or other aquifers following over-pumping

2.2.5 OTHER

Site selection for precipitation sampling is covered in Chapter 9. The study of salt-water bodies is beyond the scope of this manual. A good treatment of sampling in estuaries is provided in WQS (pp. 303-317). Figure 2.4 shows a sampling network for a hypothetical estuary (WQS, p. 314).

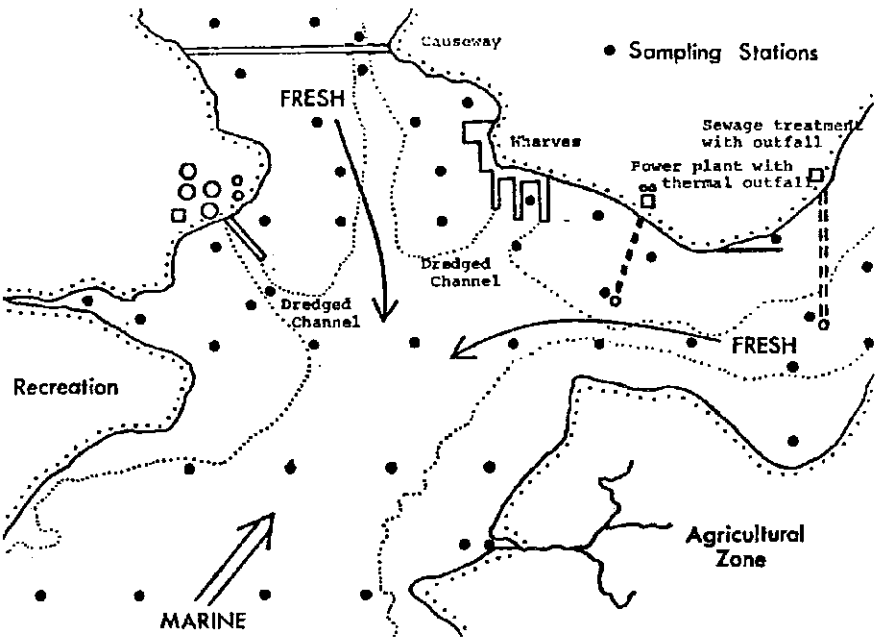


Figure 2.4 Sampling stations in a hypothetical estuary

2.3 Representative samples

Sampling is the process of collecting a representative portion of the environment to learn about the whole environment. Reported data are no better than the confidence that can be placed in the representativeness of the sample.

2.3.1 TIME VARIABILITY

Water resources may exhibit both time and space variability. For example, water below power dams or below waste water treatment plants may show weekly cycles. Some variables, such as dissolved oxygen, commonly exhibit a diurnal cycle, requiring a composite flow-weighted sample. Full delineation of such cycles by spectral analysis is lengthy and expensive, requiring at least 100 equispaced observations over a period 10 times as long as the period of the longest cycle and at intervals no longer than one-third of the shortest (DNM, p. 195).

It is much more difficult to ensure that groundwater samples are representative. The assimilative capacity of the aquifer is limited, and flow rates generally so slow, that highly localized contamination can be present and persist for long periods without detection.

2.3.2 SPACE VARIABILITY

Variability in space is more straightforward. The distance downstream to complete mixing is roughly proportional to the stream velocity and to the square of the width of the channel. Rivers are usually sufficiently shallow that vertical homogeneity is quickly attained below an influx of new material. Lateral homogeneity is much more slowly attained. Thus, wide swift-flowing rivers may not be completely mixed for many kilometres downstream from the input point (DNM, pp. 119-127). In one study, mixing in the Columbia River was incomplete three miles (4.8 km) below an outfall at Trail, British Columbia, and complete after 10 miles (16 km). The Ottawa River joins the St. Lawrence River just west of Montreal (Canada). The waters of the two rivers do not reach complete mixing until below Portneuf, approximately 200 km downstream.

Various protocols are recommended for determining the exact location in the cross-section of the river for obtaining a representative sample, e.g. six samples analysed in duplicate, at three positions across the river and two depths (SRS, section 6.1.4), or mid-depth samples at the quarter points, or other equal-distance points across the width of the river. If a representative sample cannot be obtained, it is advisable to look for another site, either immediately upstream or downstream, where such a sample can be obtained. The other alternative is to obtain a flow-weighted composite sample from samples collected on a set of cross-section verticals. This procedure is time-consuming (GEM, Chap. 1, p. 12; Chap. 2, p. 22; CPQ, section 5.B.4.b.1).

Longitudinal mixing downstream of irregular or cyclic discharges into a river will have a secondary influence on the location of a sampling site. Their effects need to be taken into account in deciding frequency of sampling and when interpreting data (SRS, p. 11; WQS, pp. 261-262).

The degree of mixing in lakes will depend on the configuration of the lake and the location of inlets and outlets. Where the lake is elongated or dendritic, with many branches, or consists of a number of basins, mixing will be poor. Many lakes also exhibit the phenomenon of seasonal thermal stratification. During spring and summer, the surface layers of the water become warmer and less dense. They float upon the cold, denser layer below and there is a resistance to vertical mixing. The warm surface layer is known as the epilimnion and the colder water trapped underneath is the hypolimnion. Between the two is a shallow layer of rapid change in temperature called the thermocline. Because the hypolimnion does not undergo

re-aeration, it becomes depleted of dissolved oxygen, often completely (GEM, Chap. 1, pp. 15, 17).

In the fall, the thermocline sinks as the epilimnion cools, until the surface reaches a temperature close enough to that of maximum density (4°C) that it becomes more dense than the hypolimnion, at which point the lake quickly "overturns", leading to vertical mixing. Figure 2.5 shows the kinds of sampling regimes required at different times of the year (GEM, Chap. 2, p. 23).

In the case of groundwater, if the well casing is perforated such that it accesses more than one aquifer, it may be necessary to collect a sample from a particular depth without mixing it with water from other layers.

2.4 Frequency of sampling

Sampling frequency depends on the purpose of the network, the relative importance of the sampling station, the range of measured values, the time variability of the parameter of interest and on the availability of resources.

Time variability has been mentioned in section 2.3.1. Sometimes the data collected prior to project design include such information, but usually it is determined as the project progresses.

There have been a number of proposals as to how to establish the time variability. For example, GEM (Chap. 2, section 2.6.3) recommends that weekly samples be taken for one year; daily samples on seven consecutive days, once in each quarter; hourly samples over a 24-hour period, once in each quarter; and every four hours for a period of seven consecutive days in each quarter. To lighten the analytical load in such an intensive sampling regime, it may be necessary to reduce the number of determinands (parameters to be determined) to some which are representative of the time variability expected. For examples of different sampling regimes for three rivers in Finland, see Table 2.2 (QMS, p. 10).

For lake stations the recommendation is to sample five consecutive days during the warmest part of the year and five consecutive days every quarter. Special cases include temperate-zone lakes that experience stratification (LTM, section 6). These should be sampled at least six times a year, together with the occasional random sample, to cover the following periods: during open water prior to summer stratification, during mixing following summer stratification, under ice and during the periods of snowmelt and runoff. Similarly, additional samples of rivers should be taken if possible after storm events and during snowmelt and runoff.

For groundwater, a few weekly or fortnightly samples should establish the characteristics of the station, but longer interval sampling should cover a full year.

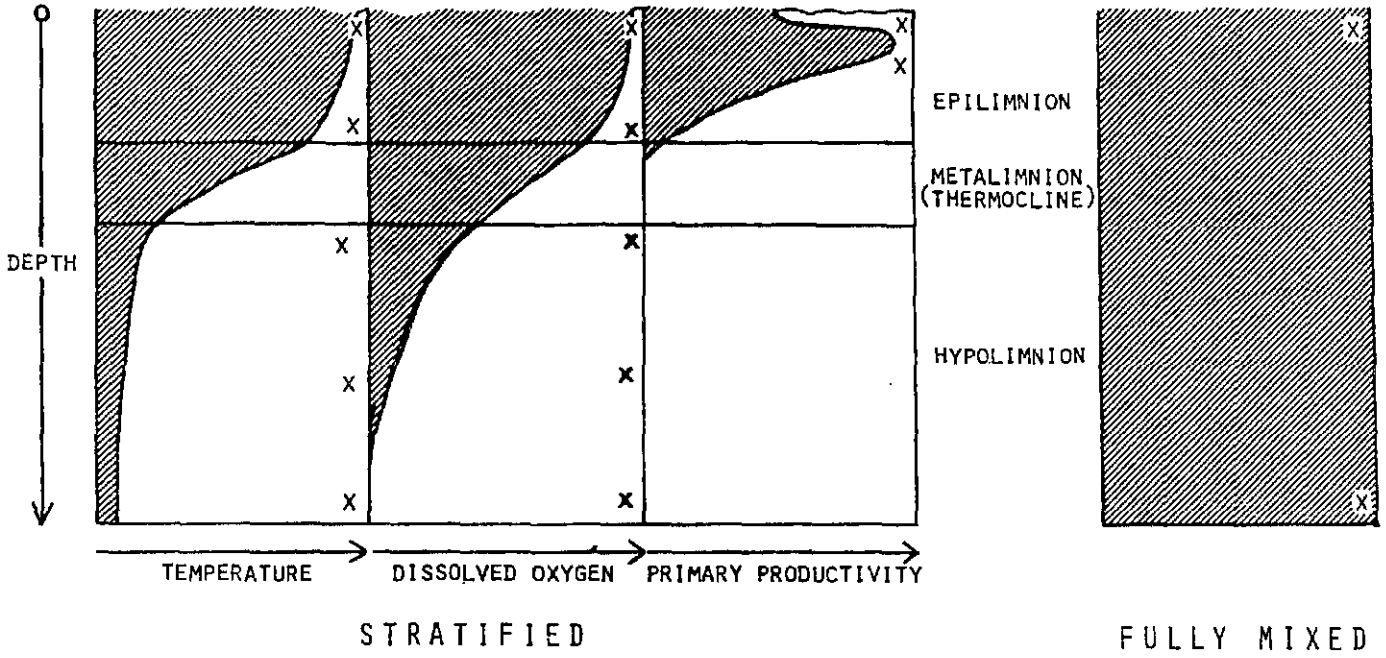


Figure 2.5 Minimum sampling points for a lake when stratified and when fully mixed

TABLE 2.2 An example of sampling intervals for river systems

Parameter	Samples per time unit		
	Porvoonjoki	Tervajoki	Hiidenjoki
pH	very rarely	1/6 day	1/2 month
Conductivity	1/4 day	1/1 day	1/2 day
DO saturation %	1/1 day	1/4 day	1/12 day
Turbidity	1/1 day	3/1 day	1/3 day
Chloride	3/1 day	1/6 day	1/4 month

When parameters are plotted against time, some cyclic variation may be apparent amidst the random fluctuations. However, smaller cyclic effects may be hidden unless the data are subject to spectral analysis to obtain a power spectrum (HSS, section 4.3; WQS, section 6.8.8). As mentioned in section 2.3.1, detection of cyclic events requires a sampling interval no longer than one-third of the shortest cycle time and sampling over a period at least 10 times longer than the time of the longest cycle. Therefore, long-period cycles will not be verified in the initial surveys, but become apparent during the operation of the network. To detect the cyclic variations some randomization of sampling is desirable, for example sampling on different days of the week or different hours of the day.

Several different strategies have been recommended for averaging out daily or weekly variations when the changes throughout the day or week, respectively, are of no interest (e.g. SRS, pp. 26-27). For daily variations, these might be sampling at different times of the day throughout the year, with each portion of the day equally represented, or taking composite samples equally spaced throughout the 24 hours, a popular choice where automatic sampling devices are available.

When the desired sampling frequencies have been selected, they will sometimes require more resources than are available. To reduce the resource requirements composite samples may be used, although with some loss of information. A review

of the objectives of the programme is another alternative. For example, a relaxation in the required accuracy of the data can result in significant reduction in the level of resources needed for the project.

To economize, a reduction of the number of sampling locations should be considered first (SRS, p. 37; GEM, Chap. 2, p. 9). The water quality at one location may also correlate sufficiently well with that at another to allow reduction of the frequency at one of the two locations. Statistical analysis of past data may also show that some determinands are sufficiently well correlated with one another that one can be used to provide an adequate estimate of the other.

Identification of sources of pollution requires high frequency of sampling and probably the use of auxiliary stations (TNW, p. 44). Where compliance standards are involved accurate data may be necessary, involving some 18 to 24 samples for meaningful statistical analysis.

USE OF STATISTICS IN SELECTING SAMPLING FREQUENCIES

A basic goal of many water-quality monitoring programmes is to establish the statistical distribution of the concentration of a water-quality determinand over a given period of time. This can then be used to detect trends in water-quality parameters over time or distance and extreme values which may require action of some kind, e.g. correction of a problem or regulatory action.

Several references deal with probability and statistics applied to water quality (see, for example, DNM or GDS). In using these concepts and the techniques based on them, the water-quality person must be aware of the associated constraints. Most of the formulas and examples in the published literature refer to normally or quasi-normally distributed data. Unfortunately, many water-quality parameters, especially toxic organic chemicals and heavy metals, only rarely follow this distribution. In such cases other, more appropriate, statistical methods must be used.

If some water-quality data already exist at a given location and if they are normally distributed, then one can calculate the number of samples one needs to collect to determine an average value with a pre-established limit of error, E, for a given period of time, e.g. day, week, month, year or season.

$$n \geq \frac{t_{\alpha/2} \cdot S^2}{E}$$

The value of $t_{\alpha/2}$, Student's "t" constant, is obtained from statistical tables for a given level of certainty for the values obtained from these statistical calculations. In routine water-quality monitoring, values of 80-95 per cent certainty are acceptable. Lower values result in too great uncertainty in the statistics obtained from the data collected. Higher values require considerable additional expenditures. S^2 is the sample variance obtained from existing data:

$$S^2 = \frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n - 1}$$

where x_i is a measured value and $\bar{x}$ is the mean of all x_i, i.e. the sum of all x_i divided by n, the number of measured values. The standard deviation is approximated by the value of S.

Because $t_{\alpha/2}$ is also a function of the "degrees of freedom", i.e. n-1, an iterative process is used: an initial n is estimated, $t_{\alpha/2}$ is obtained from the table, a new value for n is then obtained followed by a new value for $t_{\alpha/2}$, and so on until n does not change. Note that when the result for n is a non-integer, n is taken as the next higher integer.

Example: A set of six chloride concentration values has a mean of 240 mg/l and a standard deviation of 20 mg/l. Assuming a normal distribution, how many values are needed to ensure, at a 90 per cent confidence level, that the annual mean does not differ by more than 10 mg/l from the true mean? This might be important, for example, in a case where the monitoring programme has as one of its objectives to find out whether or not there is a long-term trend in the chloride concentration at a given site. (Note: The normal distribution is symmetrical about the mean value. Because of this symmetry the statistical tables only give the values for one-half of the normal distribution. Thus, the $t_{0.45}$ refers to a 45 per cent confidence interval on one side of the mean (i.e. 100 times the numbers in the top row of Table 2.3). If both sides are considered then the confidence interval is 90 per cent).

Assume an initial n = 10. From Table 2.3, $t_{0.45}$ at 9 degrees of freedom is 1.83. Therefore

$$n \geq \frac{1.83 \times 20^2}{10} \cong 14$$

For the new iteration $t_{0.45}$ at 13 degrees of freedom is 1.77. The new n is:

$$n \geq \frac{1.77 \times 20^2}{10} \cong 13$$

Repeating the calculation once more will not change n. Therefore, at least 13 samples/year will have to be collected and analysed for chloride content to ensure that the conditions stated are met. Hydrologic considerations will require that the 13 samples be collected at such times during the year that the whole range of flow regime is represented. More details can be found in DNM (p. 155ff). Another treatment of this problem is found in HSS, section 4.2, which includes graphical solutions and also deals with the related problem of determining the number of samples needed to achieve a required accuracy for extreme values.

2.5 Flow measurements

Water quality, expressed as either concentrations or loads, is directly related to flow. Consequently, data on river discharge are required as part of the design and operation of a water-quality monitoring network. There is also a direct requirement for flow measurements when flow proportional composite samples are collected (3.1.2.2) or the results are averaged across sections of a stream (2.3.2). Other uses would include prediction of the arrival downstream of an accidental spill, tracing the origin of a pollutant back up a chain of stations; estimating the distance downstream from an outfall for complete mixing (2.3.2) or the time for a groundwater pollutant to reach a given well; or calculating the part of the variability of water-quality parameters which is due to changes in the discharge.

All efforts should be made to colocate flow measurement and water-quality stations. If this is not possible or if no flow-measurement stations are available, there are methods of estimating flows that will meet most needs. These range from time-of-travel measurements, such as observation of surface floats (multiplied by a coefficient of from 0.85 to 0.95 depending on various characteristics of the stream) and dye, salt or other tracer injections, to the use of current meters (HSS, section 2.4, and SRS, section 6.3). For a more thorough treatment reference may be made to such sources as the two-volume *Manual on Stream Gauging*, WMO-No. 519, 1980.

TABLE 2.3 Student's "t" constants as a function of degrees of freedom and confidence level (α)

Degrees of Freedom (n-1)	α/2									
	0.495	0.490	0.475	0.450	0.40	0.30	0.25	0.20	0.10	0.05
1	63.66	31.82	12.71	6.31	3.08	1.376	1.000	.727	.325	.158
2	9.92	6.96	4.30	2.29	1.89	1.061	.816	.617	.289	.142
3	5.84	4.54	3.18	2.35	1.64	.97	.756	.584	.277	.137
4	4.60	3.75	2.78	2.13	1.53	.941	.741	.569	.271	.134
5	4.03	3.36	2.57	2.02	1.48	.920	.727	.559	.267	.132
6	3.71	3.14	2.45	1.94	1.44	.906	.718	.553	.265	.131
7	3.50	3.00	2.36	1.90	1.42	.896	.711	.549	.263	.130
8	3.36	2.90	2.31	1.86	1.40	.889	.706	.546	.262	.130
9	3.25	2.82	2.26	1.83	1.38	.883	.703	.543	.261	.129
10	3.17	2.76	2.23	1.81	1.37	.879	.700	.542	.260	.129
11	3.11	2.72	2.20	1.80	1.36	.976	.697	.540	.260	.129
12	3.06	2.68	2.18	1.78	1.36	.873	.695	.539	.259	.128
13	3.01	2.65	2.16	1.77	1.35	.870	.694	.538	.259	.128
14	2.98	2.62	2.14	1.76	1.34	.868	.692	.537	.258	.128
15	2.95	2.60	2.13	1.75	1.34	.866	.691	.536	.258	.128
16	2.92	2.58	2.12	1.75	1.34	.865	.690	.535	.258	.128
17	2.90	2.57	2.11	1.74	1.33	.863	.689	.534	.257	.128
18	2.88	2.55	2.10	1.73	1.33	.862	.688	.534	.257	.127
19	2.86	2.54	2.09	1.73	1.33	.861	.688	.533	.257	.127
20	2.84	2.53	2.09	1.72	1.32	.860	.687	.533	.257	.127
21	2.83	2.52	2.08	1.72	1.32	.859	.686	.532	.257	.127
22	2.82	2.51	2.08	1.72	1.32	.858	.686	.532	.256	.127
23	2.81	2.50	2.07	1.71	1.32	.858	.685	.532	.256	.127
24	2.80	2.49	2.06	1.71	1.32	.875	.685	.531	.256	.127
25	2.79	2.48	2.06	1.71	1.32	.856	.684	.531	.256	.127
26	2.78	2.48	2.06	1.71	1.32	.865	.684	.531	.256	.127
27	2.77	2.47	2.05	1.70	1.31	.855	.684	.531	.256	.127
28	2.76	2.47	2.05	1.70	1.31	.855	.683	.530	.256	.127
29	2.76	2.46	2.04	1.70	1.31	.854	.683	.530	.256	.127
30	2.75	2.46	2.04	1.70	1.31	.854	.683	.530	.256	.127
40	2.70	2.42	2.02	1.68	1.30	.851	.681	.529	.255	.126
60	2.66	2.39	2.00	1.67	1.30	.848	.670	.527	.254	.126
∞	2.58	2.33	1.96	1.645	1.28	.842	.674	.524	.253	.126

For purposes of the water-quality monitoring network, an area-x-velocity estimation of flow will often suffice. Cross-sectional areas can be calculated from depth profiles which in turn can be taken with a "lead line", a weighted line marked up from the weight in feet or metres.

Since the flow rate, depth and cross-sectional area vary during a day as well as from day to day and from season to season, flow rates at the time of sampling need to be known. The most critical flow rates are in times of drought, when the stream's capacity to assimilate wastes and pollutants will be at its lowest, and during floods, when substances which might otherwise never reach the water system are washed off from the surface of the land, thus reaching the water body through the runoff.

Figures 2.6, 2.7 and 2.8 are flowcharts summarizing much of the material so far in this chapter (GEM, Chap. 2, p. 11; SRS, p. 78; and GEM, Chap. 2, p. 10, respectively).

2.6 Water-quality parameters

The parameters which characterize water quality may be classified in several ways. In terms of the kinds of measurements, they are physical properties (e.g. temperature, electrical conductivity, colour, turbidity), inorganic chemical components (e.g. dissolved oxygen, chloride, alkalinity, fluoride, phosphorus, metals), organic chemicals (e.g. phenols, chlorinated hydrocarbons, polycyclic aromatic hydrocarbons and pesticides), and biological components, both microbiological such as faecal coliforms, and macrobiotic, such as worms, plankton and fish, which can indicate the ecological health of the aquatic environment.

A second classification is according to the importance attached to the parameter. This will vary with the type of water body, the intended use of the water and the objectives of the monitoring programme. Within the project GEMS/WATER, water-quality variables are grouped within two categories, the second with three subclasses:

(a) Basic variables;

(b) Use-related variables;

  (i) Drinking water supplies;

  (ii) Irrigation;

  (iii) General quality for aquatic life.

Tables 2.4 and 2.5 list the parameters included in these two groups.

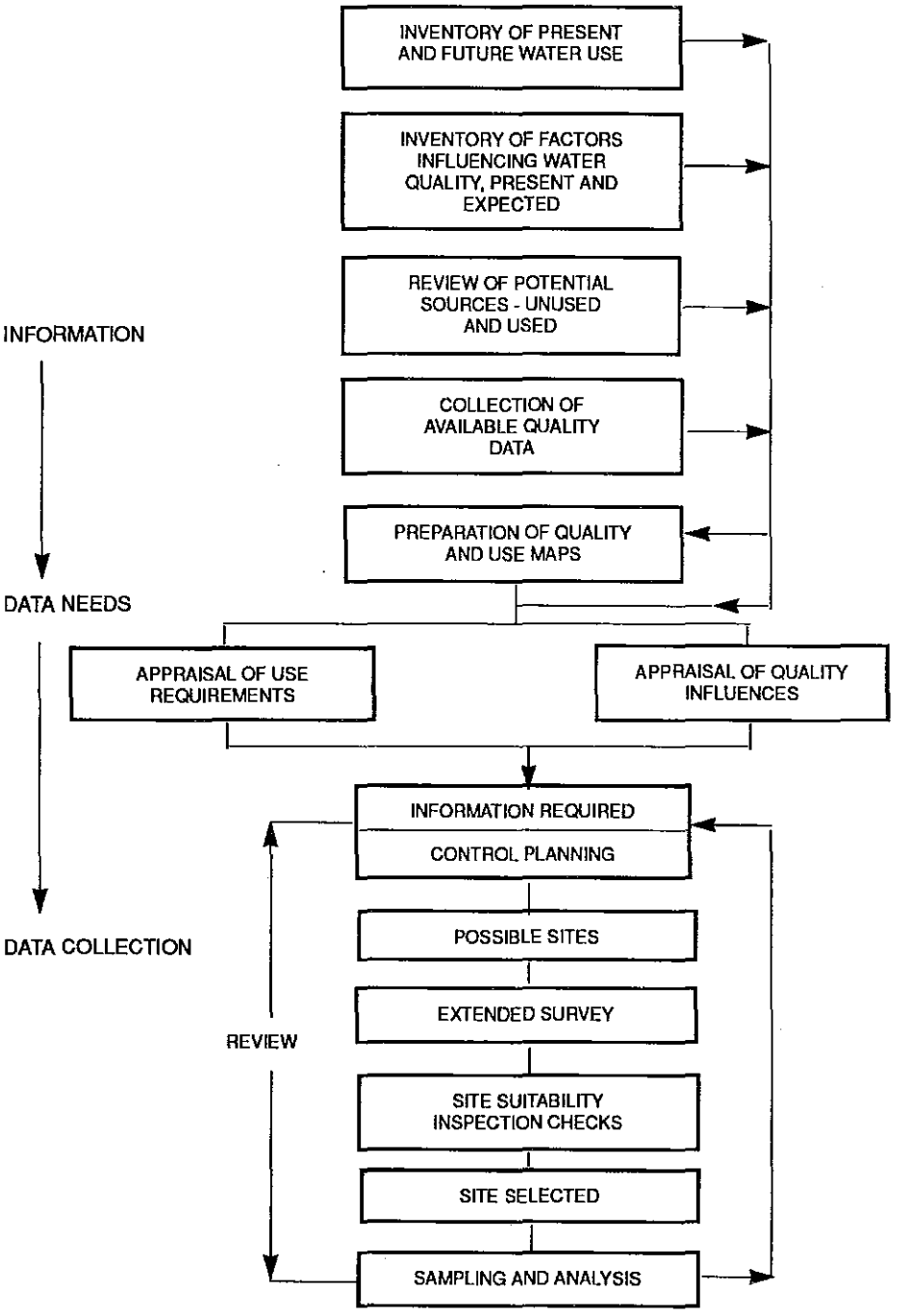


Figure 2.6 Flow diagram for selection of water sampling sites

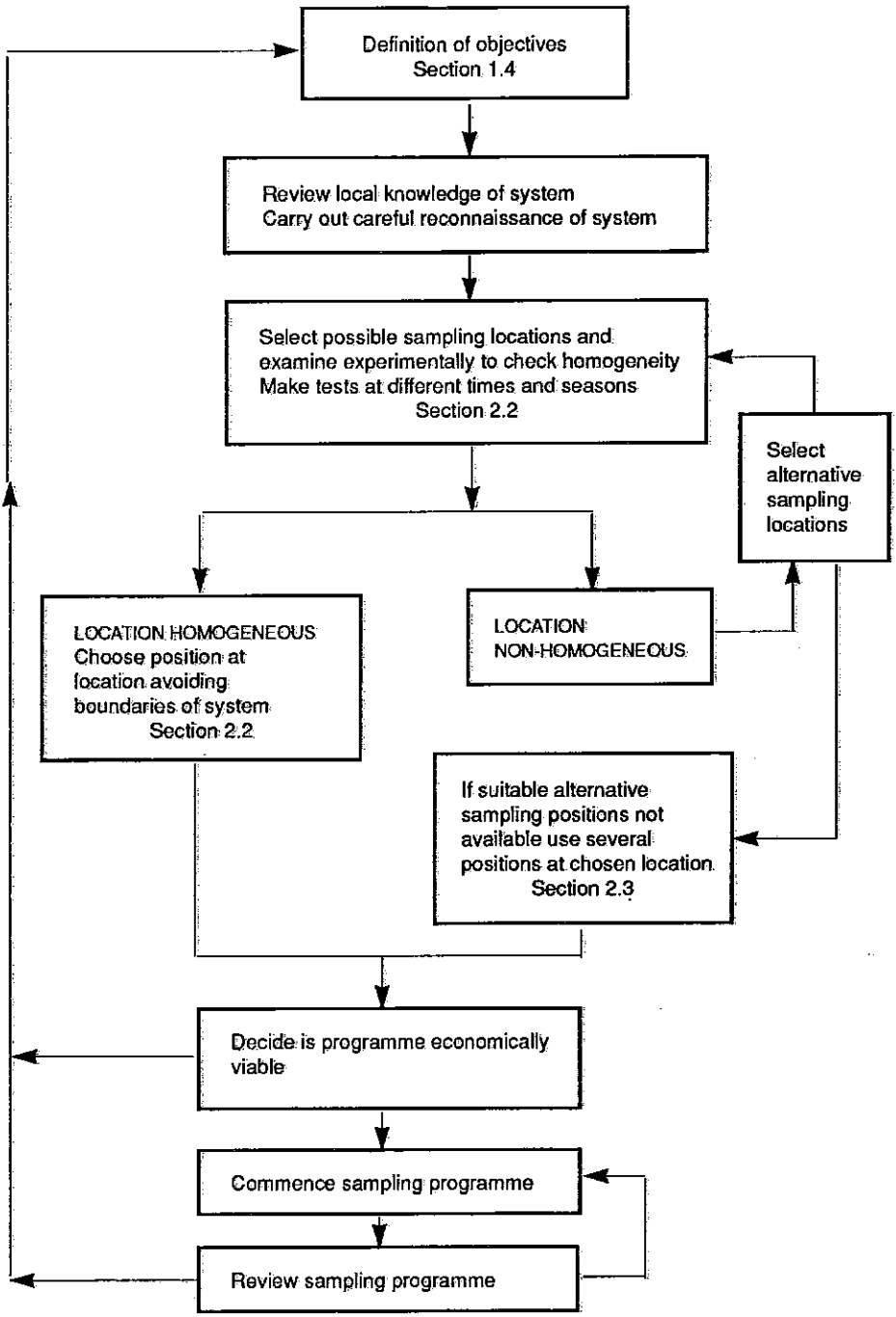


Figure 2.7 Flow diagram for selection of sampling location and position

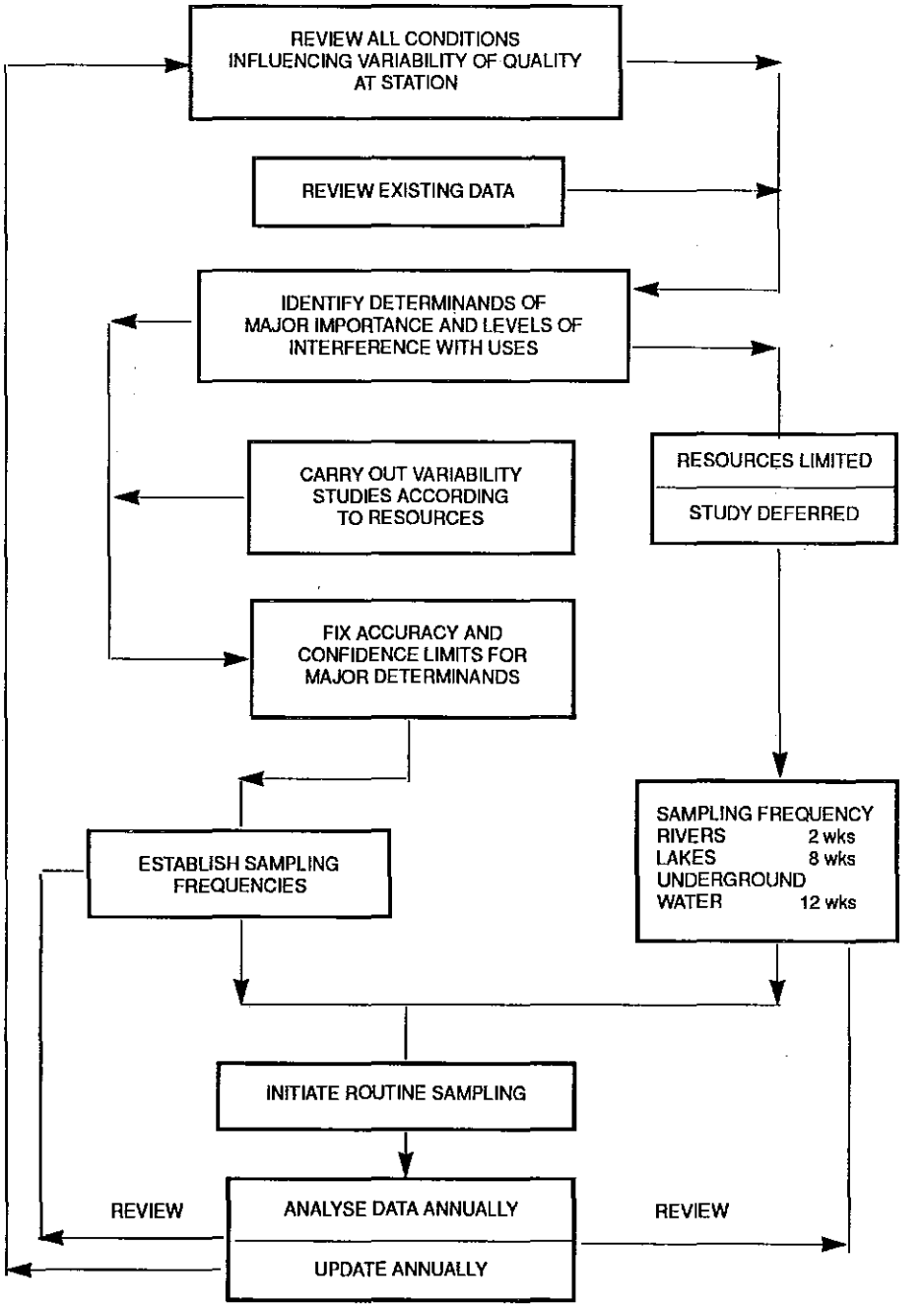


Figure 2.8 Flow diagram for assessment of sampling frequency

TABLE 2.4 Basic variables (GEMS)

	Rivers	Lakes and reservoirs	Groundwaters
Temperature	X	X	X
pH	X	X	X
Electrical conductivity	X	X	X
Dissolved oxygen	X	X	X
Nitrate	X	X	X
Nitrite	–	–	X
Ammonia	X	X	X
Calcium	X	X	X
Magnesium	X	X	X
Sodium	X	X	X
Potassium	X	X	X
Chloride	X	X	X
Sulfate	X	X	X
Alkalinity	X	X	X
BOD	X	–	–
Total suspended solids	X	–	–
Chlorophyll a	–	X	–
Transparency	–	X	–
Orthophosphate	X	X	–
Total phosphorus (unfiltered)	X	X	–
Instantaneous discharge	X	–	–

TABLE 2.5 Use-related variables (GEMS)

		Rivers	Lakes and reservoirs	Groundwaters
(a)	Drinking water supply (1):			
	Total coliforms (6)	X	X	X
	Faecal coliforms (6)	X	X	X
	Arsenic	X	X	X
	Cadmium	X	X	X
	Chromium	X	X	X
	Lead	X	X	X
	Mercury	X	X	X
	Selenium	X	X	X
	Cyanide	X	X	X
	Fluoride	X	X	X
	Nitrate (2)	X	X	X

Table 2.5 (contd)

		Rivers	Lakes and reservoirs	Groundwaters
	TOC1 (3)	X	X	X
	Dieldrin (3)	X	X	X
	Aldrin (3)	X	X	X
	DDT	X	X	X
	Copper (4)	X	X	X
	Iron (4)	X	X	X
	Manganese (4)	X	X	X
	Zinc (4)	X	X	X
(b)	Irrigation:			
	Sodium (2)	X	X	X
	Calcium (2)	X	X	X
	Chloride (2)	X	X	X
	Boron	X	X	X
(c)	General water quality (e.g. aquatic life):			
	Silica, reactive	X	X	–
	Kjeldahl nitrogen	X	X	–
	COD	X	–	–
	TOC	X	–	–
	Chlorophyll a (2)	X	X	–
	Hydrogen sulphide	–	X	X
	Iron	–	X	–
	Manganese	–	X	–
	PCBs	X	X	–
	Aluminium (5)	X	X	–
	Sulfate (5)(2)	X	X	–
	ph (5)(2)	X	X	–

(1) As in *WHO Guidelines for Drinking Water Quality* (1982).
(2) Already mentioned in basic variables.
(3) Total organochlorine compounds (TOC1), dieldrin, aldrin and DDT are considered as representative of the major categories of organic pollutants listed in WHO guidelines.
(4) Selected aesthetic quality variables listed in WHO Guidelines but not covered under basic variables.
(5) Variable also indicating a global change in water quality resulting from acidification.
(6) These variables are also to be monitored in the case of recreational use of the waterbody.

A third classification, highly relevant to sampling procedures, is according to stability:

(a) Conservative, do not change materially with time;

(b) Non-conservative, change with time but can be stabilized for at least 24 hours by appropriate treatment;

(c) Non-conservative, change rapidly with time and cannot be stabilized.

The first two groups can be measured by taking representative water samples for subsequent analysis in the laboratory. The third group, which includes temperature, pH and dissolved oxygen, need to be measured *in situ* or in the field immediately the sample has been taken. The second and third groups include most of the toxic substances of environmental concern. Work is under way in various parts of the world to develop methods for measuring the concentration in the field, for screening the samples for the presence of these toxic substances, either *in situ* or in the field, or for extracting them in the field and thus stabilizing them for subsequent laboratory analysis.

Automatic monitoring

Measurement of certain parameters can be carried out continuously or at short intervals (e.g. seconds, minutes, hours) by automatic monitoring equipment and the values recorded. The number of determinands which can be so measured at present is limited; the equipment is expensive and it needs close and skilled supervision and maintenance. The voluminous amount of data collected requires methods for handling it (GEM, Chap. 3, p 12). Automatic monitoring can be of value in special situations, such as to provide warning in a water-treatment plant or for intensive study of the temporal variability at a given site.

Three types of installations are in use (WQS, section 4.4). In one type, the water is pumped and the measurements are made on shore. Other instruments use probes immersed in the body of water and make the measurements *in situ*. A more recent type is the self-contained, battery-operated instrument which can be operated as much as 300 m below the surface.

