GEMS: GLOBAL ENVIRONMENT MONITORING SYSTEM

# GEMS/WATER OPERATIONAL GUIDE

**Third edition**

**Prepared under the joint sponsorship of the**

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UNEP/WHO/UNESCO/WMO PROGRAMME ON GLOBAL WATER QUALITY MONITORING AND ASSESSMENT

GEMS/WATER OPERATIONAL GUIDE

# FOREWORD

This is the third edition of the GEMS/WATER Operational Guide. Its purpose is to guide the implementation of the global GEMS/WATER programme at the national level.

GEMS/WATER is an international programme on water quality monitoring and assessment, jointly implemented by WHO, WMO, UNESCO and UNEP. It has now twelve years of solid achievements behind it. During those twelve years it has assisted countries in establishing and strengthening their water quality monitoring operations and has provided methodological and quality assurance support. It has also produced periodical assessments on the state of the world freshwater resources. These achievements have been made possible by the active involvement in the programme by national network participants all over the globe.

Understandably, a programme of this nature has to adapt to changing situations and respond to a growing demand for solid data and information on environmental matters. Thus, in 1991, the second phase of the programme was initiated to align the programme with the changing needs of the decade ahead.

A responsive programme requires a responsive operational structure, hence, this third edition of the GEMS/WATER Operational Guide. And, of course, this is not intended as the final edition. As the programme grows and includes new or improved methods as well as enhanced co-ordination activities in the field of water pollution monitoring and interpretation at national and international levels, further revisions will emerge. One such revision, to incorporate better the hydrological and descriptive data required to assist the production of comprehensive assessments, is already foreseen. It is the aim of the GEMS/WATER programme during this second phase, not only to strengthen and harmonize monitoring operations at an analytical level, but also to provide the necessary information and tools to support the sustainable management of freshwater resources.

We welcome any comments you might wish to make on this edition in order to improve the Operational Guide further and to align it with the needs of network participants whose inputs have made this global effort possible. We look forward to such continued close cooperation towards the goal of making the world of tomorrow a better today for us all.

UNEP/WHO/UNESCO/WHO PROGRAMME ON GLOBAL WATER QUALITY MONITORING AND ASSESSMENT

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# INTRODUCTION

## Project Background and Initiation

The Global Environment Monitoring System (GEMS) is a collaborative effort of the world community to acquire, through monitoring and assessment, the data and information needed for the national management of the environment. GEMS is a United Nations system wide mechanism, serviced by a small Programme Activity Centre within UNEP, to co-ordinate and catalyse environmental monitoring and assessment activities conducted by the specialized United Nations Organizations and national and international institutes. The four Organizations which are participating directly in this project have a continuing interest in the assessment and monitoring of water resources. The World Health Organization's programme on water quality monitoring was developed in response to WHA resolution 25.43 which particularly requested the Organization to collaborate with governments and the appropriate international bodies in developing a water quality surveillance system to deal effectively with international water pollution problems of particular public health importance. The United Nations Educational, Scientific and Cultural Organization's International Hydrological Programme is concerned with scientific studies on water quality and the United Nations Environment Programme supported UNESCO project on the establishment of a world register of rivers. Information on the existing hydrological stations network and facilities is available through the World Meteorological Organization's Hydrology and Water Resources Programme and, in addition, this Organization is concerned with the principles and techniques of hydrological network design and operation.

Ever since its formation, UNEP has been involved in and supported a series of water pollution monitoring related activities. Thus, the present project is part of UNEP's Global Environment Monitoring System (GEMS) which today consists of the following groups of activities: atmosphere and climate, environmental pollutants and earth's renewable resources. The project on global water quality monitoring and assessment (GEMS/WATER) belongs to the sub-group on environmental pollutants together with air and food monitoring and human exposure assessment.

In 1974, WHO, with the assistance of UNEP, began to plan the development of a global health-related water quality monitoring programme. In January, 1975, a meeting of experts was held at the Federal Institute of Hydrology in Koblenz, Federal Republic of Germany, to prepare the basic framework for the programme. This meeting was followed by a series of consultations with other international organizations. In November 1976 a joint UNEP/WHO/UNESCO/WMO programme on global water quality monitoring (GEMS/WATER) was established and supported by the Environment Fund of UNEP. Approaches, methods and scope of the programme were outlined and agreed upon at an inter-regional meeting of experts in December 1977 (1).

The objectives set at the beginning of the programme were:

(a) to collaborate with Member States in the establishment of new water monitoring systems and to strengthen existing systems;

(b) to improve the validity and comparability of water quality data within and between Member States;

(c) to assess the incidence and trends of the pollution of water by some persistent and hazardous substances on a long-term basis.

The programme is implemented through close collaboration of all participating organizations. To assure that the programme develops in a globally consistent fashion, it is centrally co-ordinated. However, its implementation is regionalized as much as possible. This means that the WHO Regional offices in collaboration with their counterparts on UNESCO, WMO and UNEP are responsible for the programme within their regions. Regional references laboratories assist them in this task.

In each participating country a government agency or institution is identified as the focal point for carrying out the programme within the country (National Centres). The WHO Collaborating Centre for Surface and Ground Water Quality at the National Water Research Institute (NWRI), Canada Centre for Inland Waters (CCIW) serves as the global data centre.

## Programme Implementation during Phase One

The GEMS/WATER programme was first reviewed in 1983 at an inter-regional meeting of experts convened at the CCIW (2) to evaluate the design and achievements of the project. While the objectives of the programme remained the same stronger orientation on data requirement relevant to the assessment of human exposure to pollutants was recommended.

During the first ten years of programme operations (i.e. GEMS/WATER - Phase One), substantive progress can be demonstrated in the five following areas.

- Monitoring methodology has been developed with regard to network design, sampling and analytical procedures, and data processing. This was made available on a broad basis to water, health, and environmental agencies for their water quality monitoring programmes. A number of national water quality monitoring networks in developing countries have been modelled in accordance with the GEMS/Water Operational Guide (3) of which two editions were issued and made available in more than 1,500 copies in English, French and Spanish.

- A standardized global network has been established for the first time in freshwater bodies, which covers not only surface, but also groundwaters. A total of about 450 stations were formally designated in 59 countries. Routine data submission has been achieved for 344 stations comprising 240 river stations, 43 lake stations and 61 groundwater stations. 42 countries from all continents are actively participating and contributing to the global data bank established at the National Water Research Institute in Canada where more than 500,000 data points have been accumulated. Data summaries covering the period 1979 to 1987 have been published (4,5,6).

- Training of national staff has been a prime concern of the programme. A total of 14 training courses, most lasting 2 weeks, have been organized in all continents in English, French and Spanish. These courses covered subjects such as monitoring methodology and analytical quality control. A total of 269 trainees attended from national health and water authorities and participating laboratories in 56 countries.

- Analytical quality control (AQC) was early recognized as a cornerstone of data reliability and comparability. Accordingly a regular quality control programme was operated through the USEPA Environmental Monitoring Systems Laboratory (EMSL). On a biennial basis, quality control check samples were sent to 250 laboratories world-wide and 80 laboratories in 40 countries participated in an inter-laboratory comparison study. (See references 7,8).

- Global assessment of freshwater quality was undertaken by the programme for the first time in 1987/88. A condensed assessment report highlighting global issues and future monitoring needs was prepared by a group of scientists and reviewed by a governmental expert group in 1988 (10). A fully comprehensive publication appeared in late 1989 entitled "Global Freshwater Quality: A First Assessment" (11).

After ten years of operation, the programme was reviewed by a group of UNEP/WHO government designated experts in Geneva in 1988 (10). The experts recommended that the design and implementation of Phase Two of the programme needed review with respect to overall geographic coverage, measurements of trace metals and organics and the usefulness of monitoring data for global assessment of water quality and trend analysis. Following this request, a consultation to review GEMS/WATER activities was held at NWRI in April 1989 to outline the revised monitoring structure and provide guidance for future programme development for GEMS/WATER Phase Two.

## GEMS/WATER Phase Two

A group of experts convene in Leningrad (1990) to review the GEMS/WATER Programme design in light of emerging global priorities (12). They came to the conclusion that emphasis should be shifted from monitoring to the interpretation of data and to the assessment of water quality issues and trends, and a revised set of long-term objectives was agreed upon as follows:

(1) To provide water quality assessments to governments, the scientific community and the public on the quality of the world's freshwaters relative to human health aquatic ecosystem health, and other global environmental concerns; specifically to:

- (i) define the status of water quality;
- (ii) identify and quantify trends in water quality;
- (iii) define the causes of observed conditions and trends;
- (iv) identify the types of water quality problems that occur in specific geographical areas; and
- (v) provide the accumulated information and assessments in a form that resource management and regulatory agencies can use to evaluate management alternatives and make necessary decisions.

(2) To provide to governments, the scientific community and the public information on the transport and, if necessary, assessments of the fluxes of toxic chemicals, nutrients and other pollutants from major river basins to the continent/ocean interfaces.

(3) To strengthen national water quality monitoring networks in developing countries, including the improvement of analytical capabilities and data quality assurance.

A restructured network of 40-50 baseline stations, 300-400 trend stations, and 60-70 global river flux monitoring stations was proposed. More efforts will also be required to prepare the conceptual approach to regional monitoring networks for groundwaters.

During Phase Two, a Standing Committee of Experts on Freshwater Quality will oversee the programme and prepare global assessments.

Pollutants to be Measured

During Phase One of the programme, the water quality variables to be monitored fell into three categories - basic, optional and globally significant. The first group included those which were considered important for the general assessment of water quality. The monitoring of these variables did not require expensive and complicated instrumentation and it was envisaged that they would be measured at all the sites included in the global network. The second group included a number of substances which may be of importance at given locations. Accordingly, they were not measured everywhere but only at the locations where they were known or suspected to be present in concentrations of concern. The third group of variables included those substances whose discharge into the environment is of long-term significance because they are toxic, persistent and bio-accumulable. At the Burlington meeting in 1983 (2) these categories were abandoned and, in light of the increased focus on water use for public supply regrouped into basic variables and use-related variables. The previous basic list was slightly expanded to include more inorganic water constituents. The use-related variables included lists for drinking-water supply, irrigation, and general water quality such as support of aquatic life. Also, the frequencies of sampling were revised to cover minimum monitoring requirements.

At the Leningrad meeting in 1990 (12) a revised list of variables for GEMS/WATER Phase Two was proposed. The list include essential basic monitoring variables and other variables intended to measure one or several pollution issues (e.g., organic waste pollution, irrigation, agrochemicals, industrial effluents, mining pollution, acidification). Several new parameters were added. The largest departure from the previous set of variables is that the sampling and analysis of particulate matter is recommended. This is in recognition of the crucial role played by particulate matter in the transport and fluxes of pollutants.

Analytical Quality Control

During Phase One, one of the basic aims of the programme was is to improve the validity and comparability of water quality data. To this end, a three-step approach was applied. First, analytical methods capable of achieving these requirements were identified. The participating laboratories were urged to use these methods. A compilation of reference methods, based on a EURO Manual (13) was prepared and made available. Second, each participating laboratory was requested to establish a continuing programme of intra-laboratory analytical quality control. Standard samples were provided for this purpose. Third, a series of inter-laboratory comparison studies, coordinated by the global reference laboratory, were carried out. The first global inter-laboratory study has been completed in 1983 with about 80 laboratories participating. The results were published and discussed in the World Health Statistics Quarterly in 1986 (7). Quality control samples have been distributed to GEMS/WATER laboratories for free through 1990. The USEPA's Environmental Monitoring Systems Laboratory at Cincinnati has periodically conducted formal performance evaluation study for GEMS/WATER laboratories.

During Phase Two, the GEMS/WATER Standing Committee of Experts on Freshwater Quality will develop data quality objectives for the participating programmes. Quality assurance will continue as in Phase One, but be augmented with additional performance evaluation studies and training workshops, particularly on quality control for field sampling and data management.

Data Reporting

The National Water Research Institute (NWRI) at the Canada Centre for Inland Waters functions as the global data centre (GLOWDAT). The water quality data and the relevant hydrological information is collected by each National Centre. The water quality data are forwarded directly to the global data centre or through WHO Regional Offices, on a quarterly or semi-annual basis. The hydrological information is forwarded via WMO's Global Runoff Data Centre (GRDC) at the Federal Institute of Hydrology in Koblenz, Germany. The data are then processed, validated and analyzed. The NWRI prepared and published summary reports (4,5,6). Separate data evaluation reports, regional summaries, global assessment reports etc. were also prepared during Phase One (9,10,11).

During Phase Two, Yearbook of GEMS/WATER data will be published. These reports will consist of standardized statistical summary of monitoring results from all stations by country. Major global assessment of water quality will be published every five years. Once the revised network for Phase Two is in full operation, publication of issue specific reports will be done. The issue-specific reviews will deal with important water quality problems.

Technical Support

The implementation of the programme and the operation of the network is supported through various measures. Two technical guidelines were developed prior to the initiation of this project which are of direct use, one on the planning of water quality surveys (14) by UNESCO and WHO, and one on analytical methods (13) by the WHO Regional Office for Europe (WHO/EURO). Due to the reorientation of the programme, the "Water Quality Surveys" guide was extensively revised, and a new guide entitled "Water Quality Assessments" has been published (15).

In addition, the GEMS/WATER Operational Guide is specifically prepared to instruct all project participants on the commonly applied methods, including a new standard format for data reporting. This present publication is the third edition of the GEMS/WATER Operational Guide.

## GEMS/WATER Operational Guide

The present guidebook was prepared in order to ensure as much harmonization of the project operations as is possible on a global level. All major technical instructions were compiled which concern field staff, laboratory personnel, data processors and national coordinating offices, i.e. all participants in this project. The current revised version includes the modifications proposed by the Leningrad group of experts (12) in particular a new list of variables and a new data reporting format.

Chapter I on the "Selection of Global Network Stations" gives the major criteria for the selection of sampling sites to be included in the global network. Practical instructions on site selection for lakes, rivers and groundwater stations are given. In addition this chapter contains forms for the collection of additional information relevant to the sampling stations.

Chapter II on "Sampling Frequencies and Methods" describes the minimum sample collection programme for different water bodies, i.e. rivers, lakes, and groundwaters and for the different types of GEMS/WATER stations, i.e., baseline, trend and global river flux. Also, it includes detailed methods for the sampling process, the preservation of samples in the field, the field quality assurance, and the field measured variables.

Chapter III on "Analytical Methods" presents the revised list of variables as recommended by the experts meeting in Leningrad (12). It provides a brief description of the variables and its importance for water quality and outlines the prescribed methods of analysis. Detailed analytical methods are not presented in this current edition but can be found in the previous edition of the Operational Guide or in references listed at the end of the chapter.

Chapter IV on the "Monitoring of Particulate Matter Quality" presents the importance of sampling the particulate matter in water quality surveys. Detailed instructions on field and laboratory work, and on data evaluation are provided.

Chapter V on "Microbiological Analysis" briefly presents the considerations that have to be taken into account when planning for microbiological monitoring.

Chapter VI on "Biological Monitoring" outlines three types of biomonitoring, i.e. the measurement of phytoplankton biomass, community structure monitoring, and the analysis of biological tissues.

Chapter VII on "Analytical Quality Control" describes in detail the scheme for intra and inter laboratory procedure to achieve the accuracy targets specified for the project.

Chapter VIII on "Quantative Hydrological Measurements" discusses the role of hydrological measurements in water quality monitoring in accordance with other World Meteorological Organization guides and manuals. It gives technical instructions on basic hydrological techniques.

Chapter IX on "Data Processing and Reporting" provides procedures and instructions pertinent to the collection, transfer and storage of data within the project. Forms are provided for the identification of stations and for the reporting of data with the necessary coding. Output options from the centralized computer at the WHO Collaborating Centre at the NWRI of the Canada Centre for Inland Waters are also presented.

Chapter X on "Data Analysis and Presentation" presents typical outputs for presentation of data in the yearbook of GEMS/WATER data.

## References

(1) Interregional Review Meeting on the UNEP/WHO/UNESCO/WMO Project on Global Water Quality Monitoring, Geneva, 12-16 December 1977 (WHO doc. ETS/78.3)

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## CHAPTER I: THE SELECTION OF GLOBAL NETWORK STATIONS

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## 1.0 INTRODUCTION

The monitoring of water quality to give reliable and usable data cannot be carried out cheaply and care must be taken to ensure that analytical and other resources are employed to the best advantage. The first steps in the planning of a water monitoring system should therefore be to decide what data is needed and how it will be used. Sampling sites should then be chosen with a view to obtaining the required essential information with a minimum of effort. This chapter provides guidance on the choice of appropriate sampling stations.

## 2.0 THE GEMS/WATER NETWORK

### 2.1 Objectives of the Monitoring

The monitoring activities undertaken during Phase Two of the GEMS/WATER Programme will be in support of three assessment goals:

1. Determination of natural freshwater qualities in the absence of significant direct human impact.

2. Determination of long-term trends in the levels of critical water quality indicators in freshwater resources.

3. Determination of the fluxes of toxic chemicals, nutrients, suspended solids and other pollutants from major river basins to the continent/ocean interfaces.

Meeting the monitoring data requirements means that a highly selective network of strategically located monitoring stations be created and operated in the major freshwater bodies of the world. Three types of monitoring stations are envisaged in the revised global monitoring network: baseline, trend, and global river flux stations.

Many of the monitoring stations in the revised network will be a continuation of existing "baseline" or "impact" stations, albeit with a possible change in designation or location. New stations will also have to be established.

Sampling and analysis will include particulate matter in addition to water because of the crucial role this medium plays in defining the pathways and fluxes of pollutants. Biota will also be sampled at selected stations because this medium offers the opportunity of integrated pollution monitoring in locations where chemical analyses cannot cope with the multitude of substances present in the water.