Parameters currently being measured include pH, temperature, specific conductance, turbidity, dissolved oxygen, chloride, redox potential, stage height, sunlight intensity and ultra-violet absorbance.

Automatic monitoring has apparently been quite successful in some jurisdictions (AFC, QMS) and new technology is being developed.

2.7 Field quality assurance

The field quality-assurance programme is a systematic process which, together with the laboratory and data-storage quality-assurance programmes, ensures a specified degree of confidence in the data collected for an environmental survey. A field quality-assurance programme involves a series of steps, procedures and practices.

2.7.1 General measures

(a) All equipment, apparatus and instruments should be kept clean and in good working condition, with records kept of calibrations and preventive maintenance. Many of the techniques and practices for achieving this are given elsewhere in this manual;

(b) Records should be kept of all repairs to the instruments and apparatus and of any incidents or experiences which may affect the success of the study;

(c) Conditions of the working area should be such that they encourage and maintain a completely safe environment;

(d) It is essential that standardized and approved methodologies, such as those recommended in this manual, be used by field personnel. If any changes to the approved methods are made, they should be documented and experimental data obtained to ensure that the results which have been obtained are at least as good as before.

Quality assurance depends on the people who do the work. It is recommended that each monitoring project have a person responsible for implementing and carrying out the quality assurance (SAQ, p. 16).

2.7.2 The sample collector

The success of a water-quality monitoring programme relies upon the validity of the sampling, emphasizing the key position of the field personnel (GEM, Chap. 2, p. 25). In addition to collecting samples, the field person is required to carry out field and *in situ* measurements. Skill and technical training are required. The person often operates alone and will be called upon to exercise initiative and ingenuity in the course of the work; he/she therefore needs to have a thorough understanding of the purpose and principles of sampling procedure. Furthermore, the field person has more direct knowledge of the water body and its behaviour throughout the year than the other members of the team and can often be of considerable assistance in interpreting unexpected results or locating sources of observed changes.

The members of the laboratory staff should be given the opportunity of accompanying the field team on occasion. In this way, both components of the team will acquire an understanding of the other's needs and problems.

2.7.3 PREVENTION OF SAMPLE CONTAMINATION

The quality of data generated in a laboratory depends on the integrity of the samples that arrive at the laboratory. Consequently, the field investigator must take the necessary precautions to protect samples from contamination and deterioration.

There are many sources of contamination; the following are some basic precautions to avoid them:

(a) Field measurements should always be made on a separate sub-sample, which is discarded once the measurements have been made. They should never be made on the same water sample which is sent to the laboratory for analysis;

(b) Sample bottles, new or used, must be cleaned. For recommended methods, see Tables 3.1 and 3.2 in Chapter 3;

(c) Only the type of sample bottle recommended for each parameter should be used (see Tables 3.1 and 3.2 in Chapter 3 and Tables 6.1 and 6.2 in Chapter 6);

(d) Water sample bottles should be used for water samples only. Bottles that have been used in the laboratory to store concentrated reagents should never be used as sample containers;

(e) Before being used in the field, all preservatives must be tested and the containers spot-tested for cleanliness;

(f) Recommended preservation methods must be used (e.g. section 6.2 and Tables 6.1 and 6.2 in Chapter 6). All preservatives should be of analytical grade. They should be provided and certified by the analytical laboratory;

(g) When preserving samples, the possibility of adding the wrong preservative to a sample or cross-contaminating the preservative stocks is minimized by preserving all the samples for a particular group of parameters together;

(h) Solvent-rinsed Teflon or aluminum foil liners should be used to prevent contamination from the bottle caps of water samples which are to be analysed for organic compounds;

(i) The inner portion of sample containers and caps must not be touched by bare hands, gloves, mitts or other objects;

(j) Sample containers must be kept in a clean environment away from dust, dirt, fumes and grime. Vehicle cleanliness is an important factor in eliminating contamination problems;

(k) Petroleum products (e.g. gasoline, oil and exhaust fumes) are prime sources of contamination. Spills or drippings (which are apt to occur in boats) must be removed immediately. Exhaust fumes and cigarette smoke can contaminate samples with lead and other heavy metals. Air-conditioning units are also sources of trace metal contamination;

(l) The sample collector should keep his/her hands clean and refrain from smoking while working with water, sediment or biota samples;

(m) Filter units and related apparatus must be kept clean, using procedures such as acid washes and soaking in special solutions, and should be wrapped in solvent-rinsed aluminum foil;

(n) Bottles which have been sterilized must be kept sterile until the sample is collected. If the sterile heavy-duty paper or aluminum foil has been lost or if the top seal has been broken, the bottle should be discarded;

(o) All foreign and especially metal objects must be kept out of contact with acids and water samples;

(p) Specific conductance should never be measured in a sample that was first used for pH measurements. Potassium chloride diffusing from the pH probe alters the conductivity of the sample;

(q) Samples must never be permitted to stand in the sun; they should be stored in a cool place - ice chests are recommended;

(r) Samples must be shipped to the laboratory without delay; the travel time for a sample from a sampling site to the laboratory is one of the elements considered in the network design.

Additional sampling precautions related to water conditions at a particular location (shallow water) or season (winter) are discussed in section 3.4.

2.7.4 QUALITY ASSURANCE

Quality assurance is an essential and integral element of a field programme. In addition to standardized field procedures, field quality assurance requires the submission of blank and duplicate samples to test the purity of chemical preservatives; to check any equipment used in sample collection or handling for contamination (sample containers, filtering equipment and the like); and to detect other systematic and random errors occurring from the time of sampling to the time of analysis. Replicate samples must also be collected to check the reproducibility of the sampling. The timing and frequency of blank, duplicate and replicate samples are established in the project design (cf. FSN, section 7.3).

2.7.4.1 Bottle blanks

Prior to a field-sampling trip, it is recommended that one sample bottle for every 10 of each type being used during the sampling trip should be selected at random, filled with ultrapure distilled water,* preserved in the same manner as field samples, and set aside for submission with the field samples for analysis for the parameters of interest as "bottle blanks". This should detect any widespread contamination caused by the bottle-washing process.

2.7.4.2 Sampler blanks

Periodic "sampler blanks", consisting of ultrapure distilled water poured into or permitted to pass through the sampler, should be prepared and analysed in the laboratory for the parameter(s) of interest.

2.7.4.3 Filter blanks

If water samples are "field filtered" to determine dissolved components, the field filters should be prewashed in the laboratory with a solution that can remove any contaminants which might affect the accuracy of measurement of the parameter of interest. Immediately after being washed, the filters should be sealed in plastic Petri dishes for transport in the field. Filtering apparatus, such as funnels, should be prewashed in the laboratory using the same procedure, and then sealed in polyethylene bags (Zip-Lock or Whirl-Pak in Canadian practice) for transport in the field.

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* In the Canadian practice, ultrapure distilled water is obtained by passing distilled water through a Corning model AG-11 all-glass distillation unit and then through a Millipore Super Q Ultrapure Water System containing a prefilter cartridge, an activated carbon cartridge and a mixed bed de-ionization cartridge.

A daily "filter blank" should be prepared by passing a sample of ultrapure distilled water through one of the prewashed filters in the filtration apparatus, preserving it in the same manner as the water samples, and then returning it to the laboratory for analysis for the parameter(s) of interest.

2.7.4.4 Field blanks

Daily "field blanks" (one blank is suggested for every five to 10 water samples) should be prepared in the field at the end of each day's sampling by filling the appropriate sample bottles with ultrapure distilled water, adding preservative in the same manner as it was added to the water samples, capping the bottles tightly and transporting them to the laboratory in the same manner as the water samples. Field blanks need only be prepared for samples to be analysed for parameters that require chemical preservation.

2.7.4.5 Duplicate samples (splits)

Duplicate samples are obtained by dividing one sample into two or more identical sub-samples. This should be done periodically to obtain the magnitude of errors owing to contamination, random and systematic errors, and any other variabilities which are introduced from the time of sampling until the samples arrive at the laboratory.

2.7.4.6 Replicate samples (temporal)

These are two or more samples taken at the same location sequentially at specified intervals over a specific period of time. They are taken to measure the uncertainty due to temporal variations of various parameters in the water body. The number and frequency of these samples are usually determined by a pilot study, as discussed under 2.4.

2.7.4.7 Spiked samples

At least once at each sampling point, control samples for each parameter being measured should be prepared by spiking a four-way split of a single water sample with three different levels of the parameter of interest, within the concentration-range capability of the analytical method employed. The information gained from these control samples is used to reveal any systematic errors or bias in the analytical methodology, which is important in interpreting the data.

CHAPTER 3

COLLECTING SURFACE-WATER SAMPLES

3.1 Types of surface-water samples

The type of surface water-sample to be collected is determined by a number of factors such as:

(a) The objectives of the study, including the parameters of interest and the precision and accuracy needed;

(b) The characteristics of the system being studied, including the flow regime, climatic conditions, industrial inputs, groundwater infusions, tributaries, the homogeneity of the body of water and the aquatic life present;

(c) The resources available, i.e. manpower, equipment and materials.

It is recommended that the design of the field-sampling programme be tested and assessed by a pilot project or in the initial rounds of sampling to ensure both its effectiveness and efficiency with respect to the objectives of the study. For example, assumptions about the temporal and spatial homogeneity of a river or lake can be tested by cross-sectional and vertical sampling, or the frequency of analysis of water-quality parameters can be re-examined. Other elements of the sampling programme, such as ensuring that an adequate volume of water is collected or that the shipping of samples is satisfactory, can also be checked during the pilot project.

3.1.1 Grab samples

A "discrete" grab (or spot) sample is one that is taken at a selected location, depth and time, and then analysed for the constituents of interest.

A "depth-integrated" grab sample is collected over a predetermined part or the entire depth of the water column, at a selected location and time in a given body of water, and then analysed for the constituents of interest.

The collection of grab samples is appropriate when it is desired to (HSS, section 2.2):

(a) Characterize water quality at a particular time and location;

(b) Provide information about minima and maxima;

(c) Allow collection of variable sample volumes;

(d) Deal with a stream which does not flow continuously;

(e) Analyse for parameters which are likely to change;

(f) Establish the history of water quality based on relatively short time intervals.

3.1.2 COMPOSITE SAMPLES

A composite sample is obtained by mixing several discrete samples of equal or weighted volumes in one container, an aliquot of which is then analysed for the constituents of interest, or by continuously sampling the flow.

There are two main types of composite sample.

3.1.2.1 Sequential, or time, composite

This composite is made up by:

(a) Continuous, constant sample pumping; or

(b) Mixing equal water volumes collected at regular time intervals.

3.1.2.2 Flow-proportional composite

This composite is obtained by:

(a) Continuous pumping at a rate proportional to the flow;

(b) Mixing equal volumes of water collected at time intervals which are inversely proportional to the volume of flow; or

(c) Mixing volumes of water proportional to the flow collected during or at regular time intervals.

A composite sample provides an estimate of average water-quality condition over the period of sampling. Advantages and disadvantages of the different methods of compositing are discussed in HSS, 2.2.4, and a diagram of a setup for type (c) above is shown in HSS, 2.3.3. An obvious advantage is in the economy of

reducing the number of samples to be analysed. On the other hand, composite samples cannot detect changes in parameters occurring during the sampling period.

3.2 Collecting a representative water sample (cf. section 2.3)

For water-quality sampling sites located on a homogeneous reach of a river or stream, the collection of depth-integrated samples in a single vertical may be adequate. For small streams a grab sample taken at the centroid of flow is usually adequate (CPQ, section 5.B.4.b.1).

For sampling sites located on a nonhomogeneous reach of a river or stream, it is necessary to sample the channel cross-section at the location at a specified number of points and depths. The number and type of samples taken will depend on the width, depth, discharge, the amount of suspended sediment being transported and the aquatic life present. Generally, the more points sampled along the cross-section the more representative the composite sample will be. Three to five verticals are usually sufficient and fewer are necessary for narrow and shallow streams.

One common method is the EWI (equal-width increment) method, in which verticals are spaced at equal intervals across the stream. The EDI or equal-discharge increment method requires detailed knowledge of the streamflow distribution in the cross-section in order to subdivide the cross-section into verticals proportional to incremental discharges (CPQ, section 5.B.4.b.1).

The following general guidelines apply to the collection of a water sample:

(a) Do not include large nonhomogeneous particles, such as leaves and detritus, in the sample;

(b) Face the sampling apparatus upstream to avoid contamination. Sampling from the upstream side of a bridge enables the collector to see whether any floating material is coming downstream and aids in the prevention of contamination of the sample from paint chips or dirt from the road;

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

(d) Maintain accurate records on the field-sampling sheets of possible sources of interference, environmental conditions and problem areas (section 5.2.1).

3.3 Field equipment and techniques

3.3.1 GRAB-WATER SAMPLERS

Grab samplers may be divided into two broad categories: those appropriate for taking samples in which only non-volatile constituents are of concern and those for taking samples in which dissolved gases and other volatile constituents must be analysed. Grab sample types can also be divided into discrete (surface or specific depth) and depth-integrating samplers. Both depth-integrating samplers and discrete samplers may be used to collect water for the determination of non-volatile constituents; a "multiple" sampler can also be used for this purpose.

No simple technique is available for obtaining a representative sample of a surface film such as oil or grease. A grab sample can be taken with a solvent-cleaned glass bottle opened just below the surface, but the sample will only be qualitative (SRS, 8.4.4; GDS, 12.1.1).

A grab sample may be taken using a "sampling iron" (section 3.3.1.1) with an appropriate bottle, a Van Dorn bottle (section 3.3.1.2), a Kemmerer-style bottle (section 3.3.1.2) or a pump-type sampler (section 3.3.1.2). Composite samples can be made from several grab samples or they can be obtained with special composite samplers (e.g. integrating samplers).

3.3.1.1 Depth-integrating samplers

A depth-integrated sample may be taken by lowering an open sampling apparatus to the bottom of the water body and raising it to the surface at a constant rate so that the bottle is just filled on reaching the surface. This procedure will result in a sample which approximates a theoretical depth-integrating sample. A sampling iron used for this purpose is briefly described below.

A very simple method is to take a sample through the whole depth, by selecting a flexible, clear plastic tube, weighted at one end, with an internal diameter designed to give a sufficient sample volume (e.g. 4 litres), lower the weighted end to the desired depth, pinch off the tube at the surface, raise the tube and drain the contents into a sample container (LTM, section 5.2.4).

Depth integration may not be possible in shallow streams where the depth is insufficient to permit integration. In such cases, care must also be taken not to disturb the river bottom when taking a sample. One suggestion in such cases is to dig a hole in the bottom, let the stream settle and sample down to the top of the hole.

Sampling Iron

This apparatus is a device which is made of iron and painted with a rust inhibitor. The weight of the sampler shown (Figure 3.1) is approximately 2.7 kg.

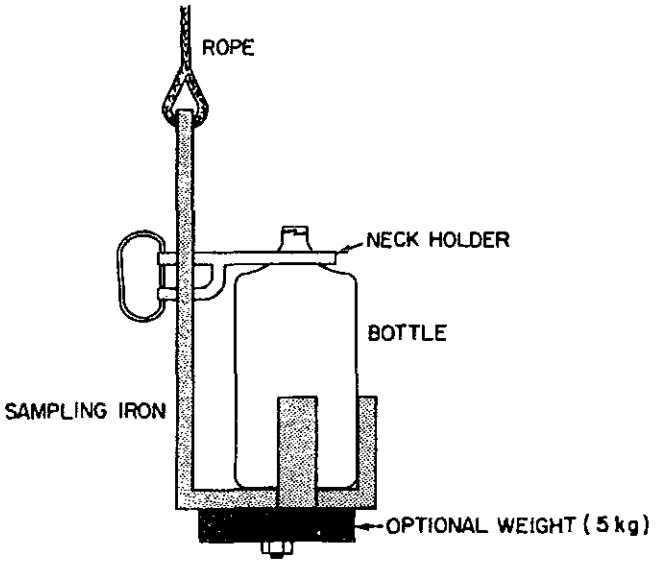

Figure 3.1 Sampling iron

Typically, this design permits the use of a 2 litre sample bottle when the bottle-neck holder is in the uppermost position; smaller bottles may be used when the holder is located in lower positions.

The sample bottles are placed in the sampler and secured by the neck holder. In some cases, sampling irons may have provision for additional weights to ensure a vertical drop in strong currents.

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

3.3.1.2 Discrete samplers

Discrete samplers are used to collect water at a specific depth. An appropriate sampler is lowered to the desired depth, activated and then retrieved. Van Dorn, Kemmerer and pump-type samplers are frequently used for this purpose. Other varieties are depicted in WQS, SRS and GEM: Meyer's sampling bottle (WQS, p. 134); Dussart sampler (WQS, p. 134; SRS, p. 97); depth immersion samplers (GEM, p. 13; SRS, p. 90); the rat-trap bottle (SRS, p. 98); Ruttner's bottle (SRS, p. 93); Friedinger's alternative to Kemmerer or Van Dorn (WQS, Fig. 21; SRS, p. 95); various forms of double-bottle systems (SRS, pp. 91-2). For a small stream, a household bucket on the end of a rope may be adequate.

Van Dorn bottle

The Van Dorn bottle is designed for sampling at a depth of 2 m or greater. The sampler, shown in its two configurations in Figure 3.2, is available in both polyvinyl chloride and acrylic plastic materials so that it may be used for general or trace metal sampling. Neoprene or silicone seals are available. The silicone seals are required for trace-metal sampling. The end seals are made of semi-rigid moulded rubber or rigid machined plastic with gaskets. A drain valve is provided for sample removal. The horizontal configuration should be used when samples are taken at the bottom, at the sediment-water interface, or when samples are required from a narrow band of the depth profile (e.g. chemocline, thermocline). Sampler volumes from 2 to 16 litres are available.

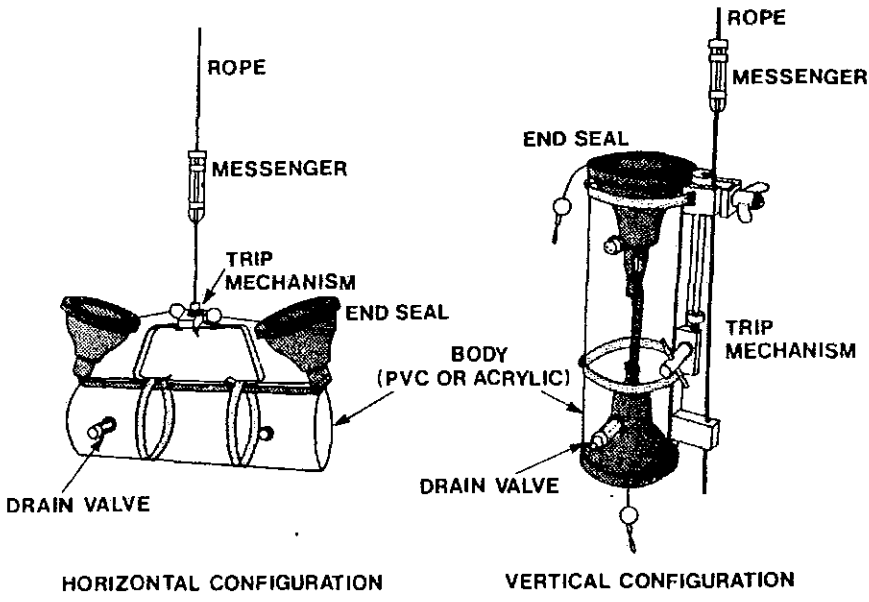

Figure 3.2 Van Dorn bottle

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

(a) Open the sampler by raising the end seals;

(b) Set the trip mechanism;

(c) Lower the sampler to the desired depth;

(d) Activate a metal or rubber messenger to "trip" the mechanism that closes the end seals of the sampler;

(e) Transfer the water sample from the Van Dorn bottle to individual sample containers via the drain valve.

Kemmerer sampler

The Kemmerer-style sampler is one of the oldest types of messenger-operated vertical samplers. It is commonly used in water bodies with a depth of 1 m or greater. The Kemmerer sampler, which is shown in Figure 3.3, is available in brass and nickel-plated brass for general water sampling. For trace metal sampling, Kemmerer samplers are made of polyvinyl chloride and acrylic plastic with silicone rubber seals. Both metal and plastic samplers are available in volumes ranging from 0.5 to 8 litre.

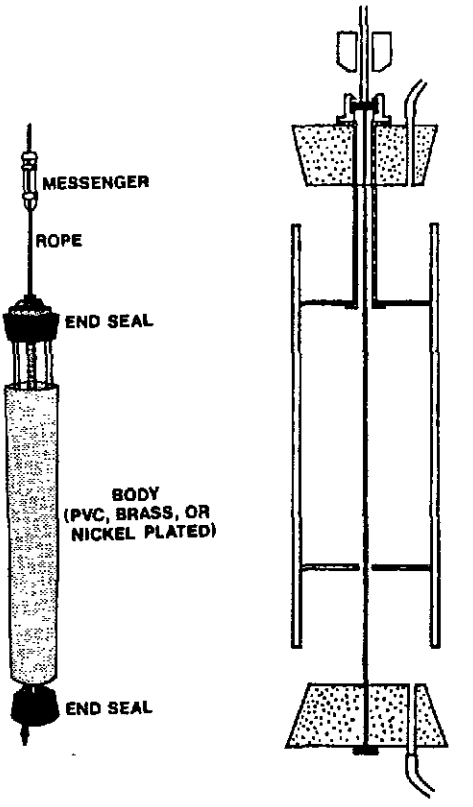

Figure 3.3 Kemmerer sampler

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

Both the Van Dorn and Friedinger (Figure 3.4) samplers have the advantage over the Kemmerer bottle that their lids do not lie in the path of the flow of water through the sampler; the Kemmerer lids are held over the openings, which can cause eddies and limited disturbance of stratification.

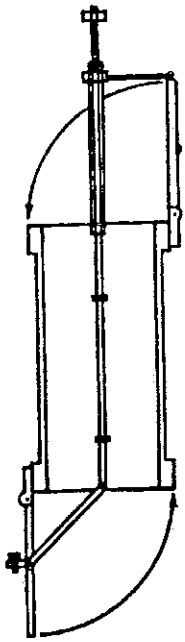

Figure 3.4 Friedinger sampler

Pumps

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

The following are general procedures:

(a) Place the input hose at the water depth specified by the sampling programme. Take care not to pump up oil, algal mats or other debris;

(b) Purge the pump and hoses with water from the station to be sampled before the actual water sampling begins;

(c) Each pump should be operated according to the instruction manual for that particular pump;

(d) Fill the type and number of sample bottles required at each station from the output hose.

Note: Take care not to contaminate the pump system. Do not permit the hoses to drag on the ground when the system is being transported.

Collecting samples in shallow waters presents special problems. A double-bottle pump system for this use is shown in Figure 3.5 (WQS, Fig. 23).

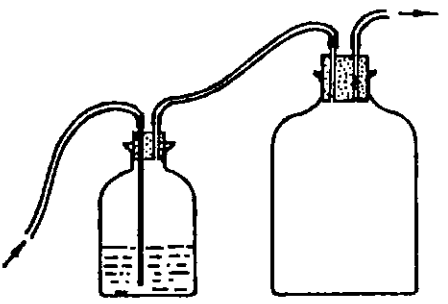

Figure 3.5 Pump-sampler system for shallow waters

Multiple sampler

A "multiple" sampler (Figure 3.6) permits the simultaneous collection of several samples of equal or different volumes at a site. Each sample is collected in its own bottle. When the samples are of equal volume, information concerning the instantaneous variability between the replicate samples can be obtained.

The sampler may be altered to accommodate different sizes and numbers of bottles according to the requirements of specific programs. This may be done by

changing cup sizes, length of cup sleeves and the configuration and size of openings in the clear acrylic top.

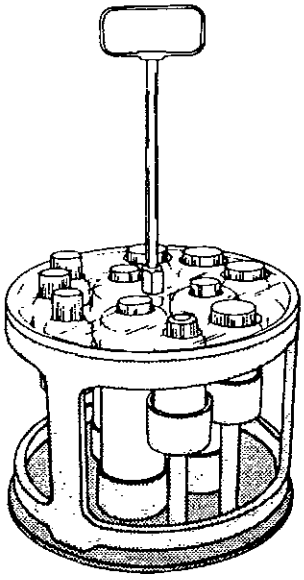

Figure 3.6 Multiple sampler

3.3.2 DISSOLVED-OXYGEN SAMPLER

A typical sampler for collecting samples for determining dissolved oxygen concentration and biochemical oxygen demand is illustrated in Figure 3.7. Other samplers such as the Dussart bottle have also been used, and a multiple sampler is shown in WQS, Figure 17. As these must be pulled up open, some admixture with upper layers is possible. If certain grab samplers are fitted with bottom drain tubes, they may be used by running the sample into the bottom of the analysis container.

The samples should be collected in narrow-mouthed biochemical oxygen demand (BOD) bottles that have bevelled glass stoppers to avoid entrapment of air in the samples. The procedure is outlined below:

(a) Place a 250- to 300-ml BOD bottle in the sampler and fasten the lid of the sampler in place, ensuring that the filling tube on the inside of the lid is positioned inside the BOD bottle;

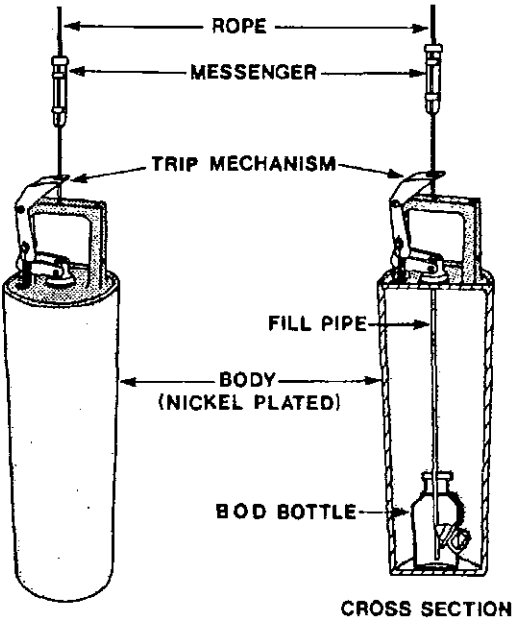

Figure 3.7 Dissolved-oxygen sampler

(b) Lower the sampler into the water to the required depth and leave it there until air escaping from the sampler can no longer be seen;

(c) Retrieve the sampler and remove the lid. If bubbles are present in the bottle, tap the sides of the BOD bottle with the glass stopper. This procedure will release all trapped air bubbles. Place the special bevelled stopper in the BOD bottle and then remove the bottle from the chamber of the sampler.

Note: Sampling of shallow streams is not advisable with this sampler. If it is necessary to sample a shallow stream, gently tilt the bottle downstream, minimizing sample agitation (bubbling).

3.3.3 Automatic samplers

Automatic samplers range from elaborate instruments with flexible sampling programmes requiring external power and permanent housing to simple, portable, self-contained devices such as a submerged bottle whose rate of filling is determined by a slow air bleed.

These devices can sometimes be programmed to sample over extended periods of time, but in order to meet the suggested maximum time limit of 24 hours to analysis 24-hour samplers are most common. They reduce costly personnel requirements if frequent sampling is required. If the site has automatic flow measurement then they can also provide flow-proportional samples. Both composite and individual sample models are available.

Regular maintenance and scrupulous cleanliness are essential if the samples are to be representative. It is difficult to obtain representative samples of suspended solids because of gas release on pumping which may also be a problem in sampling for dissolved gases.

An extensive list of automatic samplers and their capabilities is provided in Table 2.4 of HSS.

3.4 Sampling procedures as influenced by station location and season

The use of proper sampling techniques and good judgement to obtain representative water samples is of utmost importance. In the field, various sampling situations occur which require different sampling techniques. Situations in which water is shallow are handled in a manner and with apparatus different from that used at deep-water sites. Field technicians must be equipped to handle these situations. In addition, special considerations and precautions must also be taken during periods of ice and snow (section 3.4.3).

Since the fluvial characteristics of a sampling station can change with season, annual maximum and minimum flows and year-round accessibility should be considered when establishing a sampling station. When visiting an existing sampling station or when establishing a new site, the field investigator should take a variety of sampling equipment so that he or she is prepared for any situation. Some of the practical sampling considerations related to location and season of sampling are outlined in the following sections.

3.4.1 Sampling procedures from bridges, abutments, boats and aircraft

Sampling from bridges is often preferred because of its ease of access, exact identification of the sampling point, ability to control the position of sampling and capability of sampling safely under all conditions of flow and weather. Boats provide more flexibility, and the long travel time between stations can be avoided if a small boat can be trailed behind a car. The sampling point must be identified by triangulation from landmarks, care must be taken not to disturb bottom sediments, and there are navigation, high flow and storm hazards to consider. Aircraft, including helicopters, are expensive but fast and flexible. Tests have shown that the disturbance of water under helicopters does not significantly affect the dissolved-oxygen

concentration (GEM, Chap. 1, section 5).

The following are general procedures:

(a) Attach sufficient rope to permit the sampler to reach the required maximum depth. The other end of the rope should be secured to a permanent fixture on the bridge, boat or aircraft;

(b) Ensure that all of the lines that are suspending the samplers ("sampling irons", Van Dorn and Kemmerer types) remain in the vertical position to enable the accurate estimation of the depth of sample. Depending on the sampler used, weights may be added; the greater the stream velocity, the heavier the weight required. Every effort should be made to keep boats and float planes on location by anchoring or by the use of the boat's motor;

(c) When sampling from a boat, sample from the upstream side; if sampling from a float aircraft, sample from the upstream and outer side of the pontoons to minimize the chance of contamination from engine-oil leaks;

(d) When sampling, it is important that the sampling bottle not be permitted to touch the bottom of the river or lake to avoid contamination from stirred-up sediment. To prevent this, it is useful to predetermine the water depth;

(e) Rinse the sampler three or four times with the water to be sampled unless the sampler contains a bottle which contains a preservative or is sterile;

(f) Obtain the required sample volume for field tests, then repeat the procedure to fill the remaining bottles.

(g) Carry out the required preservation procedures for each sample. See section 6.2 on preservation techniques.

3.4.2 Sampling procedures from shores, stream banks and wharves

Bankside sampling should only be used where no alternative is possible (GEM, Chap. 1, section 5). If no other option is available, the sample should be taken where the water is turbulent or from the outside bank of a bend where the water is fast and deep.

A "sampling iron" is often used when water samples are collected from shores, stream banks and wharves.

The following are general procedures:

(a) Insert an open clean sampling bottle into the metal holder provided, ensuring that the ring clamp is securely locked in the holder frame by a key ring or suitable pin. Attach sufficient rope to the holder to permit sampling at the desired depths. Secure the other end of the rope to a permanent fixture on the bank or wharf. Sampling weights should be added as required, as dictated by stream velocity;

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

(c) Pull the bottle and holder in quickly to prevent the bottle from touching or becoming snagged on the bottom of the stream;

(d) Rinse the sampling bottle three or four times with the water collected in step (c). It is important that the sample bottle be well rinsed with the water to be sampled before the sample is collected;

Note: If preservative has been added to the bottle prior to sampling or if the bottle is sterile, do not rinse.

(e) Repeat steps (b) and (c);

(f) Rinse a beaker three or four times with the sampled water. Refill the beaker and carry out the field tests;

(g) After completion of field tests, repeat the sampling procedure to fill the remaining bottles required for laboratory tests;

(h) Carry out the required preservation procedures for each sample. See section 6.2 on preservation techniques.

3.4.3 WINTER SAMPLING PROCEDURES

Sampling of ice and snow under winter conditions requires somewhat different techniques. *The safety precautions outlined in section 13.7 should be followed.*

The following are general procedures:

(a) Overlying snow should be removed from the ice surface to provide a suitable working area;

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

(c) Except in the case of shallow flowing streams, samples must not be taken from the hole in the ice but should be taken as a depth-integrated sample below the ice cover (section 3.3.1.1);

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

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

(f) If a pump system is being used, power should be available to warm the lines (e.g. heating tapes) and sampler; large plastic bags around the lines and sampler will help to keep them from cooling.

3.5 Preparation for field trips

An instructive narrative account of a hypothetical week for a typical national water-quality monitoring network region in the USA is given in FSN, Appendix D, p. 179.

3.5.1 General preparation

(a) Obtain specific instructions on sampling procedures;

(b) Prepare an itinerary according to the sampling schedule (see also Chapter 13);

(c) Prepare lists of required equipment and materials;

(d) Ensure that all sample bottles have been cleaned in accordance with standard procedures;

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

(f) Prepare checklist (section 3.5.4).

3.5.2 Bottle washing and preparation

Sample bottles are usually provided by the analytical laboratory. The two major types of container materials are plastic and glass. Borosilicate glass is inert to most materials and is recommended when glass containers are required, such as when collecting samples to be analysed for organic compounds. Polyethylene is inexpensive and adsorbs fewer metal ions. It is used for samples which will be analysed for inorganic constituents, e.g. major ions and metals. Polyethylene containers should not be used for trace organic samples such as pesticides and some volatile substances which can diffuse through plastic walls. Light-sensitive samples require opaque or non-actinic glass containers. Narrow-mouthed bottles with pointed glass stoppers for dissolved gases have been described above (3.3.2). Containers for microbiological samples must withstand sterilization, either by autoclaving or with ethylene oxide.

Bottle caps are a potential source of problems. Glass stoppers may seize up, particularly with alkaline samples. Cap liners other than Teflon may introduce contaminants or absorb trace samples.

Containers and cleaning procedures for specific determinands are given in Tables 3.1 and 3.2. For additional information, see HSS, section 3.4.1; SRS, section 9; GST, section 5.3; and GPH section 3.2.2 and table.

3.5.3 Selection of sample volume

The volume of sample required depends on the type and number of parameters to be analysed, the analytical method and the expected concentrations of the parameters in the water. Laboratory personnel will specify the sample volume required. The required sample volume can be determined by listing all of the parameters that are preserved in the same way, totalling the volume needed for preparation and analysis and then multiplying by two for duplicate and three for triplicate analyses.

The following points should be kept in mind (SRS, section 8.1):

(a) When contact with air is to be avoided, e.g. when determining dissolved gases, substances that react with air, pH and conductivity in waters of low conductivity, the sample container should be completely filled;

(b) When samples require vigorous shaking before taking aliquots for analysis, the container should not be completely filled;

(c) Where both requirements must be met, completely fill the bottle but add pieces of clean, sterile inert solid such as beads. Precautions for sampling then will depend on how sensitive the determinand is to air;

(d) When the sample contains discrete particles, e.g. undissolved materials, bacteria and algae, a volume of sample larger than usual may be needed to minimize errors arising from statistical variation in the number of particles present in a given volume of sample.

3.5.4 Checklist prior to field trip

(a) Check and calibrate meters (pH, specific conductance, dissolved oxygen, turbidity) and thermometers;

(b) Replenish supplies of reagents for dissolved oxygen determinations as well as reagents for chemical preservation;

(c) Obtain fresh buffer solutions; pH values for the buffers should be close to the values expected in the field;

(d) Obtain KCl solution for pH probes;

(e) Obtain road maps, station-location descriptions, field-sampling sheets, sampling bottles, labels, samplers, preservation reagents, pipettes and equipment manuals;

(f) Obtain writing materials, extra rope and a comprehensive tool box;

(g) Obtain charging cords if the equipment has in-field charging capabilities;

(h) Obtain distilled water and clean beakers for pH, blanks and buffer measurements;

(i) If field filtering is required, obtain filtering apparatus;

(j) If microbiological sampling is to be done, obtain sterile bottles and ice chests. Ice chests are recommended for all sample storage;

(k) Check the contents of the emergency first-aid kit.

TABLE 3.1 Washing procedures and containers for water samples

Parameter(s) to be analysed	Recommended container*	Washing procedure
Acidity Alkalinity Calcium Chloride Fluoride Hardness Magnesium pH Sodium Sulphate Colour Specific conductance Turbidity Nonfilterable residue Potassium Arsenic	1000 ml polyethylene	Rinse three times with tap water, once with chromic acid,† three times with tap water, once with 1:1 nitric acid and then three times with distilled water in that order
Nitrogen; ammonia Nitrogen, nitrate nitrite Carbon, total organic Nitrogen, total	250 ml polyethylene	Rinse three times with tap water, once with chromic acid,† three times with tap water and three times with distilled water in that order
Phosphorus, total	50 ml glass (Sovirel)	Rinse three times with tap water, once with chromic acid,† three times with tap water and three times with distilled water in that order

* Teflon containers can also be used to replace either the recommended polyethylene or glass containers.

† Chromic acid - 35 ml saturated $Na_2Cr_2O_7$/1 l reagent grade conc. H_2SO_4.

‡ Chromic acid should not be used when the sample will be analysed for chromium.

§ Ultrapure distilled water is obtained by passing distilled water through a Corning model AG-11 all-glass distillation unit and then through a Millipore Super Q Ultrapure Water System containing a prefilter catridge, an activated carbon cartridge and a mixed bed deionization catridge.

** Special grade acetone - pesticide grade when GC analysis to be performed, UV grade for LC analysis.

Table 3.1 *(contd)*

Parameter(s) to be analysed	Recommended container*	Washing procedure
Aluminum Antimony Barium Beryllium Cadmium Chromium‡ Cobalt Copper Iron Lead Lithium Manganese Molybdenum Nickel Selenium Strontium Vanadium Zinc	500-1000 ml polyethylene (depending upon number of metals to be determined)	Rinse three times with tap water, once with chromic acid,† three times with tap water, once with 1:1 nitric acid and then three times with ultrapure distilled water,§ in that order
Silver	250 ml polyethylene (amber)	Rinse three times with tap water, once with chromic acid,† three times with tap water, once with 1:1 nitric acid and then three times with ultrapure distilled water,§ in that order
Mercury	100 ml glass (Sovirel)	Rinse three times with tap water, once with chromic acid,† three times with tap water, once with 1:1 nitric acid and then three times with ultrapure distilled water,§ in that order
Organochlorinated pesticides and PCBs	1000 ml glass (amber) with Teflon-lined cap	Rinse three times with tap water, once with chromic acid,† three times with

Table 3.1 *(contd)*

Parameter(s) to be analysed	Recommended container*	Washing procedure
Organophosphorus	1000 ml glass (amber) with Teflon-lined cap	organic-free water, twice with washing acetone, once with special grade** acetone, twice with pesticide grade hexane and dry (uncapped) in a hot air oven at 360°C
Pentachlorophenol	1000 ml glass (amber) with Teflon-lined cap	Rinse three times with tap water, once with chromic acid,† three times with organic-free water, twice with washing acetone, once with special grade** acetone, twice with pesticide grade hexane and dry (uncapped) in a hot air oven at 360°C for at least 1 h
Phenolics	1000 ml glass (amber) with Teflon-lined cap	Rinse three times with tap water, once with chromic acid,† three times with organic-free water, twice with washing acetone, once with special grade** acetone, twice with pesticide grade hexane and dry (uncapped) in a hot air over at 360°C for at least 1 h
Phenoxy acid herbicides	1000 ml glass (amber) with Teflon-line cap	Rinse three times with tap water, once with chromic acid,† three times with organic-free water, twice with washing acetone, once with special grade** acetone, twice with pesticide grade hexane and dry (uncapped) in a hot air oven at 360°C for at least 1 h

TABLE 3.2 Washing procedures and containers for bottom sediments and fish-tissue samples

Parameter(s) to be analysed	Recommended container*	Washing procedure
Aluminum Barium Beryllium Cadmium Chromium Cobalt Copper Iron Lead Lithium Manganese Mercury Nickel Zinc	Polyethylene bags (Whirl-Pak or Zip-Lock)	Use as shipped from manufacturer - no washing required
Organochlorinated pesticides and PCBs	Reynolds Aluminum small freezer trays, 11.4 cm x 14 cm	Rinse three times with tap water, three times with organic-free water, twice with washing acetone, once with special grade† acetone, twice with pesticide grade hexane and dry in a hot oven at 360°C for at least 1 h

* Teflon containers can also be used to replace either the recommended polyethylene or glass containers.

† Special grade acetone - pesticide grade when GC analysis to be performed, UV grade for LC analysis.

CHAPTER 4

FIELD-MEASURED PARAMETERS

This chapter describes the measurement of some water-quality parameters. Conductivity, pH, dissolved oxygen, temperature, turbidity, colour and transparency can change during storage of a sample, and should therefore be measured *in situ* or in the field as soon as possible after sample collection.

The sample collector should also look out for any unusual features of the body of water being sampled, or any changes from previous sampling periods. These qualitative observations might include unusual colour or odour, surface films and floating objects. Any special environmental conditions should be noted such as rainfall, heavy winds, storm runoff or ice breakup.

4.1 pH measurement

The pH is a measure of the acidity or alkalinity of a solution. It is the negative of the logarithm to the base 10 of the hydrogen ion concentration. Neutral solutions have a pH of 7, acid solutions a pH of less than 7 and alkaline solutions a pH greater than 7. In unpolluted natural waters, the pH is largely controlled by a balance between carbon dioxide, carbonate and bicarbonate ions. The concentration of carbon dioxide can be altered in turn by exchanges at the air-water interface and by photosynthesis and decay processes.

Changes in pH are caused by acid rain, industrial wastes, mine drainage water or leaching of minerals. The pH is an important criterion of the quality of water because it affects the viability of aquatic life and many uses of water.

Optimally, pH is determined *in situ*, but if this cannot be done it can be determined by taking a water sample and measuring the pH as soon as possible in a field laboratory or on the shore of the water body.

The preferred method of measurement is electrometric because of its ease and greater accuracy. The pH is proportional to the electromotive force (EMF) or electrical potential between a hydrogen-ion-responsive glass membrane electrode, immersed in the sample, and a reference electrode. There are many portable battery-powered pH meters on the market today; the investigator should select the one that suits his needs best. Digital meters are preferable, since analogue (e.g. pointer on a

scale) meters are sometimes difficult to read while taking *in situ* measurements, as in a boat on rough water.

For additional information, see TNW, section 3.2.

4.1.1 Procedure for taking pH measurements

Use the manual supplied with the instrument to calibrate, operate and maintain the pH meter. The following should also be considered:

(a) The instrument, including the battery, should be thoroughly checked and then calibrated in the laboratory before it is taken to the field. The buffer solutions should be periodically checked in the laboratory;

(b) In the field, the instrument should be recalibrated before each reading with appropriate buffer solutions and according to the instructions in the operating manual;

(c) Adjust the temperature of the buffer solutions and electrodes by submerging the bottles of buffer and electrodes in the water sample. Extreme care must be taken to prevent the water from entering the buffer bottles or the filling hole of the reference electrode. An equivalent procedure is to measure the temperature of the buffer, to calibrate the meter and then to re-adjust the temperature compensation to the temperature of the sample;

(d) If the electrodes have not been used recently, or have been allowed to dry for several days, they may require 10 to 20 minutes to stabilize. If the electrodes will not stabilize, try either a new reference or a pH elecrode tip in a rubber or plastic sack (such as the finger cut from a plastic glove) containing a few millilitres of buffer solution;

(e) In dry, windy climates, a static charge tends to build on the plastic face of a pH meter, causing erratic movement of the indicator needle. Antistatic spray, such as that for phonograph records, sprayed on the meter face reduces this problem;

(f) Protect the meter from extreme temperature changes during measurement, as these affect the stability of the electronic system and, consequently, the precision of the measurement;

(g) In cold waters, slow electrode response may result from the precipitation of the saturated filling solution in the reference electrode,

thereby reducing the fluid contact. This can be remedied by permitting the filling solution to reach ambient temperature before filling the reference electrode. However, this will only remedy the situation for a few samples;

(h) Before taking a measurement, thoroughly rinse electrodes and a glass or plastic beaker with sample water. Let the electrodes stand in the sample water for at least two minutes to stabilize before taking a reading. A reading, using a fresh sample, should be repeated until reproducible results (± 0.1 pH units) are obtained.

The pH may also be determined colorimetrically by the use of pH indicators and buffer standards for visual or colorimeter comparison. This method is in general less accurate than electrometric methods, and is limited to waters with a low content of coloured substances and with little turbidity.

4.1.2 Maintenance of pH probes

When combined electrode assemblies have been stored dry for a long period, the glass membrane should be soaked in a 3-mol/l KCl solution for 12 to 24 hours before use. Meters may have a probe storage reservoir which should be filled with electrolyte. Glass electrodes that have not been conditioned before use may not stabilize properly and may require frequent recalibration.

If the pH meter shows a drift and the probe has been stored and correctly conditioned, the probe itself may require topping up with additional 3-mol/l KCl solution. Fill the probe according to specific assembly instructions. Frequent recalibration caused by electrodes with persistent drift may also be minimized by soaking the electrode in 0.1 mol/l HCl or strong alkali.

The most common cause of trouble with combined electrode assemblies is a blockage in the diaphragm. If this occurs, as indicated by persistent drifting, soak the electrode in ammonium hydroxide. For optimum performance, electrodes should be soaked for one to two hours in buffer prior to use, with buffers and samples equilibrated at the same temperature (use a constant temperature bath).

As with any piece of equipment, the meter and probe should be protected from dirt, freezing temperatures and rough handling at all times.

4.2 Conductivity measurement

Conductivity, or specific conductance, measures water's ability to conduct an electric current and depends on the concentration of ions in solution. It is measured in the field using a battery-powered Wheatstone bridge-type instrument.

Most inorganic salts, acids and bases dissociate into ions in water. Many organic substances dissociate little or not at all. Although not specific for individual substances, changes in conductivity can indicate saline intrusion and other sources of pollution. The relationship between conductivity and the concentration of dissolved solids is usually linear for most natural waters. Changes in this relationship indicate changes in the proportions of different salts and therefore changes in the sources of dissolved substances entering the water body.

In situ conductivity measurement is preferable; if this is not possible, a sample is collected and the measurement made as soon as possible, since the conductivity of a water sample may change with time. Dissolved carbon dioxide, for example, contributes to the conductivity of a body of water.

Conductivity is temperature dependent. If the conductivity measurement is not automatically temperature corrected, usually to 20° or 25°C, then the temperature at the time of measurement should also be recorded.

There are various conductivity meters available which also measure the temperature and salinity. Since probes vary and cable lengths are optional, the investigator must select the equipment to meet the requirements of the sampling programme.

Samples containing fat, grease or oil will pollute the electrodes, especially platinum black electrodes, causing erratic results. Polluted electrodes must be cleaned immediately after use.

4.2.1 Procedure for taking conductivity measurements

The manual supplied with the conductivity meter should be followed for calibration, operation and trouble-shooting.

Some general recommendations follow:

(a) The meter, including the battery, should be checked and calibrated before it is taken to the field;

(b) The instrument should be recalibrated in the field before each reading;

(c) To calibrate the instrument, KCl standard solutions with the specific conductance closest to the values expected in the field should be used (Table 4.1);

(d) Do not use the same water sample in which the pH was measured to measure the specific conductance, as KCl diffuses from the pH electrode;

(e) Ensure that the probe does not touch the sides or bottom of the sample container;

(f) Rinse sample containers and probe several times with the water sample;

(g) Repeat the procedure with a fresh sample until reproducible conductivity readings are obtained, i.e. within ±5 per cent.

TABLE 4.1 Specific conductance of KCl solutions at 25°C

Concentration mol/l	g/l	Specific conductance µS/cm
0.0001	0.007456	14.94
0.0005	0.03728	73.90
0.001	0.07456	147.0
0.005	0.3728	717.8
0.00702	0.5234	1000
0.01	0.7456	1413
0.02	1.5912	2767

Note: This table has been modified from *Standard Methods for the Examination of Water and Wastewater* (1980)

4.2.2 Conductivity meter and probe maintenance

Equipment for measuring conductivity must receive the same care and maintenance required by all sensitive instruments. Accurate readings require that the meter be protected from dirt, shocks and freezing temperatures.

4.3 Dissolved-oxygen measurement

Water in contact with air dissolves oxygen as well as the other components of air. After sufficient time, the water becomes saturated with oxygen, the equilibrium concentration being dependent on the partial pressure of the oxygen and on the temperature. The concentration of oxygen in natural waters may not be the equilibrium saturation value because of rapid changes in atmospheric pressure, water temperature, oxygen consumption by chemical reducing agents or micro-organisms, or oxygen production by aquatic green organisms.

The dissolved-oxygen concentration is important for the evaluation of surface-water quality and of waste-treatment process control.

Dissolved oxygen (DO) should be measured *in situ* or in the field, as concentrations may show a large change in a short time if the sample is not adequately preserved. Even when the sample is preserved, as in a Winkler analysis, it is advisable to run the titrations within three to six hours from the time of sampling. Dissolved oxygen concentrations may be determined directly with a DO meter or by a chemical method such as Winkler analysis. The usual measure of concentration is mg/l, but per cent saturation is also used. The method chosen will depend on a number of factors including the precision and accuracy required, convenience, equipment and personnel available and expected chemical interferences. The methods discussed in this section are DO meters, Winkler analysis and the Hach method. For very precise measurements the potentiometric method should be considered.

4.3.1 SAMPLING

(a) Collect water samples using the dissolved-oxygen sampler (details of a sampler are given in section 3.3.2). Three samples must be taken. The recorded DO value will be the average of at least two readings that are within 0.5 mg/l of each other;

(b) Measure the dissolved-oxygen concentration of the samples using a dissolved-oxygen meter or Winkler chemical analysis.

4.3.2 DISSOLVED-OXYGEN METERS

Dissolved-oxygen meters can be used to measure dissolved-oxygen concentrations *in situ*, in the field or in the laboratory. They work on one of two principles: polarographic or potentiometric. Strictly speaking, the instruments respond to activity of oxygen, not concentration; thus, fresh water saturated with oxygen gives the same reading as salt water saturated with oxygen at the same pressure and temperature, although the solubility of oxygen in salt water is less. The processes are also temperature dependent; most instruments include methods for temperature compensation. For further information see GEM, Chapter III, pp. 16-28; TNW, p. 39; and CPQ, p. 50.

The meters can be used under conditions which interfere with iodometric methods (e.g. Winkler analysis), such as samples which are highly coloured or turbid or which contain readily oxidizable or other interfering substances such as sulfite, thiosulfate, polythionate, mercaptans or free chlorine. This method can also be used to give a continuous record where needed, and can be used in conjunction with BOD measurements.

The procedure is as follows:

(a) Calibrate the instrument by placing the probe in a water sample of known dissolved oxygen concentration, i.e. determined by the Winkler method or in a freshly air-saturated water sample of known temperature. With the latter method calibration can be done by using a table listing the solubility of oxygen in water at different temperatures and pressures (GEM, Chap. 3, p. 26);

(b) Place the probe in the solution to be measured and agitate the probe. Let the probe come to temperature.

4.3.3 WINKLER ANALYSIS

There are a number of modifications of this iodometric method, particularly the Alsterberg-azide modification described here, which avoids interference by nitrite ions. This method can be used to determine dissolved oxygen concentrations in the field or laboratory with high precision (TNW, pp. 40,55; CPQ, p. 50; WQS, p. 146).

*4.3.3.1 Winkler reagents**

(a) *Manganous sulfate solution* - Dissolve 365 g manganous sulfate monohydrate, $MnSO_4.H_2O$, or 400 g manganous sulfate dihydrate, $MnSO_4.2H_2O$, or 480 g manganous sulfate tetrahydrate, $MnSO_4.4H_2O$, in freshly boiled distilled water and dilute to 1 litre. A magnetic stirrer will speed up dissolution. Store in a glass bottle;

(b) *Alkaline-iodide-azide solution* - Dissolve 400 g sodium hydroxide pellets, NaOH, in 500 ml of freshly boiled distilled water. Add the sodium hydroxide in small increments and dissolve each addition before proceeding. Add 900 g sodium iodide, NaI, while the solution is still hot. Dissolve 10 g sodium azide, NaN3, in 40 ml distilled water. Add the sodium azide solution to the first solution and dilute, if necessary, to 1 litre;

(c) *Sulfuric acid* - concentrated reagent grade;

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* As described in the *Analytical Methods Manual*, Water Quality Branch, Inland Waters Directorate, Environment Canada, Ottawa, 1981.

(d) *Potassium bi-iodate, 0.000833 mol/l [0.01 N]* - Dry a suitable amount of primary standard grade bi-iodate, $KH(IO_3)_2$, at 105°C for one hour. After cooling in desiccator, weigh out 0.3249 g and dissolve in distilled water. Dilute to 1 litre and store this solution in a tightly stoppered dark glass bottle;

(e) *Starch indicator solution* - Add 30 g of soluble starch to 1 litre of glycerol. Heat the mixture to 180°C, maintaining the temperature until the solution is transparent;

(f) *Sodium thiosulfate solution, 0.019 mol/l [0.019 N]*, 1 ml = 1.5 mg DO - Dissolve 4.8 g sodium thiosulfate pentahydrate, $Na_2S_2O_3.5H_2O$, and 0.1 g sodium carbonate, Na_2CO_3, in 1 litre of distilled water. Add a few drops of chloroform as a preservative.

(g) *Standardization procedure* - Fill a 250-ml BOD bottle with water (not chlorinated tap water). Add 1.0 ml alkaline-iodide-azide reagent, replace the stopper and mix. Add 1.0 ml concentrated sulfuric acid and mix. Add 1.0 ml manganous sulfate and mix again. Transfer 100 ml of solution from the BOD bottle to an Erlenmeyer flask and add 10.0 ml potassium bi-iodate solution. let the mixture stand for at least two minutes in the dark, then titrate the liberated iodine with thiosulfate solution to a very pale straw colour. Add four drops of starch solution. Continue the titration until the blue colour just disappears.

Normality (N_1) of thiosulfate is obtained from the expression:

$$N_1 = N_2 \times V_2/V_1$$

where

N_1 = normality of sodium thiosulfate;
V_1 = volume of thiosulfate;
N_2 = normality of the standard bi-iodate solution;
V_2 = volume of potassium bi-iodate solution (this is always 10.0 ml.).

4.3.3.2 Winkler procedure

Remove stopper from the BOD bottle and add, using pipettes placed just below the water surface, 1.0 ml of manganous sulfate reagent followed immediately by 1.0 ml of alkaline-iodine-azide solution. Restopper the bottle at once and mix the contents by shaking vigorously for at least 20 seconds or until the precipitated manganous and manganic hydroxide is evenly dispersed. No air bubbles should be trapped in the bottle. Let it stand for about two to three minutes, then shake the bottle

again. Allow the precipitate in the sample to settle at least one-third of the way down the bottle (about 10 to 20 minutes required).

Add 1.0 ml concentrated, reagent grade H_2SO_4 by permitting the acid to run down the neck of the bottle. Restopper the bottle and shake gently until the dissolution of the precipitate.

By means of a pipette transfer 100 ml of solution from the BOD bottle to an Erlenmeyer flask.

Titrate at once with thiosulfate solution to a very pale straw colour. Add four drops of starch solution. Continue the titration until the blue colour just disappears.

Calculate the dissolved oxygen content of the sample as follows:

$$\text{mg/l DO} = \frac{N \times V \times 8 \times 100}{99.3}$$

where

N = normality of sodium thiosulfate solution;
V = volume of sodium thiosulfate solution used in the titration.

This method is not applicable under the following conditions:

(a) Samples containing more than 1 mg/l of ferrous iron. However, if 1 ml fluoride solution is added before acidifying the sample and there is no delay in titration, the method can be used in the presence of up to 100-200 mg/l ferrous iron. The potassium fluoride solution is made by dissolving 40 g $KF.2H_2O$ in distilled water and diluting to 100 ml;

(b) Samples containing sulfite, thiosulfite, polythionate, free chlorine or hypochlorite;

(c) Samples with high concentrations of suspended solids;

(d) Samples containing other oxidizing or reducing materials.

In instances where this method is not applicable, a DO probe should be used.

4.3.4 HACH METHOD

The Hach* method is used for determining dissolved-oxygen concentrations in the field. It involves the same chemical reactions as Winkler titration. The reagents, except the titrant, which is PAO (phenylarsine oxide), not thiosulfate solution, are contained in individual "powder pillows" premeasured for the required concentrations.

This method can be used when results within ±0.5 to 1.0 mg/l of the true value are sufficient for the purpose of the study.

The kit contains a Hach dissolved-oxygen sampler, 300-ml BOD bottle, 60-ml BOD-type bottle, a vial and a small dispensing bottle containing the PAO titrant, as well as pillows of reagents in the dry granular form. Starch, which is not supplied with the kit, must be obtained to assist in the detection of the end point.

Sample collection

(a) After the removal of the glass stopper, place the 60-ml DO sample bottle in the sampler;

(b) Replace the sampler lid, with the sample inlet tube extending into the bottle;

(c) Lower the sampler by the chain, then pull out the stopper at the desired depth;

(d) When air bubbles stop rising from the sampler, raise the sampler by the chain and carefully remove the sample bottle;

(e) Add the contents of one pillow of dissolved-oxygen I powder (manganous sulfate) and the contents of a dissolved-oxygen II powder (alkaline-iodide-azide) pillow. Stopper the bottle carefully so that air is not trapped in the bottle (see Note (1) below). Grip the bottle and shake vigorously (see Note (2) below). A flocculant precipitate will be formed. If oxygen is present, the precipitate will be brownish orange;

(f) Let the sample stand until the floc has settled halfway and leaves the upper half of the bottle clear. Again shake the bottle and let it stand until the upper half of the bottle is clear;

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* Hach Chemical Company, Ames, Iowa, USA.

(g) Remove the stopper and add the contents of one dissolved-oxygen III powder pillow (dry acid). Carefully restopper (see Note (1)) and shake to mix. The floc will dissolve and a yellow colour will develop if oxygen is present. This is the prepared sample;

(h) Pour off the contents of the DO bottle until the level just reaches the 30-ml mark on the bottle;

(i) While swirling the sample to mix, quickly add PAO by drops, counting each drop until the samples change to a pale straw colour. Add a few drops of starch solution. Continue adding PAO until the colour changes from blue to colourless. Each drop is equal to 0.2 mg/l dissolved oxygen.

Notes:

(1) It is difficult to stopper the DO bottle without getting air bubbles trapped in the bottle. To avoid air bubbles, tip the DO bottle slightly and insert the stopper with a quick thrust. This will force the air bubbles out. If air bubbles are trapped in the DO bottle in steps (e) or (g), the sample should be discarded and the test started over.
(2) A small amount of powdered reagent may remain stuck to the bottom of the DO bottle at this point, but this will not affect the test.
(3) Do not permit the PAO solution to stand in direct sunlight, as it is decomposed by ultraviolet radiation.
(4) When the water is saturated with dissolved oxygen, small bubbles of oxygen coming out of solution in the 60-ml bottle will cause an air bubble to form at the stopper. This is unavoidable; proceed with instructions as usual.

4.4 Temperature measurement

Temperature must be measured not only as an important property of water in itself, but also because it is a variable in several of the other parameters measured in the field.

Temperature should optimally be measured *in situ*, as the temperature of any water sample will readily equilibrate with its surroundings.

Temperature measurements may be taken with a great variety of thermometers. These include alcohol-toluene, mercury-filled, bimetallic strip or electrical thermometers. The last category includes thermocouples and less portable varieties such as thermistors, quartz and resistance thermometers. In addition some meters, such as those used to measure dissolved oxygen and specific conductance, have temperature-measuring capabilities. Temperature values at specified depths can be measured *in situ* if adequate cables and probes are available. Oceanographic reversing thermometers, which are turned over to fix the reading after five minutes at the depth, or maximum-minimum thermometers may be used if suitable electrical instruments are not available. Otherwise, temperatures must be measured immediately in the field

after the water sample has been taken from the required location and depth. Thermographs, i.e. continuous recording devices, and remote-sensing devices are also available.

For further information, see GEM, Chapter III, p. 6; WQS, p. 145 and TNW, section 2.1.

In-field procedure

If a thermometer is used:

(a) Rinse the thermometer by pouring a portion of the water sample over it;

(b) Immerse the thermometer in the sample for approximately one minute or until the reading stabilizes. Do not place the thermometer in any of the sample bottles being shipped to the laboratory;

(c) Record the value in degrees Celsius on the field sheet.

4.5 Turbidity measurement

Turbidity is an optical measure of suspended sediment such as clay, silt, organic matter, plankton and microscopic organisms in a water sample. It is to be distinguished from "suspended solids", which are measured as the dried weight of particles that can be filtered out of the water sample. Turbidity is not simply a function of the amount of material present, since particle size is an important factor.

Fine-particulate matter in suspension may be stirred up by flash floods, torrential flow or passage of boats, and can be generated by mining or industrial wastes, by the formation of metal oxides such as iron or manganese, and by leaching of humic substances or growth of microbiota. Turbidity affects virtually all uses of water and adds to the cost of water treatment for these uses.

Whenever possible, turbidity should be measured in-field; otherwise, it is measured at the laboratory. The field measurement is preferable, since some of the particulate matter will settle or adhere to the container wall during transportation. Furthermore, changes in the pH of the sample may cause the precipitation of carbonates and humic acids, affecting the turbidity of the sample. When the analysis cannot be done immediately, the sample should be stored in the dark for not more than 24 hours.

Turbidity can be measured by visual methods (in Jackson Turbidity Units or JTU) or nephelometric units (in Nephelometric Turbidity Units or NTU).

To use the Jackson Candle Turbidimeter, the length of the light path through the suspension at which the outline of the standard candle becomes indistinct is compared with standard suspensions of fine silica, or Formazin polymer prepared by mixing hexamethylene-tetramine and hydrazine sulfate under standard conditons.

Nephelometric methods are preferred on account of their greater precision, sensitivity and application over a wide turbidity range. They measure light scattering by the suspended particles. The intensity of scattered light depends on many factors: the number and size of particles, their refractive indices, the wavelength of the light and the angle of scattering. Instruments of different design may give different results for the same sample (TNW, section 2.3). Colour in the sample can cause errors, as will variations in the light source. Both problems can be minimized by using an instrument which simultaneously measures and ratios the scattered and transmitted light, with both scattered and transmitted beams traversing the same path length. See also CPQ, p. 20.

In-field procedure

(a) To operate the turbidity meter, follow the manual for the instrument;

(b) Prepare calibration curves for each range of the instrument by using appropriate standards;

(c) Test at least one standard in each range to be used;

(d) Make certain that the turbidity meter gives stable readings in all sensitivity ranges used;

(e) Keep sample tubes clean both inside and out; replace them when they become scratched or etched. Do not handle the tubes in the region where the light beam enters them;

(f) Shake the sample vigorously before analysis. Readings should always be made after the same time period following the homogenizing of the sample (e.g. 10 seconds) to ensure uniform data;

(g) It is important to pour off the sample quickly and to measure the turbidity of the sample in triplicate.

4.6 Colour

The colour of the original sample may be called "apparent colour", which includes the effect of suspended material, as well as the "true colour" arising from dissolved substances. The true colour is observed after filtration or centrifugation.

(Even clean water viewed through a few metres appears light blue because of light scattering).

Colour results from the presence of metallic ions, humus and peat materials, plankton and industrial wastes. It is important other than for esthetic reasons when the water is used for potable water supplies, washing or processing water, or recreational purposes.

The hues ordinarily present in natural waters can be matched by mixtures of chloroplatinic acid and cobaltous chloride hexahydrate, 1 mg/l of the former to 2 mg/l of the latter constituting one PCU (platinum-cobalt unit). Since the platinum-cobalt standard method is not convenient for field use, the colour of the water may be obtained by visually comparing tubes filled with distilled water and closed by standard glass colour discs with tubes filled with sample and closed by plain glass discs. The coloured glass discs are in turn calibrated against platinum-cobalt.

Waters mixed with certain industrial wastes may be so different in hue from platinum-cobalt mixtures that comparison is inappropriate or impossible. In this case a filter photometer may suffice, although a double-beam spectrophotometer would be preferable if the samples can be taken to the laboratory.

Another problem is turbidity. Centrifuging may give variable results depending on the sizes of the particles, and many filters will adsorb the dissolved colour substances while removing the suspension. Use of non-adsorbing calcined filter aids is recommended (TNW, p. 22).

For further information, see TNW, section 2.2 and CPQ, p. 18.

4.7 Transparency

Transparency of water is determined by its colour and turbidity. A measure of transparency can be obtained as the depth in metres at which a 20- to 30-cm diameter disc, called a Secchi disc, usually painted in black and white quadrants, disappears when lowered slowly and vertically into the water. Standard type on white paper is sometimes used instead of the disc (WQS, pp. 57, 147).

The measurement is usually made in lakes and other deep water bodies, and is useful in assessing biological conditions.

4.8 General summary of field procedures

Regardless of the specific parameters of interest, a routine should be followed at each sampling station. The following is a general summary of procedures to

be followed at each station:

(a) Calibrate meters;

(b) Standardize sodium thiosulphate when using Winkler analysis for dissolved oxygen;

(c) Run field or *in situ* measurements for pH, conductivity, dissolved oxygen, temperature and turbidity;

(d) Rinse all bottles with sampled water except for those which contain preservatives or those used for dissolved oxygen and bacteria analyses;

(e) Collect and preserve samples according to the instruction manual;

(f) Complete field sheet accurately according to the instruction manual;

(g) Put bottles in appropriate shipping containers;

(h) Label boxes and complete field sheets with all required information.

CHAPTER 5

RECORDING OF FIELD DATA

Monitoring is undertaken to generate information. If the data are not properly presented and circulated to the information users, the monitoring programme has failed.

Proper planning of reports at the network or project-design stage can greatly reduce the time necessary to generate reports (DNM, p. 258). Standard reporting forms expedite the reporting of data. Report formats will vary greatly, depending on the network's purpose, the primary users and the budget available. Where different networks are contributing data to a national or international database, it is most desirable that the data be compatible.

The needs of the users should be paramount. It is most uneconomical to expend a large effort on gathering data which are not fully analysed or used (SAQ, p. 10). A method for receiving and utilizing feedback from the users should be arranged in order to "fine tune" the reporting procedure (DNM, p. 259).

In every step of a water-quality data-collection programme, from planning to report writing (See Figure 1.1 and Table 1.1), it is essential to record all pertinent data.

This chapter deals only with the recording of field data. The sampling location, sampling date, parameters measured in the field and the corresponding values must be recorded and kept together throughout the handling of the data. If any one of these essential items goes astray, the whole effort is wasted.

5.1 Station-location descriptions

The importance of an accurate written description of each station location and the conditions under which the samples are collected cannot be overemphasized. In fact, interpretation of water-quality data may be limited by the accuracy of such descriptions. It is therefore recommended that a precise format, such as that shown in Figure 5.1 (SWQ), be used. The following information is required:

(a) Station description - An accurate description of the sampling location includes distances to specific reference points. It is important that these reference points be long-standing and clearly identified. For example, "5 m NW of the willow sapling" is a poor location designation for a long-term sampling programme. An example of

a correct description would be, as in Figure 5.1, "30 m downstream of Lady Aberdeen Bridge (Highway 148), between Hull and Pointe Gatineau, and 15 m off pier on the left side looking downstream." The date the station was first established (sampled) should also be entered;

Sampling-location information should also include descriptions of the water body above and below the sampling station, including water depths, and describe the banks on either side of the water body and the bed material, if known. Description of the water body should include any irregularities in morphology affecting flow or water quality. These irregularities may include a bend in a river, widening or narrowing of the channel, presence of an island, rapids or falls, or the entry of a tributary near the sampling station. Description of the banks should mention slope, bank material and extent of vegetation. Bed or sediment material may be described as rocky, muddy, sandy, vegetation-covered, etc. Station-location descriptions should mention seasonal changes that may interfere with year-round sampling, such as the overturn classification of lakes: overturns once a year, twice a year, several times a year or mixes poorly (GEM, section 6.4). Additional information in the case of lakes could include surface area, maximum depth, mean depth, volume and water residence time;

(b) Observations - Enter any additional information about conditions, either natural or man-made, which may have a bearing on water quality Past and anticipated land disturbances and pollution sources should be mentioned, e.g. forest fires, road construction, old mine workings, existing and anticipated land use (LTM, section 3.4);

(c) Map - A large-scale map which locates the sampling location with respect to roads, highways and towns should be included. The combination of the map and the sketch of the station location should provide complete location information. An investigator travelling to the site for the first time should have enough information to locate the sampling station confidently and accurately;

(d) Detailed sketch of station location - Sketch the location of the sampling station (including distances expressed in suitable units) with respect to local landmarks and permanent reference points.

The form shown in Figure 5.2 also embodies many of these recommendations (GEM, Chap. 1, pp. 23-27). Forms for lakes and groundwater are shown in GEM (Chap. 1, pp. 28-35).

5.2 Station data forms

An example of a station data form used by the Canadian National Water Quality Data Bank (NAQUADAT) is shown in Figure 5.3 and a GEMS GLOWDAT form (GEM, Chap. 6, p. 6) in Figure 5.4. The information required to complete the former is as follows:

(a) Station number or code - For ease of data handling, both manually or by computer, it is recommended that a unique number be assigned to each sampling station. The station number or code can be simply an accession number, i.e. a sequential number assigned as stations are established.

The station number in NAQUADAT is representative of a more sophisticated system designed for computer processing. A 12-digit alphanumeric code is the key element in storing and retrieving data on the system. This number is composed of several subfields (cf. WQS, section 6.5.2):

(i) Type of water - a two-digit numerical code indicating the type of water sampled at any given location, such as streams, rivers, lakes or precipitation. The meaning of this code has been extended to include other types of aquatic media, and a list of all currently assigned codes is given in Table 5.1;

(ii) Province, basin and sub-basin - three pairs of digits and letters identifying the province, basin and sub-basin;

(iii) Sequential - a four-digit number, assigned usually by the regional office.

Example

NNAANNAANNNN

TYPE OF WATER PROVINCE BASIN SUBBASIN SEQUENTIAL

Station number 00BC08NA0001 indicates that the sampling site is on a stream, in the province of British Columbia in basin 08 and sub-basin NA, and the sequence number is 1. Station 01ON02IE0009 is on a lake, in the province of Ontario, in basin

number 02, in IE sub-basin, the sequential number being 9.

Another well-known coding system for sampling points is the River Mile Index used, for example, by the Environmental Protection Agency of the USA as part of the STORET system. In this system, the location of a sampling point is defined by its distance and hydrological relationship to the mouth of the river system. It includes major and minor basin codes, terminal stream numbers, direction and level of stream flow, mileages between and to confluences in the river system and a code to identify the stream level on which the point is located.

(b) Co-ordinates - Geographical co-ordinates are recorded as latitude and longitude, UTM co-ordinates and distance upstream from a reference point such as a reference station or a river mouth. In GEMS (Figure 5.4), longitude and latitude are given together with national grid references, if available. In NAQUADAT (Figure 5.3), all geographical co-ordinates are stored as latitude and longitude, with minutes and seconds given as a fraction of a degree. If the initial information has been given in UTM units, the system automatically converts it to latitude and longitude before storing it. For the GEMS station form, one entry is the WMO code for the octant of the globe for the northern hemisphere: 0, 1, 2 and 3 for 0-90°W, 90-180°W, 180-90°E and 90-0°E, respectively. The corresponding codes for the southern hemisphere are: 5, 6, 7 and 8 for 0-90°W, 90-180°W, 180-90°E and 90-0°E (GEM, Chap. 6, p. 7).

Latitude and longitude values, if used, are obtained from 1:50 000 or 1:250 000 topographical maps. Points on a 1:250 000 map can be located to about ±200 m and on a 1:50 000 scale to about ±40 m (WQS, section 6.5.1). If necessary and if available, navigational charts can be used to provide more accurate values than the topographical maps.

The last entry, Pr, in the latitude and longitude fields in Figure 5.3, is a code for the estimated precision of the co-ordinates. Table 5.2 shows various formats for latitude and longitude values with the corresponding precision codes. For instance, if the location was determined to the nearest 10 seconds, then a 5 would be entered in the Pr column. If the locations were determined on a 1:250 000 or 1:500 000-scale map, the location would probably be determined to the nearest minute, and therefore a 7 would be used.

The UTM grid co-ordinates field in Figure 5.3 consists of the subfields UTM zone, given on topographical maps; northing and

easting, obtained from topographical maps; and Pr, obtained from Table 5.2.

(c) Reference station - Many times it is useful to know the distance of a sampling location from a given reference point. NAQUADAT uses the "Reference Station" for this purpose. This point could be, for example, the mouth of a river or the confluence point of two rivers. The distance of the sampling location from this reference point is then given as a "station parameter" (see below).

Besides providing a more precise identification of a station location, the distance from a reference point can be used for obtaining "concentrations vs. distance"-type plots often used in water-quality data interpretation.

(d) Narrative description - It is recommended that the narrative description begin with the name of the river, stream, lake or reservoir followed by its location (e.g. upstream or downstream) and its distance (to 0.1 km or better) from the nearest town, city, important bridges, highways or other important fixed landmarks. The name of the province, territory or other geopolitical division should also be included. It is recommended that only dictionary-approved abbreviations be used and that strictly local names for landmarks be avoided.

The "Narrative Description" section in Figure 5.3 is free-format and supplements the geographical co-ordinates in specifying the sampling location. Although the forms used usually show only five lines, NAQUADAT permits up to 99 lines of 38 characters each to be used for the "Narrative Description." The GLOWDAT form in Figure 5.4 has a similar section.

(e) Station parameters - The station parameters contain additional information about the sampling location. They can include, for example, codes for the average depth of water at the sampling station or the distance downstream from a reference station.

5.3 Field sheets

Perhaps one of the most important steps in a sampling programme is the recording on the field sheets of observations, sampling date, time, location and the measurements made. All field records must be completed before a station is left.

The interpretation of water-quality data cannot be accomplished without all supporting information. Observations of weather, dead fish, algal growth, slicks on the water surface and other phenomena may make a significant difference in explaining the data collected. The collector should not hesitate to record all observations, no matter how trivial they may seem.

Three examples of a systematic format for recording field analyses and observations are provided in Figures 5.5 to 5.7. The formats shown in Figures 5.5 and 5.6 are appropriate for those groups using the NAQUADAT, GLOWDAT (GEM, Chap. 6, pp. 10-11) or similar computer systems for storing their results. The format of Figure 5.7 can be used by any group doing water-quality work. Both formats can be adapted to fit situations specific to a particular agency.