A comprehensive assessment of global water quality is possible only if major aquifers are also monitored. This is particularly relevant in countries where the surface water resources are scarce and groundwaters constitute the major water resource available. Groundwater quality problems have reached critical levels throughout entire sub-continents, but little routine monitoring of groundwater quality exists worldwide; concepts for regional sampling designs and well selection are just beginning to be developed. A special design effort will be required during Phase Two of GEMS/Water to develop regional monitoring of groundwaters. In the interim, operation of the existing groundwater stations from Phase One will continue.

### 2.2 Definition of GEMS/Water Stations

BASELINE STATIONS are typically located in headwater lakes or undisturbed upstream river stretches where no direct diffuse or point-sources of pollutants are likely to be found. They will be used to establish the natural water quality conditions; to provide a basis for comparison with stations having significant direct human impact (i.e., trend and global river flux stations); to determine, through trend analysis, the influence of long-range transport of contaminants and of climatic changes. This type of station remains unchanged in Phase Two of the project.

TREND STATIONS are typically located in major river basins, lakes or aquifers. They will be used to follow long-term changes in water quality related to a variety of pollution sources and land uses; to provide a basis for the identification of causes or influences on measured conditions or identified trends.

GLOBAL RIVER FLUX STATIONS are located at the mouth of major rivers. They will be used to determine integrated annual fluxes of critical pollutants from river basins to oceans or regional seas. Some trend stations on rivers may also serve as global river flux stations.

### 2.3 Site Selection

#### 2.3.1 Selection Criteria

The selection of GEMS/Water stations for Phase Two of the programme take into consideration the following site specific criteria.

| Station Type | Basic Selection Criteria | Type of Water |
|---|---|---|
| Baseline station | - in small undisturbed basins,<br>- no source of pollutants,<br>- no direct human activities, (including roads),<br>- Avoid basin with a high proportion of metal-bearing rocks,<br>- at least 100 km from major air pollution source (i.e., cities, industries etc.) | - Headwater lakes (water residence time: 0.5-2 years)<br>- upstream river stretches |
| Trend station | - in medium-sized basins,<br>- moderate timeframe response to pollution and changes in land-uses,<br>- range of pollution inducing activities/or/single dominant activities (e.g., industrial, municipal, agricultural, mining etc.). | - Lakes/Reservoirs water residence time: 1-3 years<br>- Rivers<br>- Groundwaters |
| Global River Flux station | - basin priorization scheme includes importance of drainage area, population, major human activities, and significance of the river to receiving coastal waters,<br>- most downstream station not influenced by tides,<br>- station must be representative of the cross-sectional characteristics of the river,<br>- availability of flow measurement data at the location of water quality monitoring station. | - Rivers |

### 2.3.2 Revised Network

The revised GEMS/Water network should have a minimum of 10 baseline stations to start with; the optional number would be of 40 to 50 stations distributed throughout all continents. The number of baseline stations should represent a reasonable coverage of major climatic, hydrological and phytogeographic regions of the world.

Since trend stations are intended to represent human impacts on water quality, the number of trend stations should be high to address the numerous water quality issues facing the world's freshwater resources. The monitoring network will begin with about 100 and will eventually expand to between 300 and 400 trend stations. The network must cover all major human influences upon water quality. Most of the stations will be located in basins with a range of pollution-inducing activities. However, in order to determine the water quality impacts of important and specific human activities, some stations will be located in basins with single, dominant activities. When making the transition from Phase One to Phase Two, a number of previously termed "impact stations" will fulfil the criteria for trend station. Some trend stations may also serve as global river flux stations, where appropriate.

The global river flux stations will be used to determine fluxes of organic and inorganic contaminants, and fluxes of other water constituents (e.g., carbon, nitrogen, phosphorous) contributing to geochemical cycles. It is estimated that a total of 60 to 70 stations located in major world's basin will be required to ensure a global coverage and that major land masses, oceans and regional seas are adequately represented. For calculation of chemical fluxes, it is also essential that water flow measurements be obtained at the location of the global river flux station.

### 2.3.3 Water Quality Issues

The choice of stations will be influenced by the type of water pollution issue(s) to be monitored, its importance and magnitude related to the different water uses. In Phase Two of the GEMS/Water programme, seven issues of significance at the global and/or continental or sub-continental level were selected:

- organic wastes from municipal sewage discharges and agro-industrial effluents;

- eutrophication of surface waters as a result of point and non-point input of nutrients and organics;
- irrigation areas which are threatened by salinization and polluted irrigation return waters;
- agro-chemical use, fertilizers and pesticides leading to surface and groundwater contamination;
- industrial effluents containing a variety of toxic organics and inorganics;
- mining effluents and leachates from mine tailings affecting surface and groundwaters on a large scale;
- acidification of lakes, rivers and even groundwaters resulting from the long-range atmospheric transport of pollutants.

### 2.3.4 Water Uses

The choice of stations will also be influenced by the various uses of the water and by their location, relative magnitude and importance. The degree of risk of accidental pollution will also be an important factor. The location of a river use downstream of a large urban area or of an underground water source near to industrial tips will impose a greater risk, requiring more supervision, than similar uses located upstream of any significant polluting discharges or remote from any potential pollutants. It must be remembered that the use of the storage of agricultural chemicals and the transport of chemicals by road-tanker can both create serious hazards in relatively unpopulated areas.

| Use | Criteria |
|---|---|
| **All Waters** | |
| Drinking and domestic use | Population served. |
| Agricultural irrigation | Annual value of crops and population employed. |
| Livestock watering | Numbers of animals, annual commercial value, population employed. |
| Industrial use<br>- low grade - e.g. cooling<br>- high grade - e.g. food and drink | <br>National and local importance of factory.<br>Annual value of products, population employed. |
| **Surface waters** | |
| Commercial fisheries | Quality and value of catch, importance as a food, population employed. |
| Sporting fisheries | Number of people and frequency of use, membership of clubs, value of fishing rights. |
| Recreation<br>bathing<br>boating<br>amenity | Number of people, frequency of use, membership of clubs, distance from urban areas, access to alternative waters. |
| Navigation<br>(risk of silting or aquatic vegetation) | Quality and value of goods transported, people employed. |
| Drainage<br>(risk of silting or obstruction causing floods) | Potential damage, remedial costs, population affected. |

## 2.4 Use of Data

The utilisation of data may be divided into operational and control or planning and research purposes. The data will be used at different organizational geographical levels.

### 2.4.1 Operation and Control

Operational and control purposes will include:

1. Identification of areas in need of improvement and an assessment of the urgency.

2. Protection of water users by determining the effectiveness of control measures for maintaining or improving the quality of the water.

3. Measurement of changes in quality over periods of time to detect and measure trends and to propose anticipatory action.

4. Assessment of the effect of changes of input to the water system.

5. Determination of water quality where international frontiers are crossed.

6. Assessment of the total pollutant loads discharged by rivers, at the tidal limit of fresh water, into marine waters.

The first four uses are likely to be mainly but not exclusively of local or regional interest covering a single river basin, lake or aquifer whereas items five and six may be concerned with international interests and obligations.

### 2.4.2 Planning and Research

Planning and research will cover the use of the data for:

1. Provision of information on the quality of water potentially available to meet future requirements.

2. Prediction of the effect of intended changes of input upon the quality of water.

3. Assistance in estimating the effect of proposed hydrological changes upon the water regime (impoundment of a river, change in depth of a lake; artificial recharge of an aquifer, etc.).

4. Preliminary consideration in the formulation of mathematical models.

5. Information on the incidence and trends of specific dangerous substances.

## 3.0 PLANNING OF SITE SELECTION

### 3.1 The Process

Because of the heavy cost involved in routine sampling and analysis it is well worth devoting time and effort to careful planning of the monitoring system. The site selection should be carried out in a logical sequence as described below and it is strongly recommended that all the information collected and the considerations and the reasons for the decisions reached at each stage should be written down and archived. Not only does "writing maketh an exact man" it also ensures that exact records will be readily available for future reference.

Preliminary surveys are a necessary step not only to select stations but also to check the sampling site accessibility, the available sampling means (bridge, boats etc), the time elapsed between sampling and laboratory analysis and the cost of a sampling trip.

### 3.2 Assembly of Information

1. The first step is to carry out a review and prepare an inventory of all the factors which may influence, either directly or indirectly, the quality of the water body. These will include all discharges or abstractions, both point and diffuse, likely to have a significant effect. It will also cover background information such as geography, topography, climate and weather, hydrology, hydrogeology, land use, urbanisation, industrialisation and agriculture. The review should include, as far as possible, any proposed or likely changes, both short and long term in these factors.

2. The next step is to assemble all the available information on the uses of the water and their magnitudes, quality requirements, and relative importance, and to prepare an inventory. This should also include all proposed and likely changes in use and consequent requirements in both quality and quantity.

3. Potential future sources of water pollution should be listed and described. Present and future water treatment should be described to identified re-use or re-cycling capabilities.

4. There may already be some quality data available for the water body, or some part of it, and this should be collected. The age of the data will of course affect their value.

5. At this stage maps can be prepared illustrating the more important aspects of present water quality issues and future influences and uses.

## 3.3 Appraisal of Data Needs

On the basis of the information collected it should now be possible to:

a. Appraise the relative importances of the different type of water pollution issues and land-use.

b. Appraise the relative importance of factors influencing the quality of water for different uses.

c. Decide what information is needed to meet the appropriate control, planning and base line requirements and the monitoring of specified hazardous substances.

d. Select potential sites, or localities for sites, which should provide the required information.

## 3.4 Preliminary Surveys

As far as possible preliminary surveys covering the areas of potential sampling sites should be carried out. These will assist in the identification of places where water quality is most unsatisfactory or critical. The analyses should include the basic variables and any others which the assembled information indicates may be present in significant concentration. The surveys should not be confined to the proposed stations but should be widespread covering other practicable sampling points in the water body. It is desirable to carry out the surveys over a representative period but even a single survey should, in conjunction with the background information, provide useful guidance.

For rivers, the preliminary survey may include several stations on a given river section and should check the lateral mixing at each site. Such surveys may be effected during extreme environmental conditions such as the rainy season for tropical regions, or in winter for nordic or mountain stations. In lakes, the preliminary survey should be realized on vertical profiles at the time of maximum algal production and just before the winter overturn. For groundwaters, surveys should be carried out to draw a preliminary picture of water quality based on several boreholes, wells and/or springs in order to choose the most representative stations.

## 3.5 Review

When the sampling and analysis begins the data will be fed back to those responsible for control and planning of water quality. After a suitable period, there should be examination of the data produced to decide whether or not it is meeting the information requirements. Consideration should be given to any changes in the sampling locations which might improve the value of the data and it may be that a single, extended survey would be justified.

Even where a monitoring system is already in operation a comprehensive re-examination employing the planning sequence described may be of value and could lead to a more efficient utilisation of resources.

The sequence for the selection of sites is shown in Figure 1.

## 3.6 Site Records

Basic information required for river, lake and groundwater sampling stations are annexed to this chapter and indicate the information which should be available for each station. It includes details of location, physical and flow conditions, quality influences, water uses and sampling and analytical details. These sheets could form the basis of a comprehensive record for each station which would, inter alia, be useful for reference in interpreting data obtained at the station, particularly when the inevitable changes in staff occur.

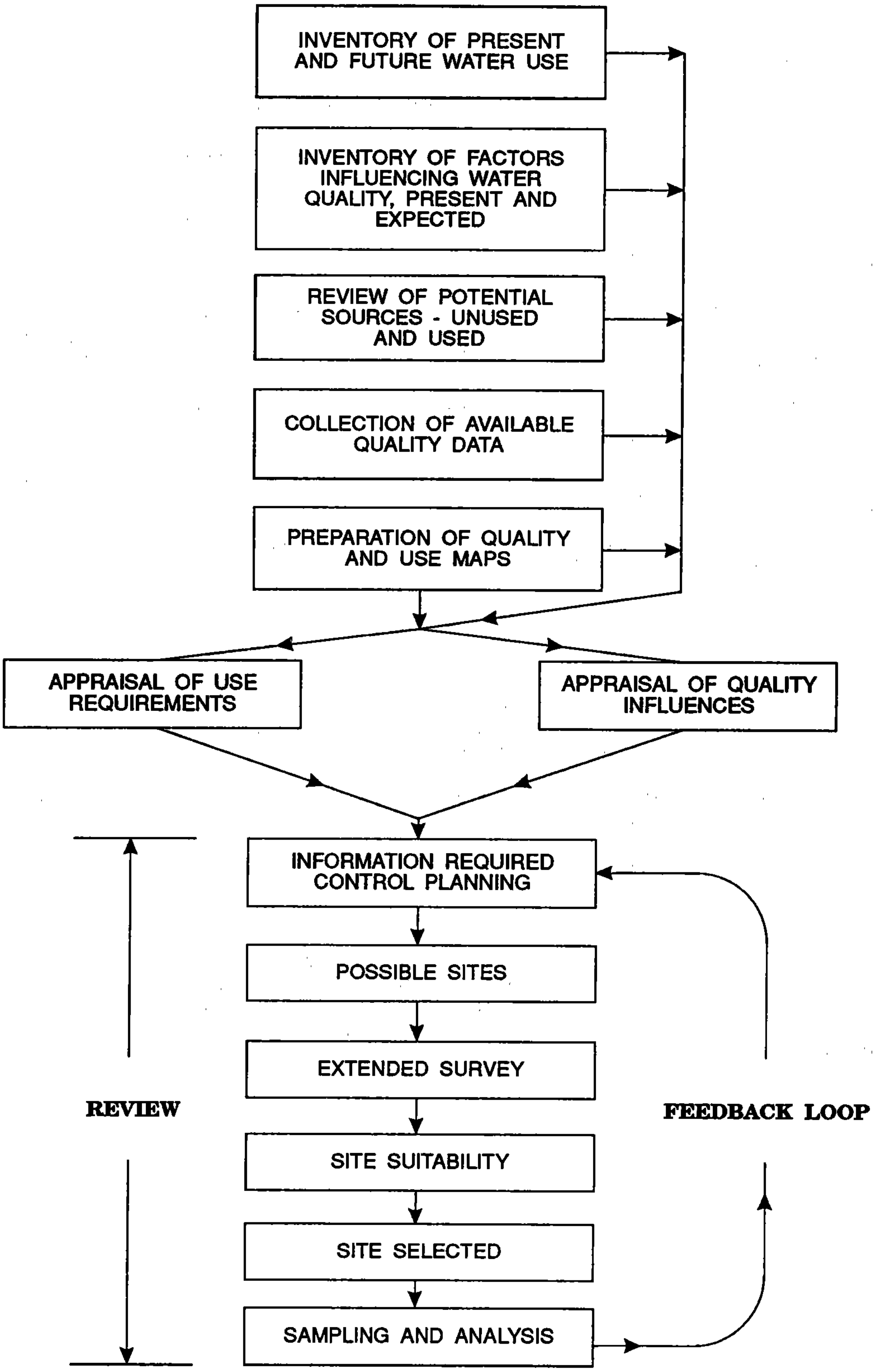



Figure 1: Scheme for selection of water sampling sites

## 4.0 SITE REQUIREMENTS FOR RIVERS

When the general location of a sampling station has been decided on the basis of the foregoing considerations there are still several practical factors which will influence its exact position. These are described below.

### 4.1 Representativeness

The sample must be representative, that is, the variables in the sample must have the same value as the water body at the place and time of sampling. For a sample to be representative therefore the water body must be fully mixed at the sampling place.

In rivers there may be appreciable delays in the lateral dispersion of discharges or tributaries depending upon the velocity, turbulence and size of the river downstream. There may also be delays in vertical mixing, particularly when there are temperature differences between the influent and the river.

All proposed river sampling stations should be examined for homogeneity over the cross-section at the sampling point. This is accomplished by sampling at intervals across the river at various depths. Details of suggested sampling arrangements according to the size of the river are given in Table I. The variables employed can be those measured in situ in the field such as conductivity, dissolved oxygen, pH or temperature. It is to be expected that, even when dissolved substances are fully mixed, vertical variations in the concentration of suspended solids are liable to occur according to the velocity of the water. The tests for homogeneity should be repeated to cover both high and low flows.

Table 1: River sampling to test for cross-sectional homogeneity

| Annual average discharge $m^3$/sec | Classification name | Number of Sampling points | Number of Sampling depths[1] |
|---|---|---|---|
| Less than 5 | small stream | 2 | 1 |
| 5-150 | stream | 4 | 2 |
| 150-1000 | river | 6 | 3 |
| Greater than 1000 | large river | minimum of 6 as in "river"; add more stations as river size increases by a factor of 2 | 4 |

[1] Samples should be collected, as far as possible, at least 30 cm below the surface or 30 cm above the bottom and care should be taken not to disturb bottom deposits.

Sampling procedures for non-homogeneous rivers can be tedious and it may be desirable to move the station downstream to a homogeneous zone if the data requirements are still met there satisfactorily. In some rivers, particularly large ones, this may not be possible because new influents enter before upstream discharges are mixed and the river may rarely, if ever, become homogeneous.

### 4.2 Flow Measurement

When sampling at a river, especially for global river flux stations, the discharge of the river at the station should be ascertained to enable the mass discharge of the different variables to be calculated. This information is required for the proper management of the water resource, and to decipher the water quality variations observed at the station. In selecting water quality monitoring stations, therefore, consideration should be given to the feasibility of siting them at or near established flow measuring stations. Ideally the gauging station should be at the sampling site but if it is situated at a point upstream or downstream where no significant change in flow has occurred this can be satisfactory. It is sometimes possible to compute the flow indirectly from two or more gauging points. If no gauging facility is available it may be necessary to install one to serve the sampling station. It should be borne in mind that if the sample collector has to carry out any lengthy gauging procedure it will be at the expense of his sampling time. Please refer to Chapter VIII of this guide for further guidance on quantative hydrological measurement.