Detailed instructions are given in SWQ, section 5.2.1 and in GEM, Chap. 6, pp.12-13, for filling out the respective forms. The information required for Figure 5.7 is as follows:

(a) Sampling site and date - The station number is obtained from the station data form. This should suffice to identify the sampling site. Unfortunately, there is still no general agreement on the recording of dates, viz. day, month, year or year, month, day. The 24 hour clock seems to be standard. Care needs to be taken that the time zone and "standard" or "daylight saving" ("summer") time, where used, are also specified;

(b) Field-measured parameters - On a well-prepared form, the analytical method used in the field and the units of the measurements are already printed. Where alternative methods are possible, care must be taken that the appropriate codes are recorded, e.g. measurements *in situ* or field of pH, temperature, specific conductance or dissolved oxygen. In addition, general observations should be included under "Remarks". Items of a routine nature which are entered here include wind direction and velocity, per cent cloud cover, snow depth, fish kills and any apparent physical changes at the site or its vicinity such as in the turbidity, vegetation cover, slope of the banks or floating objects on the water;

(c) Instrument calibration

  (i) Dissolved-oxygen meter model - Enter make and model number of dissolved-oxygen meter;

  (ii) Winkler calibration - Enter dissolved-oxygen concentration measured in milligrams per litre (to be used to calibrate dissolved-oxygen meter);

(iii) Meter reading before adjustment - Enter meter reading prior to adjustment based on Winkler calibration in milligrams per litre;

(iv) Conductivity meter model - Enter make and model number of meter used;

(v) pH meter model - Enter make and model number of meter used;

(vi) Calibration buffers used - Enter pH range for which meter is calibrated;

(vii) Remarks - Record any problems such as erratic needle movement or continual slow drift;

(d) Water-quantity measurement data - Record the description of the gauge and location along with the stage height and time;

(e) Sampling

(i) Sampling apparatus used and procedures - Enter type of water sampler used (e.g. "sampling iron," metal Kemmerer) and type of sample taken (e.g. grab-point or depth-integrated samples);

(ii) Sample specifics - Record for each water-quality parameter or group of parameters the bottle used, volume of water collected, means of preservation and whether or not a sample was collected for quality-control purposes. Consult Chapter 6 for recommended bottles, sample sizes, and preservation techniques;

(f) Quality control remarks - Record the specifics of the quality control carried out, e.g. duplicates, blanks and spiked samples with the time of collection;

(g) General remarks - Enter any general field observations which may affect water quality. These observations may include unusual colour or odour of the water, excessive algal growth, oil slicks, surface films or a heavy fish kill. Observations recorded in this section may prompt the field investigator to take additional "observation-based" samples, beyond those required by the project design. The type of samples and their preservation should be consistent with the type of analysis the investigator thinks is warranted by the

prevailing conditions. If additional samples are collected but not exactly at an established station, the description of the location should be accurately recorded. This kind of information and the additional samples will prove very useful in the interpretive phase of the study.

*

* *

DOE, INLAND WATERS DIRECTORATE, WATER QUALITY BRANCH

STATION LOCATION DESCRIPTION

REGION QUEBEC

PROVINCE QUEBEC BASIN OTTAWA RIVER

STATION DATA

Type	Prov.	Basin	Sub-Basin	Segment		
00	04	02	L	11	003	6

Latitude (N+)				Longitude (W+)				Pr
S	Deg	Min	Sec	S	Deg	Min	Sec	
	45	27	25.0		075	42	08.0	5

UTM Zone		Easting		Northing (N+)	Pr
	S	0		S	

STATION LOCATION

ON GATINEAU (Reservoir / Stream / Lake / River)

at LADY ABERDEEN BRIDGE near PT. GATINEAU Prov. QUE.

Located in _____ Sec. _____ Tp _____ Rge _____

Established APRIL 1978

Distance from base to station 1.5 Km

Distance from station to site of analysis 17 Km

Location of station with respect to towns, bridges, highways, railroads, tributaries, islands, falls, dams, etc.:

30M DOWNSTREAM OF LADY ABERDEEN BRIDGE (HIGHWAY 148) BETWEEN HULL AND POINTE GATINEAU AND 15M OFF PIER ON LEFT SIDE (LOOKING DOWNSTREAM)

Description and location of nearby hydrometric installations

BASKATONG DAM ABOUT 190 KM UPSTREAM
FARMERS RAPIDS ABOUT 25 Km UPSTREAM

SPECIMEN

Figure 5.1 Station-location description forms and maps

STATION DESCRIPTION

DIRECTION OF FLOW:

SOUTH EAST

DESCRIPTION OF CHANNEL ABOVE STATION:

PERMANENT LOG BOOM ON RIGHT, GRADUAL CURVE TO LEFT.

DESCRIPTION OF CHANNEL BELOW STATION:

GRADUAL WIDENING BEFORE EMPTYING INTO OTTAWA R.; MAIN CURRENT ON LEFT, SLIGHT BACKWATER ON RIGHT.

DESCRIPTION OF LEFT BANK:

APPROX. 3M DROP TO RIVER; SLOPE ALLOWS ONLY SHRUBBY VEGETATION.

DESCRIPTION OF RIGHT BANK:

EDGE OF PARKLAND; GENTLE SLOPE

BED: rocky, gravel, sandy, clean, vegetated.

PROBABLY WOOD CHIPS, MUDDY

APPROXIMATE DIMENSIONS AND DESCRIPTIONS OF LAKES AND/OR RESERVOIRS

NONE

OBSERVATIONS

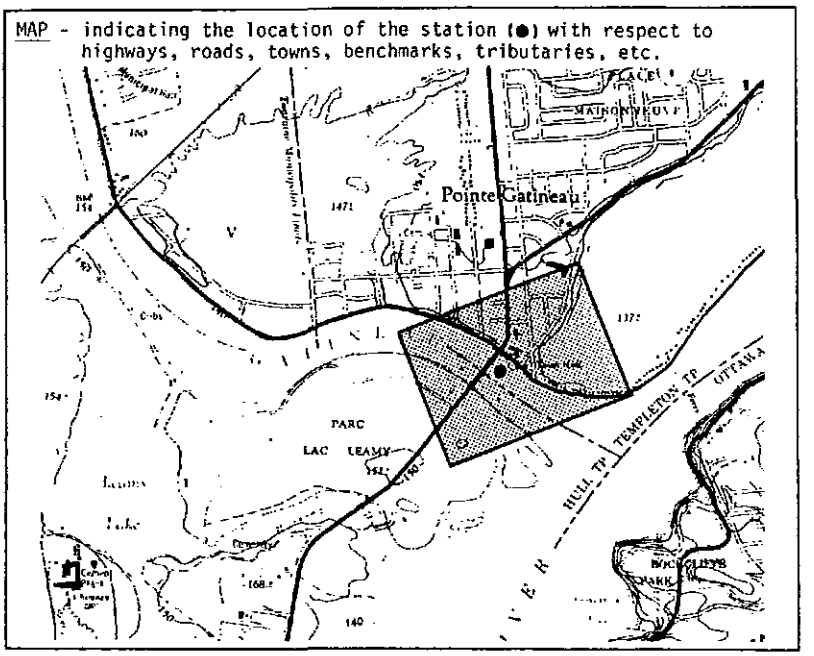
NATURAL CONDITIONS AND/OR CONTROL INSTALLATIONS WHICH MAY AFFECT FLOW REGIMES:

BASKATONG DAM
FARMERS RAPIDS

SOURCES OF CHEMICAL OR PHYSICAL INPUTS:

LOGS, LOCAL SEWAGE INPUT.

Figure 5.1 *(contd)*



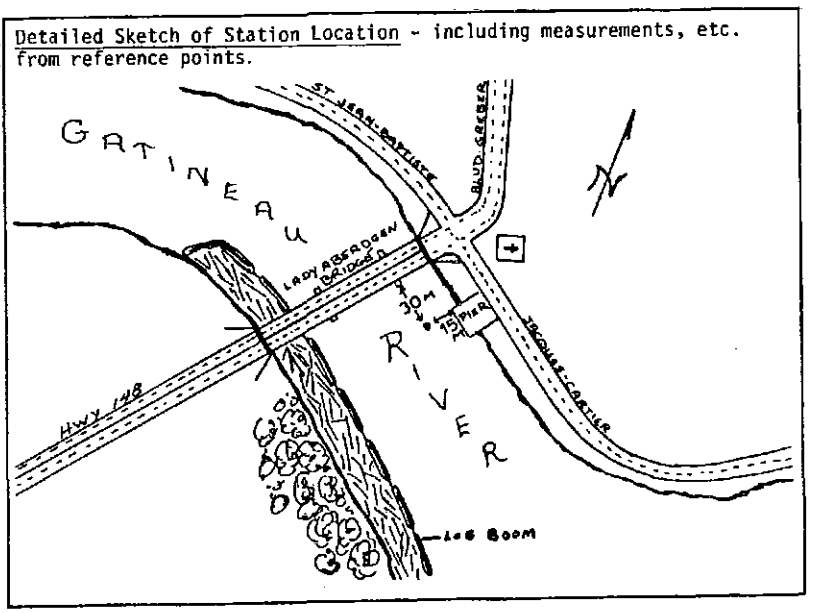


Figure 5.1 *(contd)*

UNEP/WHO/UNESCO/WMO PROJECT ON GLOBAL WATER QUALITY MONITORING

WHO REGION : . . . . . .

COUNTRY : . . . . . .

COUNTRY INFORMATION
SHEET IV (page 1 of 5)

RIVER SAMPLING STATION SUGGESTED FOR
INCLUSION IN THE GLOBAL NETWORK

EXISTING OR PROPOSED (please mark)

A. LOCATION OF SAMPLING SITE

1. Name of river :

2. Longitude and latitude :

3. National grid reference (if available) :

4. Local reference of position (name of bridge, nearby village etc.) :

5. Distance in river length

from source : . . . . . ; above tidal limit : . . . . . .

6. Countries passed through

upstream of station :

downstream of station :

B. PHYSICAL CONDITIONS

1. Width of river

average : . . . . . maximum : . . . . . minimum : . . . . . .

2. Depth of river (in middle)

average : . . . . . maximum : . . . . . minimum : . . . . . .

3. Character of river banks (indicate accessibility) :

Figure 5.2 River sampling station forms (GEMS))

UNEP/WHO/UNESCO/WMO PROJECT ON GLOBAL WATER QUALITY MONITORING

WHO REGION : . . . . . .

COUNTRY : . . . . . COUNTRY INFORMA
SHEET IV (page

RIVER SAMPLING STATION SUGGESTED FOR
INCLUSION IN THE GLOBAL NETWORK

4. Nature of river bottom :

5. Aquatic vegetation :

6. Stream velocity (at middle)

average : . . . . . maximum : . . . . . minimum : . . . . . .

7. Extent and seasonal regularity of flow variations :

C. FLOW CONDITIONS

1. Nearest flow gauging station (location and type) :

2. Best available means of assessing flow at point and time of sampling :

3. Rate of flow

average : . . . . . Maximum : . . . . . minimum : . . . . . .

4. Rate of flow when full to the bank (flood point) :

D. UPSTREAM INFLUENCES

1. Nearest significant pollution input (type and distance) :

2. Nearest significant clean water input (type and distance) :

Figure 5.2 *(contd)*

UNEP/WHO/UNESCO/WMO PROJECT ON GLOBAL WATER QUALITY MONITORING

WHO REGION : . . . . . .

COUNTRY : . . . . . .

COUNTRY INFORMATION
SHEET IV (page 4 of

RIVER SAMPLING STATION SUGGESTED FOR
INCLUSION IN THE GLOBAL NETWORK

3. Depth at which sample is taken :

4. Method of sampling (from bridge or boat, by wading or else) :

5. Sampling equipment used :

6. Sampling difficulties due to extremes of flow (frequency and seasons) :

7. Ease of access by vehicle to sampling station :

8. Laboratory carrying out analysis (please refer to Sheets no. II):

9. Distance from laboratory, means of sample transport and normal time :

10. Frequency of routine sampling :

G. ANALYSIS (for existing stations only)

1. List of determinations carried out at sampling station and methods employed :

2. Normal time elapsing between sampling and commencement of analysis :

Figure 5.2 *(contd)*

UNEP/WHO/UNESCO/WMO PROJECT ON GLOBAL WATER QUALITY MONITORING

WHO REGION : . . . . . .
COUNTRY : . . . . . .

COUNTRY INFORMATION
SHEET IV (page 5 of 5

RIVER SAMPLING STATION SUGGESTED FOR
INCLUSION IN THE GLOBAL NETWORK

3. **Sample storage conditions :**

4. **List of determinations carried out routinely and methods employed :**

5. **List of determinations carried out occasionally and methods employed :**

6. **Significant trends and changes in water quality parameters during past years :**

Figure 5.2 *(contd)*

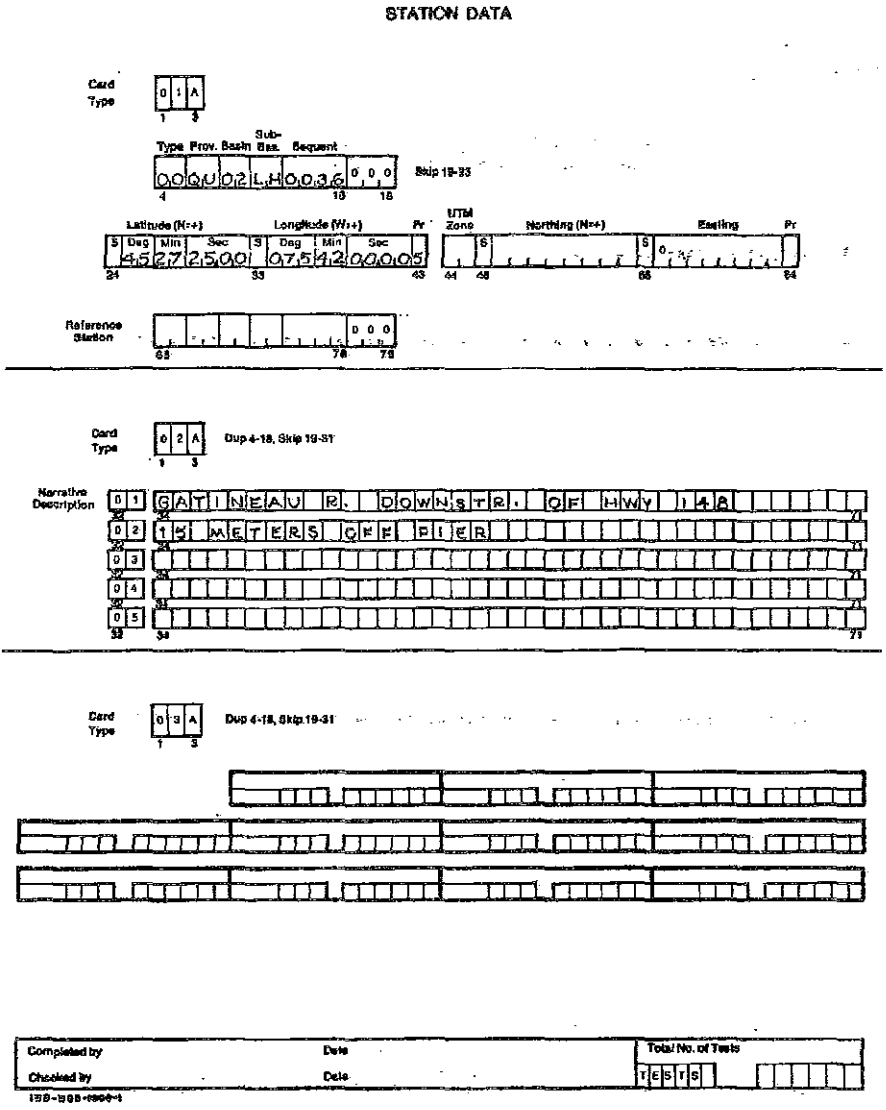
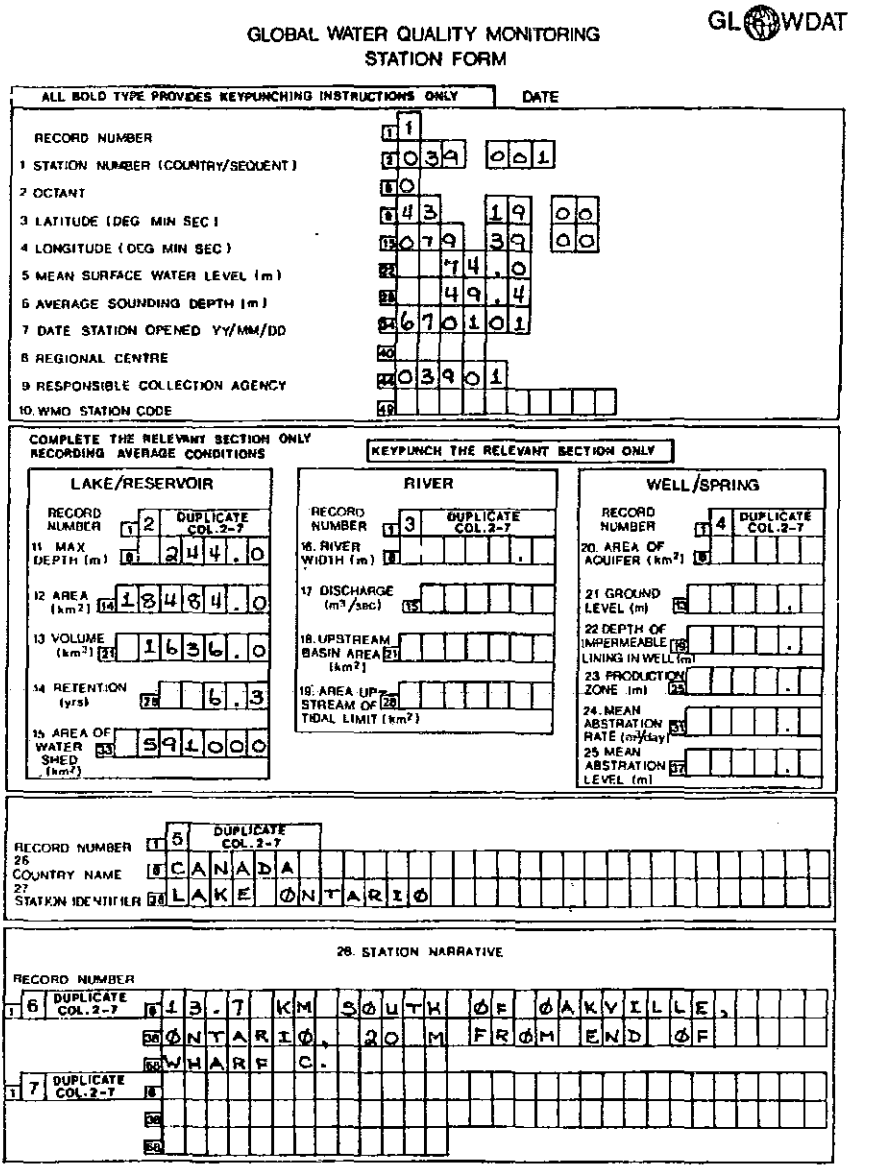


Figure 5.3 Station data form (NAQUADAT)


GLOBAL WATER QUALITY MONITORING
STATION FORM

GLOWDAT

ALL BOLD TYPE PROVIDES KEYPUNCHING INSTRUCTIONS ONLY — DATE

RECORD NUMBER 1 1
1 STATION NUMBER (COUNTRY/SEQUENT) 2 0 3 9 0 0 1
2 OCTANT 8 0
3 LATITUDE (DEG MIN SEC) 9 4 3 1 9 0 0
4 LONGITUDE (DEG MIN SEC) 15 0 7 9 3 9 0 0
5 MEAN SURFACE WATER LEVEL (m) 22 1 4 . 0
6 AVERAGE SOUNDING DEPTH (m) 28 4 9 . 4
7 DATE STATION OPENED YY/MM/DD 34 6 7 0 1 0 1
8 REGIONAL CENTRE 40
9 RESPONSIBLE COLLECTION AGENCY 42 0 3 9 0 1
10 WMO STATION CODE 48

COMPLETE THE RELEVANT SECTION ONLY RECORDING AVERAGE CONDITIONS

KEYPUNCH THE RELEVANT SECTION ONLY

LAKE/RESERVOIR
RECORD NUMBER 1 2 DUPLICATE COL. 2-7
11 MAX DEPTH (m) 8 2 4 4 . 0
12 AREA (km²) 14 1 8 4 6 4 . 0
13 VOLUME (km³) 21 1 6 3 6 . 0
14 RETENTION (yrs) 28 6 . 3
15 AREA OF WATER SHED (km²) 33 5 9 1 0 0 0

RIVER
RECORD NUMBER 1 3 DUPLICATE COL. 2-7
16 RIVER WIDTH (m) 8 .
17 DISCHARGE (m³/sec) 15 .
18 UPSTREAM BASIN AREA (km²) 21 .
19 AREA UPSTREAM OF TIDAL LIMIT (km²) 28 .

WELL/SPRING
RECORD NUMBER 1 4 DUPLICATE COL. 2-7
20 AREA OF AQUIFER (km²) 8 .
21 GROUND LEVEL (m) 15 .
22 DEPTH OF IMPERMEABLE LINING IN WELL (m) 18 .
23 PRODUCTION ZONE (m) 25 .
24 MEAN ABSTRATION RATE (m³/day) 31 .
25 MEAN ABSTRATION LEVEL (m) 37 .

RECORD NUMBER 1 5 DUPLICATE COL. 2-7
26 COUNTRY NAME 8 C A N A D A
27 STATION IDENTIFIER 28 L A K E Ø N T A R I Ø

28 STATION NARRATIVE

RECORD NUMBER
1 6 DUPLICATE COL. 2-7 8 1 3 . 7 KM SOUTH OF OAKVILLE,
28 ONTARIO, 20 M FROM END OF
60 WHARF C.
1 7 DUPLICATE COL. 2-7 8
30
50

Figure 5.4 Station data form (GLOWDAT)

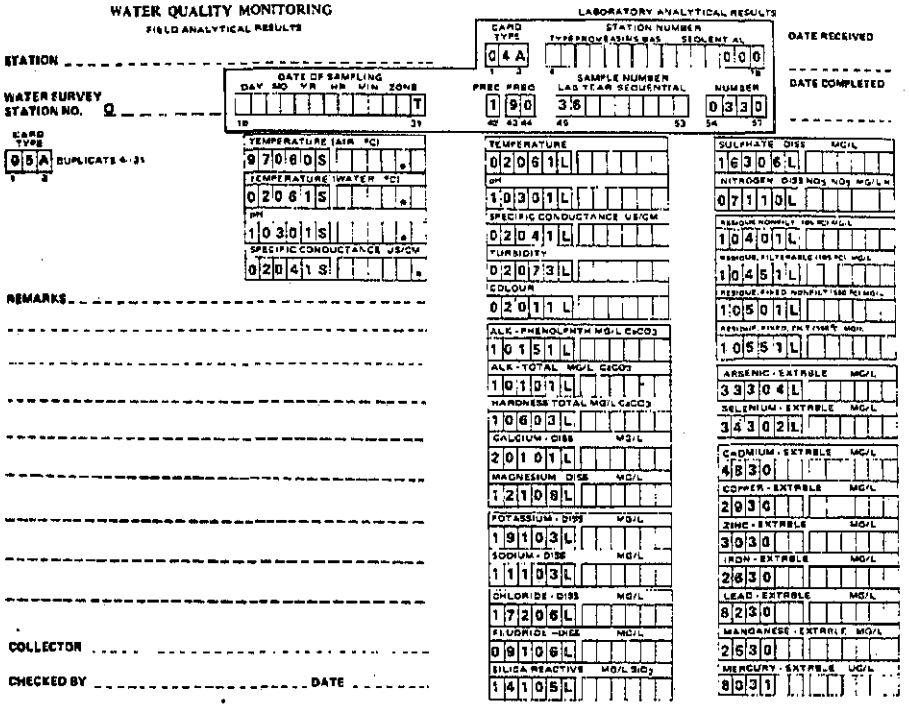


Figure 5.5 Field sheet for use with NAQUADAT or similar computer system

GLOBAL WATER QUALITY MONITORING
DATA FORM

GLOWDAT

1 ADDITION CHANGE (A,C,D) — A
2 STATION NUMBER (COUNTRY SEQUENT) — 03900 1
3 DATE SAMPLE TAKEN (YY MM DD) — 81 10 09
4 TIME SAMPLE TAKEN (HH 00-23)(MM 00-59) — 15 45
5 SAMPLE DEPTH IN METRES — 0.0
6 INTEGRATED SAMPLE — V=VERTICAL H=HORIZONTAL; T=IN TIME F=FLOW

STATION LAKE ONTARIO
TYPE LAKE
COMPLETED BY K. MILES
DATE OCTOBER 9 1981
AGENCY 03901

ALL BOLD TYPE PROVIDES KEYPUNCHING INSTRUCTIONS ONLY

DETERMINAND	CODE	AQC FLAG	VALUE	DETERMINAND	CODE	AQC FLAG	VALUE
Instanc. Discharge m^3/s	97167		150.0				
Water Temperature °C	02061		6.5				
pH pH units	10302		8.1				
Conductivity µS/cm	02041		368.0				
Suspended Solids mg/l	10401		22.5				
Alkalinity mg/l	10101		141.0				
Chloride mg/l	17205		9.4				
Dissolved oxygen mg/l	08102		10.9				
Biochem.oxygen demand mg/l	08201		6.1				
Ammonia mg/l	07554		0.3				
Nitrate + Nitrite mg/l	07105		0.172				
Orthophosphate mg/l	15254	L	0.005				
Faecal coliform no/100 ml	36011		85.0				

Figure 5.6 Field sheet for use with GLOWDAT

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 5.7 General formal for a field-sampling sheet

SAMPLING APPARATUS USED AND PROCEDURES

SAMPLE SPECIFICS

	Container Material	Vol. Collected	Preservation	Quality Control
Major Ions				
Metals				
Organics				
Pesticides & Herbicides				
Mercury				
Phenols				
Nutrients				
BOD & COD				
Others				

QUALITY CONTROL REMARKS

GENERAL REMARKS

MODE OF TRANSPORT

Figure 5.7 *(contd)*

TABLE 5.1 NAQUADAT codes for types of aquatic media

Type	Code	Subtype	Code
Surface water	0	Stream - channel	0
		Lake	1
		Estuary	2
		Ocean - sea	3
		Pond	4
		Impounded reservoir	5
		Harbour	6
		Ditch	7
		Runoff	8
		Unknown	9
Groundwater	1	Well - sump	0
		Spring	1
		Piezometer well	2
		Tile drain	3
		Bog	4
		Household tap	8
		Unknown	9
Waste - treated and untreated	2	Industrial	0
		Municipal	1
		Mining	2
		Livestock waste	3
		Unknown	9
Precipitation	3	Rain	0
		Snow	1
		Ice (precipitated)	2
		Mixed precipitation	3
		Dry fallout	4
Treated supply	4	Municipal	0
		Industrial	1
		Mining	2
		Private (individual)	3
		Other communal works	4
		Municipal distribution	5
		Municipal treatment plant (intermediate)	6
		Treatment residue or sludge	7
		Other	9
Sediments, soils	5	Stream channel	0
		Lake bottom	1
		Stream bank	2
		Lake bank	3
		Contaminated by soil	4
		General soil	5
		Effluent irrigation soil	6

Table 5.1 *(contd)*

Type	Code	Subtype	Code
		Sludge conditioned soil	7
		Other	8
Industrial wastewater	6	Storm water	0
		Primary influent	1
		Primary effluent	2
		Finaf effluent	3
		Sludge	4
		Special problem	5
		Other	6
Municipal wastewater	7	Raw	0
		Primary lagoon effluent	1
		Secondary lagoon effluent	2
		Conventional primary effluent	3
		Conventional secondary effluent	4
		Advanced wastewater treatment effluent	5
		Disinfected effluent	6
		Raw sludge	7
		Digested sludge	8
		Other	9
Miscellaneous wastewater	8	Raw	0
		Primary lagoon effluent	1
		Secondary lagoon effluent	2
		Conventional primary effluent	3
		Conventional secondary effluent	4
		Advanced wastewater treatment effluent	5
		Disinfected effluent	6
		Raw sludge	7
		Digested sludge	8
		Other	9
Aquatic biota	9	To be categorized later (e.g., fish, phytoplankton, benthos, macrophytes, periphyton, zooplankton)	

Source: Whitlow and Lamb (1982).

TABLE 5.2 Formats and precision codes for sampling locations

Latitude and longitude*					
DEG†	MIN	SEC	Rounding off to the nearest:	Code	Radius (r)‡
XXX	XX	XX.XX	±0.03 sec or better	0	r ≤ 1 m
XXX	XX	XX.X0	±0.1 sec	1	1 m < r ≥ 3 m
XXX	XX	XX.X0	±0.3 sec	2	3 m < r ≤ 10 m
XXX	XX	XX.00	±1 sec	3	10 m < r ≤ 30 m
XXX	XX	XX.00	±3 sec	4	30 m < r ≤ 100 m
XXX	XX	XX.00	±10 sec	5	100 m < r ≤ 300 m
XXX	XX	XX.00	±30 sec	6	300 m < r ≤ 1 km
XXX	XX	00.00	±1 min	7	1 km < r ≤ 3 km
XXX	XX	00.00	±5 min	8	3 km < r ≤10 km
XXX	XX	00.00	±10 min or worse	9	r ≤ 10 km

* X represents an actual number (0-9) and 0 is a zero.

† The DEG subfield for latitude has only two digits; DEG subfield for longitude must have leading zero if < 100.

‡ Radius, in metres, from the specified location within which the sample was taken.

Source: *NAQUADAT Users Manual (Demayo and Hunt, 1975).*

CHAPTER 6

FIELD FILTRATION AND PRESERVATION PROCEDURES

In an aquatic environment, inorganic and organic substances can be found in a variety of forms such as free or complexed, dissolved, particulate or sorbed onto suspended sediments and biomass, and associated with the bottom materials.

Although the question has been addressed in the scientific literature, so far no clear consensus has emerged on which chemical-physical species of a substance should be measured when monitoring water quality. This depends on the particular system being studied, on the purpose of the study and the biological availability of the various species of the substances being studied. The issue of biological availability is also far from being resolved. For many substances, their biological availability is directly proportional to their concentration in the dissolved phase. Also in the case of most metals, for example, the concentration in the dissolved phase is typically low compared with that associated with the suspended or colloidal particles. However, the greatest quantity of each element, sometimes over 90 per cent, occurs in the dissolved phase because the particulate matter forms only a small percentage of the total mass of the sample. For these reasons, in water-quality work it is very important to have the capability of measuring the "dissolved" constituents. The operational definition used by several authorities for "dissolved" phase is that which passes through a 0.45-nm membrane filter (FMW; CPQ, section 5.B.6.c.2; SWQ, p. 31; cf. GEM, Chap. 6, section 2.5).

6.1 Filtration

For separation of dissolved from particulate matter, sample filtration is recommended. Centrifugation requires more equipment, settling requires more time, and both cannot be easily calibrated and may increase contamination hazards (GEM, Chap. 6, section 2.5.1). Optimally, the filtration should be carried out in the field during or immediately after sample collection and must be followed by the appropriate preservation.

The total concentrations of metals may be determined using a second unfiltered sample collected at the same time. This sample will then undergo a complete digestion in the laboratory which converts the metals to water-soluble compounds.

Samples requiring analysis for organic constituents are filtered immediately after collection, using a glass-fibre filter or a metal membrane (CPQ, section

5.B.6.c.2). After filtration, the filtrate may be analysed for dissolved organic constituents and the filter supporting the particulate fraction is available for particulate organic analysis.

Adsorption and absorption of dissolved substances on the filter material can be a serious problem. Various suggestions have been made as to the best materials to use. GEMS recommends organic filters (polycarbonate, cellulose, acetate) for mineral substances, and glass-fibre filters for organic compounds, although glass fibre may absorb chlorinated hydrocarbons (GEM, Chap. 6, p. 18). A semiquantitative method of detecting how serious adsorption may be is to refilter a filtrate through a fresh filter and determine either the amount retained on the filter or the change in concentration between the two filtrates. Blank determinations should be carried out on unused filters.

The filter and filtration apparatus require laboratory pretreatment and should be rinsed with a portion of the collected sample before the filtrate is collected, i.e. by discarding the first 150 to 200 ml of filtrate. This technique minimizes the risk of altering the composition of the samples by the filtering operation. The filtrate for metals analysis should be preserved as outlined in Table 6.1; the filtrate for anion analysis does not require special preservation. The volume of sample needed is indicated by laboratory personnel.

The filtration procedure requires maintaining a vacuum in the filtration apparatus; either an electrical or manual pump must be used. If an electrical type is employed filtration will require access to electrical services or the operation of a mobile power unit. Vacuum may cause changes in the pH due to loss of carbon dioxide, resulting in precipitation of some metals. For this reason and to reduce losses due to adsorption on the walls of the container, metal samples are often acidified.

6.1.1 General apparatus-washing procedures

The following are the Canadian practices (SWQ, section 6.1.1). There are further suggestions in GEMS (GEM, Chap. 6, section 2.5.1) on the handling of filters such as pretreatment for filters intended for re-use, including solvent extraction in addition to baking at 300°C for those used for organics.

If it can be managed, parallel use of several filtering kits can accelerate the filtration procedure.

(a) Before or after each field trip:

  (i) Wash and scrub filtration units with non-phosphate detergent;

  (ii) Rinse with tap water and soak overnight in 5 per cent HCl;

(iii) Clean inside (only) of tubing by soaking for 16 hours or more with 5 per cent HCl;

(iv) Rinse unit and tubing with tap water followed by distilled or de-ionized water;

(b) Before each filtration:

(i) Rinse unit and tubing with distilled or de-ionized water;

(ii) Continue with procedures as outlined in section 6.1.2;

(c) After the last filtration of the day:

(i) Rinse unit with 5 per cent HCl (pump through the tubing);

(ii) Scrub as necessary;

(iii) Rinse with tap water followed by distilled or de-ionized water.

Note: If at any time the unit appears to contain residue from filtration which has not been removed by procedures outlined in (b) and (c), proceed to (a).

6.1.2 Filtration procedures

The following are examples of detailed directions for two different filtration procedures in Canadian practice (SWQ, section 6.1.2).

6.1.2.1 Particulate carbon and nitrogen

Immediately following the collection of the required sample:

(a) Using a pair of tweezers, place a pretreated* weighed glass-fibre filter paper on the filtration holder, taking care not to touch the paper with fingers. Place the filtration bowl on the filter and clamp or twist securely;

---

* Clean the glass-fibre filters by placing them in a preheated muffle furnace (450°C) for one hour to remove organic matter. Do not use filters that are bent. Store filters in a sealed dry container.

Note: Both the filtration bowl and vacuum flask must be acid-washed and stored in heat-sealed polyethylene bags. Each filtration unit may only be used once between acid washes.

(b) Filter a measured volume of the well-shaken water sample. Record the volume of water filtered;

(c) After the water sample has passed through the filter, wash the inside of the filter bowl with a few millilitres of carbon- and nitrogen-free distilled water to ensure that all particulate material is on the filter;

(d) Acid wash to remove carbonates by carefully adding 2-5 ml 0.05 mol/l sulfuric acid (0.3 per cent v/v) to the filter. Continue filtering;

(e) Rinse the filter with 2-5 ml carbon- and nitrogen-free distilled water;

(f) Remove the filtration bowl and continue filtering until all excess water has been removed from the filter;

(g) Transfer the filter to a labelled petri dish. Store the petri dishes at 4°C;

(h) Periodically, distilled-water blank filters should be prepared using the filtration steps above to monitor the background concentration levels.

6.1.2.2 Chlorophyll a

Again, a reminder that peristaltic pumps should not be used to sample cells because of likely cell damage.

(a) Filter samples for chlorophyll a immediately;

(b) Preserve the sample with 0.2 ml of $MgCO_3$ suspension (1.0 g $MgCO_3$ in 100 ml H_2O) just as the last of the sample is being filtered;

(c) Mount a clean filter head (such as a Millipore Pyrex filtering head) and a GF/C filter (Whatman) or a Millipore filter of suitable pore size;

(d) Mix the sample well in a 500-ml polyethylene bottle. Exposure to

light must be avoided;

(e) Pass as much sample as possible through the glass filter paper and record the volume. Non-turbid samples will generally pass through the filter completely (approximately 450 ml); highly turbid samples may only pass 50-100 ml;

(f) Do not allow the GF/C filter to dry between filtering sequences;

(g) After the sample is filtered, rinse the sides of the filter head with approximately 50 ml of demineralized water;

(h) Allow the GF/C filter to dry five seconds after the rinse has passed;

(i) Fold the GF/C filter in half using two pairs of forceps, place it in a labelled petri dish and then place the petri dish in a sub-zero freezer unit;

(j) Record the total volume of filtered samples on the labelled petri dish.

6.2 Preservation techniques

Between the time that a sample is collected in the field and until it is actually analysed in the laboratory, physical changes and chemical and biochemical reactions may take place in the sample container which will change the intrinsic quality of the water sample.

For several determinands, preservation is not possible and the measurements must be done in the field. When field analysis is not practicable (bulky or complex equipment, power supply required, special analytical skills), the use of mobile laboratories should be considered (SRS, section 10.1). Even when the constituent to be measured is reasonably stable, it is usually necessary to preserve the samples before shipping to prevent or minimize changes with time. This is done by various procedures such as keeping the samples in the dark; adding chemical preservatives; lowering the temperature to retard reactions; freezing samples; extracting them with different solvents, field column chromatography or a combination of these methods.

Limited knowledge is available on the preservation of water samples and research is under way in many countries to improve and standardize preservation techniques (WQS, section 4.2; GEM, Chap. 2, note 3 to Table 3). It is suggested that any recommendations on sample preservation be regarded as tentative until their efficiency has been experimentally tested (SRS, section 10.2.5).

6.2.1 CONTAINERS

The use of appropriate containers is very important in preserving the integrity of the sample. (GPH, section 3.2.2; GEM, Chap. 2, section 3.4).

In choosing a container one must consider:

(a) Leaching of container material by the sample, e.g. organic compounds from plastics or sodium, silica or boron from glass;

(b) Sorption of substances present in the sample on the container walls, e.g trace metals by glass or organic substances by plastic;

(c) Direct reaction of the sample with the container, e.g. fluoride and glass.

The smaller the concentrations of the species to be determined in the sample, the more important these aspects become.

Many publications contain recommendations on which type of container should be used for particular determinands. These recommendations do not always agree (SRS, section 10.2.3). The containers and the preservation methods recommended by the Water Quality Branch, Environment Canada, are summarized in Tables 6.1 and 6.2. Other lists are given in GEM, Chap. 2, Table 3; WQS, Table 11, pp. 156-163; and in the table attached to GPH. Detailed discussions of sample handling are also to be found in HSS, Chap. 10.

6.2.2 CHEMICAL ADDITION

This method, which includes acidification, is used for preserving the water samples for a variety of tests, including most dissolved metals and phenoxy acid herbicides. Care must be taken in using only "reagent"-grade chemicals such that the water sample is not contaminated by impurities in the added preservatives. Some samples for biological analysis also require chemical preservation.

Several authorities note that mercuric chloride is often added as a biocide, to a level of 40 mg/l or even higher. In addition to the difficulty of avoiding contamination in laboratories which analyse for trace amounts of mercury, use of this preservative entails adverse environmental effects which should be considered. Although methods for reclaiming mercury from wastes before disposal exist, it is recommended that acidification to a pH of 1.5 be considered as an alternative to the use of mercury salts (GPH, section 3.2.5; HSS, section 10.2.2).

As a general rule, it is preferable to use relatively concentrated solutions of preserving agents; corrections for the dilution of the sample by the small volume of

preserving agent will then be small or negligible.

Potential interference of the preservative with the analysis requires that procedures be carefully followed. For example, an acid can alter the distribution of suspended material and can lead to dissolution of colloidal and particulate metals (SRS, section 10.2.4). Thus the order, filtration and then acidification, becomes very important.

6.2.3 Freezing

Freezing is acceptable for certain analyses but is not a general preservation technique because it can cause physico-chemical changes, e.g. formation of precipitates and loss of dissolved gases, which might affect the sample composition. Also, solid components of the sample change with freezing and thawing, and a return to equilibrium followed by high-speed homogenization may be necessary before any analysis can be run.

Never freeze water samples in glass bottles. They burst.

6.2.4 Refrigeration

Refrigeration at 4°C or in melting ice is a common preservation technique which is widely used in field work. It has the advantage that no substance is added to the sample which could interfere with future analyses. However, it does not maintain the complete integrity of all constituents. In some cases it may affect the solubility of some constituents and cause them to precipitate. Refrigeration is often used in conjunction with chemical addition (Table 6.1).

When glass containers are filled to the brim, they should be stored at a lower temperature, down to 4°C, to avoid development of high expansion pressures on warming.

6.2.5 Practical aspects of preservation

An important practical aspect of preservation is a consistent routine to ensure that all samples requiring preservation receive the immediate treatment they need. This is particularly important when chemical preservatives are added, since these additions may not produce an easily detectable change in sample appearance. It may be advisable to mark or flag each preserved sample to ensure that no sample is forgotten or treated more than once.

Safe and accurate field addition of chemical preservatives also require special precautions. Precalibrated Repipets™ and other automatic pipettes ensure accurate field addition as well as eliminate the safety hazard of pipetting acids by mouth. It is necessary when using automatic pipettes to check that air bubbles are absent

from the delivery tube. Automatic dispensers must be primed so that subsequent samples will receive the correct aliquot of preservative. It is important that each pipette be unique to a preservative so that there is no possibility of cross-contamination from one preservative to another. Finally, it is advisable to label clearly all preservative bottles used in the field with their contents and the volume to be used, e.g. conc. nitric acid, add 2 ml/l of sample. It is often convenient to add the preservative in the laboratory before the sample containers are taken to the field. Another alternative is to use colour-coded or labelled sealed vials containing premeasured preserving agents. Although more expensive, this method has the advantage of simplifying the field procedure, thus lessening the possibility of errors and contamination.

*

* *

TABLE 6.1 Sample containers and preservation for constituents in water

Parameter	Recommended container*	Preservative	Maximum permissible storage time
Acidity	Polyethylene	Cool, 4°C	24 h
Alkalinity	Polyethylene	Cool, 4°C	24 h
Aluminum	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Antimony	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Arsenic	Polyethylene	Cool, 4°C	6 months
Barium	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Beryllium	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
BOD	Polyethylene	Cool, 4°C	4 h
Boron	Polyethylene	Cool, 4°C	6 months
Cadmium	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Calcium	Polyethylene	Cool, 4°C	7 days
Carbamate pesticides†	Glass	H_2SO_4 to pH <4, 10 g Na_2SO_4/L sample	Preferable to extract immediately
Carbon, inorganic	Polyethylene	Cool, 4°C	24 h
Carbon, organic‡	Polyethylene	Cool, 4°C	24 h
Carbon, particulate	Plastic petri dish	Filter using GF/C filter; cool, 4°C	6 months
Chloride	Polyethylene	Cool, 4°C	7 days
Chlorinated hydrocarbon pesticides†	Glass	Cool, 4°C	Preferable to extract immediately
Chlorophyll	Plastic petri dish	Filter on GF/C filter; freeze -20°C	7 days
Cholesterol	Glass	1 mL Conc. H_2SO_4/L sample	24 h
Chromium	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Cobalt	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
COD	Polyethylene	Cool, 4°C	24 h
Colour	Polyethylene	Cool, 4°C	24 h
Copper	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Coprostanol	Glass	1 mL Conc. H_2SO_4/L sample	24 h
Cyanide	Polyethylene	1 mL 10% NaOH/100 mL sample	24 h
Dissolved oxygen Winkler titration	Glass	Fix on site	6 h
Fluoride	Polyethylene	Cool, 4°C	7 days
Hardness	Polyethylene	Cool, 4°C	24 h
Iodide	Polyethylene	Cool, 4°C	24 h
Iron	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Lead	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Lithium	Polyethylene	2 mL Conc. HNO_3/L sample	6 months

* Teflon containers can also be used to replace either the polyethylene or the glass containers shown in the table.

† In some WQB regions, depending upon the specific compound to be analyzed within these groups and the method of analysis employed, certain organic solvents are also added to samples in the field in measured amounts. Preliminary research results have shown that this might be a better method of preservation than only cooling to 4°C.

‡ In some WQB regions these parameters are measured from the same bottle. Therefore the preservation method is the same, i.e. 2 mL 30% v/v H_2SO_4/L sample + cool 4°C. This method of preservation for organic carbon and total phosphorous has not been corroborated by any WQB studies.

§ If the whole sample is autoclaved in the original sample container.

Note: This table has been adapted from the *Analytical Methods Manual* (Water Quality Branch, 1981).

Table 6.1 *(contd)*

Parameter	Recommended container	Preservative	Maximum permissible storage time
Magnesium	Polyethylene	Cool, 4°C	7 days
Manganese	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Mercury	Glass or Teflon	1 mL Conc. H_2SO_4, 1 mL 5% $K_2Cr_2O_7$ solution/100 mL sample	1 month
Molybdenum	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Nickel	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Nitrogen			
Ammonia‡	Polyethylene	Cool, 4°C, 2 mL 40% H_2SO_4/L	24 h
Kjeldahl	Polyethylene	Cool, 4°C	24 h
Nitrate + nitrite‡	Polyethylene	Cool, 4°C	24 h
Organic nitrogen	Polyethylene	Cool, 4°C	24 h
Organic-particulate	Plastic petri dish	Filter using GF/C filter; cool, 4°C	6 months
NTA			
Polarographic	Polyethylene	Treated with 0.5% of 37% solution of formaldehyde; filter using 0.45-μm membrane filter	24 h
GLC	Glass	5 mL Conc. HCl/L sample	24 h
Oil and grease	Glass	Cool, 4°C, 5 mL 1 + 1 H_2SO_4/L (H_2SO_4 to pH <2)	24 h
Organophosphorus pesticides*	Glass	Cool, 4°C, 10% HCl to pH 4.4	No holding; extraction on site preferable
Pentachlorophenol	Glass	H_2SO_4 to pH <4, 0.5 g $CuSO_4$/L; cool, 4°C	24 h
pH	Polyethylene	None	6 h
Phenolics	Glass	H_3PO_4 to pH <4, 1.0 g $CuSO_4$/L; cool, 4°C	24 h
Phenoxy acid herbicides	Glass	H_2SO_4 to pH <2; cool, 4°C	Preferable to extract immediately
Phosphorus			
Dissolved	Glass	Filter using 0.45-μm membrane filter on site	24 h
Inorganic	Glass	Cool, 4°C	24 h
Ortho	Glass	Cool, 4°C	24 h
Total‡	Glass	Cool, 4°C	1 month§
Potassium	Polyethylene	Cool, 4°C	7 days
Residue	Polyethylene	Cool, 4°C	7 days
Selenium	Polyethylene	Cool, 4°C	6 months
Silica	Polyethylene	Cool, 4°C	7 days
Silver	Polyethylene	0.4 g Disodium EDTA/100 mL sample	10 days
Sodium	Polyethylene	Cool, 4°C	7 days
Specific conductance	Polyethylene	Cool, 4°C	24 h
Strontium	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Sugar	Glass	Cool, 4°C	24 h
Sulphate	Polyethylene	Cool, 4°C	7 days
Turbidity	Polyethylene	Cool, 4°C	7 days
Vanadium	Polyethylene	2 mL Conc. HNO_3/L sample	6 months
Zinc	Polyethylene	2 mL Conc. HNO_3/L sample	6 months

TABLE 6.2 Sample containers and preservation for constituents in sediment

Parameter	Recommended container	Preservative	Maximum permissible storage time
Carbon	Polyethylene or polypropylene bag or jar	Freeze, -20°C	6 months
Chlorinated hydrocarbon pesticides	Glass jar or aluminum cannister	Freeze, -20°C	Extract as soon as possible
Mercury	Polyethylene or polypropylene bag or jar	Freeze, -20°C	6 months
Metals	Polyethylene or polypropylene bag or jar	Freeze, -20°C	6 months
Nitrogen	Polyethylene or polypropylene bag or jar	Freeze, -20°C	6 months
Oil and grease	Glass jar or aluminum cannister	Freeze, -20°C	Extract as soon as possible
Phosphorus	Polyethylene or polypropylene bag or jar	Freeze, -20°C	6 months

Note: This table has been adapted from the *Analytical Methods Manual* (Water Quality Branch, 1981).

CHAPTER 7

SAMPLING FOR RADIOACTIVITY MEASUREMENTS

7.1 Sources of radioactivity in water

Excessive levels of radioactivity are deleterious to several beneficial uses of water, and are especially significant in relation to human and animal health (WQS, section 2.7). Radionuclides in water emit radiation of the following types:

- Alpha particles, which are helium nuclei; they do not penetrate materials deeply. This means that they deposit all of their energy close to their source and are therefore very dangerous when ingested or inhaled;

- Beta particles, which are high velocity electrons; they are moderately penetrating and moderately dangerous;

- Gamma and X-rays, which are short-wave-length electromagnetic radiation, deeply penetrating and moderately dangerous.

Neutrons, highly penetrating uncharged particles, are very dangerous but less important since neutron emitters are seldom encountered as water pollutants.

Radioactivity in water may be of natural or man-made origin. The main natural processes that introduce radioactivity into water are the weathering of rocks containing radioactive minerals and fallout of cosmic-ray-produced nuclides. The major sources of man-made radioactivity are uranium mining, the nuclear-power industries, nuclear weapons testing and the peaceful applications of nuclear materials and devices.

The principal radionuclides introduced naturally into surface and groundwaters are uranium, radium-226, radium-228, radon, potassium-40, tritium and carbon-14. All but the last two derive from radioactive minerals. In areas where radioactive minerals are abundant, natural uranium is the major radioactive constitutent present in water. Tritium and carbon-14 are produced by the interaction of cosmic-ray neutrons with nitrogen in the upper atmosphere. The tritium is eventually rained out as tritiated water and the radiocarbon is incorporated into atmospheric carbon dioxide. Both radionuclides are also produced by thermonuclear weapons

testing. Tritium is also an activation product and since 1970, the nuclear-power industry has probably been the largest source of tritium.

Strontium-90 and cesium-137 are the major man-made radioisotopes of concern in water.

Dissolved and particulate radioactivity in water is controlled by the same mechanisms that affect other constituents in the geohydrologic environment. The geochemical behaviour of a daughter element may be grossly different from that of the radioactive parent, although its occurrence, distribution and transport may be governed by the parent.

The International Commission on Radiological Protection recommends maximum permissible body burdens for various radioisotopes, from which maximum permissible concentrations in water are derived (WQS, section 2.7).

The SI radioactivity units are:

- *Becquerel* (Bq) - Corresponds to one disintegration (transformation) per second (dps);
- *Gray* (Gy) - Represents the absorption of one joule of energy per kilogramme of tissue and measures the biological effectiveness of radiation dose;
- *Sievert* (Sv) - Measures the radiation dose equivalent and is obtained by multiplying the absorbed dose with a quality factor (Q). Q depends on the nature of radiation. For example, Q is 1 for beta particles and gamma rays whereas for alpha particles it has a value of 20 (USEPA, 1981).

Equivalence to older units:

- *1 curie* (Ci) is equal to 3.7 x 1010 Bq (or dps);
- *1 rad* is equal to 100 ergs/g, or to 0.01 Gy;
- *1 rem* is equal to 0.01 Sv or to 100 ergs/g x Q.

7.2 Collection and preservation of samples

Acceptable containers are polypropylene, polyethylene or Teflon (HSS, section 10.8.2). They should be pretreated by filling them with concentrated nitric acid for a day, rinsing with detergent and then rinsing several times with purified water. The principal problem encountered in preserving these samples is adsorption

on the walls of the container or on suspended matter (GPH, p. 12).

Samples are collected in 4-litre bottles. To keep metals in solution and minimize absorption, 2 ml of concentrated HCl per litre of sample, or nitric acid to 1 per cent concentration, are added and then the bottles are shipped to the laboratory.

The procedure used in the National Radionuclides Monitoring Program of Environment Canada is to sample for radioactivity measurements monthly and then to analyse an annual composite sample. This is made up by mixing, in a separate bottle, 400-ml aliquots from each monthly sample. If a significant level of radioactivity over the background levels is found, then the samples making up the composite are analysed individually to locate the sample(s) which has (have) the higher-than-expected radioactivity level.

Detailed instructions for analysis of radioisotopes associated with water quality are given in CPQ, pp. 113-63, including recommended containers and preservation methods.

CHAPTER 8

SAMPLING FOR BIOLOGICAL ANALYSIS

Natural and treated waters vary greatly in biological quality. The "saprobic system" of water-quality assessment is a rating system based on biological activity (WQS, section 2.5.2). Changes in the community of plants and animals living together in a specific area can also be used to indicate water quality, the lack or abundance of certain species being indicators of problems (for the ecosystems approach to the classification of water quality, see IWQ).

8.1 Microbiological analysis

The presence of living fecal coliform bacteria indicates an incursion of inadequately treated sewage. The complete absence of coliforms, and especially fecal coliforms, is mandated by the World Health Organization for any drinking water supply (GDW, Table 6, p. 19). Other micro-organisms responsible for human diseases are sometimes to be found in water, e.g. the cholera and typhoid agents, salmonella, pseudomonas and certain single-celled animals such as those that cause amoebiasis.

It is very important that all water samples submitted for microbiological analysis be collected as aseptically as possible in order to reflect accurately microbiological conditions at the time of sample collection.

Only some of the essential information for sampling for microbiological analysis is given here. More detailed information about the various aspects of microbiological sampling and analysis is found in specialized manuals such as *Methods for Microbiological Analysis of Waters, Wastewaters and Sediments* (National Water Research Institute, Environment Canada, Burlington, Ontario, 1978).

8.1.1 Sample containers

Microbiological samples are usually collected in sterile 200-ml or 500-ml wide-mouthed glass or non-toxic plastic bottles with screw caps. Plastic containers should be checked to make sure that they do not shed microscopic particles capable of confusing some kinds of bacterial counts. Metal and certain rubber containers may exert a bacteriostatic effect. If capped, the bottle cap should have an autoclavable silicone rubber liner. If stoppered, the bottle mouth should be covered with sterile heavy-duty paper or with aluminum foil secured with string or an elastic band.

Where the standard is "no coliforms in 100 ml", the failure to find one in a small sample by no means ensures their absence. It would be statistically more meaningful to examine more or larger samples (GDW, section 2.4.2.1).

8.1.2 SAMPLE PRESERVATION

Whenever possible, water samples should be analysed immediately after collection. If immediate processing is impossible, samples should be stored in the dark, in melting ice. Storage under these conditions minimizes multiplication and die-off problems up to 30 hours after collection. Samples should never be frozen.

If samples are suspected of containing concentrations greater than 0.01 mg/l of heavy metals such as copper, nickel or zinc, their bacteriostatic or bactericidal effects should be minimized by the addition of a sequestering agent such as ethylenediaminetetraacetic acid (EDTA), 0.3 ml of a 15 per cent solution for each 125 ml of sample (HSS, section 11.3.2).

Residual chlorine would not often be expected in natural waters, but if present should be destroyed by addition of thiosulfate, 0.1 ml of a 10 per cent solution of sodium thiosulfate for each 125 ml of sample.

8.1.3 SAMPLING PROCEDURE

A discussion of the advantages and disadvantages of several samplers under various circumstances is included in SRS, section 8.2.4. Objections to the use of open-ended cylinder samplers (contamination by carry-down of bacteria from upper layers, bactericidal effect of metals during the short residence times) have been found to be unsupported by the facts (SRS, p. 47). Composite sampling is not recommended (HSS, Fig. 11.1) because of the great variability of samples.

The following instructions are for use of a simple bottle sampler:

(a) Remove, as one unit, the protective paper and stopper of the sample bottle;

(b) Do not rinse the sterile bottle;

(c) If the sample is to be collected in a hand-held fashion, hold the sample bottle near the base and plunge the bottle, neck downward, below the water surface 25-40 cm. Tilt the bottle so that the neck points slightly upward and during filling push the bottle horizontally forward in a direction away from the hand to avoid contamination. If a current is present, direct the mouth of the bottle against the current;

(d) If a bacteria-sampling apparatus is used, fit the bottle into the spring clamp with the bottle mouth downward. The mechanism is designed so that the bottle is then rotated to the upright position under the water surface by the mechanical sampler;

(e) Remove bottle and decant sufficient water to leave a space of 3-4 cm between stopper and water line;

(f) Replace cap or stopper and paper covering, fasten cover and label bottle (if not prelabelled) with a waterproof marking pencil;

(g) Place the bottle in an ice chest;

(h) Record the time of sampling and depth of sample, water temperature and ambient temperature on the field-sampling sheet. Description of the location can be obained from the station-location description sheet.

8.2 Macrobiota

There are several categories of multicellular species which may be monitored for a number of different reasons (HSS, section 10.7.1).

Fish are used as a food supply and a recreational resource and, as the peak of the food chain, are indicative of a variety of water-quality conditions depending on their type and age. Benthic macroinvertebrates (organisms living on or near the bottom which are retained by a standard sieve) are indicators particularly of recent pollution events because of their low mobility and sensitivity to stress. Periphyton, a sessile plant which grows clinging to surfaces, and plants that grow in the mat attached to it are some of the primary producers of aquatic organic matter, particularly in shallow areas. Macrophytes are large plants, often rooted, which cover large areas in shallow water and may interfere with navigation and recreational uses of a water body. Plankton is small free-floating plants and animals; the former, phytoplankton, is primarily algae, whose growth is an indirect measure of, among other things, the concentration of nutrient chemical parameters; the latter, zooplankton, is found at all depths in both standing and flowing waters.

Many of these organisms can be troublesome in water treatment. For example, algae clog filters, consume extra chlorine, adversely affect odour and taste of water, and some are toxic. Others species may be carriers of disease-causing organisms, such as the snails which carry guinea-worm larvae or schistosomes (GDW, sections 3.2 and 3.3).

Depending on the information desired, many different studies can be made on these specimens, from counts and identification, through wet, dry and ash-free

weight, to tissue analysis and enzyme determinations (HSS, section 10.7.1.8).

8.2.1 SAMPLING METHODS

Distributions of sampling locations are recommended in HSS, section 7.4.4.

Fish can be collected actively, as with seines, trawls, electro-fishing, chemicals, and hook and line, or passively, as with gill nets, trammel nets, hoop nets and traps.

Macroinvertebrates may be qualitatively sampled by many methods, depending on their habitats and other parameters (GST, section 4.2.3.3). Two methods in addition to nets are multiple-plate samplers, Figure 8.1 (from HSS, p. 167), and the basket sampler (described in WQS, p. 142). These are left suspended in place by floats for periods of four to eight weeks, then carefully raised to the surface, with a net underneath, for dislodgement of the specimens. Bottom samplers are described in Chapter 10.

Plankton can be collected using the water samplers described in Chapter 3. There are also specially designed samplers such as the Juday plankton trap, which encloses about 5 litres of sample at the desired depth and filters out the plankton. It is rather expensive and awkward to handle from a boat (WQS, p. 138). Zooplankton requires large samples, and a metered nylon net can also be employed.

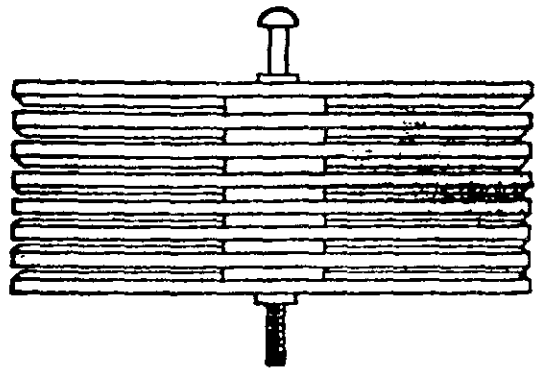
Periphyton can be sampled by exposing anchored or floating slides at the site for at least two weeks (GST, section 4.2). An example of the latter is shown in Figure 8.2 (HSS, p. 166).

For macrophytes, a garden rake can be used in shallow water and dredges in deeper water. From a boat, a cutting knife on the end of a pole or a simple grapple can be used (WQS, section 3.7). For some purposes, self-contained underwater breathing apparatus has been found to be useful.

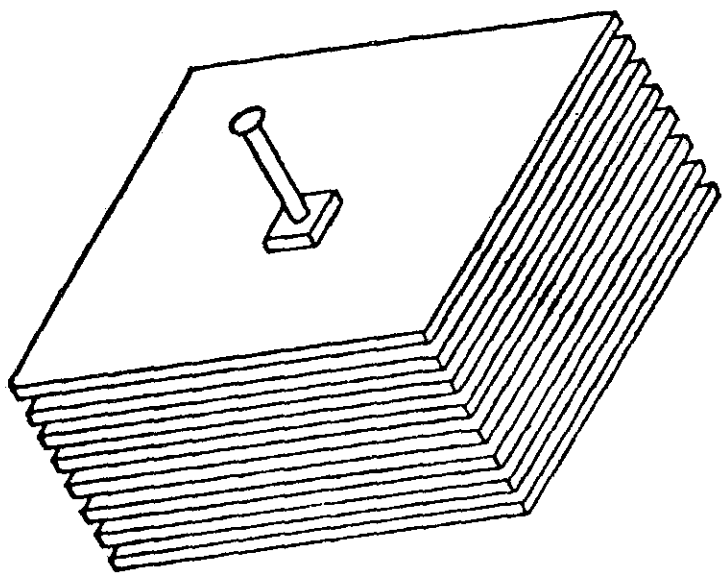
8.2.2 SAMPLE PRESERVATION

In WQS (p. 141) it is recommended that a suitable stain such as rose bengal be added before any fixatives. At a later date, the preserved animals can be picked out by personnel with less biological training because the colour causes them to stand out against the background.

Tables recommending methods for the preservation of specimens of macrobiota are given by GPH and HSS (pp. 234-240). The former is included here as Table 8.1. Canadian practice prefers the use of lugol solution rather than formaldehyde for periphyton and the planktons.

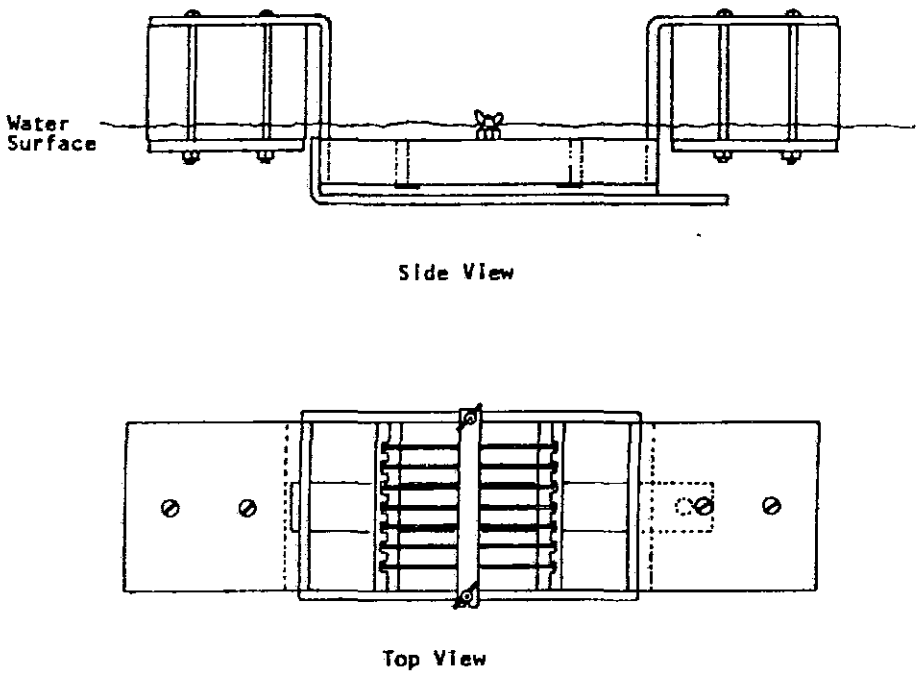


Side View



Hester-Dendy

Figure 8.1 Macro-invertebrate multiple-plate sampler



EPA periphyton sampler. Plexiglass frame supported by two styrofoam floats. Rack holds eight glass microscope slides (30).

Figure 8.2 Periphyton floating-slides sampler

TABLE 8.1 Techniques generally suitable for the preservation of samples

BIOLOGICAL ANALYSIS

The biological parameters to be determined are generally numerous and may sometimes vary from one biological species to another. For this reason it is impossible to draw up an exhaustive checklist of all the precautions that should be taken to preserve samples for this type of analysis. The information below therefore only relates to certain parameters generally studied for various animal or vegetable groups.

It should be noted that before carrying out any detailed study, it is essential to choose the parameters of interest.

1	2	3	4	5	6
Counting and identification					
Benthic macroinvertebrates	P or G	Addition of ethanol	Laboratory	1 year	
Fish	P or BG	Addition of 10% (m/m) formaldehyde, 3 g of sodium borate decahydrate and 50 ml of glycerol per litre	Laboratory	1 year	This analysis should preferably be carried out as soon as possible.
Macrophyton	P or G	Addition of 5% (m/m) formaldehyde	Laboratory	1 year	
Periphyton	P or opaque G	Addition of 5% (m/m) neutral formaldehyde and storage in the dark	Laboratory	6 months	
Phytoplankton	P or opaque G	Addition of 5% (m/m) neutral formaldehyde or mercuriolate and storage in the dark	Laboratory	6 months	
Zooplankton	P or G	Addition of 5% (m/m) formaldehyde or a lugol solution	Laboratory		
Fresh and dry mass					
Benthic macroinvertebrates Macrophytes Periphyton Phytoplankton Zooplankton	P or G	Cooling to between 2 and 5°C	On site or in the laboratory	24 hrs	Do not freeze to -20°C The analysis should be carried out as soon as possible and not later than 24 h.
Fish			On site		
Mass of ash					
Benthic macroinvertebrates	P or G	Filtration and cooling to between 2 and 5°C	Laboratory	6 months	
Macrophytes		Freezing to -20°C	Laboratory	6 months	
Periphyton		Freezing to -20°C	Laboratory	6 months	
Phytoplankton		Filtration and freezing to -20°C	Laboratory	6 months	
Calorimetry					
Benthic macroinvertebrates Phytoplankton Zooplankton	P or G	Cooling to between 2 and 5°C then filtration and storage in a desiccator	Laboratory	24 h	The analysis should preferably be carried out as soon as possible and in all cases within 24 h.
Toxicity tests	P or G	Cooling to between 2 and 5°C	Laboratory	36 h	The preservation period will vary according to the method of analysis to be used.
		Freezing to -20°C	Laboratory	36 h	

CHAPTER 9

PRECIPITATION SAMPLING

In recent years it has become increasingly apparent that deposition of atmospheric pollutants to aquatic ecosystems is of major ecological significance. Most notable in this regard have been the effects on aquatic biota resulting from acidic precipitation in Scandinavia, eastern Canada and north-eastern United States, damage to forests in various parts of the world, and the discovery of toxic contaminants in lakes and icefields far removed from anthropogenic sources.

Rain and snow contribute not only hydrogen ions but also significant amounts of other chemical constituents including trace metals, nutrients, sulfates and organic compounds. Precipitation on land then undergoes a complex series of interactions as it percolates through the soil to become groundwater. Acid rain, for example, may dissolve metallic components such as aluminum and mobilize them for transportation ultimately into surface waters. Material deposited by rain generally interacts with surface or groundwaters within a short time, while snowpacks on ice or frozen ground accumulate both wet and dry deposition over a longer period. At the time of spring thaw this whole amount is delivered to the surface or groundwater at once, greatly intensifying the effects of the accumulated pollutants (SPN, section 3.5). In fact, it has been shown that three-quarters of the soluble material is carried off by the first third of the melt water (CAP, p. 12).

For a complete picture of the atmospheric transport of toxic substances, both the wet and dry precipitation must be sampled and analysed as well as the air itself. Precipitation is an effective scavenging agent for many atmospheric substances, solid, gaseous and aerosol. Before they are removed by rainout (removal processes in the cloud) or washout (removal processes below the cloud), most major pollutants are converted to aerosols. Gaseous components are removed by dissolution in the water droplets or trapping in ice crystals. The partitioning of a gas between air and water is governed by Henry's law (SPN, section 3.2). Particles such as dust or other aerosols are removed in-cloud by serving as nuclei for droplet or ice crystal formation and washed out below the cloud by impaction with rain or snow. Other mechanisms for scavenging of materials from the atmosphere are absorption and deposition at the surface, e.g. solution of gases and trapping of particles at water surfaces.

Particulate analysis, both of "dry deposition" (material deposited outside periods of precipitation) and that of material suspended in the air (aerosols), is made uncertain as an indicator of atmospheric composition by local sources of particles

such as resuspended dust. Deposition at the surface is controlled by the flux (rate of downward motion), which in turn is a function of particle size; by the turbulence of the air flow; and by the roughness and stickiness of the surface. For example, particulate matter deposited in a coniferous forest is almost 100 per cent retained, whereas the same material deposited on a ploughed field can be easily resuspended.

This chapter discusses the criteria necessary for the collection of liquid and frozen precipitation samples and of surface deposition. For the analysis of atmospheric deposition over longer periods than are usual in a water-quality monitoring network, several other substrates have been found useful in providing a record of past depositions (CAP, p. 9). These include naturally growing mosses (which quantitatively retain some metals), ice cores from glaciers and bottom sediments.

The material contained in this chapter has been adapted primarily from CAP, SPN and SWQ, Chapter 9.

9.1 Site selection

As for a surface water-quality monitoring network, the selection of sampling sites and the type and frequency of sampling in a precipitation-sampling network depend on the objectives of the monitoring programme.

One objective could be to monitor the temporal and spatial variations of constituents of precipitation over a large geographical area to follow long-range transport of airborne pollutants. Sampling sites in such a network would be located distant from local or regional sources of pollution, and would be selected to represent major geographic and climatic areas (SPN, section 2.2). It could further be desired to establish monthly, seasonal or annual cycles or long-term trends. For the definition of monthly cycles, for example, it is necessary to sample frequently - at least weekly - over a minimum of one year. For the establishment of trends, one approach is to sample at more or less equally spaced intervals, at least monthly, over a period of at least 10 years for statistical significance (SPN, section 5.3).

Another objective could be to monitor and control local or regional emissions. Estimates of the local impact of large sources require intensive short-term sampling with a large number of collectors to establish the pattern of deposition; the number of collectors could be reduced in number if the exact location of the plume in each event could be located (CAP, p. 13).

Finally, data could be required to develop and test mathematical models which have specific sampling needs. Typical models utilizing these data would be designed to simulate the emission, transformation and interaction, transportation, deposition and effects on receptors of pollutants on a local, regional or continental scale.

In general, sampling sites should be selected to give accurate and representative information concerning the temporal and spatial variation of precipitation deposition of chemical constituents of interest. Important factors to take into consideration are prevalent wind trajectories, sources for compounds of interest, frequency of precipitation events (rain, snow, hail) and other meteorological and atmospheric processes that influence the wet deposition.

Local criteria to consider are:

(a) No moving sources of pollution, such as routine air, ground or water traffic should be within 1 000 m of the site;

(b) No surface storage of agricultural products, fuels or other foreign materials should be within 1 000 m of the site;

(c) Samplers should be installed over flat undisturbed land, preferably grass covered surrounded by trees at distances greater than 5 m from the sampler. There should be no wind-activated sources of pollution nearby such as cultivated fields or unpaved roads. Zones of strong vertical eddy currents, eddy zones leeward of a ridge, tops of wind-swept ridges and roofs of buildings should be particularly avoided because of strong turbulence;

(d) No object taller than the sampler should be within 5 m of the site;

(e) No object should be closer to the sampler than a distance of 2.5 times the height by which the object extends above the sampler. Particular attention must be given to overhead wires;

(f) The collector intake should be located at least 1 m above the height of existing ground cover to minimize coarse materials or splashes from being blown into it.

(g) Automatic samplers require power to operate lids and sensors, and in some cases for refrigeration in the summer and thawing in the winter. If power lines are used, they must not be overhead. If generators are used, the exhaust must be located well away and downwind from the collector;

(h) To address issues on a continental scale, sites should preferably be rural and remote, with no continuous sources of pollution within 50 km in the direction of the prevalent wind direction and 30 km in all other directions.

It may not be possible to meet all of these criteria in all cases. The station-location

description should refer to these criteria and indicate the exact characteristics of each location chosen as a sampling site.

In the case of large lakes, the precipitation over the lake may not be as heavy as along the shores and the proportion of large particles smaller. To sample in the middle of a lake, the sampler can be mounted on a buoy, rock, shoal or small island (SPN, section 4.2.2).

Location and warning lights of buoy collectors require approval from the responsible navigational regulatory agency. The buoy should not be near a navigational lane or channel, yet should be safely accessible by a boat. The sampler height should be high enough above the water that splashing or wave spray does not affect the sample. The mooring of a buoy should be secure, but in colder climates it should be capable of being replaced in winter by an ice-based sampler.

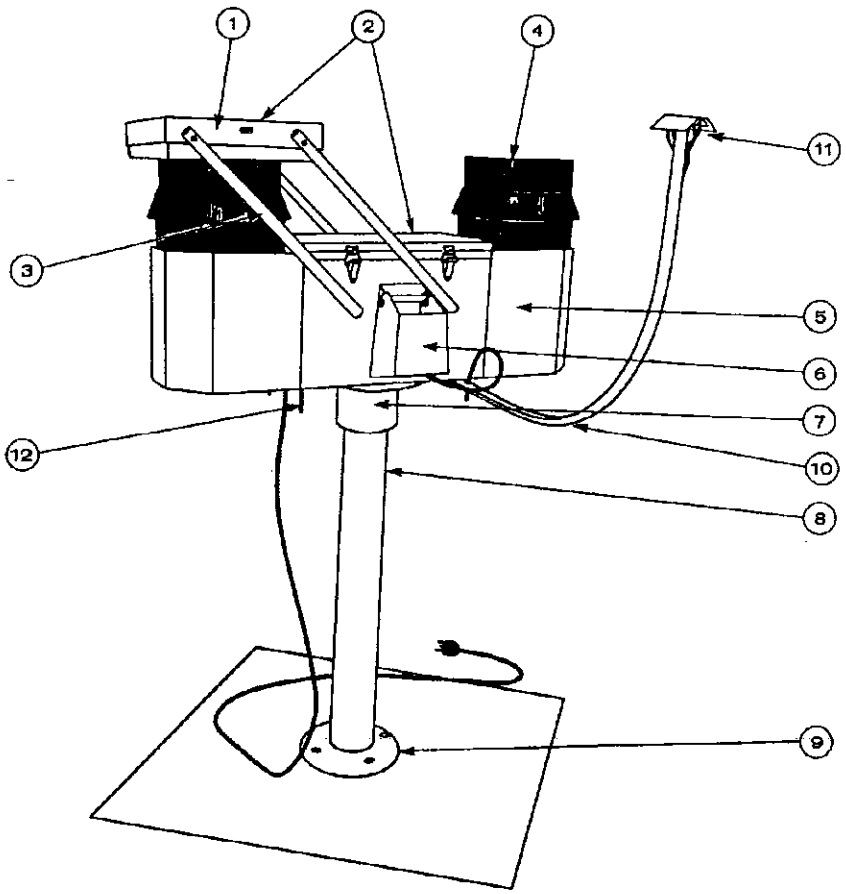
9.2 Sample collectors

Event sampling is the preferred method for sampling precipitation. Each rain shower, storm or snowfall would constitute an event. Analysis of event precipitation samples enables the determination of the nature of the pollutants associated with a particular storm and makes possible the use of wind trajectory analysis to determine probable sources. However, this sampling regime is very demanding of analytical resources. The same statistical considerations concerning frequency of sampling apply here as for surface-water sampling (section 2.4). Similarly, the sample volume is determined by the analytical needs (section 3.5.3). The size of the collecting surface of the sampler and the minimum volume of sample needed for analysis will determine the minimum amount of rainfall which can be considered an event. For example, if the collecting surface measures 2 500 cm^2 (e.g. a square collecting funnel 50 cm to the side or a round funnel with a diameter of 56.4 cm) and the minimum amount of sample needed for analysis is 1 litre, given a collection efficiency of 80 per cent, the amount of rainfall needed to collect sufficient sample is:

$$\text{Amount of rainfall} = \frac{1000\ cm^3}{2500\ cm^2} \times \frac{1}{0.8} = 0.5\ \text{cm or 5 mm.}$$

Many types of collectors have been used to sample precipitation, from a plastic, stainless steel or glass container placed on location at the beginning of a precipitation event to a sophisticated sequential sampler designed to collect precipitation samples automatically at selected intervals during an event.