4.3 Accessibility

The sample collector normally has to carry an appreciable burden of sampling kit and water samples and the distance he can walk from his transport is limited. Furthermore, the more difficult of access is the site the fewer the number of samples he can take in a working day. The sampling site should also be accessible under all conditions of weather and flows. Accessibility is therefore an important consideration particularly in regions exposed to severe climatic conditions (freezing temperatures, heavy rains etc.)

4.4 Distance from Laboratory

The samples will contain three types of variables, conservative such as chloride which will not change with time, non-conservative but preservable such as ammoniacal nitrogen and non-conservative non-preservable such as the B.O.D. The time taken to transport the samples to the laboratory will govern the range of determination which can be carried out for a particular sampling site. Travel times greater than 24 hours between the site and the laboratory will, for some water quality determinations render the site unsuitable.

4.5 Safety

The collection of lake or river samples can be hazardous, particularly under bad weather conditions or high flows, and in considering a site due regard must be given to this aspect. If there is no alternative to a hazardous site, full precaution must always be taken and the necessary safety equipment provided and used.

4.6 Disturbing Influences

If the sampling station is located a short distance below a weir the dissolved oxygen content will tend to be high and if it is above a weir, it will be low. Successive samples at such points will give comparable results but they will not be generally representative for the river. Similarly location below a stretch or river with an unrepresentative growth of vegetation will yield samples influenced by photosynthesis and respiration.

It is desirable to avoid land-water boundaries, e.g. banks or shorelines for sampling because the water is less likely to be representative of the main body.

4.7 Sampling Facilities

There is a range of sampling facilities possible and their availability will be limited by local circumstances. They all have advantages and disadvantages and are described below.

<u>Bridges</u>

Sampling from bridges is usually preferred by sample collectors because of their ease of access, the exact identification of the sampling point, the ability to control the lateral and vertical positions of sampling and the capability to sample safely under all conditions of flow and weather. Disadvantages are hazards from road traffic, and difficulties with river traffic particularly as sampling is normally carried out on the down stream side of the bridge. Hydraulic conditions may assist in mixing and can enhance the dissolved oxygen content if there is an appreciable deficit but this is rarely significant. Bridge sampling is normally the most expeditious and economical form of river sampling.

<u>Boats</u>

Boats provide a more flexible form of sampling, permitting it to be carried out at any point along or across the river. It is, however, necessary to accurately identify the sampling point usually by reference to one or more land marks. Care is necessary to ensure that the boat does not disturb bottom sediments which may be included in the sample. There may be hazards from other navigation as also from high flows or storm conditions and lifejackets should be available. The time of travel of a boat between stations is protracted and the flexibility of boat travel is offset by the fewer stations which can be sampled. A quicker alternative, provided suitable launching sites are available, is to use a small boat trailed behind a car, or a boat may be left permanently near the sampling station.

<u>Wading</u>

Where rivers are sufficiently shallow it is possible to take samples by wading. They must be taken upstream of the wader who inevitably disturbs the bottom. This can result in representative samples but it can be less satisfactory for the sampler who should use a staff and may consider it desirable to wear a lifeline anchored to the bank.

<u>Bankside</u>

This form of sampling should only be used when no alternative is possible. The sample should preferably be taken where the water is turbulent, or from the outside bank of a bend where the water is usually fast and deep. The sampler should always wear a lifeline firmly attached to land.

Cable ways

Cable ways used for current velocity measurements can also be employed quite satisfactorily (with adaptation for river sampling). Their use is restricted to smaller rivers.

Helicopter

Sampling by helicopter has the advantage of flexibility, for a sample may be taken at any point on a river or lake, however difficult of access, and its other great advantage is its speed. It is possible to visit and sample at a large number of stations in a short time and the operation of sampling is easy and quick. Tests indicate that the disturbance of the water does not affect the dissolved oxygen concentration significantly. The cost is high but should be considered in relation to the total cost of sampling and analysis of the number of samples.

## 4.8 Sampling Devices

Whenever possible, it is recommended to sample with a winch and a horizontal sampling bottle that can be closed by sending a messenger. The bottle material and its cleanliness must meet the requirements set up for the analysis of trace substances. As an example, plastic devices should be avoided when carrying out trace organic analyses. More information on sampling equipment may be obtained in Chapter II.

# 5.0 SITE REQUIREMENTS FOR LAKES

## 5.1 General Characteristics

A lake may be defined as a partially enclosed body of fresh water surrounded by land; it may be of natural or artificial origin e.g., reservoirs.

The behaviour of lake water is subject to a wide range of influences operating over three dimensions unlike river water which is often virtually unidimensional. Because of the complexity of the behaviour of lake water the factors giving rise to spatial and temporal variations in the distribution of the quality of lake waters are given in detail.

A lake may be characterised by morphometric, hydrological, chemical, biological and sedimentological parameters depending on its age, history, climate, and water budget. Each lake will develop its own response to these combined factors causing major variations of water quality in both space and time.

## 5.2 Water Budget

The composition of the water in the lake will be influenced by the water budget - that is, by the balances between inputs and outputs. The water budget is not the sole deciding factor however because there is an interchange between sediment and water and a build up of organic matter by biological activity.

The major inputs are usually tributary rivers and streams which may carry a range of materials of both natural and artificial origin. There may be point discharges directly into the lake of both sewage and industrial wastes. There will also be diffuse discharges from land drainage influenced by agricultural activities. There may also be sub-lacustrine water from underground sources and rainfall may introduce foreign matter. The measurement of input from these latter diffuse sources is, of course, difficult.

Most of the outputs are a direct reversal of inputs, along similar pathways. The major output will be the river through which the lake water discharges, and there may be abstractions for public and industrial use. The abstracted water after use may be returned to the lake but is sometimes diverted to the outlet river. There may also be sub-lacustrine movement of water out of the lake into adjoining aquifers. Finally there will be loss of water from evaporation.

The theoretical time for retention or residence time of the lake will be the total water inputs divided by the lake volume. It can vary from some months for shallow lakes to several decades and more for the greatest and deepest lakes. The residence time is the minimum time taken to reach equilibrium after a major change in input. In practice this rarely occurs unless the lake is fully mixed. The degree of mixing will vary according to the configuration of the lake and the location of the inlets and outlets. Where the lake is elongated or dendritic, with many branches, or consists of a number of basins, lateral mixing will be poor and related variations in water quality will occur. Stratification of the water will also reduce the effective volume of water available for dilution of a changed input.

## 5.3 Trophic Classification of Lakes.

When considering the primary production, four major types of lakes can be distinguished:

<u>Oligotrophic</u>: Nutrient (mostly phosphorous and nitrogen compounds) materials are present in small concentrations and limit the biotic production to low levels. The rate of decay of organic matter balances its production.

<u>Mesotrophic</u>: The supply of nutrients is increased and there is a corresponding increase in biota and organic matter which begins to accumulate. Bottom oxygen is not always found at saturation.

<u>Eutrophic</u>: The lake become rich in nutrients, biota flourish and organic matter accumulates at a high rate, largely as bottom deposits, which consume the oxygen of bottom waters, sometimes completely.

<u>Dystrophic</u>: There are excessive accumulations of organic matter mostly of humic nature that limit biological activity. Most of these lakes are shallow and acidic and are in the process of becoming marsh.

These four types can occur naturally and there is sometimes a slow trend from oligotrophy to eutrophy due to natural processes resulting from filling and ageing.

When nutrients inputs increase - through atmospheric precipitations, rivers, direct runoff, collected wastewaters, groundwaters etc. - as a result of various human activities, there is a rapid change towards the eutrophic stage, which depends mostly on the input rate of nutrient (phosphorous mainly) per unit lake area and on the water residence time. This enhancement of a natural process can be considered as an organic pollution. Its effects are, among others, anoxia of bottom waters, decrease of transparency, increase in particulate organic matter in surface waters, changes in plankton and fish species etc.

5.4 Stratification and Water Mixing.

Another characteristic of lakes which will influence sampling procedures is thermal stratification caused by the influence of temperature on water density (the maximum density of water is at 4°C).

In temperate regions, during spring and summer the surface layers of the water become warmer and their density decreases. They float upon the colder and denser layer below and there is a resistance to vertical mixing. The warm surface layer is known as the epilimnion and the colder water, which is trapped underneath is the hypolimnion. The epilimnion can be mixed by wind and surface currents and maintains a fairly even temperature. Between the two layers is a shallow zone where the temperature changes from that of the epilimnion to the temperature of the hypolimnion. This zone is called the metalimnion or the thermocline. The hypolimnion does not undergo direct reaeration from the atmosphere and may become depleted of dissolved oxygen if the levels of organic matter are high. Under anoxic conditions reduction of various compounds in the sediments can occur converting them into soluble reduced forms which diffuse into the hypolimnion. Substances produced in this way include ammonia, nitrate, phosphate, sulphide, silicate, iron and manganese compounds.

As the weather becomes cooler, the temperature of the surface layer falls and the thermocline sinks even lower. When the surface layers reach a temperature at which they are denser than the water of the hypolimnion there is an "overturning" of the lake water, which occurs quite quickly and results in a vertical mixing of the lake water.

Thermal stratification does not usually occur in large lakes unless the depth is at least 10 meters and in very deep lakes it may persist throughout the winter. It does not normally arise in small shallow lakes, particularly where there is a high rate of flow through.

If a lake becomes covered with ice an inverse thermal stratification can occur with a layer of colder water on top of the main body at 4°C. When a lake is frozen over rearation virtually ceases and anoxic and reducing conditions can arise.

In tropical and equatorial regions, deep lakes are usually stratified throughout the year. This permanent stratification results in a natural and continuous anoxia of bottomwaters (meromixis). Shallow tropical lakes may, on the other hand, be mixed completely several times a year.

The frequency of the overturn and the consequent mixing depends upon the local climate and lakes may be classified on this basis:

1. Monomictic - once a year - temperate lakes that do not freeze
2. Dimictic - twice a year - temperate freezing lakes
3. Polymictic - several times a year - shallow temperate or tropical lakes
4. Amictic - poor mixing - deep tropical lakes
5. Meromictic - incomplete mixing - mainly amictic lakes but sometimes deep monomictic and dimictic lakes

Lateral mixing is influenced by wind generated currents but the effect is usually confined to the surface layers.

5.5 Seasonal and Vertical Variations of Biological Activity.

The biota in the lake will greatly influence the quality of waters, the effect varying according to the age of the lake. The activity of most immediate consequence is photosynthesis carried out, mainly by phytoplankton, in the upper layer of the lake (the trophogenous zone, which generally corresponds to the warm waters of the epilimnion). This results in an uptake of nutrients such as nitrogen, phosphorous and silica with a production of oxygen and an adsorption of carbon dioxide, free or combined, giving rise to an increase in pH value.

In cold and temperate regions, the photosynthesis cycle follows a marked seasonal pattern with a winter minimum and a summer maximum, while in the tropics the algal productivity, and its influence on water chemistry,is more evenly distributed.

In bottom waters, the bacterial degradation of the algal detritus that "rains" from the trophogenous zone leads to a regeneration of inorganic nitrogen, phosphorous, an increase of $CO_2$, a shift towards acidic pH, and, most of all, a decrease in oxygen. This $O_2$ depletion is directly related to the amount of organic detritus that recycles the bottom waters and inversely linked to the extension of the hypolimnion.

At the turnover periods, the lake water quality is homogenous from top to bottom, except for meromictic lakes where only the top layer is mixed. The lake chemistry is therefore more complex than in rivers and groundwaters and results from external (water inputs, chemistry, water balance and evaporation) and internal processes (biological activity, water mixing) which lead to marked temporal and vertical water quality variations.

5.6 Selection of Sites

When selecting a lake/reservoir station, there should be a comprehensive collection of information and an appraisal of the information requirements. There will be a need for data on the lake characteristics such as volume, surface area, mean depth, water renewal time together with such information as is available on the thermal, bathymetric, hydraulic and ecological characteristics.

There is usually a high degree of dispersion and dilution of discharges into a lake and sampling stations concerned with specific may measure and detect impacts more readily if they are located fairly close to the influent or effluent point. The data from such stations will be restricted to more local uses.

For the GEMS/WATER programme, because of good lateral mixing and the volume of water involved, a single station near the centre of the lake will normally be adequate for the monitoring of baseline or trend conditions. If the lake is divided into bays or basins more than mor station will be needed. As a guideline, the number of sampling points could be equal to the rounded value of the log of the lake area in $km^2$.

A preliminary survey will be necessary and should ideally be based upon a network grid or transects but the work involved is considerable and a more limited survey should suffice. Study of the collected information should give indications as to the most suitable areas for sampling for specified purposes and checks at one or two points in these areas should demonstrate their value. In selecting stations it should be borne in mind that the time taken and the labour involved in sampling at a lake station is greater than the sampling of river or groundwater stations.

5.7 Lake Sampling and Depth Profiles.

Lake sampling is normally carried out from a boat. The station is usually identified from a combination of landmarks on the shore and depth profiles with echo sounding. Precise identification of the station each time is not easy but this is usually immaterial because of the good lateral mixing.

A number of samples will need to be taken at vertical intervals. This is described in Chapter II. The following minimum programme is recommended:

- two depths (surface and bottom) if lake depth does not exceed 10 m;
- three depths (surface, thermocline and bottom) for lakes not deeper than 30 m;
- four depths (surface, thermocline, upper hypolimnion, bottom) for lakes of at least 30 m depth;
- in lakes deeper than 100 m additional depths may be considered.

6.0 SITE REQUIREMENTS FOR GROUNDWATER

6.1 Ground Characteristics

The aquifer

Groundwater is held in porous rock such as sandstone, in porous sediments such as sands or gravels or in the fissures of fractured rock such as limestone. The body of rock or sediments containing the water is described as an aquifer and the upper water level in the saturated body is termed the water table. The media in an aquifer are characterised by porosity and permeability. Porosity is the ratio of pore and fissure volume to the total volume of the media. It is measured as percentage voids and denotes the storage or water holding capacity of the media. Permeability is a measure of the ease with which fluids in general may pass through the media under a potential gradient and it indicates the relative rate of travel of water or fluids through media under given conditions. For water it is termed hydraulic conductivity. The following table gives the porosity and hydraulic conductivity for a number of typical media.

Table 2: Ranges of porosity and hydraulic conductivity for selected porous media

| Material | Porosity % | Hydraulic Conductivity cm/sec at 20°C |
|---|---|---|
| Clay | 45 - 55 | $10^{-4}$ - $10^{-10}$ |
| Silt | 40 - 50 | $10^{-3}$ - $10^{-7}$ |
| Sand | 30 - 40 | $10^{-1}$ - $10^{-4}$ |
| Gravel | 30 - 40 | $10^{-1}$ - $10^{-2}$ |
| Sandstone | 10 - 20 | $10^{-5}$ - $10^{-7}$ |
| Limestone | 1 - 10 | $10^{-7}$ - $10^{-9}$ |

Unless the aquifer contains connate waters, i.e., strongly linked to minerals, the groundwater is part of the hydrological cycle although its time span may extend over many years.

Soil

Overlying the inorganic rock of the aquifer is a layer of soil containing 5 - 10% of organic matter. The inorganic component of the soil consists of particles of a wide range of sizes and the organic matter comprises animal and plant debris in varying stages of decomposition. The soil is inhabited by a large variety of living organisms. There is a great diversity of soil types but they all influence the character of the water as it percolates through the soil down into the aquifer.

### 6.2 Influences on Groundwater Quality

The quality of the water abstracted or emerging from an aquifer depends upon the composition of the water recharged into the ground, the interaction between the water and the media of the aquifer and the reactions which take place in the aquifer. The overlying soil also plays an important role particularly in physical filtration and biochemical reactions.

There are a number of subterranean interactions that may cause a removal of dissolved substances or a change in their composition. These are summarised below.

Physical Processes

1. Dispersion (dilution) - the dispersion capacity is directly dependent upon groundwater velocity i.e., hydraulic conductivity and gradient, and inversely proportional to porosity.

2. Filtration - its efficacy depends upon the particle size of the soil and aquifer.

3. Gas movement - assists in maintaining aerobic conditions and biochemical oxidation.

Geochemical Processes

1. Complexion - increases the ionic species in the water.

2. Acid/base reactions - most constitutents increase in solubility with decreasing pH value.

3. Oxidation/reduction - for example under reducing conditions iron and manganese become more soluble, chromium less soluble, nitrogen compounds and other substances may be reduced. Under oxidising conditions nitrogen compounds may be oxidized and iron and manganese become less soluble.

4. Precipitation/solution - reactions between cations and anions may lead to precipitation or to solution, e.g. calcite or $CaCO_3$.

5. Adsorption/desorption - ions and molecules may be retained and released according to concentrations in the water.

Biochemical Processes

1. Decay and respiration - microorganisms may oxidise and decompose a wide variety of organic and some inorganic chemicals.

2. Cell synthesis - nutrients may be taken up and their movement in the ground retarded.

Some of these processes can remove or destroy certain pollutants e.g., decomposition of organic substances, but others such as adsorption merely delay the onward passage of pollutants. Nevertheless such action reduces their maximum concentration in the water and can be of value when spasmodic or irregular variations in quality occur.

6.3 Artificial Influences

Pollution of underground water arises most commonly from the percolation of polluted water from the surface and the various actions and interactions described provide a considerable degree of protection for underground water, more particularly for that drawn from deep parts of the aquifer. However when polluted water does penetrate to the point of abstraction the consequences are serious. Because of the slow rate of travel of the water in the aquifer and the large volume of subterranean water there is usually a considerable time lag between the casual activity and the appearance of the pollutant in the abstracted water. This will vary according to the hydraulic conductivity, the hydraulic gradient and the porosity. For similar reasons the time required to flush out the polluted water will be long, even longer because of the "drag out" effect. Under such circumstances the recovery process is sometimes regarded as irreversible and the source abandoned.