Two types of automatic collectors are the Aero-Chem Metrics device (CPQ, section 5.B.5.a) and the Sangamo Type A precipitation collector (Figure 9.1), which is the current (1986) standard collector in Canadian practice. It is a "double bucket"collector; one bucket is used to collect the wet deposition while the other bucket collects



1. Moveable cover
2. Splash screens
3. Cover support arms
4. Collection buckets
5. Housing
6. Cover plate
7. Mounting flange
8. Mounting pipe (7.5 cm I.D.)
9. Companion flange (18 cm)
10. Sensor head support arm
11. Sensor head
12. Housing vents and drain spouts

Figure 9.1 Sangamo Type A precipitation collector

the dry deposition. The collector is equipped with an automatic sensing system which detects precipitation, liquid or frozen. At the onset of a precipitation event, the sensor detects it and the cover is moved from the "wet" bucket to the "dry" bucket. On cessation of the event, the cover automatically returns over the "wet" bucket.

The sample container normally used with the sampler is a black polyethylene vessel. It consists of two parts. The top part is a removable rim which has been specially fabricated to ensure a sharply defined uniform area of collection. Both the rim and the bucket must be rinsed with distilled, de-ionized water each time a sample is removed. When sampling precipitation for organic contaminants a stainless steel or glass bucket must be used.

When the direction from which the precipitation comes and its amounts are part of the information desired, associated meteorological measuring instruments can be utilized. Equipment has been designed in which a wind vane directs the precipitation to one of a number of bottles depending on the direction of the wind (SPN, section 6.5.4).

New, all-weather samplers, especially for collecting samples for analysis of toxic organic compounds in precipitation, are under development. They incorporate not only recent advances in electronics but also extract the organic compounds onto resin columns, thus preserving the sample and facilitating its shipment to the laboratory for analysis.

9.2.1 Snow collectors

The aerodynamics of a snow collector differ from those of a rain collector (SPN, section 6.4.2). Falling snow blown by the wind often travels close to the horizontal and would not be entrapped by a rain collector. In addition, wind eddies around the opening of the collector can generate turbulence inside and remove some of the snow. More modern snow collectors are similar to the rain collectors except that they are heated to thaw and store the entrapped snow as liquid in a compartment beneath the sampler.

9.2.2 Dry-deposition collection

Many of the problems in snow collection also apply to collection of dry deposition. The two-bucket collectors provide a measure of the amount, but considerable controversy exists about the relevance of such measurements (CAP, p. 17). The air turbulence around such devices is not the same as at the surface of a lake, for example, which leads to differences both in absolute collection efficiency and relative efficiency between different particle sizes. Other methods have been suggested such as glass plates coated with sticky materials and shallow pans with liquids, aqueous ethylene glycol or mineral oil.

9.3 Sample collection procedures

9.3.1 Definition of the end of the month

For regimes in which monthly returns are submitted, the end of the month should be defined. A convenient definition used in Canadian practice is that the month ends at 17.00 GMT on the last day of the current month. In the event that precipitation is occurring at the station at 17.00 GMT on the last day of the month, the end of the month is taken as the date and time that the precipitation ceases.

9.3.2 Sample-handling procedures

Depending on the sampling frequency, e.g. event or monthly, the sample is removed from the collector at the end of the event or of the month, using the following procedures:

(a) Remove the bucket from the collector and carry it to a clean area free from smoke, dust, gasoline, oil, and any other materials that might contaminate the sample;

Note: Hands must be clean. Those surfaces which will come in contact with the precipitation samples (i.e. inside surface of the collection bucket) must not be touched. If the sample is frozen, i.e. snow or ice, it must be allowed to melt at room temperature before proceeding.

(b) Using a graduated flask, measure the volume of the sample to the nearest 10 ml and note this figure on a Sample History Form together with the period over which the precipitation was collected, e.g. 25-07-81 to 26-07-81, 420 ml;

(c) Carefully pour the sample into a large, e.g. 8-litre, storage container and recap the container immediately;

(d) Using the rinse bottle and de-ionized, distilled water, thoroughly rinse the bucket, rim and flask. Assemble the vessel and place it back in the collector. Cover the graduated flask after rinsing it.

For shipping the sample to the laboratory for analysis:

(a) Carefully pour the sample into a sample shipping bottle, filling it to within about 2 cm of the top if there is sufficient sample. Screw the top onto the shipping bottle securely;

(b) Discard any sample remaining in the graduated flask;

(c) Using the rinse bottle and de-ionized, distilled water, thoroughly rinse the storage container and the graduated flask. Cover the graduated flask;

(d) Complete the Sample History Form. Fill out a sample identification label, of the type shown in Figure 9.2, and stick it onto the sample bottle;

(e) Prepare the labelled sample bottle, including the completed history form, for transmission by the selected means to the analytical laboratory for chemical analysis.

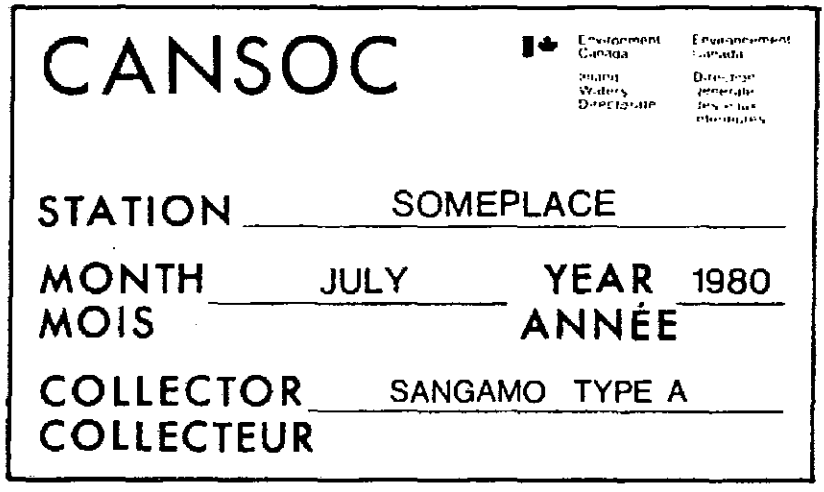


Figure 9.2 Example of a label for a precipitation sample

9.3.3 Prevention of sample contamination

Careful handling of equipment and samples to prevent contamination is extremely important. The dissolved substances in a precipitation sample have very low concentrations and any contamination will produce erroneous results.

Those surfaces which will come in contact with the precipitation samples must not be touched, i.e. the inside surface of the collection vessel. If transfer of the sample must be carried out, extreme care must be taken with cleanliness of the funnel and the transfer must be done in a dust-free area with no person smoking nor any other form of pollution in the vicinity (SPN, section 7).

It is essential that all operations be carried out in as clean a manner as possible. The following contaminants should be strictly avoided:

(a) Gasoline;

(b) Oil;

(c) Cigarette smoke and ash;

(d) Organic liquids;

(e) Other volatile materials that can lead to contamination of the sample by vapours or smoke;

(f) Other materials such as dust and dirt.

If it is suspected that the sample has been contaminated with any of these materials, then it should be reported on the Sample History Form.

For the use of blanks to ensure that no contamination is introduced during any of the procedures see section 2.7.4.

9.4 Records of precipitation samples

The interpretation of the results of the chemical analysis requires information on any phenomena likely to affect the chemical constituents or the physical collection of precipitation. Thus, it is necessary to maintain a carefully prepared record pertaining to each sample. A Precipitation Sample History Form must be provided for this purpose. An example of a completed Precipitation Sample History form is shown in Figure 9.3. The information which must be included in any such form is:

(a) Station name and number;

(b) Type of collector (enter the full name);

(c) The day, month and year that the collection was begun and completed;

(d) The volume of the sample (to the nearest 10 ml is usually sufficient);

(e) The height (in mm) of water collected in the standard precipitation gauge during the same period.

Space should be included to enter any observations of situations which may affect the samples, together with the time of the occurrence. A partial list of events of the type which should be recorded follows:

(a) High winds, their direction and intensity (if available);

(b) Unusual amounts of blowing dust;

(c) Blowing snow, i.e. snow particles raised by the wind;

(d) Missed precipitation events with an estimation of amount missed, whenever possible;

(e) Snow and ice capping of the collection vessel;

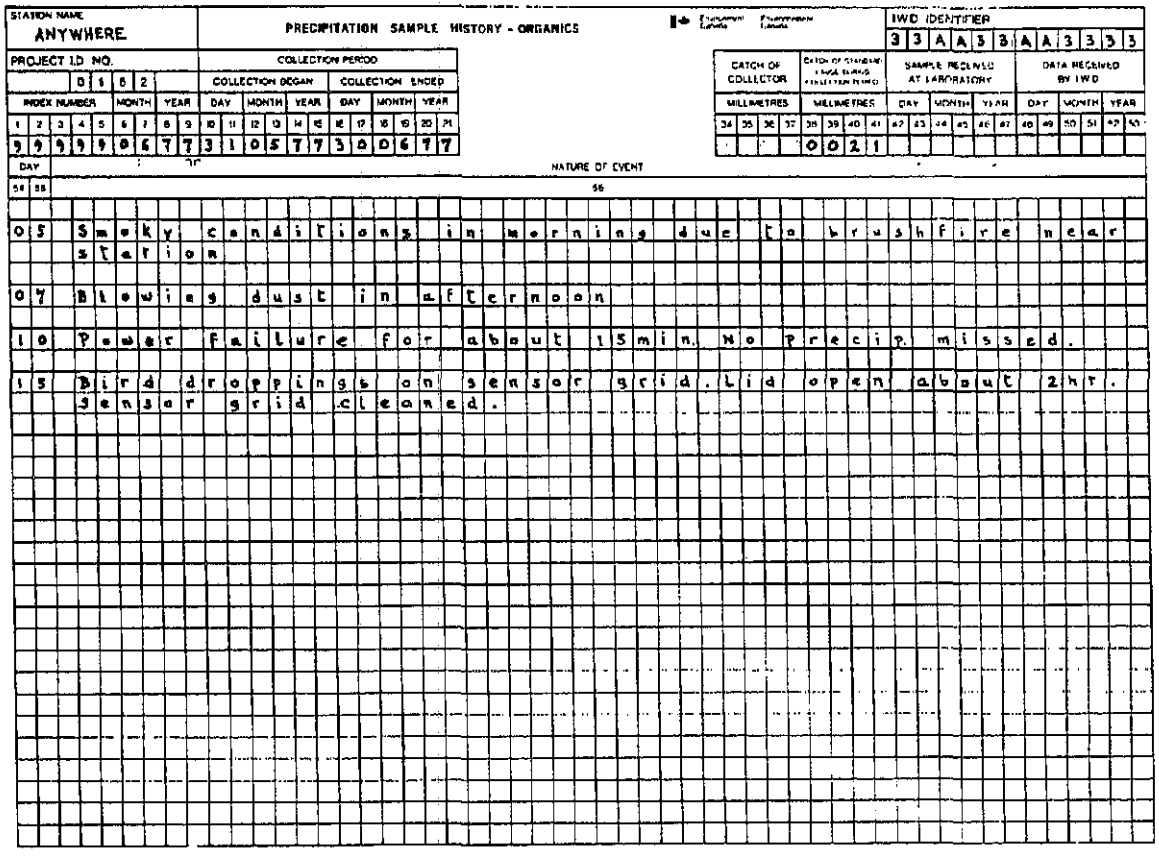
(f) Objects found in the collection vessel. Indicate the nature of the object, such as leaf, insect, paper, bird droppings;

Note: If objects are found in the collection vessel, do not attempt to remove them, as further contamination may result.

(g) Power failure.

*

* *



STATION NAME: ANYWHERE

PRECIPITATION SAMPLE HISTORY - ORGANICS

IWD IDENTIFIER: 3 3 A A 3 3 A A 3 3 3 3

PROJECT I.D. NO.: 0 1 6 2

INDEX NUMBER	COLLECTION PERIOD BEGAN DAY	MONTH	YEAR	COLLECTION PERIOD ENDED DAY	MONTH	YEAR	CATCH OF COLLECTOR (MILLIMETRES)	CATCH OF STANDARD RAIN GAUGE (MILLIMETRES)	SAMPLE RECEIVED AT LABORATORY DAY	MONTH	YEAR	DATA RECEIVED BY IWD DAY	MONTH	YEAR
99999	06	77	31	05	77	30	06	77						
								002	1					

DAY	NATURE OF EVENT
05	Smoky conditions in morning due to brushfire near station
07	Blowing dust in afternoon
10	Power failure for about 15 min. No precip. missed.
15	Bird dropping on sensor grid. Lid open about 2 hr. sensor grid cleaned.

Figure 9.3 Example of a completed precipitation sample history form

CHAPTER 10

SEDIMENT SAMPLING PROCEDURES

Three major types of particulate matter can be distinguished in rivers and lakes, although the distinction is not absolute. One type can be converted into another by changes in water velocity. The types are (GEM, Chapter VII, section 1.1.1):

(a) Suspended matter - particles maintained by water turbulence in suspension above the bed of the water body. In rivers the total amount and particle size vary greatly with stream flow. In lakes the amount is usually small, less than 10 mg/l, and consists mostly of organic lacustrine detritus and very fine soil material;

(b) Bedload (or "traction-load") - that part of the particulate matter which remains in almost constant contact with the river bed and is moved by rolling, sliding or hopping much more slowly than the water velocity;

(c) Deposited matter - results from a decrease in water energy, leading to settling, coarse particles first. Lake sediments tend to be fine particles, while those in rivers are much more heterogeneous.

A scale of grain sizes is given in Table 10.1 (GEM, Chap. VII, Table 1, p. 4).

Sediment plays an important role in water quality. Part of the assimilative capacity of natural-water systems for inorganic materials, e.g. metals and organic substances such as pesticides and herbicides, is due to the ability of the sediment to bind them, thus removing them from the water. On the other hand, many toxic substances bound to the sediment can be released to the surrounding waters by a variety of chemical and biochemical reactions, thus making them available to the organisms living in these waters.

The binding power of sediments depends on the chemical nature of the substance to be bound and of the particles, and on the surface-to-mass ratio of the sediment particles. Small particles, particularly those of organic origin, can have surface areas of many square metres per gram. Thus they are capable of absorbing large amounts of dissolved materials. Table 10.2 (GEM, Chap. VII, p. 8) indicates some of the specificities of adsorption.

TABLE 10.1 Grain-size scales for sediments *(after Shepard, 1963)*

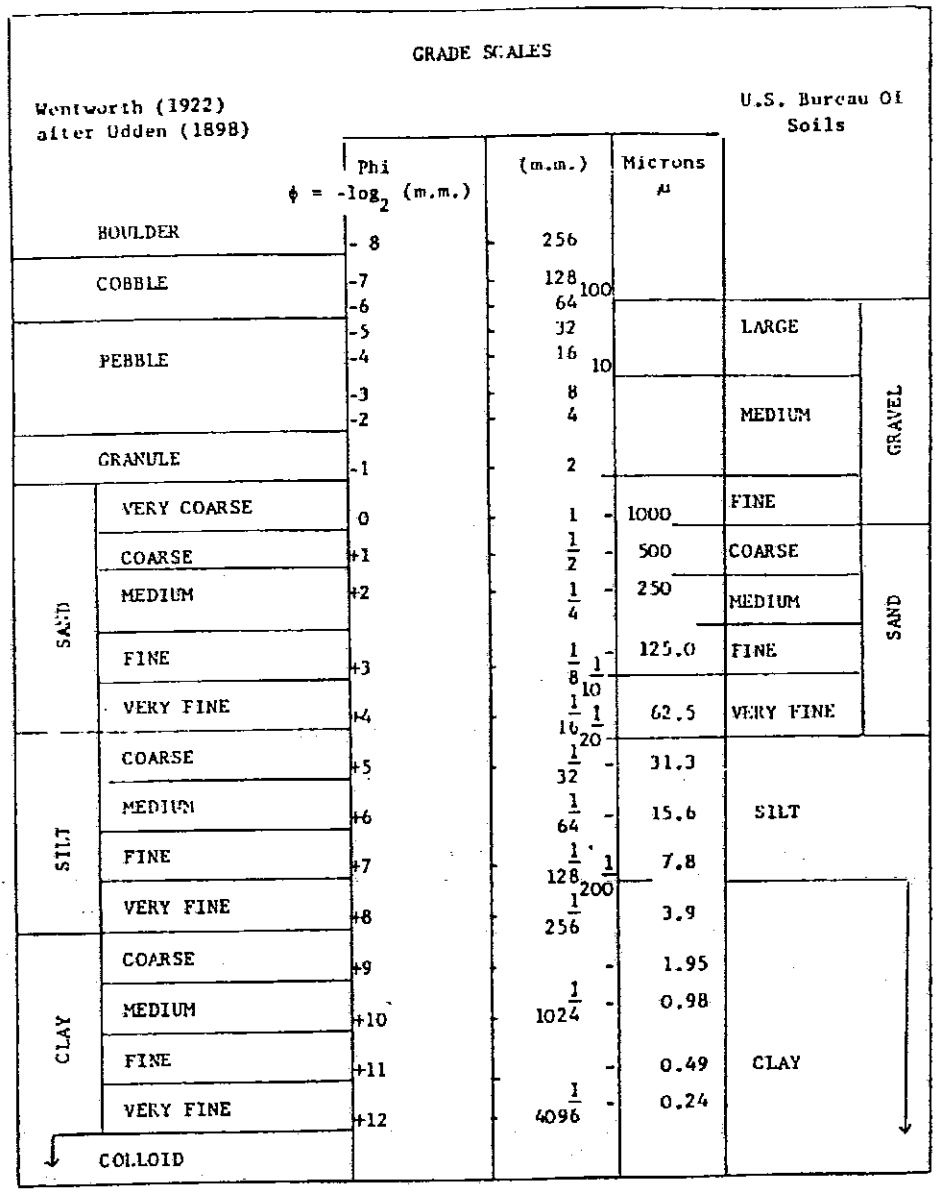


TABLE 10.2 Speciation of pollutants in particulate matter

Pollutant or Nutrient	*Phase or form*							
	Electro-statically adsorbed	Specifically adsorbed	Organic matter	Bound to carbonates	Occluded in Fe-Mn oxides	Bound to Sulfides	Specific Minerals	Silicates and other residual minerals
Organic matter	o	x	xx	o	x	o	o	o
Nitrogen	x (NH_4^+)	x	xx	o	o	o	o	o
Phosphorus	x (PO_4 - P)		xx (Nucleic acids, phospho-lipids)	o	xx	o	xx (Apatites)	o
Arsenic	x	x	x	o	x	x	xx (Arsenates)	x
Trace metals	x	x	xx	x	xx	x	x	xx
PCBs & other chlorinated compounds	(i)	xx	x	o	o	o	o	o
Polycyclic aromatics	(i)	xx	x	o	o	o	o	o
Other hydrocarbons	(i)	xx	x	o	o	o	o	o

Relative abundance: o = None; x = Little; xx = Abundant; and (i) = Depends on the polarity of organic molecules.

Lake and stream sediments often reflect recent additions of heavy metals before they are detectable in the overlying water. Poorly soluble pollutants, such as polychlorobiphenyls (PCBs), will be present in fine sediments at concentrations many orders of magnitude higher than their concentration in water. While the water analysis may therefore indicate no detectable concentrations, a water body may still be heavily polluted with organic and inorganic material in the sediments indicating that contamination has occurred or is occurring. With water-insoluble and fat-soluble substances, even higher concentrations may be found at the top of the food chain, but in many cases sediment sampling is nonetheless preferred to sampling of biota (SRB, section III.1.3). Bottom sediment samples reflect the historical input to streams, lakes and estuaries with respect to time, application of chemicals and land use. Also, for bottom-feeding organisms sediments may be more important than water as a source of organic and inorganic substances.

Suspended-sediment samples are collected in much the same way as surface-water samples in that they are intended to be representative of a region of the water body. On the other hand, bottom sediments are specific to a particular location on the bed of the water body.

10.1 Site selection

Most of the selection criteria outlined in Chapter 2 also apply to sampling for sediments; therefore, only additional special recommendations will be described here.

10.1.1 Rivers

The quality of suspended material across a section of a river is much less variable than its quantity. An integrated sample obtained by mixing water from several points in the water column according to their average sediment load can be considered as representative of the quality of particles in the cross-section, as long as there is good lateral homogeneity.

The best place to sample bottom deposits in fast-flowing rivers is in shoals, at channel bends and at mid-channel bars or other sheltered areas where the water velocity is at its minimum (GEM, Chap. VII, section 2.2.2; SRB, section III.4).

Where sediment transport data are required, it is necessary to locate the sampling sites near a water-quantity gauging station so that accurate stream discharge information is available at all times. Sampling locations immediately upstream from confluences should be avoided, as they may be subject to back-water phenomena. In streams too deep to wade, it may be advantageous to locate sampling sites under bridges or cableways. When sampling from bridges, the upstream side is normally preferred. Sampling on the downstream side of the bridge presents limited upstream visibility (cf. section 3.2). Sampling in areas of high turbulence, near piers, must be

avoided. Sediment samples collected near piers are often unrepresentative of the general sediment transport characteristics. Attention must also be paid to the accumulation of debris or trash on the piers, as this can seriously distort the flow and hence the sediment distribution. Finally, sampling sites should be accessible during floods, since sediment transport rates are high during these times.

10.1.2 Lakes

The basic sampling site should be located at the geographic centre of the lake, which is also usually near the deepest part of the lake. If the deepest point is far from the centre of the lake, if there are many lacustrine basins, or if the lake is very large (area > 500 km^2), several base stations may be needed.

If each sediment type must be sampled in each region of a lake, data from acoustic surveys - echo-sounders - can be used both to identify the type of surficial material (sand, gravel or mud) and to indicate the presence of layering below the surface (SRB, section III.3.2).

Secondary sampling sites should be located between the base station and major tributary inlets or pollutant sources. A common strategy is to place points down the long axis of the lake with occasional cross lines. Three to five stations should usually give a good approximation of the sediment quality of an average-size lake (GEM, Chap. VII, section 2.2.1). For statistical validity, however, a larger number of sampling sites will probably be required.

10.2 Sample collection

10.2.1 Sampling frequency

Most of the considerations governing water sampling frequency (section 2.4) apply to sediment sampling. A few additional observations are included here.

Sampling frequency in lakes is affected by the generally low concentrations of suspended sediment. Sediment traps should be operated during the periods of maximum and minimum algal productivity and at times of high input of sediment from rivers.

Repeat sampling of bottom sediments in lakes needs to take into account the rates of sediment accumulation (SRB, section III.2.2). Basins in cool temperate climates often have accumulation rates of the order of 0.1-0.2 mm/yr. A resampling period of five years would then be too soon to provide worthwhile new information, unless the presence of a new pollutant is be tested.

For identification of peak pollution loads in rivers, two cases must be considered. For pollution from point sources, sampling should be done during low-flow

periods when pollution inputs are less diluted. On the other hand, when pollutants originate from diffuse sources such as runoff from the land of agricultural nutrients or pesticides, sampling must be focused on flood periods during which the pollutant is washed out of the soil (GEM, Chap. VII, p. 15).

If one of the objectives is to quantify the transport of sediment in the river system, it should be noted that peak concentrations of sediment do not necessarily correspond with times of peak flow. They may be simultaneous or lagging (SRB, section III.4.2). Also, a series of high flow rates will lead to progressively lower sediment peaks - an "exhaustion effect" arising from depletion of material available for resuspension.

10.2.2 Sample integrity

For some purposes bed-sediment samples can be disturbed, i.e. the individual particles can be rearranged relative to each other and it is unimportant if the volume and shape of the sample is altered from the actual conditions of the deposit. However, for many purposes undisturbed samples are required. When the purpose of sampling is to obtain information related to the vertical composition of the deposits or on the distribution of contaminants from a certain depth, undisturbed core or high-quality dredge samples should be taken. It must be noted, however, that in rivers and shallow lakes frequent resuspension of bottom sediments leads to homogenization of the upper layer.

10.3 Samplers

To collect valid suspended sediment samples, samplers and sampling procedures must be designed to represent accurately the water-sediment system being studied. The procedures and apparatus employed for sediment sampling depend on the type of sediment being sampled. For example, since adsorption is greatest on the smallest grains, the loss of the fine material in low-density deposits must be minimized during any sampling process; the methodology and the equipment used for sampling suspended sediments are different from those required for sediment deposits. In addition to retaining fines, a bottom-material sampler must usually be able to maintain the integrity of the layers.

10.3.1 Suspended-sediment samplers

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

(a) Integrating samplers;

(b) Instantaneous or grab samplers;

(c) Pumping samplers; and

(d) Sedimentation traps.

The US series of integrating samplers is designed such that the intake nozzle is oriented into and parallel to the flow. As a result, the water-sediment mixture moves from the stream into the intake with minimum acceleration, thus providing the most accurately representative sample (SED, section 3.D.1.b.1.b).

In lakes, the first two types are unlikely to provide enough material after filtration for even the most basic analyses. Most of the published work on suspended matter in lakes has used sedimentation traps, although microbial processes continuing within them during the lengthy residence times required to obtain even small samples and the complex physics of trap entry raise doubts about how representative the analyses may be (SRB, section III.3.7). Sedimentation traps for use in lakes and reservoirs are cylinders of plastic for metallic determinands and glass or metal for organic compounds. The cylinder should have a height-to-width ratio larger than five, with nothing above the opening such as lattices, lids, baffles or collars. It is necessary to prevent the mooring system from moving by using an appropriate sub-surface float (GEM, Chap. VII, section 2.4.1). Traps should be retrieved after no more than one month to minimize mineralization and microbial degradation of suspended organic matter.

A minimum of 500 mg of suspended matter is needed for some basic analysis purposes and 5 g for a fuller range of parameters. The volume of water which should be sampled to obtain the required amounts of suspended sediments can vary from a few to thousands of litres depending on the suspended-sediment concentration. For large volumes only pumping systems are practicable, and a continuous-flow centrifuge is preferable to filtration (SRB, section III.3.7). At throughputs of about 6 l/min, this is a lengthy process. An alternative is transport back to the laboratory in tanks. New procedures are also being developed, e.g. combining centrifugation with solvent extraction in the field (Canadian Water Quality Branch).

In smaller rivers, direct hand sampling can be performed by wading, using a simple bucket if that is all that is available. If the suspended-sediment load is sufficiently high, grab or depth-integrating samplers may be used followed by pressure filtration through a 0.45-nm filtration system. Pumped centrifugation is required only where specialized analyses are to be undertaken.

10.3.2 Bottom-sediment samplers

Exposed surface sediment may be collected directly into sterile containers using a sterilized spatula or spoon (SRS, section 8.2.4.4). Sediments covered by water require special sampling equipment.

Because the topmost layer of the sediment is the most recent and is the site of the most intensive microbiological activity, it is usually important that the sampler not stir the sediment surface or cause change in the sediment layers. Thus the sampler must be lowered so as not to create a pressure wave that may displace the softest surface sediments. The sampler must penetrate far enough into the sediments to include the desired layers, but not so far that sediment spills out the top. Further, the sample must not be subject to washout on the way up.

The weight of many of these samplers and also the mass of the line necessary in deep water require that a hand- or power-operated winch be available.

10.3.2.1 Core samplers

Gravity and piston corers are used to collect undisturbed samples of river, lake, reservoir and pond deposits. Samplers of this type are essentially tubes which are forced into the bed of the system. A few such samplers are illustrated in Figures 10.1 (SWQ, p. 44) and 10.2 (HSS, p. 163). Samples are retained inside the barrel of the sampler by a partial vacuum formed above the sample and/or by a core retainer at the lower end. In shallow waters, a simple tube can be pushed into the sediment by hand and closed at the top or both ends by stoppers.

A number of other core-type samplers are mentioned in SRS, section 8.2.4.4.2 and SED, section 3.D.2.c, and compared in HSS, Table 5, p. 157 and SRB, Table IV.2, pp. 98-99.

Where plastic can be used for the barrel of corers, it is advantageous to use transparent material such that the sample can be visually examined. When layers are extruded and cut off for examination, the problem of contamination by the wall of the corer can be avoided by taking samples from the centre of the core if the internal diameter of the corer is sufficiently large (at least 5 cm).

Some gravity-type corers have a plastic liner. The steel cutting head at the base of the sampler holds the liner in place. The corer is allowed to accelerate to achieve the desired penetration. A check valve at the top retains the sample as it is raised to the surface. The cutting head is removed, exposing the plastic liner which is capped and withdrawn. The liner can be cut off above the sample and again capped and labelled for further handling (SED, section 3.D.2.c.1.a).

Most core samplers lack positive seals to hold a moist sample in place as the sampler is withdrawn from the water. Also, collection of representative samples at the water-sediment interface is difficult. Considerable effort has been devoted to proposed solutions for these problems (CPQ, section 5.B.5.c).

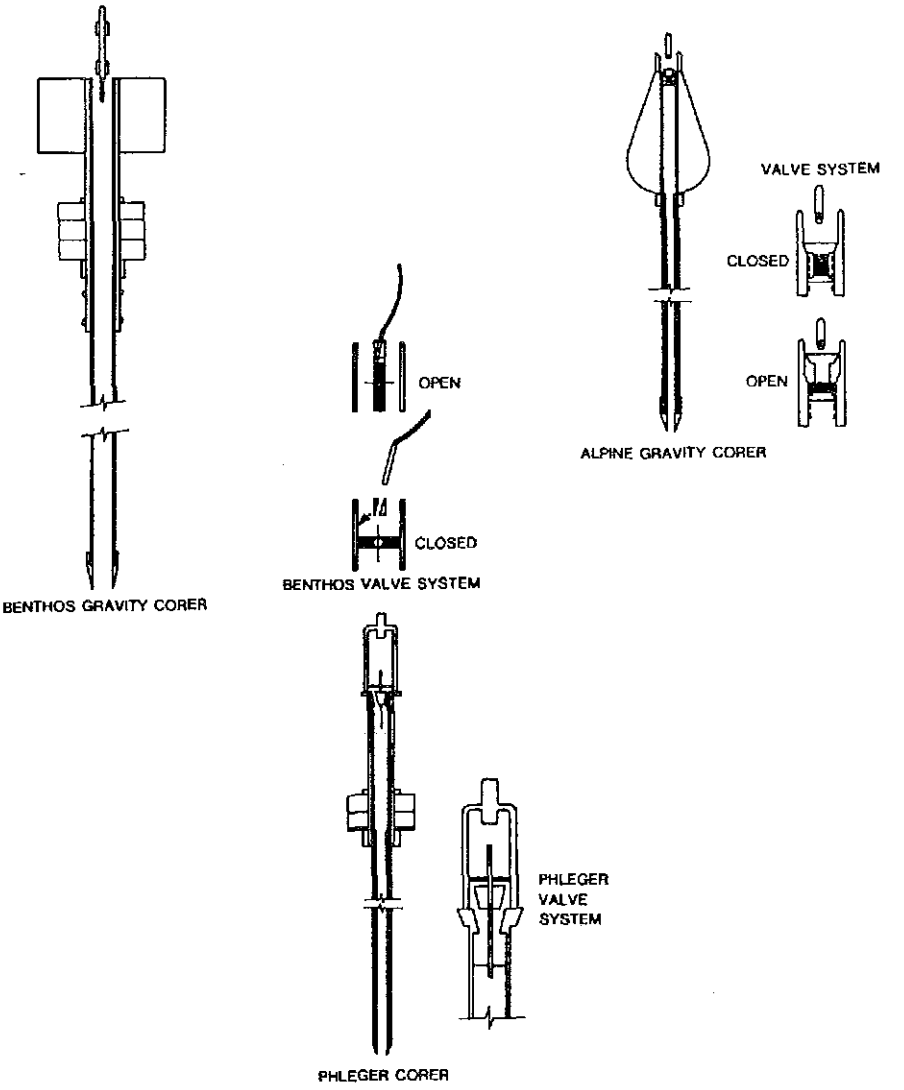


Figure 10.1 Examples of sediment corers *(from Mawhinney and Bisutti, 1981)*

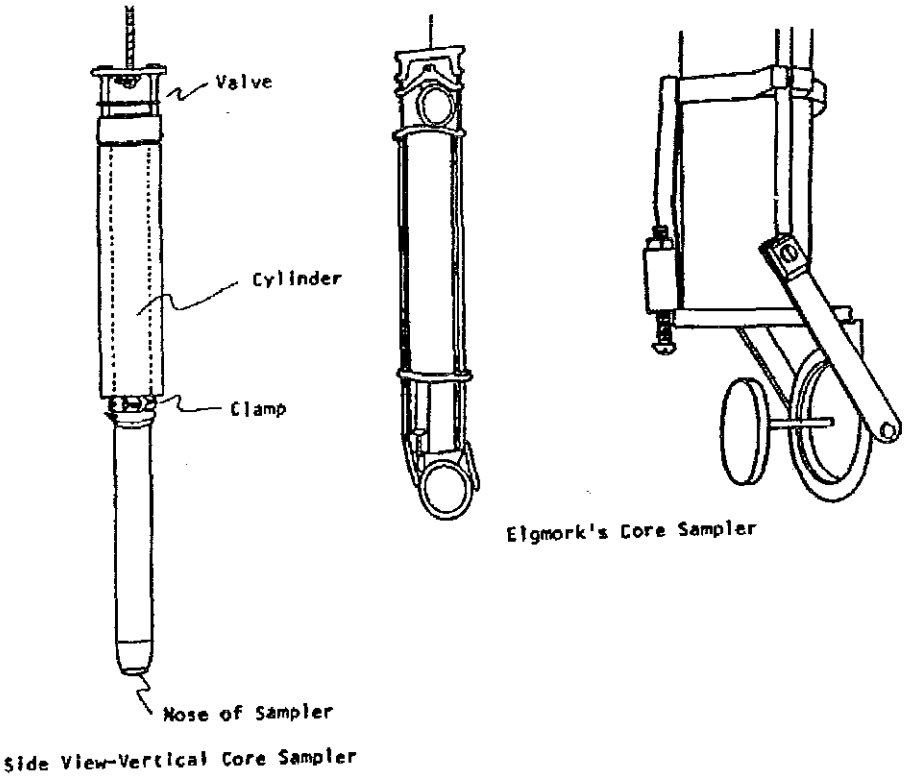


Figure 10.2 Core samplers

10.3.2.2 Grab samplers

Grab samplers are more commonly used than core samplers for collecting deposited sediments, as they are often much lighter and in some circumstances much easier to use. If properly used, the grab sampler encloses a volume of the bed material and isolates the sample from water currents during its ascent to the surface to yield a reasonably good undisturbed sample. Grab samplers are compared in Table 10.3 (HSS, Table 7.4, p. 156).

TABLE 10.3 Comparison of bottom grabs

Device	Advantages	Disadvantages
Polar	Safe, easy to use, prevents escape of material with end plates, reduces shock wave, combines advantages of others, preferred grab in most cases	Can become buried in soft sediments
Ekman	Use in soft sediments and calm waters, collects standard size sample (quantitative), reduces shock wave	Not useful in rough water; not useful if vegetation on bottom
Tall Ekman	Does not lose sediment over top; use in soft sediments and calm water, standard sample size, reduces shock wave	Not useful in rough waters, others as for Ekman
Peterson	Quantitative samples in fine sediments, good for hard bottoms and sturdy and simple construction	May lose sampled material, premature tripping, not easy to close; does not sample constant areas; limited sampling capacity
Smith-Mcintyre	Useful in bad weather, reduces premature tripping, use in depths up to 1500 m (3500 ft), flange on jaws reduced material loss, screen reduces shock waves, good in all sediment types	Large, complicated and heavy, hazardous, for samples to 7 cm depth only, shock wave created
Hayward Orange Peel	Easy to operate, commercially available in various sizes, does not rust easily, does not require messenger, good bottom penetration, takes undisturbed sample of top sediment	Difficult to determine sampling cover, 2 cables required, active washing during sampling, jaws do not close tightly, soft sediment fouls closing mechanism
Diver	Can determine most representative sampling point and current velocity	Requires costly equipment and special training

The Shipek grab sampler consists of a steel shank, weight and a sampling bucket (Figure 10.3). The steel bucket is the inner part of a pair of concentric half cylinders with closed ends, and is rotated at high torque by two helically wound external springs. It is lowered through the water column in an inverted position (convex upward) until it contacts the sediment surface. The internal weight mounted above it continues to drop and triggers a release mechanism which frees the inverted bucket. The bucket rotates 180° on its axis at high speed, cutting a continuous curve through the sediment until it is stopped in a position concave upwards. In most cases the rotational shear is far greater than the sediment shear strength, and consequently the cutting action is very clean (producing minimal disturbance) particularly in soft clays, muds, silts and sands. The bucket is held in this closed position during the return to the surface, and is released by pulling outwards on its pivot pins and a clean-cut undisturbed bottom sample is recovered. Difficulty has been experienced in ensuring that the sampler goes down straight, but this can be rectified by attaching a plastic float at the upper end of the device (SRS, section 8.2.4.4.1).