Artificial pollution of groundwater may arise from either diffuse or point sources. The more common sources are given in Table 3.

Table 3: Artificial Sources of Groundwater Pollution

| Type of Pollution | Point Sources | Diffuse Sources |
|---|---|---|
| Domestic Sewage | Cesspool and septic tank | Artificial recharge with treated sewage |
| | Leakage from sewage systems | Excessive distribution of sludge on farm lands |
| | Infiltration from stabilization ponds | |
| Domestic Solid Waste | Leachate from garbage waste disposal and sanitary land fills | |
| Agriculture Wastes | From animal feedlot areas | Rainwater, irrigation water and the solution of fertilizers and biocides |
| Industrial Wastes | Leaching from industrial waste sites | Disposal of industrial wastes by by land irrigation |
| | Disposal of industrial wastes including cooling water by discharge into boreholes | |
| | Accidental spillages during use, storage or transport | |
| | Leakage from tanks and pipelines | |
| General | | Artificial recharge with surface water |
| | | Natural recharge by polluted river, lake or rain water |
| | | Intrusion of saline water from sea or other aquafers following overpumping |

## 6.4 Selection

The planning programme given in Figure 1 is, with some modification, applicable to the selection of sites for groundwater monitoring stations. It will be necessary to obtain hydrogeological information, as far as it is available, and to seek specialist advice in this field throughout the planning sequence.

The first step will be the choice of aquifer and its relative importance will be assessed from its total yield, the population served, its value to industry and agriculture and the magnitude of threats to its water quality.

The assembled information about the aquifer should describe its hydrological situation, i.e. the location, depth and area of the aquifer and its geological and mineralogical characteristics. Water levels, hydraulic gradients, transmissivity and velocity and direction of water movements should be known. Wherever possible information should be illustrated by plans, profiles and diagrams. In some countries the information available may be incomplete and stations may have to be accepted in the hope that the information can be obtained later.

Background information will be needed on existing and potential influences on water quality. Details of land use should be recorded and Table 3 will serve as a guide to the appropriate information.

An inventory should be drawn up of all the wells, boreholes and springs fed by the aquifer together with information on their quality and its monitoring.

The larger and more uniform the aquifer the more representative will be the samples from a single station. The choice of station will usually be restricted to existing abstraction points or springs. It may however be decided to incur the cost of drilling new boreholes either to provide information on the quality of water of a potential new source or to act as advance warning impact stations by interposing them between a major pollution hazard and an important abstraction point. The proximity of the sampling station to the laboratory will be a consideration.

The area covered by a well will vary with its yield. A high yielding well of, say, 2 cubic metres per minute will draw its water from a large area whereas a smaller yielding well of, say, 0.2 litres per second will produce water representative only of local conditions. A high yielding well, because its heavy drawdown affects hydraulic conditions, may influence indirectly the quality of the water withdrawn.

It is unlikely that groundwater which contains any of the specified dangerous substances will be withdrawn for use. Where wastes containing any of those substances have been used for recharge or where the natural geochemistry suggests their possible presence the water should be examined for those substances.

Where information about the quality of water withdrawn from the selected aquifer is inadequate, attempts should be made to carry out an analytical survey of existing wells. The data so obtained will, in conjunction with the inventories and background information, assist in the choice of a representational sampling pattern.

## 7.0 ANNEXES

### 7.1 BASIC INFORMATION ON RIVER SAMPLING STATIONS

[GENERAL]

1) Name: ____________________

2) Country, continent: ____________________

3) Longitude and latitude of sampling site: ____________________

4) Altitude:_______ m above sea level.

5) Local reference of position (name of nearby village, bridge, etc):____________________

6) Distance in river length:
from the source: ________ km; above tidal limit: ________ km;

7) Major drainage basin to which the river belongs: ____________________

8) Countries pass through:
upstream of station: ____________________

downstream of station: ____________________

9) GEMS/Water station type (Baseline, Trend, Global River Flux): ____________________

10) GEMS/Water station code: ____________________

[RIVER CONDITIONS]

11) Width of river at sampling station:

average: ________ m; maximum: ________ m; minimum: _______ m.

12) Depth of river at sampling station:

average: ________ m; maximum: ________ m; minimum: _______ m.

13) Character of river banks (accessibility etc.): ____________________

____________________

14) Nature of river bottom: ____________________

____________________

15) Aquatic vegetation: ____________________

____________________

16) River velocity (at middle):

average: ____________ cm/s; maximum ________ cm/s; minimum __________ cm/s.

17) Nearest flow gauging station (location, type and distance from water quality sampling station): ____________________

____________________________________________________________

18) WMO code of flow gauging station (where appropriate): ____________________

19) Best available means of assessing flow at point and time of sampling: ____________________

____________________________________________________________

20) Rate of flow:

average: ________ $m^3/s$; maximum: __________ $m^3/s$; minimum ____________ $m^3/s$;

21) Rate of flow when full to the bank (flood point): __________ $m^3/s$

22) Extent and seasonal regularity of flow variations (natural or regulated): ____________________

____________________________________________________________

23) General water characteristics (hardness pH, salinity, humic substances, suspended matters, etc.): ____________________

____________________________________________________________

____________________________________________________________

____________________________________________________________

[DRAINAGE BASIN]

24) Upstream drainage basin area: ________ $km^2$.

25) Geological characteristics (use e.g., Koppen classification): ____________________

____________________________________________________________

____________________________________________________________

26) Geological characteristics (upstream basin): ____________________

____________________________________________________________

____________________________________________________________

____________________________________________________________

27) Land characteristics, upstream basin (natural vegetation, forestry, agriculture, urbanization, etc.): ____________________

____________________________________________________________

____________________________________________________________

28) Population in the upstream basin (year of reference): ________________ (19__).

29) Main cities upstream of sampling site: ______________________________________________

______________________________________________________________________

______________________________________________________________________

[ANTHROPOGENIC INFLUENCE FACTORS]

30) Main water body utilizations (drinking and domestic, agricultural, industrial, recreation, navigation, fisheries etc.):________

______________________________________________________________________

______________________________________________________________________

31). Nearest significant pollution input (type, distance, control measure): ______________________________

______________________________________________________________________

______________________________________________________________________

32) Other pollution types (specify), characteristics and trends, and control measures: ________________________

______________________________________________________________________

______________________________________________________________________

______________________________________________________________________

______________________________________________________________________

33) Water abstractions (location, type of use, volume, number of people served, surface irrigated): ______________

______________________________________________________________________

______________________________________________________________________

______________________________________________________________________

______________________________________________________________________

34) Natural conditions influencing water quality: ________________________________________

______________________________________________________________________

______________________________________________________________________

35) Other relevant explanatory informations (narrative, no figures): ________________________________

______________________________________________________________________

______________________________________________________________________

[SAMPLING AND ANALYSIS]

36) Water quality variations over cross-section (checks for homogeneity): __________

37) Location of sampling point in river: __________

38) Depth at which sample is taken: __________ m.

39) Method of sampling (from boat, bridge etc.): __________

40) Sampling equipment used: __________

41) Sampling difficulties due to extremes in flow (frequency and seasons): __________

42) Accessibility of sampling station: __________

43) Frequency of routine sampling: __________

44) Laboratory carrying out analysis: __________

45) Distance from laboratory, means of sample transport and normal time: __________

46) List of determinations carried out at sampling site, and methods used: __________

47) Average time elapsing between sampling and commencement of analysis in laboratory: __________

48) Sample storage conditions: __________

49) List of determinations carried out routinely and methods used: ______________________

_____________________________________________

_____________________________________________

_____________________________________________

_____________________________________________

50) List of determinations carried out occasionally and methods used: ______________________

_____________________________________________

_____________________________________________

_____________________________________________

_____________________________________________

51) Significant trends and changes in water quality parameters during past years: ______________________

_____________________________________________

_____________________________________________

_____________________________________________

_____________________________________________

52) Completed by: ______________________ 53) Date: ______________________

## 7.2 BASIC INFORMATION ON LAKES AND RESERVOIRS SAMPLING STATIONS

[GENERAL]

1) Name: ______________________________

2) Country, continent: ______________________________

3) Approximate latitude and longitude (ranges for large lakes): ______________________________

______________________________

4) Altitude: ______________m above sea level.

5) Local reference of position (name of nearby village etc.): ______________________________

6) Location of sampling site in the lake relative to shore: ______________________________

7) Countries bordering the lake: ______________________________

8) River basin to which the lake belongs: ______________________________

9) Origin: ______________________________

10) Lake type (for reservoirs, types and the year of construction): ______________________________

______________________________

11) GEMS/Water station type (Baseline, Trend): ______________________________

12) GEMS/Water station code: ______________________________

[LIMNOLOGICAL]

13) Surface area: ______________ $km^2$.

14) Maximum length: ______________ km.

15) Maximum width: ______________ km.

16) Length of shoreline: ______________ km.

17) Volume: ______________ x 10 $km^3$.

18) Maximum depth: ______________ m.

19) Mean depth: ______________ m.

20) Thoretical filling time (= water volume/annual inflow): ______________ yr.

21) Names (mean discharge rates) of main tributaries and outlets:

Tributaries: ____________ ( m³/sec), ______ ( m³/sec) ____________

____________ ( m³/sec) ____________

Outlets: ____________ ( m³/sec) ____________

22) Annual water level variation: ________ m ___ natural ___ regulated.

23) Main upstream and downstream water bodies (in case of lake chain):

Upstream: ____________

Downstream: ____________

24) Freezing period: ____________

25) Stratification type and cycle: ____________

____________

26) Water characteristics (hardness, chemical type, pH type, salinity, humic substances, suspended matter, turbidity, etc.): ____

____________

____________

____________

27) Transparency ___ high ___ medium ___ low

28) Trophic characteristics: ___ oligotrophic ___ mesotrophic

___ eutrophic ___ hypertrophic ___ dystrophic ___ others ( )

29) Trends (optional figures of mean P, N and chlorophyll contents) may be given: ____________

____________

[DRAINAGE BASIN]

30) Drainage basin area (except lake area): ____________ $km^2$.

31) Maximum altitude: ____________ m.

32) Mean altitude: ____________ m.

33) Climatic characteristics (use e.g., Koppen classification): ____________

____________

____________

34) Geological characteristics: ______________________________

______________________________

______________________________

35) Land characteristics (main natural vegetation, forestry, agriculture, urbanization, etc.): ______________

______________________________

______________________________

______________________________

36) Population in the basin (year of reference): ______________________ (19 )

37) Main cities directly on lake (figures optional):

______________________________

[ANTHROPOGENIC INFLUENCE FACTORS]

38) Main water body utilizations (drinking and domestic, agricultural, industrial, recreation, navigation, fisheries etc.):

______________________________

______________________________

39) Pollution types (characteristics and trends) and control measures:

______________________________

______________________________

______________________________

______________________________

40) Water abstractions (location, type of use, volume, number of people served, surface irrigated etc.):

______________________________

______________________________

______________________________

41) Other relevant explanatory information (narrative, no figures):

______________________________

______________________________

[SAMPLING AND ANALYSIS]

42) Depth(s) at which samples is taken: ______________ m.

43) Method of sampling (from boat, bridge etc.): ______________________________

44) Sampling equipment used: ______________________________

45) Sampling difficulties (due to weather conditions, etc.): ______________________________

______________________________

46) Accessibility of sampling station: ______________________________

______________________________

47) Frequency of routine sampling: ______________________________

48) Laboratory carrying out analysis: ______________________________

______________________________

49) Distance from Laboratory, means of sample transport and normal time: ______________________________

______________________________

50) List of determinations carried out at sampling site and methods used: ______________________________

______________________________

______________________________

______________________________

51) Average time elapsing between sampling and commencement of analysis in laboratory: ______________________________

52) Sample storage conditions: ______________________________

______________________________

53) List of determinations carried out routinely and methods used:

______________________________

______________________________

______________________________

______________________________

______________________________

54) List of determinations carried out occasionally and methods used:

______________________________

______________________________

55) **Significant trends and changes in water quality parameters during past year:** ____________________

______________________________________________

______________________________________________

______________________________________________

56) **Completed by:** ______________________________________________

57) **Date:** ______________________________________________

## 7.3 BASIC INFORMATION ON GROUNDWATER STATIONS

[GENERAL]

1) Station name (or name of geographical area): ______________________

2) Country, continent: ______________________

3) Longitude or latitude: ______________________

4) Altitude: ____________ m above sea level.

5) Local reference of position (name of nearby village etc.): ______________________

6) Location of site in aquifer: ______________________

______________________

7) Countries covering aquifer: ______________________

______________________

8) GEMS/Water station code: ______________________

[CHARACTERISTICS OF AQUIFER]

9) Aquifer type (confined or unconfined): ______________________

10) Aquifer size and extent: ____________ $km^2$, ______________________

______________________

11) Climatic characteristics: ______________________

______________________

12) Geology of aquifer: ______________________

______________________

13) Topography of surface area over aquifer: ______________________

______________________

14) Direction of water flow in aquifer: ______________________

______________________

15) Estimation of population in area covering aquifer: ______________________

16) Additional information on aquifer: ______________________________

______________________________

______________________________

______________________________

[ANTHROPOGENIC INFLUENCE FACTORS]

17) Pollution sources potentially influencing water quality (type and magnitude of pollution threat): ______________

______________________________

______________________________

______________________________

18) Other conditions influencing water quality in aquifer: ______________________________

______________________________

______________________________

______________________________

19) Water abstractions from aquifer (location, type of use, volume, number of people etc.): ______________

______________________________

______________________________

______________________________

20) Water abstractions from station (type of use, volume, number of persons, etc.): ______________

______________________________

______________________________

21) Number of wells within 5 km radius of sampling station: ______________________________

22) Total yield of wells within 5 km radius of sampling station: ______________________________

23) Groundwater level under static condition: ______________________________

24) Groundwater level during normal withdrawal: ______________________________

25) Seasonal variations in groundwater level at station: ______________________________

______________________________

______________________________

**[SAMPLING AND ANALYSIS]** (for reference see Figure 2, Page 29)

26) Type of abstraction at station (drilled well, dug well, spring): ______________________________

27) Method of groundwater withdrawal: ______________________________

28) Ground level of sampling station: ______________m above sea level.

29) Depth of impermeable lining in sampling well: ______________m.

30) Mean abstraction level: ______________m above sea level.

31) Mean abstraction rate: ______________$m^3$/day.

32) Sea water intrusion: ______________________________

______________________________

______________________________

33) Methods of sampling (equipment used): ______________________________

______________________________

34) Frequency of routine sampling: ______________________________

______________________________

35) Laboratory carrying out analysis: ______________________________

______________________________

______________________________

______________________________

36) Distance of station from laboratory, means of sample transport and normal time: ______________

______________________________

37) List of determinations carried out at sampling station and methods used: ______________

______________________________

______________________________

______________________________

______________________________

38) Average time elapsing between sampling and commencement of analysis in the laboratory: ______________

______________________________

39) Sample storage conditions: ______________________________________________

______________________________________________

40) List of determinations carried out routinely and methods used: ______________________

______________________________________________

______________________________________________

______________________________________________

______________________________________________

41) List of determinations carried out occasionally and methods used: ______________________

______________________________________________

______________________________________________

______________________________________________

42) Significant trends and changes in water quality parameters during past years: ______________

______________________________________________

______________________________________________

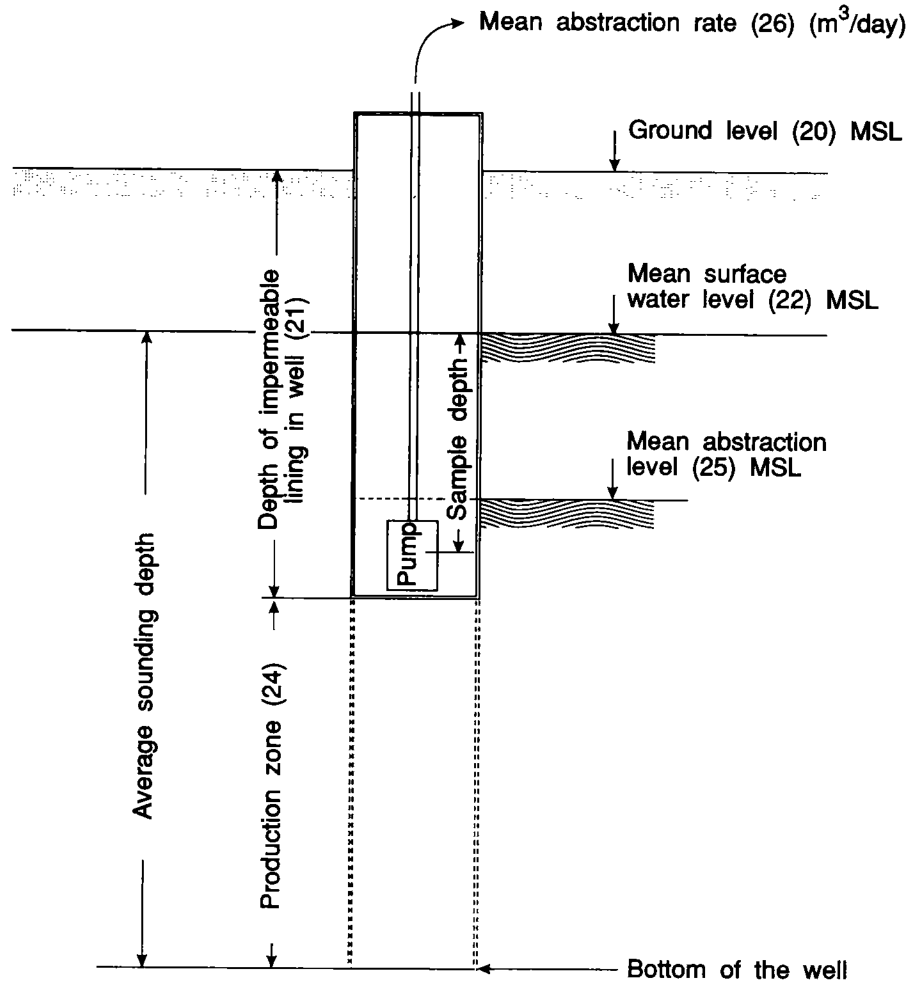
______________________________________________

______________________________________________

43) Completed by: ______________________________________________

44) Date: ______________________________________________

Figure 2: Schematic representation of groundwater levels




Notes:

1. All levels are expressed in meters above the mean sea level (MSL)
2. Depth of impermeable lining in well (21) is measured from the ground level (20)
3. Average sounding depth is measured from the mean water surface level (22)
4. The production zone (24) can also be the total thickness of the aquifer layers at different depths

UNEP/WHO/UNESCO/WMO PROGRAMME ON GLOBAL WATER QUALITY MONITORING AND ASSESSMENT

GEMS/WATER OPERATIONAL GUIDE

# CHAPTER II: SAMPLING FREQUENCIES AND METHODS

Revised by the WHO Collaborating Centre for Surface and Ground Water Quality

National Water Research Institute
Canada Centre for Inland Waters
Burlington, Ontario
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## 1.0 INTRODUCTION

The collection of water samples may seem a relatively simple task. However, more than the simple dipping of a container into water is required to obtain representative water samples and to preserve their integrity until they are analyzed in the laboratory. A representative sample can be easily obtained from rivers and lakes which are relatively homogeneous, whereas many bodies of water have significant spatial and temporal variations and the collection of a representative sample becomes much more complex. The procedures in this manual will aid investigators in collecting reliable, representative water samples.