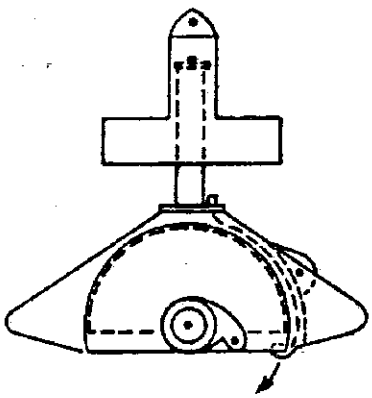


Figure 10.3 Shipek grab sampler *(from Mawhinney and Bisutti, 1981)*

The Shipek sampler functions well as a result of the mechanism which permits the bucket to close with its separation plane aligned in the horizontal rather than in the vertical. Good samples can still be retrieved even when bucket closure is prevented by pebbles or similar material, 2-5 cm across. With the bucket properly rotated, sample washout is completely avoided and the body of the sampler protects the bucket from washout on ascent. It is cumbersome and difficult to sterilize, but as the quantity of material collected is rather large (400 cm^2 to a depth of 10 cm at the centre), it is possible to obtain material which has had no appreciable contact with the equipment.

The Mini-Shipek sampler works exactly as the standard Shipek described above except that, as the name implies, it takes a considerably smaller sample. This sampler is used basically from small boats by hand.

The Birge-Ekman dredge (Figure 10.4) is available in a number of models and sizes (about 15x15 cm, 24x24 cm and 30x30 cm) all basically similar in design. The standard model consists of a brass or stainless-steel box with a pair of free-moving hinged flaps. During descent, these flaps are forced open by the pressure of water passing through the open box. On ascent, the flaps cover the upper surface of the box and prevent disturbance of the material inside it. Pivot points on opposite sides of the box serve as mounting points for a pair of spring-tensioned scoop-like jaws. The jaws are held open by wires which lead up to an externally mounted trigger assembly. This is normally triggered by a surface-release messenger weight. The jaws are designed to overlap to prevent washout during retrieval. The commonest size, 15x15 cm, weighs about 4.5 kg. With the jaws closed, the maximum depth of their cut is about 4.5 cm. The maximum sample surface area is approximately 230 cm^2 with a maximum sample capacity of about 3.9 litres.

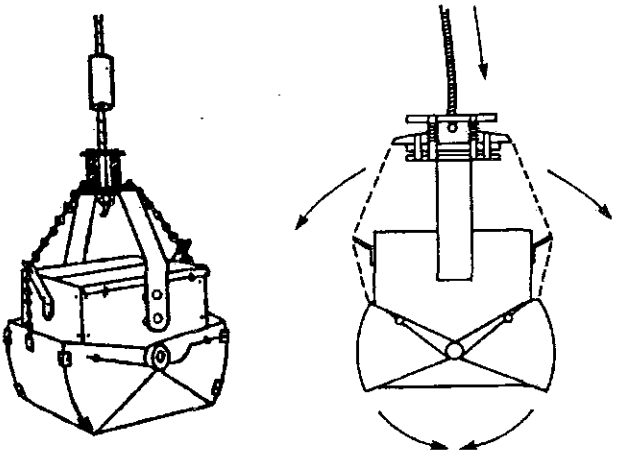


Figure 10.4 - Birge-Ekman dredge *(from Mawhinney and Bisutti, 1981)*

The Birge-Ekman dredge is suitable for soft clays, muds, silts and silty sands. The sampler should be used during calm water conditions, typically in small lakes or restricted areas. The lack of sample disturbance, square cross-section and moderate penetration make this sampler suitable for detailed studies, e.g. biological and geochemical, of the top 2-3 cm of bottom sediment. It is lightweight and easy handling makes it well suited to small-boat operations.

The sampler performs well except when used in very coarse or shelly sediment. Under these conditions, material may be trapped between the jaws, preventing their closure. In this case washout may be severe. Due to the overlapping of the jaws, a slight imperfection of closure can be tolerated.

Another problem can be sampling in deep water. The line has to be in one continuous length without joints because the messenger has to be sent down the line.

Other dredges are described in WQS, section 3.5, including the Surber sampler (Figure 10.5). This is a lightweight representative of the category of dredge nets used for collecting biological specimens.

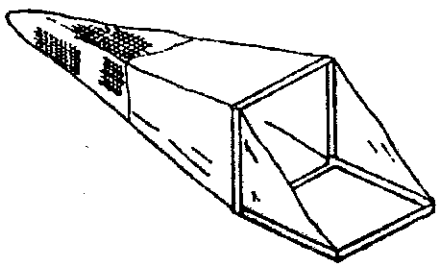


Figure 10.5 Surber sampler

10.4 Sample handling and preservation

Many of the compounds are found in the sediments at very low levels. Special care is therefore necessary to avoid contamination.

Samples for trace metal and organic analysis also require preservation. Table 6.2 lists a number of parameters and methods of preservation. Collection bottles should be precleaned by thorough washing, as outlined in section 3.5.2.

10.4.1 Suspended sediment

As soon as possible after collection, the sample should be filtered. The filtrate can then be used for measuring the dissolved constituents. Preservation procedures, as outlined in section 6.2 and Table 6.2, should be followed.

The analysis of a suspended-sediment sample is often limited on account of the difficulty in obtaining sufficient material for the many subsamples required for the different analyses. A composite of a large number of representative samples may be necessary.

10.4.2 Bottom sediment

Samples of sediment for routine particle-size analysis can be transported and stored without refrigeration.

Bottom sediments and their interstitial water may come from a highly reducing anoxic environment in which the concentration of dissolved substances is much higher than in the water above, and even just above the sediment surface. A number of components can be rapidly oxidized on exposure to air, such as ferrous iron, precipitating as a result and carrying other components with them. If these interstitial waters are to be studied, they should not be processed in the field or stored but returned for handling in an inert atmosphere (SRB, section IV.1.5).

With these provisos, the following general procedures are recommended (GEM, Chap. VII, section 2.5.3):

(a) The overlying water should be carefully siphoned off until only 1 cm of water remains above the sediment-water interface; the water should then be transferred to a bottle and filtered;

(b) The upper layer of the sediment ("fluid mud") should then be siphoned off, filtered and kept as representative of the top layer of the core;

(c) The core is carefully sealed at the bottom and at the top, then brought to the laboratory in a vertical position, avoiding any tilting if possible;

(d) If the slicing operation cannot be performed on the fresh sediment shortly after sampling, freezing is recommended unless cellular biological specimens are among the determinands.

CHAPTER 11

GROUNDWATER

Groundwater exists in the pores of sedimentary rocks, such as sandstone; in sediments, such as alluvial sands and gravels and glacial till; and in the fissures of fractured rocks. Its upper surface, the water table, is the level at which the water pressure is equal to the atmospheric pressure. The water-soaked environment below the water table is known as the saturated zone, and the region above the water table is known as the unsaturated zone (vadose zone, zone of aeration) (WQS, section 10.1). Permeable geological formations which store and transmit significant quantities of water are known as aquifers. In a given region there may be several aquifers one above the other separated by impermeable layers of rock.

The quality of groundwater is subject to change and deterioration as a result of the activities of man on the overlying cover of soil. Localized point sources of pollution include cesspools and septic tanks, leaks in municipal sewers and waste ponds, leaching from garbage dumps and sanitary landfills, runoff from animal feedlots, industrial waste discharges, cooling water returned to recharge wells, and leaks from tank cars or pipelines. Larger geographical areas may suffer degradation of groundwater quality because of irrigation-water returns, the recharging into aquifers of treated sewage or industrial effluents, and intrusion into fresh-water aquifers from neighbouring highly saline or seawater aquifers.

Soils and rocks have the capacity to remove many contaminants from water percolating through them, by exchange of aqueous ions with minerals, by adsorption onto soil particles and by chemical and microbiological action (WQS, section 10.4). The self-purification ability of groundwater has caused it to be long regarded as the best water resource for any type of use. This capacity is not, however, unlimited, and increasing large-scale abstraction of groundwater has caused a number of serious pollution episodes and gradual degeneration of groundwater quality over large groundwater bodies. These groundwater pollution problems can be properly studied and monitored only on the basis of sound knowledge of the aquifer water in question. Groundwater monitoring is discussed in detail in GWM and GRW.

Although, as in the case of surface waters, water quantity is very important when discussing groundwater quality, this section refers only to procedures involved in groundwater-*quality* monitoring. Many hydrogeological questions of interest may also be answered by studies of the sampling areas (see GRW). However, they are beyond the scope of this manual, although they help to define the environment of

aquifers and provide information useful in planning an overall monitoring system. For example, seismic refraction data can be used to locate the water table boundary between saturated and unsaturated zones (GRW, section 2.D.1.b.4.b).

11.1 Site selection and sampling frequency

Section 2.2.4 describes some of the considerations in selecting sampling sites for groundwater monitoring. An existing well is a low-cost choice although they are not always at the best location or made of non-contaminating materials. A well that is still in use and pumped occasionally is preferable to one which has been abandoned. Abandoned or unused wells are often in poor condition with damaged or leaky casings and corroded pumping equipment; it is often difficult to measure their water levels and they may be safety hazards.

The information described in section 5.1 is needed to identify each site, together with the following (GRW, Table 2.2, section 2.A.1):

(a) Aquifer tapped;

(b) Well depth, size and type of casing or finish; location and type of perforations in the casing;

(c) Elevation of land surface and the survey measuring point;

(d) A diagram and photograph of the well showing access to it and the measuring point;

(e) The local name of the well and its owner's name;

(f) Use of the well.

Changes in groundwater can be very slow and are often adequately described by monthly, seasonal or even annual sampling schedules (GRW, section 2.G.1.a).

11.2 Sampling procedures

Water samples can be collected from the flow of flowing wells and most conveniently from the flow of pumping wells. Portable pumps are available for pumping down and then sampling non-pumping wells. In open wells, and particularly when it is desired to sample from specific depths, samples can also be taken by grab samplers of the type described in section 3.3.1, except that they often need to be of small external diameter to fit in casings which may often be only 5 cm in diameter. In some cases, selected zones in a well can be temporarily isolated for pumping with mechanical or inflatable packers.

Samples and water levels from perched layers - saturated regions sitting on less permeable layers in the unsaturated zone - can be obtained by the use of piezometers, tubes with a porous region near the bottom which can be pushed or driven into the soil to the desired depth. Other samples from the unsaturated zone can be obtained by embedding a porous ceramic cup in good contact with the soil, or with a bed of fine sand to ensure good contact, with a vacuum tube leading to the bottom. Soil water is drawn into the cup by the suction and raised into a sample bottle in the vacuum line. If the installation is below the level from which suction can lift the sample, the material can be sucked from the porous chamber through a checkvalve into a second chamber, from which it can then be forced to the surface by nitrogen pressure.

11.3 Field measurements

The basic measurements for surface water (Chapter 4) are also basic in groundwater-quality monitoring, with the exception of turbidity which should not be a problem.

Detailed sampling procedures as well as a description of the instrumentation used in the sampling of groundwater are given in UTS (Chap. 6), GRW and GWM. Some of the problems of ground water sampling are discussed in GSG.

There are two additional basic field measurements: water level and the redox potential. Air can penetrate the unsaturated zone, but the combination of chemical and biochemical action in the soil can lead to anoxic reducing conditions. The relative oxidizing and reducing power of the water is measured by the redox or oxidation-reduction potential (GRW, section 2.G.2.e).

11.3.1 Water level

In non-flowing wells, the water level should be measured with steel measuring tapes before the well has been pumped to obtain the static level. The tape is weighted at the bottom with a lead weight attached sufficiently loosely that it can be sacrificed if the weight becomes lodged in the well. The lower end of the tape is rubbed over a blue carpenter's chalk to provide a surface which will show the wetting level. Tapes are very accurate but are difficult to use if water is dripping down the wall and may constitute a hazard if the well has an automatic pump, since it is not easy to tell when the tape has reached the water surface.

Two other methods free from these handicaps are also used. An electrical method consists of two-conductor electric tapes with conductivity probes at the bottom (again loosely attached, since the probe is larger than the tape and prone to become lodged) which detect the water level on contact. The other method uses air lines lowered well below the surface and bubbled to determine the pressure needed to

purge the line of water (GRW, section 2.A.6.a). The pressure can then be converted into depth of water and the depth subtracted from the length of the air line to locate the water level. Recording devices can also be used to monitor changes in water levels: floats or electromechanical water-seeking probes and submerged mechanical or electrical pressure gauges.

If the well penetrates more than one aquifer and the casing is perforated to allow contact with each aquifer, the measured water level is a composite affected by the heads and hydraulic properties of all the aquifers (GRW, section 2.A.7).

Flowing wells - springs or artesians - belong to aquifers whose water table is above the ground surface. For these wells, a sanitary seal (a small pipe threaded at the top and fitted with an expandable rubber packer at the bottom) can be fitted to the pipe at the top of the well. If the water table is not too high above ground level, a hose or plastic pipe can be attached to determine the height of rise of the water. Otherwise, a pressure gauge can be fitted, preceded by a pressure snubber to reduce water hammers when the flow is cut off.

The times from prior pumping of a non-flowing well or closing off of a flowing well to the time of a reasonably steady level or pressure measurement should be recorded and duplicated on succeeding visits to the site, since it may be impracticable to wait until a slow-filling well returns to complete equilibrium.

11.3.2 Redox potential, Eh

The redox potential, Eh, is measured by determining the potential between a noble metal electrode and a reference electrode in the sample. This value is compared to the value obtained with the same electrodes using a stable solution of known Eh value which has been determined relative to a standard hydrogen electrode (hydrogen gas at one atmosphere pressure and 25°C in contact with platinum metal). The final result is reported in millivolts and is temperature dependent. In natural systems the measurement has many interferences. It has been used to explain the concentration of some elements that have more than one oxidation state under natural conditions, e.g. iron (GRW, 2.G.2.e).

The procedure is described in detail in GRW, section 2.G.2.e.2.b and the apparatus is shown in Figure 11.1 (GRW, Fig. 2-40, p. 105). The combination electrode is equilibrated at sample temperature with the working redox standard fluid (value A in millivolts), then with the sample (value B). Several reference electrodes may be used in the combination electrode, such as the common calomel and silver-silver chloride electrodes. In GRW the recommended redox standard fluid is a potassium ferrocyanide-potassium ferricyanide mixture named after the investigator, ZoBell, who described its use in 1946. The measurement of the combination electrode in the ZoBell solution is used to check the electrodes against the expected value, read from Figure 11.2, before proceeding further (GRW, Fig. 2-39). The

temperature-corrected value for the ZoBell solution against the standard hydrogen electrode is determined (value C) from a graph, Figure 11.3 (GRW, Fig. 2-41). The Eh value is then calculated as:

$$Eh = B - A + C$$

11.3.3 ZoBell solution

ZoBell redox reference solution is prepared by dissolving 1.4080 g of potassium ferrocyanide, 1.0975 g of potassium ferricyanide, and 7.455 g of potassium chloride in distilled water to make 1.000 litre of solution. This solution is stable for several months in an opaque bottle out of sunlight. *It is poisonous and should be handled with care* (GRW, section 2.g.2.e.2.a).

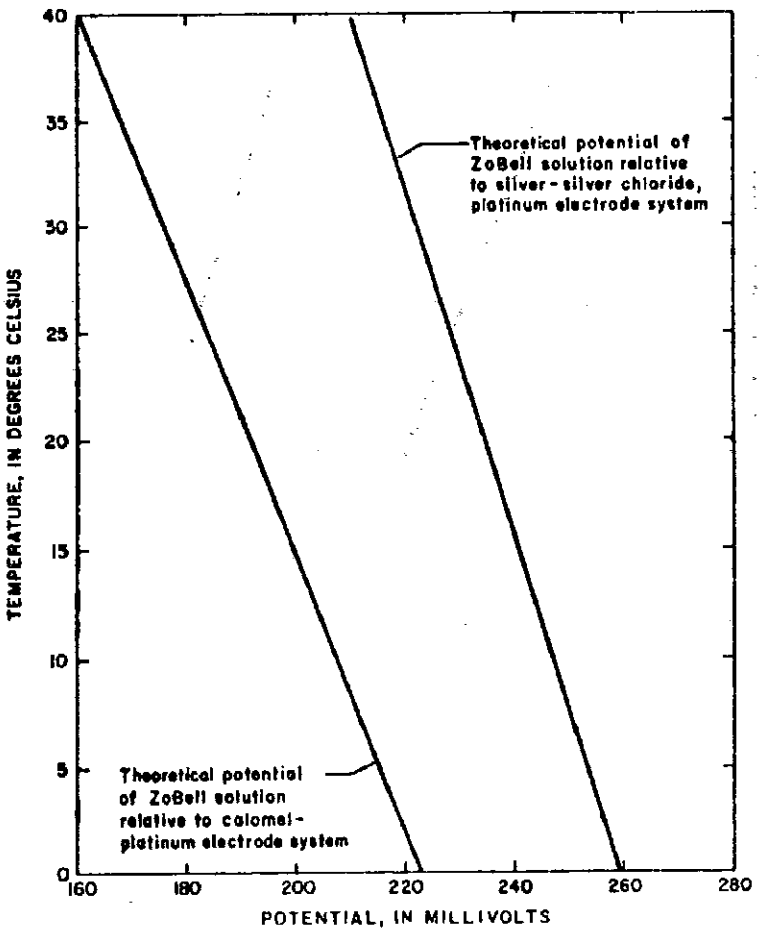


Figure 11.1 Eh measuring cell

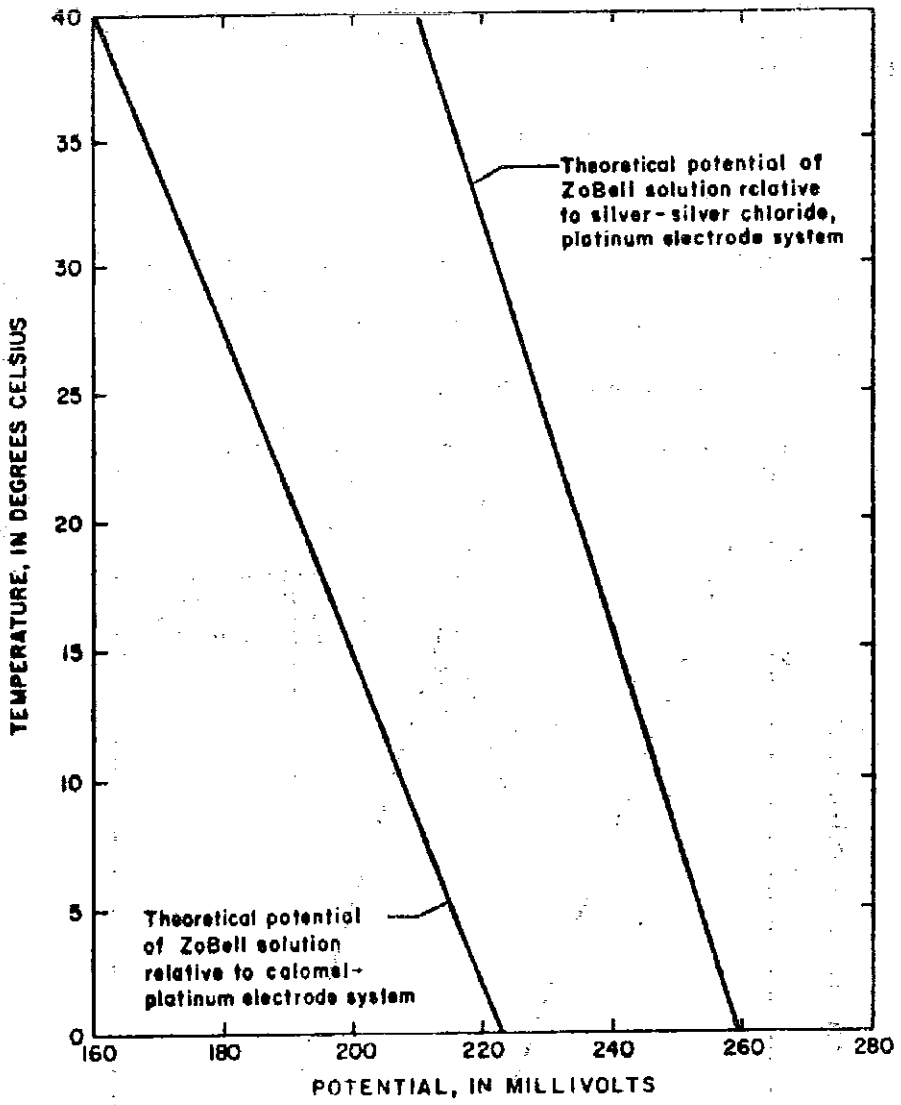


Figure 11.2 The potential of ZoBell solution, relative to reference electrode systems, at various temperatures

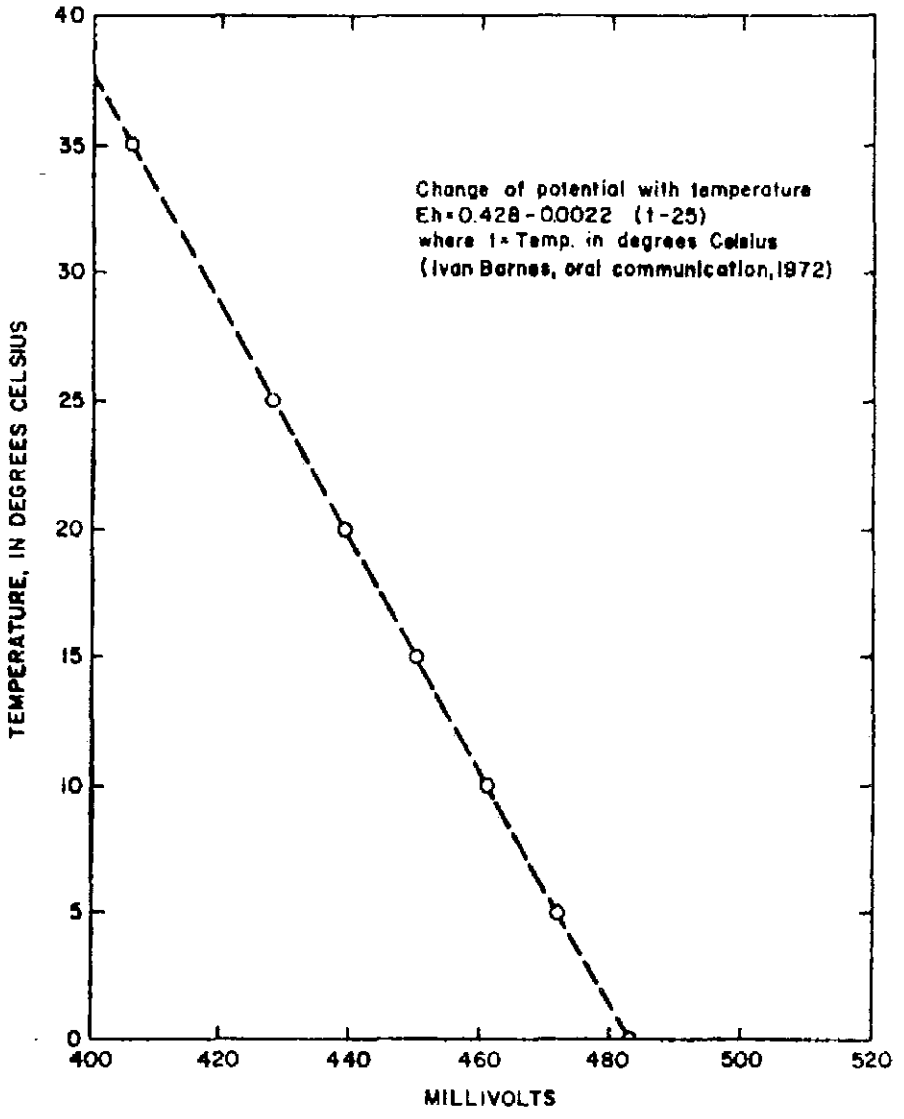


Figure 11.3 The potential of ZoBell solution, relative to the standard hydrogen electrode, at various temperatures

CHAPTER 12

SHIPPING OF SAMPLES

Once collected, water samples must be transported to the laboratory. The mode of transport will depend upon the geographic location and on the maximum permissible time lapse before analysis for each parameter. The field investigator is responsible for delivering the samples to the air, bus, train or postal terminal or express courier office on schedule so that there will be minimal delay in sample transport. Logistics for sample shipping and storage should be determined before fieldwork is initiated.

12.1 Preparation for shipping

During packing, the samples from one location must not be separated into different shipping boxes or coolers unless all bottles of one size must be shipped together because of container size.

If samples from one station must be divided and placed in two cartons, a copy of the field-sampling sheet pertaining to the bottles must be enclosed in each box. (See section 5.3 for a description of field-sampling sheets.) This could require two or more field sheets (carbon paper or a similar system is useful). In addition, a clear identifier label must be attached to each sample (see sections 12.2 and 12.3 for details on labels). Before shipping, always check that all sample bottles recorded on the field-sampling sheets have been placed in the carton. Indicate the shipping date and mode of transport on the field-sampling sheet.

Preparation for shipping should follow these steps:

(a) Fold the field-sampling sheets and place them in plastic bags. The bags will protect the field sheets should spillage occur during transport;

(b) Pack samples well to prevent breakage, affix identification, destination and FRAGILE labels to each carton or cooler. (Section 12.2 contains a description of shipping labels). Mark the tops of cartons or coolers as THIS END UP in red ink or secure sticker. Also, number the boxes or coolers in a shipment, e.g. 1 of 4, 2 of 4, 3 of 4 and 4 of 4. This informs the receiver of the number of pieces to expect;

(c) Keep a list of samples packed in each carton or cooler.

The investigator should also retain a copy of the field-sampling sheets.

12.2 Shipping labels

Labels which clearly identify the source and destination of the sample bottles increase the efficiency of sample shipping. An example of a shipping label is provided here.

All shipping labels should include a clearly written, precise destination address, including postal code, if any. Any delay in shipping on account of incomplete addressing must be avoided. If a particular person is in charge of the analytical side of the project, the label should be marked to his or her attention. Also included on the shipping label is the sender's name and address and the date of shipping.

FROM: John Doe
351 St. Joseph Blvd
Hull, P.Q. K1A 0E7

SHIP TO: P.O. Box 5050
867 Lakeshore Dr.
Burlington, Ontario
L7R 4A6

DATE:
FEB. 12/81

ATTN: Jim Smith

Shipping labels on all boxes must be clearly legible. Preprinted or pretyped self-sticking labels are recommended.

12.3 Labels or tags on individual bottles

Each bottle should be clearly marked. As a minimum, each label should state:

(a) The station code number; a narrative description is optional;

(b) Sampling date and time;

(c) Parameters that are to be analysed from that specific bottle; prearranged codes can be used to indicate certain groups of parameters;

(d) Whether or not the sample is preserved and with what; coloured labels can be used to indicate the preservation method; and

(e) Collector's identity (initials).

A number of methods may be used to label individual bottles. Labels may be applied directly to each bottle with a water-insoluble marker or they may be written on masking tape, which is then attached to the sample bottle. Information may also be written on commercially available tags and then attached to the bottle with elastic bands, string or tape. Elastic bands should not be used on sample bottles for metals or metal blanks.

12.4 Chain of custody

On occasion, samples may form part of a case for regulatory action. In such cases, the local rules of evidence will dictate how the samples should be handled. This section is intended to alert collectors to the possibility of special handling. The advice of local competent legal authorities must determine the actual course of action in each jurisdiction.

In many countries, the possibility that analytical evidence may be introduced in a court of law will require the maintenance of a chain of custody from the collector to the analyst (HSS, section 3.3). The number of people in the chain should be kept to a minimum. As each transfer takes place, the transferee must sign the tag and record the date and time of the transfer.

A sample is in custody if it is:

(a) In a person's actual physical possession; or

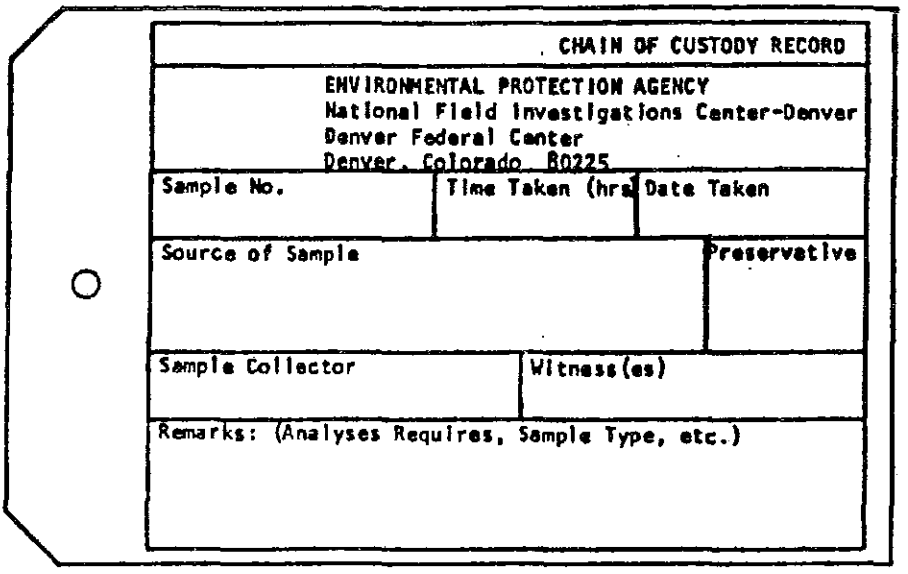
(b) In view, after being in physical possession; or

(c) In physical possession and locked up so that no one can tamper with it.

In addition to the information on an ordinary sample-identification label, a chain of custody tag should be dated, timed, signed and witnessed. In many jurisdictions the tag should be sealed (e.g. with a gummed seal) so that the tag cannot be removed and the container cannot be opened without breaking the seal. An example of a chain of custody tag is shown in Figure 12.1 (HSS, Fig. 3.1, p. 44).

Careful records of the field measurements should be kept in a bound notebook or log.

(FRONT SIDE)



(BACK SIDE)

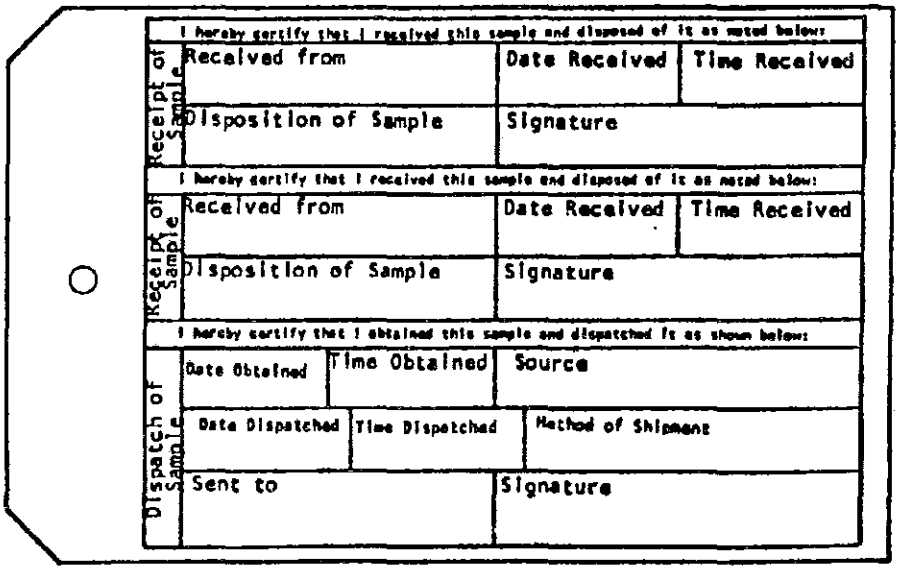


Figure 12.1 - Chain of custody record tag

CHAPTER 13

FIELD SAFETY

Samples are collected during a wide range of conditions and personnel may encounter a variety of safety and health risks. Hazards are both natural, such as those of terrain and weather, and man-made, such as traffic, electrical and chemical risks. In some situations, additional natural hazards have to be considered such as poisonous plants and dangerous animals. Some rivers contain sufficient quantities of sewage or industrial effluents to be bacteriologically, virologically or chemically hazardous.

Knowledge of the hazards that may be encountered and the means by which they can be minimized is a necessary consideration in any field project. Field personnel must receive the necessary training to become knowledgeable of the hazards they might encounter in the field, in recognizing potentially hazardous situations and in the measures which should be taken to minimize hazards to ensure their health and safety. For example, field staff must be familiar with water safety, including water survival and field first aid. Whenever available, field personnel should receive training related to other safe field practices, e.g. wilderness survival and basic methods for repairing machinery used for transportation. Refresher courses should be taken as required.

To this end all field offices should maintain a current list of relevant safety courses available from various government or private agencies, as well as a record of courses taken by their personnel. Periodic refresher courses are strongly recommended. In addition, all field personnel should be familiar with the information services available on weather, road, water and flood conditions. A current list of agencies providing this information, with addresses and telephone numbers, should be posted in an easily identifiable place within the office. Survival and first-aid kits are recommended for all field parties and they are a must for personnel working in isolated areas or in regions subject to rapid weather changes.

Periodic safety seminars in which particular safety topics are discussed with specialists or new safety procedures are introduced are also recommended.

The field-safety procedures recommended in this section are based chiefly on those prepared for Canadian personnel.

13.1 General practices

All employees should adhere to the water-safety procedures promulgated by their governments for the protection of their personnel. As an example, the *Handbook of Occupational Health and Safety*, published by the Canadian Federal Treasury Board, Ottawa, 1978, states the following under "Drowning Hazards":

"No employee shall work or be permitted to work over water or at any other work location where there is a risk of drowning unless

(1) the employee is wearing an approved life jacket or other buoyancy device of a type described in paragraph 43; or

(2) the employee is prevented from falling into the water by a safety net or platform or a safety restraining device; and

(3) the employee is accompanied by at least one other person."

In certain situations, although over water, one employee should be able to carry out the field work safely. For example, when the work is performed from the deck of a bridge and the safety of the employee is protected by an adequate guard rail, there would be no actual risk of falling and drowning. If, on the other hand, the guard rail did not provide adequate protection, i.e. was poorly designed or maintained, or for any reason the employee was required to work on, over or above the guard railing, a risk of drowning could exist and the requirements of the above paragraph would apply.

Field staff should be provided with available information concerning characteristics of water bodies under study. All field activites must be assessed to determine if abnormal weather or water conditions have altered the situations for which safety measures have been designed. Sampling should never be carried out in weather which is considered by the party leader or a party member to be hazardous to the safety and health of the field staff or likely to damage equipment.

In all situations field parties should leave accurate sampling schedules and expected itineraries in the field office. (In some jurisdictions, such as Canada, this is a requirement, not advice: "Where an employee may be working alone, or a field party is working in an isolated area, an appropriate official or authority in the area should be advised of the geographical location of the isolated field operation, its estimated duration, the normal and emergency methods of communication, and the names or numbers of personnel involved"). Employees should not leave their vehicle for distant treks without the first-aid kit supplied to each field party.

13.2 Safety precautions when sampling from bridges

Traffic may present serious problems when working from bridges. Sometimes bridges have sidewalks, footpaths or catwalks suspended at the side of the bridge for pedestrian traffic, but more often than not the sampler must walk and work in traffic lanes. When interference with the traffic cannot be avoided, suitable arrangements to divert the traffic or to place warning signs must be made in advance with police or other local authorities. For example, warning lights and "men working" signs should be erected. In addition, personnel are well advised to wear fluorescent clothing and, if sampling is being carried out in darkness or poor visibility, they should carry lights or torches (SRS, section 5).

The field technicians must take special care when sampling from bridges over navigable water as boat operators and water skiers may not be able to see apparatus suspension lines. Samples should be collected when there is no water traffic. Otherwise, special precautions such as the attachment of flags should be taken to make suspension lines visible. When working from railway bridges, a knowledge of train schedules is essential and at no time should the collector use equipment that cannot be removed quickly.

Power lines strung close to bridges can be dangerous. If samples are going to be repeatedly collected from a bridge near a power line, a warning sign indicating the presence of the power line should be installed. A hazard warning should also be noted on the site-location form.

13.3 Safety precautions while wading

Wading is one of the easiest methods to collect samples from many streams; it may also be extremely dangerous and should not be undertaken alone. Insecure river banks, fast-flowing water, waves, eddies, slippery algae and moss-covered rocks must be considered potential hazards as they may lead to serious injuries.

Wading permits the investigator to examine the stream flow and decide where to sample. Rubber boots or chest-high waders should be worn when wading. Water depth during wading operations should be checked with a pole before steps are taken. A wading rod or similar probing instrument is also useful to estimate the current and to locate holes, soft mud, quicksand and other unsafe footing. If the wader has any uncertainty about his ability to wade a stream, he or she should use an approved safety line attached to a rigid mooring and should wear an approved flotation device. An extra change of clothing is always advisable and is essential during the colder months. When wading equipment is worn, the support straps must be outside the clothing. If a hazardous situation exists or develops wading should be abandoned.

If a wader steps into quicksand, panic must be avoided. In shallow water, the best method for extrication is to fall flat on the surface and crawl to firmer ground. In deeper water the wader's effective weight can be reduced by swimming motions (SRS, p. 7).