The sections on water sampling equipment are not intended to be all-inclusive but rather to introduce common sampling equipment. Furthermore, instructions for operating sampling and field measurement equipment are not intended to replace those of the manufacturer but are to be considered as supplementary information. The sample containers, preservatives, sampling and field measurements procedures described in this manual reflect those most widely used for physical, chemical and microbiological analyses.

The quality of data collected depends first and foremost on how good the sample is, e.g., how well it represents the quality of the body of water from which it was collected and whether or not contamination has been avoided. Using the most reliable techniques for collecting samples and for making field measurements contributes to the good quality of the data, increases its precision and accuracy and contributes to the overall improvement of the water quality management process.

This chapter is the joint effort of national collaborators in the GEMS/Water programme and draws heavily on the sampling practices and experiences of the Water Quality Branch, Inland Waters Directorate of Environment Canada.

### DISCLAIMER

The inclusion of trade names, commercial products or manufacturers in this manual is for illustration purposes only and does not constitute endorsement.

## 2.0 FREQUENCY AND TIME OF SAMPLING

### 2.1 Variability of Water Quality

The quality of water in various water bodies is rarely if ever constant in time but is subject to change. While there may be some relationship between the rate of change of different variables others alter independently. In measuring the mean, maximum and minimum values of variables over a period of time the closeness of the monitored values to the true values will depend upon the variability of the variable and the number of samples taken. The larger the number of samples from which the mean is derived the narrower will be the limits of the probable difference between the observed and true means. These confidence limits are not directly proportional to the number of samples but to the square of the number. In order to double the reliability of a mean value the number of samples must be increased four fold.

### 2.2 Variability Characteristics

Variations in water quality are caused by changes (increase or decrease) in the quantity on the concentration of any of the inputs to a water body system. Such changes may be natural or man-made and either cyclic or random. Water quality variation may therefore be similarly cyclic or random. Since it is possible for some changes to occur in combination the reasons behind variations may sometimes be obscured.

#### 2.2.1 Random Variations

These are due to spasmodic, often unpredictable events. Sudden storms will lead to increased flows followed by polluted run off and leachings or to the operation of sewer overflows. Rainfall effects may be modified by flood control arrangements. There may be accidental spillages and leakages. Any of these may occur at any time and without warning.

#### 2.2.2 Cyclic Variations

Annual cycles may be the result of regular rainfall patterns, snow melts and seasonal temperature changes. The seasonal growth and decay of vegetation will also give rise to cyclical changes in the composition of the water and rates of self purification and nitrification are strongly temperature dependent. There may be daily cycles of natural origin particularly that caused by photosynthesis and affecting dissolved oxygen and pH. Industrial, agricultural and domestic activities may cause cyclical changes due to cycles of discharge and abstraction. Hydraulic manipulation of river flow such as by river regulation, or for power generation or navigation purposes tend to be cyclical but can occur randomly.

#### 2.2.3 River

The variability differs between rivers, lakes and ground waters. It is most pronounced in rivers and the ranges will be the greater the nearer the sampling point is to the source or sources of variability. As the distance from the source increases longitudinal mixing smooths out irregularities and fewer samples are needed to meet given confidence limits. However, as the distance between the source of variability and the sampling point increases not only will there be reduction in the range of variation but there will also be dilution and some variables will be reduced by self purification, deposition and adsorption. These effects must be considered if a sampling station used for quality control purpose is located some distance from the area of point of use.

### 2.2.4 Lakes

In lakes the mass of water and good lateral mixing provide an inertia against any rapid changes resulting from modifications in inputs. Many lakes exhibit marked seasonal variations due to thermal stratification, overturn and biological activity. These phenomena are described in Chapter I. Depending upon the type of lake the sampling may be carried out with a seasonal bias related to the natural cycles of the lake.

### 2.2.5 Ground Water

Ground water has a lower variability than that of either rivers or lakes. The rate of quality changes depends upon the depth of sampling, the size and porosity, i.e., the water volume of the aquifer and the hydraulic conductivity. The time elapsing between changes in land use and in surface recharge water and their effect upon the ground water will depend upon the time of percolation. Variations are often, but not invariably, seasonal with a time lag according to the rate of percolation. Direct injection into boreholes or saline intrusion from subterranean sources may take effect more rapidly. (Sources of pollution of ground water are listed in Chapter I.)

## 2.3 Variability of Individual Variables

Some generalizations based on variability studies in rivers can be made. The distribution of the values of a variable at an individual station tends to be normal and such deviations as occur are not usually sufficient to invalidate calculations made on this assumption.

The greatest range of values is found in the suspended solids concentration and the distribution tends to be log normal. This is not unexpected because the values are strongly influenced by extremes of river flow and velocity. Variables which are insoluble and therefore associated with suspended and insoluble substances tend to be less accurate than those for dissolved substances for the same number of samples.

## 2.4 Time of Sampling

If, when cyclic variations occur, the samples are taken at constant intervals coinciding with the period of the cycle and therefore at the same point on the cycle on the cycle the successive results will be directly comparable for the purposes of assessing changes in water quality. Such samples are not, however, representative in time and give no indication of what is happening during the rest of the cycle.

The sampling programme may stipulate random sampling times but they should be spread more or less evenly throughout the year. It is usually easier to organize the cyclic variations. For example whatever time interval is decided it could be based on a multiple of 7 days $\pm$ 1 day so that the sampling day advances or retreats throughout the week. The samples may also roll through the 24 hours by using successive times based on 24 $\pm$ 1. Rolling programmes can lead to problems concerning rest days and night work for both the sample collector and the analyst and some compromises may be needed.

If the time of greatest variability or criticality of water quality is known it may be desirable either to increase the rate of sampling at such times or to divert a larger proportion of the monitoring effort to those times. In rivers such increased sampling may be desirable during low flow conditions in hot and dry seasons, or at times of seasonal or other regular industrial and agricultural activities. Lakes are particularly subject to regular periods of rapid change as a result of thermal stratification and overturning. Ground waters may exhibit regular patterns of quality but rates of change are relatively slow.

## 2.5 The assessment of sampling frequency

The assessment of the sampling frequency needed at a station in order to obtain the required data should be carried out in a planned sequence. The process, described below, may be divided into five stage:

### 2.5.1 Collection of Information

1. The collection of information of all conditions influencing water quality and its variability and on water quality needs according to use. This information will be the same as that required for site selection and described in section 3.2 of Chapter I.

2. The collection of all existing analytical data to assist in assessing the quality variations at the station. Again this information will be the same as that obtained in accordance with Section 3.2 of Chapter I.

2.5.2 Identification of Needs

The next stage is to decide what are the variables of major importance at the station having regard to the water uses and the levels at which they will interfere with existing or proposed uses. These concentrations are, in effect, local ambient quality standards.

2.5.3 Preliminary Studies

It is now necessary to ascertain the existing water quality and its variability characteristics and in particular the concentrations and variations of the variables of major importance at the station as identified at the preceding stage.

It may be that the existing analytical data will suffice but this in unlikely. Bearing in mind the need to optimize the use of valuable sampling and analysis resources it is essential to have adequate, up to date information and an intensive survey should be undertaken to make sure it is available. A comprehensive scheme is described below but its scope may need to be adjusted to accord with the local facilities.

1. Weekly samples for one year.
2. Daily samples on seven consecutive days once in every 13 weeks (4 times during the year).
3. Hourly samples over 24 hours once in every 13 weeks (4 times during the year).
4. Samples collected every 4 hours for a period of seven consecutive days once in every thirteen weeks (42 samples per period).

For surveys of this kind the number of variables may be reduced to lighten the working load and they may well be restricted to the more important variables for the station. Using a combination of the above schemes or a modification appropriate to local circumstances a wide variety of data sets can be obtained.

For example the weekly sampling programme gives the following combinations for determining the statistical characteristics of the annual mean:

| | | |
|---|---|---|
| 1. Sampling weekly | 52 x 2 | 1 set figures |
| 2. Sampling every 2 weeks | 26 x 2 | 2 sets |
| 3. Sampling every 4 weeks | 13 x 4 | 4 sets |
| 4. Sampling every 2 months | (7 x 4) | 8 sets |
| | (6 x 4) | 15 sets |

Sampling programmes 1 and 3 can be subdivided to provide characterisation of annual, quarterly, daily and hourly distributions. Sampling programme 4 provides opportunity to use special analysis for separating the variance components by magnitude and periodicity. It calls for specialist assistance.

The quality at baseline stations where the water is little affected by man's activities is unlikely to show the same degree of variability as rivers carrying used water. Subject to the background information obtained the preliminary survey above could be modified and reduced in intensity.

The initial sampling programme described above covers the sampling of rivers and these exhibit the greatest degree of variability of the three types of water under consideration. The same process and sequence is applicable to lakes and ground waters but the frequency of routine sampling will be less as will the intensity of the preliminary survey.

For lake stations the following preliminary survey is suggested:
1. Five consecutive days during the warmest part of the year.
2. Five consecutive days once every 13 weeks.

For trend stations near to use points, where variability is likely to be greater than in the main body of the lake the survey sampling could be increased.

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

2.5.4 Determination of Sampling Frequency

From the information obtained in the preceding stages it should now be possible to confirm the relative importance of the different variables and to assess the margins which exist between their present levels and the critical, interfering concentration and decide the concentration, and frequencies of their occurrences at which action should be taken. This information will provide a basis for establishing appropriate accuracy and confidence limits for the important and critical variables.

There is general agreement that when the number of samples that can be handled is strictly limited it is preferable to reduce the number of stations rather than to curtail the frequency of sampling. It is better to obtain reliable results from one station than dubious data from two. Table 1 lists the recommended annual sampling frequency for GEMS/Water stations.

Table 1: Recommended annual sampling frequencies for GEMS/Water stations

| STATION TYPES | TYPE OF WATER | | |
|---|---|---|---|
| | RIVERS/STREAMS | LAKES/RESERVOIRS | GROUNDWATERS |
| BASELINE | Minimum: 4, including high and low water stages<br><br>Optimum: 24, i.e. fortnightly sampling, and weekly for total suspended solids | Minimum: 1 at turnover (sampling at lake outlet)<br><br>Optimum: 1 at turnover and 1 vertical profile at end of stratification period | |
| TREND | Minimum: 12 for large drainage area (ca: 100,000 km$^2$)<br><br>Maximum: 24 for small drainage area (ca: 10,000 km$^2$) | EUROPHICATION ISSUE: 12, including twice monthly during summer<br><br>OTHER ISSUES:<br>Minimal: 1 at turnover<br>Maximal: 2, one at turnover, and one at maximum thermal stratification | Minimum: 1 for large, stable aquifers<br><br>Maximum: 4 for small alluvial aquifers<br><br>Karstic Aquifers: same as rivers |
| GLOBAL RIVER FLUX | LARGE BASINS (>200,000 km$^2$) (1)<br>6, for some particulate metals (2)<br>12, for all other variables<br><br>SMALL BASINS (< 200,000 km$^2$) (1)<br>24, for basic monitoring variables (3)<br>12, for expanded nutrients, organic contaminants and some expanded metal monitoring (4)<br>6, for some particulate analysis (2) | | |

(1) For global river flux stations: continuous record of water discharge and weekly sampling for total suspended solids are recommended.
(2) For particulate arsenic, cadmium, chromium, copper, lead, mercury, selenium, zinc.
(3) For temperature, pH, electrical conductivity, dissolved oxygen, calcium, magnesium, sodium, potassium, chloride, sulphate, alkalinity, nitrate plus nitrite, total phosphorus filtered and unfiltered, silica, chlorophyll a, organic carbon dissolved and particulate, organic nitrogen dissolved and particulate.
(4) For dissolved and particulate fractions of aluminum, iron and manganese; and for dissolved arsenic, cadmium, chromium, copper, lead, mercury, selenium and zinc.

### 2.5.5 Operational Experience and Review

If the preliminary surveys have to be deferred until after the commissioning of the sampling station, the following sampling frequencies may be adopted provisionally, in the absence of any indications otherwise:

| | | |
|---|---|---|
| Rivers | - | every two weeks |
| Lakes | - | every two months |
| Ground water | - | every three months |

At the end of the first year the data should be examined statistically and the frequency reviewed. Sampling more frequently than the minimum given above would assist in the evaluation of the first year's data.

The annual re-examination process should in any case be carried out for all GEMS stations. The processed data returned annually by the National Water Research Institute, (Canada Centre for Inland Waters) will include inter alia the arithmetic means and the standard deviations for all variables and it will be a simple matter to calculate the 95% or other confidence limits. The sampling programme for each station should be reviewed to decide whether or not the sampling frequency can be reduced or needs increasing. The calculations, comments and decisions should be recorded and at the same time the station records and background information should be updated.

## 2.6 Measurement of Mass Loadings

Under the GEMS system not only is the concentration of a variable measured but also the corresponding water flow in rivers to enable the mass load to be calculated. The samplings to determine the concentration are normally "spot" or "grab" samples taken over a brief period of the time and the question arises whether or not the associated flow or discharge rates should be instantaneous or average. Comparisons of mass loads calculated using both instantaneous discharge rates and the mean flows during the time since the previous sample did not reveal any significant differences at the 95% confidence level. Comparisons were also made between the use of instantaneous flows and the annual mean flows and the differences were significant. The use of the instantaneous flow figure appears to be preferable.

## 2.7 Special Sampling Procedures

### 2.7.1 Rivers

Sampling difficulties arise when the only acceptable sampling point lies in a non-homogenous, i.e. an unmixed length of a river. Individual samples will not then be representative of a water body. It will be necessary to sample over a cross section of the river to obtain average values and this can be done in a number of ways.

The river is considered in terms of a series of vertical sections across the chosen site. Discrete samples are taken in each section and analyzed separately. The results for each may then be averaged by adding them together and dividing by the number of samples. Alternatively, to save analytical work the samples may be mixed in equal proportions and the analyses of the composite will be the same as the calculated values. This average will be time weighted and ignores the differences in flow between the sections.

It is preferable to obtain flow weighted averages and this involves measuring the volume of flow in each section at the time of sampling. The cross sectional area of each section must be known and velocity profiles for each prepared. The flow in each section is multiplied by the value of the sector, the results for all sectors added and the result divided by the total flow to give the flow weighted average. Again analytical work can be reduced by preparing a composite sample containing sectional samples added in proportion to the sectional flows. The process is time consuming.

If a series of flow weighted averages are taken using analyses of individual samples it may prove possible to derive a mathematical relationship between the analytical results at one, or perhaps a few, sampling points and the flow weighted average. The use of such a relationship would greatly reduce the time and labour involved but the reliability of the result is likely to be somewhat lower. The subject is dealt with in more detail in the section on mass flow computation techniques in the chapter on Hydrological measurements.

### 2.7.2 Lakes

Many lakes exhibit the phenomenon of seasonal thermal stratification which is described briefly in Chapter I on the selection of sampling sites.

When stratification exists a number of samples will be taken vertically in the lake according to the position of the metalimnion or thermocline. A vertical profile of the stratification may be plotted from a series of vertical temperature measurements. Samples should be taken:

1. Immediately below the water surface
2. Immediately above the epilimnion
3. Immediately below the epilimnion
4. Mid hypolimnion
5. One metre above the sediment/water interface

If there is an anoxic zone it is desirable to take at least two samples in this layer. For deep lakes additional samples at say 100m intervals should be taken. When the lake is fully mixed, samples should be taken at least at points 1 and 5 above. If after turnover there is still an anoxic zone lying on the bottom this should be sampled in the neighbourhood of its upper boundary layer also.

### 2.7.3 Ground Water

Ground water samples will normally be taken at existing wells or boreholes. The water should be pumped for a time before sampling to ensure that new water is taken. The water emerging at the surface is often a mixture of waters derived from different strata. This is not of great importance provided the relative contributions from each stratum are fairly constant. If information is required about the quality from the different strata it may be possible to lower a tube or tubes down the borehold and abstract at different levels. Probes to measure conductivity for other variables may be lowered into the well and the variables profile plotted.

The ground water has usually been out of contact with air for a considerable period, dissolved gases may not be in equilibrium with the atmosphere and the emerging water may change its character quite rapidly. Dissolved carbon dioxide may be lost to the atmosphere and cause changes in the pH value of the water. If the water is anoxic, oxygen will be taken up and oxidised iron and manganese precipitated. The samples need to be taken out of contact with air and a bleed pipe from the pump delivery should pass into the sample bottles which should be left to overflow before sealing. As far as possible the analyses should be carried out on site.

## 3.0 COLLECTING SURFACE WATER SAMPLES

The location of sampling stations and the frequency of sampling must be outlined in the project design. They are established from the project objectives, and the spatial and temporal variability of the system. It is the responsibility of the field investigator to locate all sampling stations accurately. It is important to take the sample at exactly the same location each time. Only if the same location is consistently sampled can temporal changes in the water quality variable levels be interpreted with confidence. Therefore, accurate station location descriptions must be prepared on the first visit to every sampling site, and these must be carefully followed by investigators on subsequent visits. The project design must also specify the types of samples which must be collected (e.g. grab, integrated or composite; water, biota, bottom or suspended sediment) and the field or *in situ* measurements which must be taken at each location.

It is recommended that the design of the field sampling program be tested and assessed by a pilot project or in the initial rounds of sampling to ensure both its efficiency and effectiveness 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 the detection limit can be reexamined. Other elements of the sampling program, such as ensuring that an adequate volume of water is collected or that the shipping of samples is adequate, can also be checked during the pilot project.

### 3.1 Types of surface water samples

The type of surface water sample collected is determined by a number of factors, such as:
(1) The objectives of the study, including the variables of interest and the accuracy and precision needed;
(2) The characteristics of the system being studied, including the flow regime, climatic conditions, point and non-point inputs, ground water infusions, tributaries, homogeneity of the body of water, and the aquatic life present.
(3) The resources available, i.e., manpower, time, equipment and materials.

#### 3.1.1 Grab Samples

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

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

#### 3.1.2 Composite Samples

A composite sample provides an estimate of average water quality condition over the period of sampling. Such a sample is obtained by mixing several discrete samples of equal or weighted volumes in one bottle an aliquot of which is then analyzed for the constituents of interest.

The two main types of composite samples are: (1) Sequential or time composite, and (2) flow propertional composite. The time composite sample is made up by continuous, constant sample pumping or mixing equal water volumes collected at regular time intervals. The flow proportional composite is made up by continuous pumping at a rate proportional to the flow, by mixing equal volume of water collected at time intervals which are inversely proportional to the flow, or by mixing volumes of water proportional to the flow collected during or at regular time intervals.

### 3.2 Collecting a Representative Water Sample

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

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 specified, the basic required volume is a summation of the volumes requires for analysis of all the variables of interest.

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

## 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 analyzed. Grab sampler 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. Also, a "multiple" sampler can be used for this purpose. A grab sample may be taken using a "sampling iron," with a appropriate bottle, a Van Dorn bottle, a Kemmerer style bottle, or a pump type sampler. Composite samples can be made from several grab samples or they can be obtained with special 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-integrated sample. A "sampling iron" used for this purpose is briefly described here. Depth integration may not be possible in shallow streams where the depth is insufficient to permit integration.

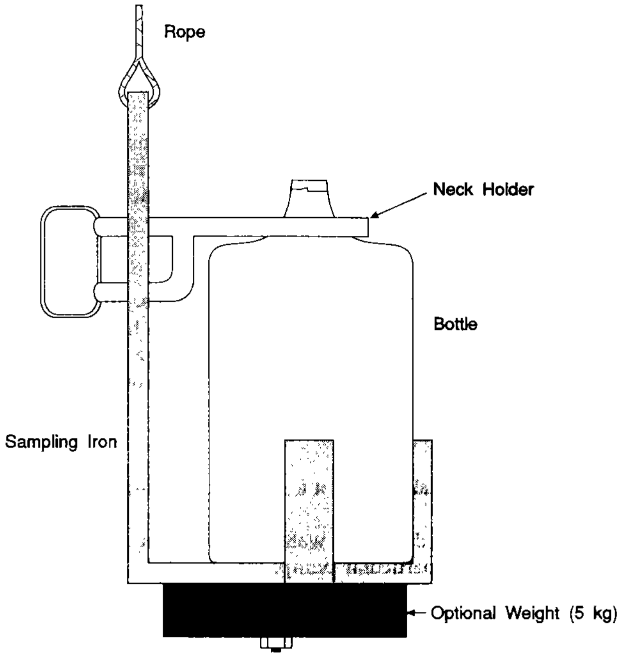


Figure 1. Sampling Iron

A Sampling Iron is a device which is of iron or steel and painted with a rust inhibitor. The weight of the sampler is approximately 2.7 kg (Fig. 1).

Typically, this design permits the use of a 2 litre sample bottle when the bottle neck holder is in the uppermost position; small 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. The Van Dorn bottle is designed for sampling at a depth of 2 m or greater. The sampler, which is shown in its two configurations in Figure 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.

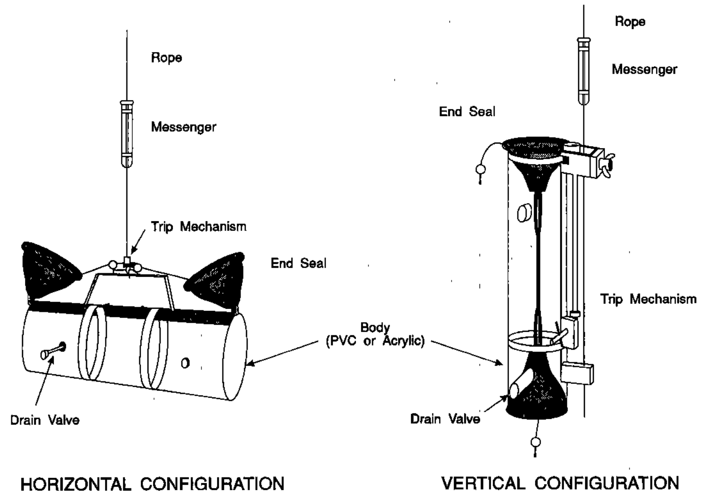


Figure 2. Van Dorn Bottle

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) Activitate 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.

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

Three types of pumps - diaphragm, peristaltic and rotary - are available to collect samples from specified depths. In general, diaphragms pumps are hand-operated; the peristaltic and rotary pumps require a power source and consequently they 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 in-field procedure is:
(a) Place the input hose at the water depth specified by the sampling program. 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.

A "multiple" sampler permits the simultaneous collection of several samples of equal or different volumes at a site. Each sample is collected in its own bottle. When the samples are of equal volume, information concerning the instantaneous variability between the replicate samples can be obtained. A multiple sampler is illustrated in Figure 4. The sampler may be altered to accomodate 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.

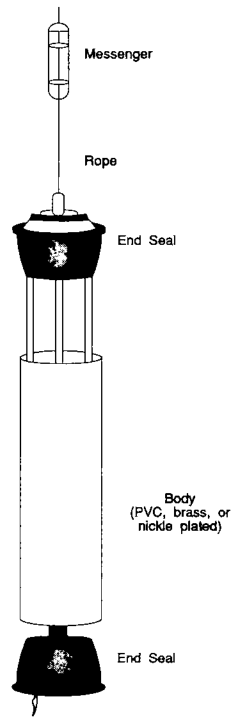


Figure 3. Kemmerer Sampler

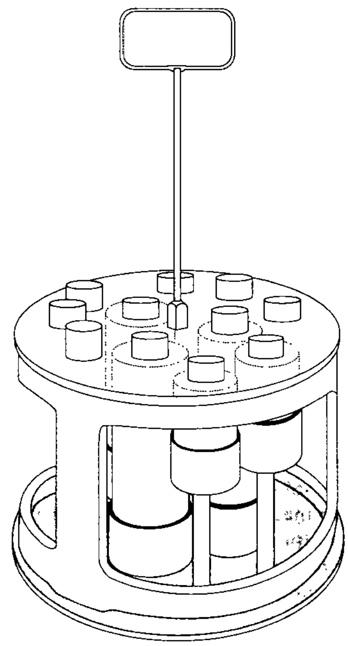

Figure 4. Multiple Sampler

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 5.

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 tub on the inside of the lid is positioned inside the BOD bottle;
(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 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.

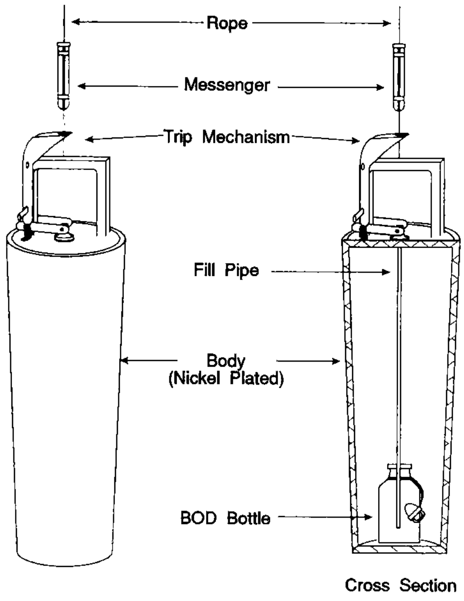


Figure 5. Dissolved Oxygen Sampler

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).

## 3.4 Preparation for Field Trips

### 3.4.1 General Preparation

(a) Obtain specific instructions on sampling procedures;
(b) Prepare an itinerary according to the sampling schedule;
(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 3.4.4).

### 3.4.2 Bottle Washing and Preparation

Sample bottles are usually provided by the analytical laboratory. The recommended cleaning procedures are shown in Table 2.

### 3.4.3 Selection of Sample Volume

The volume of sample required depends on the type and number of variables to be analyzed, the analytical method, and the expected concentrations of the variables in the water. Laboratory personnel will specify the sample volume required. The required sample volume can be determined by listing all of the variables that are preserved in the same way, totalling the minimum volume for analysis and then multiplying by 2 for duplicate and 3 for triplicate analyses.

### 3.4.4 Checklist Prior to Field Trip

(a) Check and calibrate meters (pH, specific conductance, dissolved oxygen) 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, 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 also recommended for all sample storage.

# 4.0 FIELD QUALITY ASSURANCE

The Field Quality Assurance program is a systematic process which, together with the laboratory and data management quality assurance programs, ensures a specified degree of confidence in the data collected. The Field Quality Assurance program involves a series of steps, procedures and practices which are described in the following sections.

## 4.1 General Measures

(a) All equipment, apparatus and instruments should be kept clean and in good working condition;
(b) Records should be kept of all repairs to the instruments and apparatus and of any irregular incidents or experiences which may affect the success of the study;
(c) Conditions in 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 guide, 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.

## 4.2 Prevention of Sample Contamination

The quality of data generated in a laboratory depends primarily 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 heed:

(a) Field measurements should always be made on a separate sub-sample, which is then discarded once the measurements have been made. They should never by made on the same water sample which is returned to the analytical laboratory for chemical analysis;
(b) Sample bottles, new or used, must be cleaned according to the recommended methods (see Table 2);
(c) Only the recommended type of sample bottle for each variable should be used (see Table 2);

Table 2. Washing Procedures and Containers Recommended for Water Samples

| Variable(s) to be Analyzed | | Recommended container* | Washing procedure |
|---|---|---|---|
| Alkalinity<br>Calcium<br>Chloride<br>Fluoride<br>Magnesium<br>pH | Sodium<br>Sulfate<br>Nonfilterable residue<br>Potassium<br>Arsenic | 1000 ml polyethylene | Rinse:<br>three times with tap water<br>once with chromic acid,<br>three times with tap water<br>once with 1:1 nitric acid<br>and then: three times, with distilled water, in that order |
| Nitrogen, ammonia<br>Nitrogen, nitrate and nitrite<br>Carbon, total organic<br>Nitrogen, total | | 250 ml polyethylene | Rinse:<br>three times with tap water<br>once with chromic acid<br>three times with tap water<br>and then:<br>three times with water<br>in that order |
| Phosphorus total | | 50 ml. Glass (sovirel) | |
| Aluminum<br>Cadmium<br>Chromium<br>Copper<br>Iron | Lead<br>Manganese<br>Nickel<br>Selenium<br>Zinc | 500-1000 ml polyethylene (choice of size depends on the number of metals to be determined and the quantity of sample required) | Rinse:<br>three times with tap water<br>once with chromic acid<br>three times with tap water<br>once with 1:1 nitric acid<br>and then:<br>three times with ultrapure distilled water, in that order |
| Mercury | | 100 ml Glass (sovirel) | |
| Organochlorinated pesticides and PCB's | | 1000 ml glass (amber) with teflon-lined cap | Rinse: three times with tap water,<br>once with chromic acid,<br>three times with organic-free water,<br>twice with washing acetone,<br>once with special grade** acetone,<br>twice with pesticide grade hexane and dry (uncapped) in a hot air oven at 360°C for at least 1 hour |
| Pentachlorophenol | | 1000 ml glass (amber) with teflon-lined cap | |
| Phenolics | | 1000 ml glass (amber) with teflon-lined cap | |
| Phenoxy acid herbicides | | 1000 ml glass (amber) with teflon-lined cap | |

* Teflon containers can also be used to replace either the recommended polyethylene or glass containers.
Chromic acid - 35 ml saturated $Na_2Cr_2O_7$/litre of reagent grade conc. $H_2SO_4$.
Chromic acid should not be used when the sample will be analyzed 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 Millepore Super Q Ultrapure Water System containing a prefilter cartridge, an activated carbon cartridge and a mixed bed deionization cartridge.

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

(d) Water sample bottles should be employed 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 have been tested and the glassware spot-tested for cleanliness;
(f) Recommended preservation methods must be used. All preservatives must be of analytical grade. They are usually 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 should be minimized by preserving all the samples for a particular group of variables together;
(h) Solvent-rinsed Teflon or aluminum foil liners can be used to prevent contamination from the bottle caps of water samples which are to be analyzed for organic compounds;
(i) The inner portion of sample bottles and caps should not be touched with bare hands, gloves,mitts, etc.;
(j) Sample bottles 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 (gasoline, oil, 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 a source of trace metal contamination;
(l) 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;
(m) Bottles which have been sterilized must remain 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, discard the bottle;
(n) All foreign and especially metal objects must be kept out of contact with acids and water samples;
(o) Specific conductance should never be measured in sample water that was first used for pH measurements. Potassium chloride diffusing from the pH probe alters the conductivity of the sample;
(p) Samples must never be permitted to stand in the sun; they should be stored in a cool place; ice chests are recommended;
(q) Samples must be shipped to the laboratory without delay;
(r) The sample collector should keep his/her hands clean and refrain from smoking while working with water samples.

### 4.3 Field Quality Control

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

#### 4.3.1 Bottle Blanks

Prior to a field sampling trip, one sample bottle for every ten 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 chemical analysis for the variables of interest as "bottle blanks." this should detect any widespread contamination caused by the bottle washing process.

#### 4.3.2 Sampler Blanks

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

#### 4.3.3 Filter Blanks

If water samples are "field filtered" to determine the dissolved component of certain water quality constituents, then the field filters should be pre-washed in the laboratory with a solution that can remove any contaminants which might affect the accuracy of measurement of the variable of interest. Immediately after washing, the filters should be sealed in plastic petri dishes for transport in the field. Filtering apparatus, such as funnels, should be pre-washed in the laboratory using the same procedure, and then sealed in polyethylene bags for transport in the field. A daily "filter blank" should be prepared by passing a sample of ultrapure distilled water through one of the pre-washed 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 variable(s) of interest.

#### 4.3.4 Field Blanks

Daily "field blanks" (one blank is suggested for every ten water samples) should be prepared in the field at the end of each day's sampling by filling 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.

4.3.5 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.

4.3.6 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 variables in the water body. The number and frequency of these samples are usually determined by a pilot study.

4.3.7 Replicate Samples (Spatial)

These are two or more samples taken simultaneously in a given predetermined cross section of the water body under study. They should be taken to measure the cross-sectional variations in the concentration of the variables of interest. The number and the exact location of these samples are usually determined by a pilot study.

4.3.8 Spiked Samples

At least once at each sampling point, control samples for each variable being measured should be prepared by spiking a four-way split of a single water sample with three different levels of the variable 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.

5.0 FIELD MEASURED VARIABLES

A number of variables including pH, conductivity, dissolved oxygen, temperature and transparency should be measured at the sampling site. Where possible, these measurements are taken in situ, but in all cases their values should be determined in the field as soon as possible after sample collection.

5.1 pH Measurement

The pH is a measure of the acidity or alkalinity of a solution. Neutral solutions have a pH of 7, acid solutions a pH of less than 7, and alkaline solutions a pH greater than 7. The pH should be determined in the field, immediately after sample collection. Since pH can change rapidly and significantly soon after sample collection, it is not recommended that samples for this test be shipped to the laboratory. 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. There are many portable pH meters on the market today; the investigator should select the one that suits his needs best. Digital meters are preferable, since analog meters are sometimes difficult to read while taking in situ measurements (e.g. in a boat on rough water).