13.4 Safety precautions when sampling from boats

Only boats and equipment suitable for the water system being sampled are to be used. In isolated locations, on large water bodies and where there are downstream dangers such as rapids or waterfalls, it is an absolute necessity to use the correct type of boat in proper operating condition. It is also necessary to have auxiliary power which may be relied on in case of an emergency. Before setting out onto the water, the operating condition of the boat must be checked and any irregularities corrected. Boats must not be overloaded with sampling equipment. The amount and size of equipment in a boat must comply with local small-vessel regulations.

To ensure smooth operation and to conserve time in the field, it is important to establish boat-launching sites at marinas, public piers and the like in advance of the actual sampling programme.

At least two people should be present on the boat, wearing approved flotation devices, e.g. life jackets, and operating in accordance with approved water-safety rules and regulations. When only one water-quality person is available, the assistance of another person qualified to undertake the tasks required should be obtained. Care must be exercised when choosing field assistants.

Any craft used must have good stability. Busy navigation lanes should be avoided - a small boat in the middle of a narrow dredged shipping lane will be neither safe nor popular. Regard to both the normal rules of navigation and common courtesy should be exercised. The operation of the boat must conform with the regulations of the coast guard or other competent authority. In addition, local or regional police boating regulations must be checked and followed at all times.

Boats, as with cars and trucks, must have regular maintenance and service checkups prior to a sampling trip. Gasoline, spare parts (particularly shear pins and spark plugs) and a tool box should be checked and included on each field trip. A spare motor is also recommended when sampling in remote areas, over large bodies of water or fast-flowing rivers. Sampling activities are carried out year round and as a result the field operator should be properly clothed at all times. Cold-weather clothing is described in section 13.7. Hats, mitts, gloves, socks, underwear, boots, rubber boots, waterproof clothing and replacements for the above should be carefully included in the clothing inventory. Wet clothing can lead to hypothermia. Clothing to guard against sunburn and sunstroke should be included when applicable. Sufficient emergency rations should be brought, especially when sampling in remote areas.

The weather forecast should always be checked before departing on a sampling trip. Sampling should be curtailed when weather or water conditions make it unsafe to continue.

Boat operations on flooded streams are particularly hazardous. During these periods the boat operator must cope with the fast current and also be on the alert for shallows and floating and submerged debris.

13.5 Safety precautions when handling chemicals

Acids and bases used for the preservation of water samples should be stored and handled with care. All chemicals must be securely stored during transport to prevent spillage. Care should be taken to prevent bottle and other glassware breakage during sampling; for example, overtightening of tops, rough handling of pipettes and improper packaging and storage of glass sampling bottles may result in breakage and injury during transport. Spills should be cleaned up immediately by dilution with large quantities of water, neutralization, or mopping up of the chemical followed by disposal of the contaminated material. It is recommended that gloves and an apron be carried in the field and used during such cleanup operations.

Inhalation of vapours or direct contact with skin, eyes and clothing must be avoided. Acids and bases should never be pipetted orally. Skin which has been in contact with an acid or a base should be washed immediately with plenty of water. The contaminated area may be swabbed with a neutralizing solution, followed by a washing with soap.

If any chemicals enter the eyes, they and the surrounding areas should immediately be rinsed with plenty of water for several minutes. It may be necessary to hold the eyelids open during this procedure. After first aid, all eye injuries must be treated professionally. Sufficient quantities of water should be carried to be used to rinse eyes that have been contaminated with chemicals. During winter months provision must be made to ensure that the water does not freeze.

WARNING

- Certain preservatives, such as mercury(II) chloride, acids and chloroform require extra caution. Operators shall be warned of the dangers involved in handling them, and the ways of protecting themselves from them (GPH, section 3.2.5).

- The use of mercury(II) chloride (mercuric chloride, corrosive sublimate, $HgCl^2$) is to be avoided, unless absolutely necessary. When it has been used, the mercury from any residues must be recovered (e.g. HSS, section 10.2.2.2).

13.6 Equipment

The use of electrical equipment in or near water can present electrocution hazards. Work procedures should minimize these hazards. Special care must be taken when electrofishing (SRS, section 5 and GDS, section 7.11). Equipment should never be directly wired to a power line; switches or plugs should always be available for disconnecting the equipment safely and quickly from its power supply (SPN, section 10.2).

If self-contained underwater breathing apparatus (scuba gear) or other diving equipment is used, it should always be checked to ensure reliability.

Sites where equipment is to be installed that are susceptible to flooding, vandalism or curious children should be avoided if possible. If this cannot be done, appropriate precautions such as fences and shelters should be provided.

13.7 Special precautions for cold climates

Proper garments to protect against hypothermia caused by exposure to cold temperatures and/or wet clothing must be taken.

Winter sampling requires suitable clothing to maintain a comfortable working temperature and to prevent frostbite and hypothermia. Parkas, warm hats, woollen undergarments, extra socks, mitts, proper footwear, and in some cases glasses to prevent snow blindness, should be taken. Before leaving the base, the field investigator should also check the wind-chill factor (an equivalent temperature calculated from a combination of still air temperature and the wind velocity).

Floating ice is very dangerous; even when there is no danger to a boat, changes in wind, current or tide may shift the position of ice flows and cut the boat off from shore.

Working on ice-covered lakes and rivers

Whenever work is carried out on ice, two persons should work together employing approved safety lines and other equipment, e.g. ice spikes and similar equipment related to safe working practices on ice. Winter-safety flotation devices should be worn. Field personnel should follow the guidelines respecting safe operations on ice, e.g. "Information and Guidelines Respecting Safe Operations over Ice" (Canadian Federal Public Service Commission, December 1976).

Considerable risk may be involved in collecting samples through ice if necessary precautions are not met. Employers, along with employees, must ensure that the hazards associated with any task are reduced to a minimum or eliminated. If, after the safety precautions are taken, there is still "considerable risk" associated with

a given sampling procedure, an alternative sampling method should be sought. For example, a hole of sufficient diameter to collect a sample from a bridge may be broken in thin ice by dropping a weight attached to a handline, although in this case particular care must be taken because the samples may become contaminated with road de-icing agents.

The ice in a stream is likely to be of variable thickness, and the strength of the ice cannot be estimated from the apparent thickness near the edges. In advancing across an ice-covered stream, it is advisable to test the ice with an ice chisel every few steps. It may also be hazardous to collect samples downstream from bridge supports, as the ice may be thin as a result of modified flow patterns and de-icing agents from the road surface. Field staff should be cautious when approaching ice areas covered with snow. A few centimetres of new snow can conceal thin ice. Areas with rapids should be approached with extra caution because ice is usually much thinner due to the water movement. Working from ice during breakups is particularly hazardous. Vehicles should never be driven over ice-covered bodies of water, except where winter ice roads exist and then with caution.

Field personnel must be able to recognize ice conditions and to proceed accordingly. The employees should be retrained if their knowledge of the subject is limited or outdated.

13.8 Survival kit and rations

The components of a typical survival kit are listed below. It should be noted that other articles may be beneficial and should be included as required.

Survival kit		Survival rations
Thermal blanket, 1.8 m x 2.3 m	Wool socks	Compressed food packets (1200 calories each)
Sleeping bag	Wool gloves	Dry soup mix
Tent	Balaclava	Coffee
First-aid kit	Knife, fork, spoon	Tea
Single-burner folding stove	Metal mug	Powdered milk
Solid cooking fuel	Tissues	Sugar
Flashlight	Plastic garbage bags	
Flares	Gas-line antifreeze	
Small signal mirror	Fishing line and hooks	
Candles, 15 hours, with holder	Mattock	
Windproof and waterproof matches	Insect repellent	
	Water-disinfection tablets	
	Mosquito-protection net	
	Coin for pay telephone	

CHAPTER 14

TRAINING

The establishment of a water-quality monitoring programme requires that several elements be available. These elements are summarized in Table 14.1. Most of them have already been discussed in the previous chapters.

One element which appears several times in Table 14.1 is that of trained staff. This is absolutely essential for a programme to be successful. The literature on training in the water-resources field is very scarce and in the water-quality field is non-existent. The reference section at the end of this chapter lists several titles related to training in the water-resources field.

This chapter describes only the very first steps an organization should take towards training its staff in water-quality monitoring. It does not deal with the details on how such a training programme can be set up.

14.1 Basic knowledge

The study of water quality involves the integration of a number of basic disciplines such as chemistry, physics, biology, limnology and mathematics, especially statistics; various aspects of engineering, e.g. chemical and hydraulic; geography and economics. Professionals working in the water-quality field can have their basic education in any of these disciplines. Experience has shown that, in the area of water-quality monitoring, a degree in chemistry, biology, limnology or chemical engineering, focused on environmental aspects and combined with knowledge of statistics, provides a very good basis.

14.2 Specialized training

Personnel having the basic knowledge can be trained in the specialized field of water-quality monitoring. The training can take place externally or in-house. Figure 14.1 shows a possible sequence of steps to be followed in deciding on the type of training to be provided and in establishing an in-house training programme.

14.2.1 External training

From time to time, certain universities and organizations offer courses in water-quality monitoring. For example, Colorado State University, Fort Collins,

Colorado, USA, offers each summer a one-week course on the design of water-quality monitoring networks. A course outline is shown in Table 14.2. Similarly, the Pan American Health Organization has offered a one-week course entitled "Basic concepts in the field of surface-water quality". The outline of this course is shown in Table 14.3.

In a one-week course only the basic elements of each topic can be introduced. Such an introductory course is appropriate for familiarizing the audience with the various topics and giving some idea of their complexity. For people wishing to implement a water-quality monitoring programme or already operating one, an in-depth training presentation of each topic is required. This in-depth training will not only expand the presentations in the short course but will also add new topics and "hands-on" sessions, i.e. periods in which the trainees will be required to solve problems based on real situations as well as sessions in the field and in the laboratory.

14.2.2 IN-HOUSE TRAINING

This type of training affords the greatest flexibility in both content and training methods. The training can be fitted to the exact requirements of the monitoring programme and to the available resources. Also, on the positive side, a larger number of persons can attend an in-house training programme while it would be very expensive to send so many away for training, especially when the external training is given in a different city or country.

To set up an in-house training programme requires a significant amount of preparatory work as well as availability of resources such as instructors, training materials, training aids, appropriately equipped classrooms and access to field and laboratory facilities. It is advantageous both from the technical and financial points of view to carry out the training in several different stages.

Advantages and disadvantages should be considered in deciding on whether the training will be done in-house or externally, including the relative costs of implementing and running the programmes. To aid in the decision, a cost-benefit or equivalent analysis is suggested in Figure 14.1. Any such analysis should look at both the easily quantifiable factors, e.g. the costs of facilities and supplies and the number of people to be trained, and the less tangible ones, e.g. training expertise available in the organization and having the training staff interact with the operational staff on an almost daily basis. The analysis should be done both for the short term (one month to one year) and the medium term (one to five years).

14.2.3 COMBINED TRAINING

This alternative combines external with in-house training. For example, external training is recommended when available curricula fit some of the identified training needs and when the analysis of costs and benefits shows that this type of

training is advantageous. Then the training which cannot be obtained externally will be provided in-house.

The two types of training might be combined by using an external course to train personnel who then provide in-house training.

The best way of ensuring that a trainee can perform a task satisfactorily and reliably is for one expert to show one person how to perform. This is, of course, very demanding of expert time and often impracticable. Where facilities exist, a very efficient way of using an expert trainer may be to videotape his sampling and analytical techniques, for example, and to allow the trainees to view the tapes at leisure.

14.3 References

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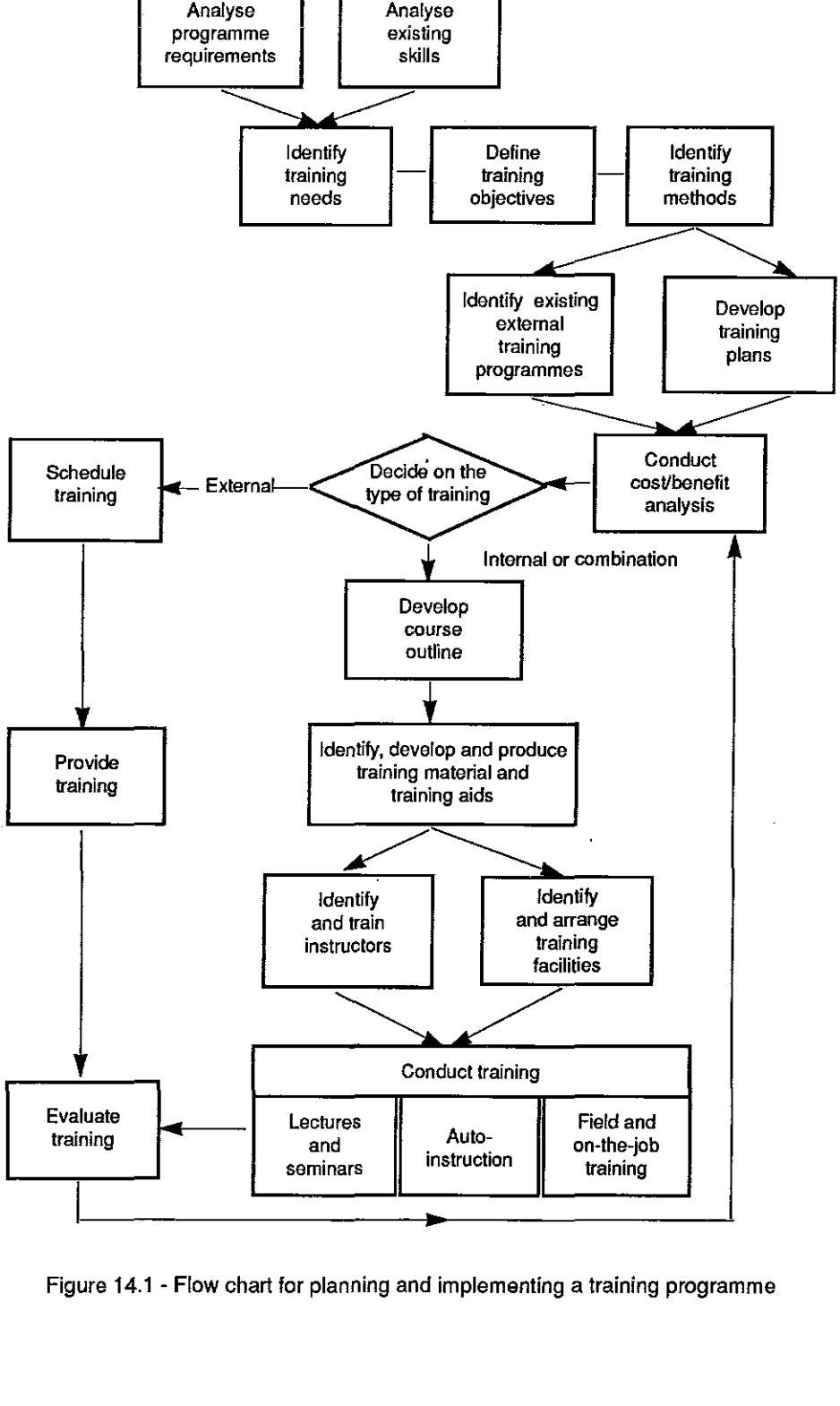

Figure 14.1 - Flow chart for planning and implementing a training programme

TABLE 14.1 Main elements needed to establish a water-quality programme

* CLEAR OBJECTIVES TIED TO IDENTIFIABLE GOVERNMENT PROGRAMMES
* ADEQUATE ORGANIZATIONAL STRUCTURE
* SAMPLE COLLECTION CAPABILITY
  - Methodology
  - Trained staff
  - Equipment
  - Chemicals
* ANALYTICAL (FIELD AND LABORATORY) CAPABILITY
  - Methodology
  - Trained staff
  - Physical facilities
  - Equipment
  - Chemicals
* DATA HANDLING, ANALYSIS AND REPORTING CAPABILITY
  - Methodology
  - Trained staff
  - Physical facilities
  - Equipment

(These elements are all interrelated)

TABLE 14.2 Outline for a one-week course on the design of water-quality monitoring networks given by the Research Institute of Colorado in co-operation with Colorado State University

Day 1	*	Introduction
	*	Water quality variables as stochastic processes
	*	Systems approach to water-quality monitoring
	*	Basic concepts of probability and stochastic processes
	*	Problem session - calculations in probability
Day 2	*	Detection of changes in water quality
	*	Problem session - calculations for analysing water quality changes
	*	Managing a water-quality monitoring programme
	*	Location of sampling stations
	*	Design considerations of a groundwater-monitoring programme
Day 3	*	Subsurface sampling
	*	Resource Conservation and Recovery Act (RCRA) monitoring implications
	*	Representative sampling
	*	Problem session
Day 4	*	Factors in selection of variables to be monitored
	*	Sampling frequency - single station
	*	Problem session - calculating sampling frequencies
	*	Sampling frequency - multiple variables and stations (network)
	*	Practical considerations in determining sampling frequencies
	*	Water-quality issues on the horizon
Day 5	*	Sampling frequency taking into account correlation
	*	Practical implications of monitoring network design
	*	Course summary folllowed by a discussion of water-quality monitoring
	*	Problems

TABLE 14.3 Basic concepts in the field of surface-water qualiy. Outline of a course given by the Pan American Health Organization

Day 1	*	Environment, hydrology and hydraulic developments
	*	Interactions between air, water, sediments, and aquatic and terrestrial organisms
	*	Basic concepts in hydrology
	*	Water-quality parameters
	*	Water-quality guidelines: uses of water; scientific, technical and economic considerations; and political and administrative principles
	*	Fate of contaminants in the aquatic environment
Day 2	*	Pollution sources and loadings
	*	Water-quality legislation and institutional structures
	*	Regulations regarding point source discharges
	*	Control of water quality: technology, planning and economic aspects
Day 3	*	Mathematical models for surface waters
	*	River models
	*	Lakes and estuaries models
Day 4	*	Design of water-quality data-collection programmes
	*	Sampling for water quality
	*	Analysis of water
	*	Water-quality data interpretation
	*	Environmental impact studies
	*	Socio-economic evaluation of environmental impact of water pollution
Day 5	*	Implementing a water-quality monitoring programme: prerequisites, objectives, organizational structure, planning, operational aspects, control and evaluation

CHAPTER 15

GLOSSARY

Absorption - the incorporation of a substance into the body of another.

Accuracy - the difference between the measured and the accepted or "true" value of the variable determined. It indicates the correctness of the measurement.

Acid extractable metal - the concentration of a metal in solution after treatment of an unfiltered sample with dilute cold or hot mineral acid.

Acidity - the quantitative capacity of aqueous media to react with hydroxyl ions. It indicates the presence of hydrogen ions originating from mineral and organic acids.

Acid mine drainage - low pH drainage water from certain mines, usually caused by the oxidation of sulphides to sulphuric acid. Mine drainage can also contain high concentrations of metal ions.

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

Algal mat - a moribund surface algal population.

Algicide - a chemical used to kill algae. Algicides are often applied to water to control nuisance algal blooms.

Aliquot - a representative sample of a larger quantity.

Alkalinity - the capacity of an aqueous medium to neutralize an acid. It indicates the presence of carbonates, bicarbonates and hydroxides and, less significantly, borates, silicates, phosphates and some organic substances. It is expressed in milligrams of $CaCO_3$ per litre.

Ambient temperature - the temperature of the surrounding medium, such as the air over a lake or river.

Analytical grade - characteristic of a chemical indicating a level of purity high enough to permit its use in chemical analysis.

Anoxic - indicates oxygen deficiency.

Aquatic life - those organisms found living or growing in, on or near water.

Aquifer - permeable geological formation of water-bearing rock, sand, soil or gravel which can supply water in useable quantities, for example to wells or springs.

Bedload - material (silt, sand, gravel) moving on or immediately above the stream bed by rolling, sliding, and sometimes making brief excursions into the flow a few diameters above the bed.

Bedload discharge - the quantity of bedload passing a transect in a unit of time.

Bedload sampler - a device for sampling the bedload.

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

Bed-material sampler - a device for sampling bed material.

Benthos - the aquatic organisms, stationary or mobile, that live at the bottom of bodies of water and depend on them for their survival.

Biochemical oxygen demand (BOD) - a measure of the quantity of oxygen used in the biochemical oxidation of carbonaceous and nitrogenous compounds in a specified time, at a specified temperature and under specified conditions. The standard measurement is made for five days at 20°C. BOD is an indicator of the presence of organic material in the water. It is normal to find a BOD of 2-3 mg/l in river waters receiving natural drainage.

Biodegradability - the characteristic of a substance that can be broken down by microorganisms.

Biodegradation - the biochemical process of the breakdown of complex organic molecules into simple molecules.

Biomass - the weight, wet or dry, of living matter in a defined area.

Biota - living organisms, including animals, plants and bacteria in a given ecosystem.

Birge-Ekman dredge - a sampler designed for the collection of the top 2-3 cm of the bottom sediment of a lake or river. This apparatus is suitable for soft clays, muds, silts and silty sands (Figure 10.4).

Blank - a sample of distilled water which is treated in the same way as an actual sample and then submitted for analysis as though it were a sample.

Bloom - a clearly visible concentrated growth or aggregation of planktonic algae in a water body.

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

Buffer - a solution used to minimize changes in hydrogen ion concentration which would otherwise take place as a result of chemical additions or reactions.

Centroid of flow - midpoint of a channel of uniform flow.

Chain of custody - documentation showing continous physical possession of evidence from discovery to courtroom.

Chemocline - a zone of rapid change, with depth, in the concentration of dissolved substances in a lake. Also the boundary between the circulating and non-circulating layers of a lake.

Coliform bacteria or coliforms - a group of bacteria predominantly inhabiting the intestines of humans and warm-blooded animals, but also occasionally found elsewhere. Fecal coliform bacteria are those organisms associated with the intestine of warm-blooded animals. They are used commonly as an indicator of the presence of fecal material and the presence of organisms potentially capable of causing disease in man.

Colony - A localized population of individuals, animals or plants. Also, a cluster of microorganisms growing in or on a culture medium. In some colonies, the individuals are structurally connected and function as a single unit.

Community - Any naturally occurring group of organisms occupying a common environment. Community and abiotic surroundings together constitute an ecosystem.

Composite sample - a sample obtained by mixing several discrete samples, or representative portions thereof, into one container (see flow-proportional and sequential composite samples).

Conductivity - see specific conductance.

Confidence interval - range of values which has a specified probability of containing the "true" value.

Confidence level - the probability that the "true" value of some parameter will be found within a specified range of values called the confidence interval.

Contamination - the presence of foreign or unwanted material which renders a

sample unfit for meaningful analysis or, generalizing, an environment unfit for intended use(s).

Cosmic-ray-produced nuclides - isotopes, usually radioactive, such as tritium, beryllium-7 and carbon-14 formed by high-energy space particles (e.g. electrons and nuclei) or cosmic rays interacting with certain atmospheric and terrestrial elements.

Cross section - a plane perpendicular to an axis such as the axis of flow.

De-ionized water - water that has passed through a column to remove charged, usually inorganic, particles.

Dendritic - having a branching tree-like structure or pattern.

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

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

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

Determinand - a measureable physical, chemical, radiological or biological characteristic of an aquatic environment (synonyms: parameter, variable).

Detritus - finely divided non-living settleable material suspended in water. Organic detritus is from the decomposition of the broken down remains of organisms; inorganic detritus is settleable mineral materials.

Diaphragm pump - a reciprocating pump in which the motion is delivered to the fluid by movement of a flexible diaphragm which isolates the fluid from the moving parts.

Discharge - the flow rate of a fluid at a given instant expressed as volume per unit of time (see stream discharge).

Dissolved concentration - the concentration of a constituent of an unacidified water sample that will pass through a 0.45-nm membrane filter. The filtration should be done immediately after sample collection.

Dissolved load - the part of the stream load that is carried in solution, such as chemical ions, yielded by weathering and erosion of the land mass.

Dissolved oxygen (DO) - the amount of oxygen dissolved in a given volume of water.

Drainage basin - the area tributary to or draining to a lake or stream (see also watershed).

Dry deposition - material deposited from the atmosphere on the Earth's surface outside periods of precipitation.

Duplicate samples - obtained by dividing one sample into two or more identical subsamples.

Ecology - the study of the relationships of organisms to their environment.

Ecosystem - a natural unit consisting of living and non-living parts interacting with each other, formed by the organisms of a natural community and their environment.

Electromotive force (EMF) - difference in electrical potential (volts) between different electrodes in the same electrolyte, identical electrodes in different electrolytes, or where both electrodes and solutions are dissimilar.

Epilimnion - the uppermost layer of water in a lake, characterized by an essentially uniform temperature which is generally higher than elsewhere in the lake and by a relatively uniform mixing caused by wind and wave action. Also, the less dense oxygen-rich layer of water that overlies the metalimnion in a thermally stratified lake.

Eutrophication - the process of over-fertilization of a body of water by nutrients producing more organic matter than the self-purification processes can overcome.

Extractable metal - see acid extractable metal.

Filterable constituent - see dissolved constituent.

Filtrate - the fluid that has passed through a filter.

Filtration - the process of passing a liquid through a filter to remove suspended matter.

Floc - small masses formed in a fluid through coagulation, agglomeration or biochemical reaction of fine suspended particles.

Flocculant or flocculating agent - a substance which, when added to water, forms a floc, thus expediting the settling of suspended matter, for example, alum, ferrous sulphate or lime.

Flow-proportional composite sample - sample obtained by: (1) continuous pumping at a rate proportional to the flow; (2) mixing equal volumes of water collected at time

intervals inversely proportional to the volume of flow; (3) mixing volumes of water proportional to the flow collected during or at regular time intervals. This sample will represent a "flow"-averaged water-quality condition over the period of time of compositing.

Flow weighted - see previous entry.

Fluvial characteristics - of or pertaining to a river or rivers; existing, growing or living in or near a stream or river; produced by the action of a stream or river.

Friedinger sampler - a messenger-operated, open-tube grab sampler for water and suspended sediment (Figure 3.4).

Gauging station - a selected location on a stream channel where discharge and other related parameters are measured continuously or periodically.

GEMS - Global Environmental Monitoring System.

Geochemistry - the science that deals with the chemical composition and the chemical reactions of the substances making up the crust of the earth.

Geohydrology - the science of underground water (synonym: hydrogeology).

Glass distilled water - water that has been freed from dissolved or suspended matter by distillation in an all-glass system.

GLOWDAT - the computerized storage and retrieval system storing water quality and related data collected as part of the GEMS/WATER global monitoring programme sponsored by United Nations Environmental Programme (UNEP). GLOWDAT is run and managed for UNEP by the National Water Research Institute, Environment Canada, located in Burlington, Ontario, Canada.

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

Groundwater - all subsurface water.

Hach method - an iodometric method of analysing for dissolved oxygen.

Hardness, total - the sum of calcium, magnesium and some other ions (e.g. iron, aluminum and manganese) concentrations in a water sample expressed as milligrams $CaCO_3$ per litre. The hardness relates to a water's capability to produce lather from soap; the higher the hardness, the more difficult it is to lather soap. Waters are classified according to their hardness as follows:

Hardness of 1 to 60 mg/l $CaCO_3$ - soft water.
Hardness of 61 to 120 mg/l $CaCO_3$ - medium-hard water.

Hardness of 121 to 180 mg/l $CaCO_3$ - hard water.
Hardness of >180 mg/l $CaCO_3$ - very hard water.

Heavy metals - metallic elements with specific gravities greater than five such as cadmium, copper, lead and zinc.

Herbicide - substances or a mixture of substances used to destroy specific vegetation.

Homogeneous - uniform in composition and structure.

Hydrological - pertaining to the study of the occurrence, circulation, distribution and properties of the waters of the Earth and their reaction with the environment.

Hypolimnion - the lowermost layer of water in a lake, characterized by an essentially uniform temperature (except during a turnover), generally colder than elsewhere in the lake and often relatively stagnant or oxygen-poor. Also the dense layer of water below the metalimnion in a thermally stratified lake.

In situ measurement - measurement made directly in the water body.

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

Lacustrine - related to, pertaining to, produced by or formed in a lake or lakes.

Macro-organisms - plant, animal or fungal organisms visible to the eye.

Macrophytes - large aquatic plants.

Membrane filter - a filter of cellulose ester with a specified pore diameter.

Mean - the average of a series of values; see sample mean, population mean.

Metalimnion - see thermocline.

Microbiota - collectively, the microscopic plants and animals of a habitat or region.

Microphyte - a microscopic plant; bacteria or smaller algae.

Molarity - the concentration of a solution expressed as the number of moles of a substance dissolved in 1 litre of solution.

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

NAQUADAT - the computerized Canadian National Water Quality Data Bank. It stores physical, chemical, biological, hydrometric and other data and information relevant to the quality of surface and groundwaters, precipitation, sediments and biota from Canadian aquatic environments.

Non-point waste source - an unconfined waste discharge.

Normality - the concentration of a solution expressed as the number of gram-equivalent weights of a substance dissolved in 1 litre of solution. Normality is abbreviated by *N*.

Nutrient - a substance, element or compound necessary for the growth and development of plants and animals.

Oligotrophic waters - waters with a low level of nutrients supporting little organic production.

Organic-free water - water free from organic substances.

Partial pressure - the pressure that would be exerted by one component of a mixture of gases if it were present alone in the container.

Particle size - the average diameter or volume of the particles in a sediment or rock, or of the grains of a particular mineral that make up a sediment or rock, based on the premise that the particles are spheres or that the measurements made can be expressed as diameters of equivalent spheres. It is commonly measured by sieving, by calculating settling velocities or by determining areas of microscopic images.

Periphyton - organisms, mostly microscopic, attached to submerged objects in aquatic environments; such organisms do not penetrate into the substrate and may or may not be sessile.

Peristaltic pump - a pump delivering an intermittent discharge by successively squeezing sections of tubing.

Pesticide - substance that kills organisms injurious to man or to the plants and animals upon which he depends for food, fibre and shelter.

pH - the negative $\log_{10}$ of the hydrogen ion activity in solution. Water with a pH of less than 7 is acidic, of 7 is neutral and of more than 7 is alkaline.

Photosynthesis - the synthesis of chemical compounds by chlorophyll-containing plants in light, especially the manufacture of organic compounds, primarily carbohydrates from carbon dioxide and a hydrogen source such as water, with the simultaneous liberation of oxygen.

Phytoplankton - collectively, all the microscopic plants, such as certain algae, living unattached in aquatic habitats.

Plankton - minute plants (phytoplankton) and animals (zooplankton) which either have relatively small powers of locomotion or drift in the water subject to the action of waves and currents. The chief constituents of phytoplankton are unicellular algae. The zooplankton consists of protozoa, small crustaceans and various invertebrate larvae.

Point sample - see grab sample.

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

Pollution - the condition caused by the presence of substances of such character and in such quantities that the quality of the environment is impaired (see also water pollution).

Population - In ecology, a group of individuals of the same type, particularly of the same species, within a community. Populations have certain characteristics not shown by individual organisms or the community as a whole. Characteristics of a population include density (size in relation to unit space), birth and death rates (natality and mortality, respectively), age distribution, sex ratio, dispersion (distribution of the individuals within the area) and growth rate.

Population (or true) mean - the average of all possible values of a quantity.

Potentiometer - a device for measuring the electromotive force or electrical potential between two points.

Precision - a measure of the reproducibility or the closeness of agreement between the data generated from replicate or repetitive measurements using the same experimental procedure. Statistically the concept is referred to as dispersion and it measures the variability of the experimental procedure, e.g. sampling, analytical or data-processing methods, resulting from random errors.

Preservative - a substance added to the sample in order to maintain components in the form they are in the water body, e.g. dissolved metals in solution.

Pumping sampler - an apparatus for sampling the water-sediment mixture by withdrawning it through a pipe or hose, the intake of which is placed at the desired sampling point.

Radioactive contaminant - a radioactive material which is present in places where it may harm life, spoil experiments or make products or equipment unsuitable or unsafe for use.

Radioactivity - the property of some elements, e.g. uranium, of spontaneously emitting alpha, beta or gamma rays by the disintegration of their nuclei.

Radionuclide - a radioactive isotope of an element.

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

Replicate samples (spatial) - samples taken simultaneously in a given cross section of the water body under study.

Replicate sample (temporal) - samples taken at the same place sequentially at specified intervals over a specific period of time.

Representative sample - a sample of a milieu or population whose composition is expected to exhibit its average properties.

Representative site - a location chosen as typical of an environment.

Reservoir - an impounded body of water or controlled lake where water is collected and stored.

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

Sample mean - an approximation to the population mean obtained by taking the average of a sample of the possible values of a quantity.

Sample variance - the square of the standard deviation. It is a measure of variability from a mean.

Sampling iron - an iron frame used in collecting water samples from rivers and lakes, designed to hold sampling bottles of different sizes.

Sampling vertical - a vertical line from the water surface to the bottom along which one or more samples are collected.

Secchi disk - a circular metal plate, 20-30 cm in diameter, painted in black and white quadrants. It is used to determine the transparency of a water body.

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

Sediment discharge - usually the mass, sometimes the volume, of sediment passing a stream transect in a unit of time. The term may be qualified, for example, as suspended-sediment, bedload or total-sediment discharge.

Sediment load - the amount of sediment passing a cross section of a river or stream, in a specified period of time (see also bedload and suspended sediment load).

Sediment transport - see sediment discharge.

Sediment yield - the total sediment outflow from a drainage basin in a specified period of time. It includes bedload as well as suspended load and usually it is expressed in terms of mass or volume per unit of time.

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

Shipek sampler - an instrument designed to collect relatively undisturbed samples of bottom surface sediments (also Mini-Shipek) (Figure 10.3).

Species - Group of related individuals with a common hereditary morphology, chromosomic number and structure, physiological characteristics and way of life, separated from neighbouring groups by a barrier, which is generally sexual in nature, and occupying a definable geographic area. Members of different species do not normally interbreed; if they do, the progeny are sterile. In binomial nomenclature each species has two names. The first is the name of the genus and the second is the specific epithet (trivial name). For example, in the species Homo sapiens, Homo is the generic name and sapiens is the specific epithet.

Species population - a group of similar organisms residing in a defined space at a certain time.

Specific conductance - a measure in microsiemens per centimetre (mS/cm) of the ability of a material such as a solution to conduct an electrical current. The conductivity of a solution depends on the concentration of ions and on the temperature.

Spectral analysis - a method of data analysis using the power spectrum of data to detect cyclical variations, their frequency and magnitude.

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

Standard deviation - a measure of the dispersion or spread of data points around the mean value of the data set obtained.

Standing crop - the biota present in an environment at a selected point in time.

Sterilization - the process of destroying all forms of microbial life on and in an object.

Stream discharge - the quantity of water passing a stream transect in a unit of time.

Supernate or supernatant - the liquid, e.g. water, above the surface of settled sediment.

Surber sampler - a light-weight dredge net for bottom biota sampling (Figure 10.5).

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

Survey - an intensive, in-depth study, usually carried out over a short period of time.

Suspended load - the part of the sediment load that is in suspension.

Suspended sediment - the component of an unacidified water sample that is retained by a 0.45-nm membrane filter.

Suspended solids - see suspended sediments.

Teflon - polytetrafluoroethylene, a man-made plastic material inert to all ordinary chemical reagents except molten alkali metals.

Thermocline - the layer in a thermally stratified lake, between the epilimnion and hypolimnion, where temperature decreases most rapidly with depth. Also, the horizontal layer of water characterized by a rapid decrease of temperature and increase of density with depth; sometimes arbitrarily defined as the layer in which the rate of temperature decrease with depth is equal to at least 1°C per metre (synonym: metalimnion).

Time composite sample - see sequential composite sample.

Time series - a set of data usually collected at equal time intervals over a long period of time.

Total concentration - the concentration of a given constituent determined in an unfiltered water or sediment sample after vigorous digestion with mineral acid(s). It can also be obtained by summing the concentrations in both filterable and unfilterable (suspended) fractions of water sample.

Total dissolved solids (TDS) - the concentration of all dissolved substances in water, usually expressed in milligrams per litre, which would remain as a solid residue after removal of the water.

Trace element - a chemical element found naturally or required for growth and health by living organisms in extremely small quantities.

Transect - a imaginary line across a river or a lake on which samples or measurements are taken to determine cross-section variations.

Turbidity - a measure of the absorption and scattering of light in water caused by suspended matter such as clay, silt, finely divided organic and inorganic matter, soluble coloured organic compounds, plankton and other microscopic organisms.

Universal Transverse Mercator (UTM) grid - a grid, which may be superimposed on any map, based upon the transverse Mercator projection.

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

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

Water pollution - the addition of harmful or objectionable materials to water in sufficient quantities to affect its usefulness adversely.

Water quality - a collective term comprising the physical, chemical and biological properties of specific waters, e.g. lake, river, drinking water distribution system, waste water and so on.

Water-quality criteria - the scientific information, e.g. concentration-effect data, used to derive water-quality guidelines.

Water-quality guideline - numerical concentration or narrative statement recommended to support and maintain a designated water use.

Water-quality objective - a numerical concentration or narrative statement established to support and protect the designated uses of water at a specified site.

Water-quality standard - a water-quality objective recognized in enforceable environmental control laws.

Watershed - all lands enclosed by a continuous hydrologic-surface drainage divide and lying upslope from a specified point on a stream (see also drainage basin).

Winkler analysis - an iodometric method for the determination of the concentration of dissolved oxygen.

Zooplankton - microscopic animals living unattached in aquatic ecosystems. They include small crustacea, such as Daphnia and Cyclops, small larvae, and single-celled animals such as protozoa.

CHAPTER 16

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