5.2 Conductivity Measurement

Conductivity (specific conductance) is a numerical expression of water's ability to conduct an electric current. Measured in microsiemens per centimetre (µS/cm) conductivity depends on the concentration of ions in solution. In situ measurements are preferable; if this is not possible, a sample is collected and measurement should be made as soon as possible, since the conductivity of a water sample may change with time. In most cases conductance readings are stable for months. Conductivity is temperature dependent. If the conductivity measurement is not automatically temperature corrected, then the temperature at the time of measurement should also be recorded. There are various conductivity meters available which may also have temperature and salinity determining capabilities. Since probes vary and cable lengths are optional, the investigator must select the equipment to meet the requirements of the sampling program.

5.3 Dissolved Oxygen Measurement

Dissolved oxygen (DO) should be measured insitu 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 3 to 6 h from the time the sample was taken. Dissolved oxygen concentrations may be determined directly with a DO metre or by a chemical method such as Winkler analysis or the Hach method. The method chosen will depend on a number of factors including the accuracy and precision required, convenience, equipment and personnel available and expected interferences. For very precise measurements the potentiometric method should be considered.

5.4. Transparency

Transparency is a characteristic of water that varies with the combined effects of colour and turbidity. The determination can be done quickly and requires only simple equipment. The main application is to surface waters in the field and particularly to limological work.

The apparatus consists of a disc 250 mm diameter, made of metal or rigid plastic and painted white. Alternatively, the disc may be painted so that a white quadrant alternates with a black one. The disc is mounted on a string or a chain which is graduated in cm with the disc at zero. When the string is held with the disc suspended on it the disc should be horizontal. It is useful to have a weight on the string below the disc to help maintain the string in a vertical position when the disc is lowered into the water.

The diameter of the disc and the pattern on its upper surface do not make significant difference to the readings obtained, but the same size and pattern of disc should be used at the same sampling station in order that a time series of determinations made over a number of years will be as free as possible from any distortions arising from differences in equipment. The disc used for transparency determination is called a Secchi disc.

The procedure is simply to lower the Secchi disc from the surface and to observe the depth at which the disc just disappears from view. The observation must be made through a shaded area of water surface. It is usual to determine the point of disappearance as the disc is being lowered, lower it a little further and then determine the point of reappearance as the disc is being raised. The mean of the two readings measured in meters is taken as the "Secchi disk transparency". The report of the transparency should state the diameter of the disc and the colour (or pattern) on its upper surface.

### 5.5 General Summary of Field Procedures

Regardless of the specific variables 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 <u>in situ</u> measurements for pH, conductivity, dissolved oxygen, temperature and transparency;
(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;
(f) Complete field sheet accurately;
(g) Put bottles in appropriate shipping containers;
(h) Label boxes and complete field sheets with all required information;

## 6.0 FIELD FILTRATION AND PRESERVATION

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 already been addressed in the scientific literature, so far no clear consensus has emerged on which chemical-physical species of substance should be measured when monitoring water quality. The decision 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 the biological availability is directly proportional to their concentration in dissolved phase. Also in the case of most metals, for example, typically the concentration in the dissolved phase is low compared with the suspended or colloidal particles. The definition most commonly used in scientific literature for "dissolved" phase is that which passes through a 0.45-μm membrane filter. Optimally, the filtration should be carried out in the field during or immediately after sample collection and must be followed by the appropriate preservation.

### 6.1 Filtration

To determine the concentration of dissolved inorganic constituents (e.g. metals and anions), it is necessary to filter the sample through a 0.45-μm membrane filter immediately after collection. The filtrate for metals analysis should be preserved as outlined in Table 3; the filtrate for anion analysis is not preserved. The volume of sample needed is indicated by laboratory personnel. The filter and filtration apparatus require laboratory pre-treatment and should be rinsed with a portion of the collected sample before the filtrate is collected.

Samples requiring analysis for organic constituents are filtered immediately after collection using a glass-fibre filter. After filtration the filtrate may be analyzed for dissolved organic constituents, and the filter supporting the particulate fraction is available for particulate organic analysis.

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.

## 6.2 Preservation Techniques

Between the time that a sample is collected in the field and until it is actually analyzed 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. It is necessary, therefore, to preserve the samples before shipping to prevent or minimize these changes. 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, extraction procedures, field column chromatography, or by a combination of these methods.

The preservation methods recommended are discussed briefly here and summarized in Table 3.

### 6.2.1 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.

### 6.2.2 Freezing

Freezing may be acceptable for certain analyses but is not used as 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 sampling change with freezing and thawing, and a return to equilibrium followed by high-speed homogenization may be necessary before any analysis can be run.

### 6.2.3 Refrigeration

Refrigeration at 4°C is a common preservation technique which is widely used in fieldwork. 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 3).

### 6.2.4 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 a chemical preservative is 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 requires special precautions. Precalibrated pipets and other automatic pipettes now ensure accurate field addition as well as eliminating 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, for example, conc. nitric acid, add 2 ml/litre of sample.

Table 3. Sample Containers and Preservation for Constituents in Water

| Variable | Recommended container* | Preservative | Maximum permissible storage time |
|---|---|---|---|
| Alkalinity | Polyethylene | Cool, 4°C | 24 h |
| Aluminum | Polyethylene | 2 ml Conc. $HNO_3$/1 sample | 6 months |
| Arsenic | Polyethylene | Cool, 4°C | 6 months |
| BOD | Polyethylene | Cool, 4°C | 4 h |
| Boron | Polyethylene | Cool, 4°C | 6 months |
| Cadmium | Polyethylene | 2 ml Conc. $HNO_3$/1 sample | 6 months |
| Calcium | Polyethylene | Cool, 4°C | 7 days |
| Carbamate pesticides | Glass | $H_2SO_4$ to pH < 4, 10g$Na_2SO_4$/1 | extract immediately |
| Carbon/inorganic/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 | Glass | Cool, 4°C | extract immediately |
| Chlorophyll | Plastic petri-dish | Filter on GF/C filter; freeze -20°C | 7 days |
| Chromium | Polyethylene | 2 ml Conc. $HNO_3$/1 sample | 6 months |
| COD | Polyethylene | Cool, 4°C | 24 h |
| Copper | Polyethylene | 2 ml Conc. $HNO_3$/1 sample | 6 months |
| Dissolved oxygen(Winkler) | Glass | Fix on site | 6 h |
| Fluoride | Polyethylene | Cool, 4°C | 7 days |
| Iron | Polyethylene | 2 ml Conc. $HNO_3$/1 sample | 6 months |
| Lead | Polyethylene | 2 ml Conc. $HNO_3$/1 sample | 6 months |
| Magnesium | Polyethylene | Cool, 4°C | 7 days |
| Manganese | Polyethylene | 2 ml Conc. $HNO_3$/1 sample | 6 months |
| Mercury | Glass or teflon | 1 ml Conc. $H_2SO_4$ plus 1 ml 5% $K_2Cr_2O_7$ | 1 month |
| Nickel | Polyethylene | 2 ml Conc. $HNO_3$/1 sample | 6 months |
| Nitrogen | | | |
| Ammonia | Polyethylene | Cool, 4°C, 2 ml 40% $H_2SO_4$/1 | 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 |
| Organophosphorus pesticides | Glass | Cool, 4°C, 10% HC1 to pH 4.4 | No holding,extraction on site |
| Pentachlorophenol | Glass | $H_2SO_4$ to pH < 4, 0.5g $CuSO_4$/1 sample Cool,4°C | 24 h |
| pH | Polyethylene | None | 6 h |
| Phenolics | Glass | $H_3PO_4$ to pH < 4, 1.0g $CuSO_4$/1 sample;Cool,4°C | 24 h |
| Phenoxy acid herbicides | Glass | Cool, 4°C | extract immediately |
| Phosphorus | | | |
| Dissolved | Glass | Filter on site using 0.45 -µm filter | 24 h |
| Inorganic | 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 |
| Sodium | Polyethylene | Cool, 4°C | 7 days |
| Electrical conductivity | Polyethylene | Cool, 4°C | 24 h |
| Sulfate | Polyethylene | Cool, 4°C | 7 days |
| Zinc | Polyethylene | 2 ml Conc. $HNO_3$/1 sample | 6 months |

* Teflon containers can also be used to replace either the polyethylene or the glass containers shown in the table.
Note: This table has been adapted from the "Analytical Methods Manual" (Water Quality Branch, Environment Canada, 1981).

## 7.0 SAMPLING FOR MICROBIOLOGICAL ANALYSIS

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 collection. Microbiological samples are usually collected in sterile 200 ml or 500 ml wide-mouthed glass or nontoxic plastic bottles with cork or screw caps. The capped or stoppered bottle mouth should be covered with sterile heavy-duty paper or with aluminum foil secured with string or an elastic band. Whenever possible, water samples should be analyzed 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 h after collection.

More information on microbiological tests is given in Chapter V of this Guide.

## 8.0 SEDIMENT SAMPLING PROCEDURES

Sediment plays an important role in water quality. Part of the assimilative capacity of natural water system for metals, pesticides and herbicides is the ability of the sediment to bind these substances, thus removing them from the water. On the other hand, many toxic substances stored in the sediment are released to the surrounding waters by a variety of chemical and biochemical reactions, thus making them available to the organisms living in these waters. Lake and stream sediments often reflect recent additions of heavy metals before elevations of such elements are detectable in the overlying water. While water analysis may therefore indicate no elevated concentrations in the soluble phase, a water body may still be heavily polluted with organic and inorganic material in sediments. The possibility of reentry of sedimented material into the water, owing to physical, chemical, or biological processes in natural situations, always exists. Also, with botton-feeding organisms, sediments may be more important than water as a source of organic and inorganic substances.

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

More information on particulate matter collection and analysis is given in Chapter IV of this Guide.

UNEP/WHO/UNESCO/WMO PROGRAMME ON WATER QUALITY MONITORING AND ASSESSMENT

# GEMS/WATER OPERATIONAL GUIDE

## CHAPTER III: ANALYTICAL METHODS

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## 1.0 INTRODUCTION

### Revised List of GEMS/WATER Variables for Phase Two of the Programme

During Phase One of the GEMS/Water programme, monitoring was undertaken according to various categories and set of variables. The group of experts attending the meeting in Leningrad in 1990, recommended a revised set of variables for Phase Two. The revised list of variables is presented in Table 1.

Table 1. Revised List of GEMS/Water Variables

General Water Quality:
- • Water discharge/level
- • Total suspended solids (R)
- • Temperature
- • pH
- • Electrical conductivity
- • Dissolved oxygen
- • Transparency (L)

Dissolved Salts:
- • Calcium
- • Magnesium
- • Sodium
- • Potassium
- • Chloride
- • Fluoride (G.W.)
- • Sulphate
- • Alkalinity

Ionic Balance:
- Sum of cations
- Sum of anions
- Sodium adsorption ratio

Nutrients:
- • Nitrate plus nitrite
- • Ammonia
- Organic nitrogen, dissolved
- Organic nitrogen, particulate
- • Total phosphorus, dissolved (R,L)
- • Total phosphorus, particulate
- • Total phosphorus, unfiltered (R,L)
- • Silica reactive (R,L)

Organic Matter:
- Organic carbon, dissolved
- Organic carbon, particulate
- BOD
- COD
- • Chlorophyll *a* (R,L)

Microbial Pollution:
- Faecal coliforms
- Total coliforms

Inorganic contaminants:
- Aluminum, dissolved
- Aluminum, total
- Arsenic, dissolved
- Arsenic, total
- Boron, dissolved
- Boron, total
- Cadmium, dissolved
- Cadmium, total
- Chromium, dissolved
- Chromium, total
- Copper, dissolved
- Copper, total
- Iron, dissolved
- Iron, total
- Lead, dissolved
- Lead, total
- Manganese, dissolved
- Manganese, total
- Mercury, dissolved
- Mercury, total
- Nickel, dissolved
- Nickel, total
- Selenium, dissolved
- Selenium, total
- Zinc, dissolved
- Zinc, total

Paticulate Matter:
- Aluminum, particulate (GRF)
- Arsenic, particulate (GRF)
- Cadmium, particulate (GRF)
- Chromium, particulate (GRF)
- Copper, particulate (GRF)
- Iron, particulate (GRF)
- Lead, particulate (GRF)
- Manganese, particulate (GRF)
- Mercury, particulate (GRF)
- Selenium, particulate (GRF)
- Zinc, particulate (GRF)

Organic contaminants:
- Aldicarb
- Aldrin
- Altrazine
- Benzene
- 2, 4-D
- DDTs
- Dieldrin
- Lindane
- Total hydrocarbons
- Total chlorinated hydrocarbons
- Total polyaromatic hydrocarbons
- PCBs
- Phenols

| | |
|---|---|
| • | Basic variables to be monitored at all GEMS/Water stations. |
| (R) | Basic variables for river stations only. |
| (L) | Basic variables for lake/reservoir stations only. |
| (G.W.) | Basic variables for ground water stations only. |
| (R,L) | Basic variables for river, lake/reservoir stations only. |
| (GRF) | Of essential importance for Global River Flux monitoring stations. |

Sampling only the water phase has been proven to be ineffective for trace metals, persistant trace organics and nutrients, a multi-media sampling approach has been recommended (e.g., suspended sediments, deposited sediments and biological tissue analysis etc). At moderate to high total suspended matter levels, the suspended sediment fraction is of primary importance in the transport of nutrients and contaminants; and for refractory substances, the sediment-associated concentration can be decisive for estimates of flux. GEMS/Water defines the upper size limit of particulate matter to be ≤ 63µm. For now, it is particularly important that both the dissolved and particulate matter fractions be analyzed at the Global River Flux monitoring stations.

Due to the associated cost, analysis of particulate matter at trend stations should be considered on a station-by-station basis. Since several laboratories do not have the capability of doing particulate matter analysis and because of current uncertainties related to the determination of dissolved concentrations, inorganic contaminants can also be reported as total concentrations.

The section which follows, provides a brief description of the variables with a summary of sample handling and analytical procedures. The detailed analytical procedures may be obtained from the various sources, including the references listed at the end of the Chapter. For GEMS/Water participating laboratories that are unable to obtain detailed procedures for specific analysis, assistance may be provided by the World Health Organization (WHO) in Geneva or by the WHO Collaborating Centre in Burlington, Ontario.

The sequence in which the variables are presented is essentially the same as that used in major reference books. The variables are presented under four main headings:

- physical and physico-chemical
- metallic elements
- non-metallic constitutents
- organic constitutents.

Analytical procedures for the microbiology and the particulate matter are described in Chapters IV and V of this Guide.

## Control of the Correctness of Analyses

Out of concern for the quality of the analyses that it provides, every laboratory should establish control procedure of the sort described in Chapter VII. However, such a procedure does not provide individual control of global validity for the analysis of each sample. Given that the existing list of basic variables of the GEMS/Water programme includes all the ion species responsible for the basic mineralization of natural waters, the ionic balance method may be used for control of each analysis. Theoretically, the sum of the anions in a water sample, expressed in milliequivalents per litre, should exactly equal the sum of the cations expressed in the same manner.

### Calculation of the ionic balance

The concentration of each ion in milliequivalents is calculated using the coefficients F in the following table.

| Cations | F |
|---|---|
| *Ca | 0.04990 |
| *Mg | 0.08224 |
| b Sr | 0.02282 |
| *Na | 0.04348 |
| *K | 0.02558 |
| b N-$NH_4$ | 0.07143 |

| Anions | F |
|---|---|
| *$SO_4$ | 0.02082 |
| *Cl | 0.02820 |
| a*$HCO_3$ | 0.01639 |
| a*$CO_3$ | 0.03333 |
| *N-$NO_3$ | 0.07143 |
| b N-$NO_2$ | 0.0714 |
| b P-$PO_4$ | 0.09686 |

We have: meq = mg/l x F.

### Notes

* Ionic forms that are obligatory for the calculation of the ionic balance.

a These ionic forms may be replaced by the Complete Alkalimetric titre (CAT, or Alkalinity) directly expressed in milliequivalents, in which case we have alkalinity in meq/l = (Alkalinity in mg/l of $CaCO_3$)/50.

b Ionic forms that should be considered if present in sufficient concentration to alter the ionic balance significantly.

The ions $H^+$ and $OH^-$ must be included in the case, respectively, of highly acid or strongly alkaline water (pH 5 or pH 9).

Although silica is very often present in quite appreciable concentration, it does not usually need to be taken into consideration because it is only very slightly ionized at the pH values encountered in natural waters.

$$\text{The ionic balance } \% = \frac{\text{meq cations} - \text{meq anions}}{\text{meq cations} + \text{meq anions}} \times 100$$

Interpretation

An ionic balance is regarded as correct if the difference between anions and cations relative to the sum of the ions is less than 2%.

A greater difference is usually an indication either of the presence in the sample of one or more ion species that have not been taken into consideration for the calculation, or of analytical errors concerning one or more of the major ion species taken for the calculation.

Validity of the method

Deviations between anions and cations may be compensated by errors in the same sense in the anion and cation divisions or in the opposite sense within the same division.

Consequently the technique is not absolute and does not suffice in itself as a control on the validity of the results. It must necessarily be accompanied by continuous analytical quality control, element by element (see Chapter VII).

Control of the ionic balance may also be combined with comparison of the measured conductivity and conductivity calculated from the measured concentrations and the equivalent conductivity of each of the main ions.

As the equivalent conductivity of the ions is given for infinite dilutions, the comparison is directly applicable only for waters having a conductivity of less than 100 µS. For waters of higher conductivity, dilution must be carried out to adjust the conductivity to around 100 µS.

## 2.0 PHYSICAL AND PHYSICO-CHEMICAL TESTS

### Temperature

1. General

Measurements of temperature are required in studies of self-purification of rivers and reservoirs, and for the control of waste treatment plants. Water temperature is important in relation to fish life. In limnological studies, temperature at different depths are measured. Data on the water temperature are necessary for cooling purposes or for process use in industry, as well as for the calculation of the solubility of oxygen and the carbon dioxide-bicarbonate-carbonate equilibrium. Identification of the water source, such as deep wells, is often possible by temperature measurement alone. The temperature of drinking water has an influence on its taste. It is also important in connection with bathing and agricultural irrigation.

2. Methods

Normally, temperature measurements can be made with a mercury-filled Celsius thermometer, etched to read with a resolution of at least 0.1°C. In lakes or reservoirs, depth temperatures are measured with a reversing thermometer, thermophone or thermistor which should be calibrated against an NIST - or equivalent certified thermometer before field use.

### pH

1. General

The pH of water approximates the activity of free hydrogen ions in water. It is defined as the negative logarithm of the hydrogen ion concentration. The practical pH scale extends from O (very acidic) to 14 (very alkaline) with the value of 7 corresponding to exact neutrality at 25°C.

The pH of natural waters is dictated to some extent by the geology of the watershed and is governed by the carbon dioxide/bicarbonate/carbonate equilibria. The range in pH for most waters is between 4.5 and 8.5 which encompasses the pH value of 5.6 for rainwater in equilibrium with atmospheric $CO_2$. The pH may be affected by the presence or organic acids and by biological processes (e.g. photosynthesis and respiration) and physical processes (turbulence and aeration) which can alter the concentration of dissolved carbon dioxide.

The concentration of hydrogen ions is a major factor in all chemical reactions associated with the formation, alteration and dissolution of minerals. The pH of water also affects transformation processes among the various forms of nutrients and metals, and influences the toxicity of pollutants consisting of acids and bases because of the effects of ionization on these compounds. The chemical speciation of many metals, their water solubility and bioavailability are determined by pH.

2. Methods

The determination of pH by conventional chemical means is not practical and the equilibria which are involved depend upon temperature. The precise scale of pH must therefore be based upon an agreed primary standard. The electrometric method of pH measurement is the most accurate and is relatively free from interferences. A ± 0.1 pH unit represents the limit of accuracy under normal operating conditions, although a laboratory pH meter with good electrodes can produce a precision of ± 0.02 pH unit and an accuracy of ± 0.05 pH unit.

### Electrical Conductivity

1. General

Electrical conductivity is a numerical expression of the ability of an aqueous solution to carry an electric current. This ability depends on the presence of ions, their total concentration, mobility, valence, and relative concentrations, and on the temperature of measurement. Solutions of most inorganic acids, bases and salts are relatively good conductors. Conversely, molecules of organic compounds that do not dissociate in aqueous solution conduct a current poorly, if at all.

Estimates of total dissolved solids can be made by multiplying the conductivity value by an empirical factor dependent upon the soluble components of the water and the sample temperature. Other practical applications include checking the purity of distilled or deionized water; evaluating variations in the dissolved mineral content of raw water or wastewater; establishing the degree of mineralization and its effect on chemical equilibria, the physiology of plants and animals, corrosion rates, etc.; estimating sample size for common chemical determinations and checking the results of a chemical analysis; and determining the amount of ionic reagent needed in certain precipitation and neutralization reactions.

The standard unit of electrical conductivity is the Siemen per meter. Conductivity is generally reported as millisiemens per meter (mS/m) at 20°C. Note that 1 m S/m = 10 µS/cm = 10 µmho/cm. Freshly distilled water has a conductivity of 0.5 to 2 µS/cm whereas natural waters have conductivity values ranging from 50 to 1500 µS/cm.

2. Methods

Electrical conductivity is measured with a self-contained instrument consisting of a source of alternating current, a Wheatstone bridge, a null indicator and a conductivity cell. Other instruments can measure the ratio of alternating current through the cell to voltage across it and therefore can provide a linear reading of conductivity. Select an instrument capable of measuring conductivity with an error not exceeding 1% or 1 µS/cm, whichever is greater.

## Total Suspended Solids

1. General

Suspended solids are composed of clay, sand, silt, finely divided organic and inorganic matter, plankton and other microorganisms in water. The concentration of suspended solids is related to seasonal factors and flow regimes, and is affected by snowmelt and rain events. Concentrations vary from one location to another depending upon hydraulic forces, vegetative cover, soil and bedrock, and anthropogenic activities such as agriculture, lumbering, mining, etc.

Suspended particles affect water clarity and light penetration, temperature, the dissolved constituents of surface water, the absorption of toxic substances such as organics and heavy metals, and the composition, distribution and rate of sedimentation of matter. Waters high in suspended solids may be aesthetically unsatisfactory for recreational activities. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with guidelines imposed by regulatory agencies for wastewater effluents.

For more information on suspended solids or particulate matter, please refer to Chapter IV of this operational guide which describes the monitoring of particulate matter quality.

2. Methods

Total suspended solids is a measure of the material collected on a glass fibre filter and dried to a constant weight at 103 to 105°C. If the suspended matter clogs the filter and prolongs filtration, the difference between the total solids content (also dried at 103 - 105°C) and the total dissolved solids (filtrate dried to constant weight at 180°C) may be used to estimate the total suspended solids.

## Transparency

1. General

Water transparency or clarity is a function of the concentration of suspended solids in the water column. A marked attenuation in light intensity with depth in turbid waters will result in a greater absorption of solar energy near the surface. The warmer surface water may reduce oxygen transfer from the air to the water and will decrease density and stabilize stratification thus slowing or precluding vertical mixing. Reduced light penetration will decrease photosynthesis and will have a direct influence on the amount of biological production occurring within a body of water. Sight-feeding fish, zooplankton migrations and benthic invertebrate reproduction may be impacted by a lower depth of light penetration.

2. Methods

Although optical devices are available for measuring the intensity of solar radiation at depth in the water column, the very simple procedure of determining transparency with a Secchi disk still retains its value. The method is to observe the depth at which a 30 cm-diameter disk, painted white or with black and white quadrants, disappears from view as it is lowered in the water column. The actual procedure is to record the point of disappearance as the disk is lowered, allow it to drop a little farther, and then determine the point of re-emergence as the disk is raised. The mean of the two readings is taken as the Secchi disk transparency.

# 3.0 METALLIC IONS

## Alkali Metals (Na,K)

1. General

Sodium is one of the more abundant elements and is a common constituent of natural waters. Concentrations range from very low values in surface waters draining highly weathered environments to relatively high values in deep groundwaters to a very high values in marine waters and certain inland water systems. Sodium at a concentration of 10.77 mg/g (salinity = 35 g/kg) is the most abundant metal ion in seawater.

The sodium concentration of waters is of concern primarily when considering their suitability for agricultural uses or boiler feed water. However, since control of sodium intake may be necessary in sufferers from certain medical conditions, the sodium intake of drinking-water may also cause concern, especially if ion exchange or soda ash softening has been employed.

While potassium ranks seventh in elemental abundance its concentration in most natural waters remains relatively low, seldom reaching 2 mg/litre in drinking-water. Occasional brines reach 100 mg/litre and sea water (salinity=35 g/kg) contains 0.399 g of K per kg, making it the fourth most abundant metal in this medium. Potassium is of little direct significance except as a component of total dissolved solids and when considering ratios of monovalent to divalent cations.

2. Sample Handling

Samples containing low concentrations of sodium and potassium or samples that are alkaline should be stored in polyethylene bottles to eliminate the potential contamination of the sample due to leaching from glass containers. Prolonged storage in plastic containers should be discouraged because of evaporated losses through the container walls or lid seal. In the presence of solids, sample filtration prior to storage would be advisable if temperature changes are apt to occur, in order to prevent ion exchanges taking place in solution.

## Alkaline - Earth Metals (Ca, Mg)

1. General

Calcium dissolves out from practically all rocks and is consequently detected in all waters. Waters associated with granite or siliceous sand may contain less than 10 mg of calcium per litre. Many waters from limestone areas may contain 30-100 mg/litre and those associates with gypsiferous shale may contain several hundred mg/litre. Calcium imparts the property of hardness to water and if present together with alkalinity or sulfate it may cause boiler scale. Some calcium carbonate is desirable for domestic waters as it provides a coating in the pipes that combats corrosion.

Magnesium is a relatively abundant element in the earth's crust and, hence, a common constituent of natural water. Waters associated with granite or siliceous sand may contain less that 5 mg of magnesium per litre. Water contacting dolomite or magnesium-rich limestone may contain 10-50 mg/litre and several hundred mg per litre may be present in water that has been in contact with deposits containing sulfates and chlorides of magnesium. Magnesium, by a similar action to calcium, imparts the property of hardness to water. This may be reduced by chemical softening or by ion exchange. Concentrations of magnesium greater than 125 mg/litre can exert cathartic and diuretic actions.

2. Sample Handling

Samples for calcium and magnesium should be collected in plastic or borosilicate glass bottles without the addition of preservative. If any calcium is formed during sample storage, it must be redissolved before analysis by the addition of nitric acid. If the analyses are to be made by atomic absorption spectroscopy, samples should be acidified by the addition of 1.5 ml of concentrated $HNO_3$ per litre of sample prior t storage in a plastic container. If the pH is not less than 2 after the addition of acid, more $HNO_3$ should be added. If analyses are to be made of the soluble metal fraction, samples should be filtered through 0.45 µm membrane filters as soon after collection as possible and then the filtrate should be acidified.

## Trace Metals (Al, Cr, Fe, Hg, Mn, Ni, Pb, Zn, Cd, Cu)

The speciation and bioavailability of trace metals in water are controlled by physical and chemical interactions and equilibria. These interactions are affected by many factors, including pH, redox, temperature, hardness, $CO_2$ concentrations, the type and concentration of available ligands and chelating agents and type and concentrations of metal ions. Concerns over metals relate to their toxicity and bio-availability, particularly for uncomplexed ions, the potential for bioaccumulation and hazards to human health. In terms of guidelines for most trace metals, the problems inherent in determining specific metal species and the fact that toxicities are often, species dependent, support the adoption of a total metal concentration as a protective water quality measure.

### Aluminum

1. General

Although aluminum is among the most abundant elements in the earth's crust, it is present only in trace concentrations in natural waters. Because aluminum occurs in many rocks, minerals, and clays it is present in practically all surface waters, but its concentration in waters at near neutral pH rarely exceeds a few tenths of a mg per litre. In addition, in treated or wastewater it may be present as a residual from alum coagulation. The median concentration of aluminium in river water is reported to be 0.24 mg/litre with a range of 0.01 to 2.5 mg/litre.

2. Sample Handling

Because aluminum may be lost from solution to the walls of sample containers, samples should be acidified by the addition of 1.5 ml of concentrated $HNO_3$ per litre of sample prior to storage in plastic containers. If the pH is not less than 2 after the addition of acid, more $HNO_3$ should be added. If only soluble aluminum is to be determined, filter a portion of the unacidified sample through a 0.45-μm membrane filter; discard the first 50 ml of filtrate and use of the succeeding filtrate, after acidification, for the determination. Do not use filter paper, absorbent cotton, or glass wool for filtering any solution that is to be tested for aluminum, because these materials will remove most of the soluble aluminum.

## Chromium

1. General

Chromium concentrations in natural waters are usually very small. In a survey in the U.S.A., the majority of the samples showed concentrations ranging between 1 and 112 μg/litre. The mean concentration was 14 μg/litre. Sea water concentrations are substantially lower, with a reported range of 0.04-3 μg/litre. Elevated chromium concentrations can result from mining and industrial processes. Chromate compounds are routinely used in cooling waters to control corrosion. Chromium in water supplies is generally found in the hexavelant form. An upper limit of 0.05 mg of hexavelant chromium per litre is allowed in drinking-water in the U.S.A. and a similar limit is allowed in WHO's European Standards for Drinking-Water, which are mirrored in the individual standards adopted by countries in Europe and the U.S.A. A pH depression in the presence of oxidizable material, such as dissolved organics, can reduce hexavelant to trivalent chromium.

2. Sample Handling

Samples should be collected in polyethylene bottles and acidified immediately after collection to prevent chromium loss on the walls of the sample container. Acidify with 1.5 ml of concentrated $HNO_3$ per litre of sample. If the pH is not less than 2 after the addition of acid, more $HNO_3$ should be added.

## Iron

1. General

Iron is an abundant element in the earth's crust, but exists generally in minor concentrations in natural water systems. The form and solubility of iron in natural waters are strongly dependent upon the pH and the oxidation-reduction potential of the water. Iron is found in the +2 and +3 oxidation states. In a reducing environment, ferrous (+2) iron is relatively soluble. An increase in the oxidation-reduction potential of the water readily converts ferrous ions to ferric (+3) and allows ferric iron to hydrolyze and precipitate as hydrated ferric oxide. The precipitate is highly insoluble. Consequently, ferric iron is found in solution only at a pH of less than 3. The presence of inorganic or organic complex-forming ions in the natural water system can enhance the solubility of both ferrous and ferric iron.

Surface waters in a normal pH range of 6 to 9 rarely carry out more than 1 mg of dissolved iron per litre. However, subsurface water removed from atmospheric oxidative conditions and in contact with iron-bearing minerals may readily contain elevated amounts of ferrous iron. For example, in groundwater systems affected by mining, the quantities of iron routinely measured may be several hundred mg/litre.

It is the formation of hydrated ferric oxide that makes iron-laden waters objectionable. This ferric precipitate imparts an orange stain to any settling surfaces, including laundry articles, cooking and eating utensils, and plumbing fixtures. Additionally, colloidal suspensions of the ferric precipitate can give the water a uniformly yellow-orange, murky cast. This coloration along with associated tastes and odours can make the water undesirable for domestic use when levels exceed 0.3 mg/litre. Since iron compounds are used extensively in water treatment the World Health Organization (1984) has proposed a guideline value of 0.3 mg/litre in drinking-water.

2. Sample Handling

In the sampling and storage process, iron in solution may undergo changes in oxidation form and it can readily precipitate on the sample container walls or as a partially settleable solid suspension. For total iron measurements, precipitation can be controlled in the sample containers by the addition of 1.5 ml of concentrated $HNO_3$ per litre of sample immediately after collection. If the pH is not less than 2 after the addition of acid, more $HNO_3$ should be added.

Mercury (Dissolved)

1. General

Mercury is not an abundant element in the earth's crust. Estimates of its abundance have moderate confidence. One source places the average crustal abundance at 80 µg/kg. This and other factors lead to generally low soluble mercury concentrations in natural waters throughout the world and in turn at one time, a false sense of security regarding public health hazards related to mercury discharges of the environment. Elucidation of the complex chemistry of mercury and its compounds in natural systems, spurred by certain highly publicized incidents of mercury poisoning, has demonstrated that rather low concentrations of mercury may be highly important if the flux through an aqueous system is high. Sediment and biological tissue accumulations and subsequent transformations of mercury forms are of primary concern relative to human health.

While there are certain regions of the world where elevated mercury levels are observed these relate primarily to specific mercury rich mineral deposits. More commonly, high mercury concentrations are related to man-made sources. Notable sources of mercury discharge in the past were chlora-alkali plants using electrolytic cells. Many parts of the world have required process modifications to reduce mercury loss. Other industries noted for high mercury use are the electronics and electrical, explosives, photography, pesticide and preservative, chemical and petrochemical catalysis, and users of the above industrial products.

2. Sample Handling

Unless samples appear to be essentially free from suspended matter, filtration through 0.45 µm membrane filters (precleaned) should be conducted at the time of sample collection. The filter may be retained for suspended mercury determination or a second sample may be collected for total mercury. While some conjecture exists as to the mechanism of loss, it is well established that large mercury losses are experienced in both glass and polyethylene containers upon storage, if the sample is not fixed with acid. General recommendations are to sample in clean polyethylene bottles and fix the sample with nitric acid, $HNO_3$, at a final concentration of 0.5 to 1%. Analysis must be conducted within seven days. Longer storage, up to 30 days, may be achieved by making the stored sample 0.05% $K_2Cr_2O_7$ when the cold vapour AAS method is to be used.

Mercury, Total

1. General

As discussed above for dissolved mercury, if present in appreciable quantities in the aqueous environment, mercury is mostly associated with particulate matter rather than in the soluble form. Therefore, the determination of total mercury on unfiltered samples would be the most advisable.

2. Sample Handling

Samples should be collected in clean polyethylene bottles and fixed with concentrated nitric acid, $HNO_3$, to a final concentration of 0.5 to 1%. Analysis should be conducted within seven days. Longer storage may be achieved by the addition of $K_2Cr_2O_7$ to 0.05%.

Manganese

Manganese is a relatively common element in rocks and soils where it exists as oxides or hydroxides in the (II), (III) or (IV) oxidation state. These compounds strongly absorb other metallic cations and, along with iron oxides, are of great importance in controlling the concentrations of various trace metals present in natural water systems. Manganese dissolved in natural water is in the divalent state. The solubility of manganese in natural water is largely a function of pH and the oxidation-reduction potential. In relatively anoxic systems of near neutral pH, considerable concentrations of dissolved manganese may develop, but oxidation and precipitation may result from slight shifts in pH and potential. Average concentrations of manganese in rivers are around 12 µg/litre, with a range of less than 1 µg/litre to 130 µg/litre.

At levels exceeding 0.15 mg/litre, manganese in water supplies stains plumbing fixtures and laundry. At higher concentrations, it causes an undesirable taste in beverages. In common with iron, its presence in drinking-water may lead to the accumulation of deposits in the distribution system. Even at a concentration of 0.05 mg/litre, manganese will often form a coating on pipes which may slough off as a black precipitate. In addition, the presence of even low levels of manganese renders a water supply unsuitable in certain industrial applications such as those for the textile dyeing, food processing, distilling and brewing, paper, plastics, and photographic industries. The World Health Organization has recommended a guideline value of 0.1 mg/litre of manganese in water intended for domestic use.

## Nickel

Nickel ranks as the 23rd element in order of abundance in the earth's crust, and occurs in nature mainly in combination with sulphur, arsenic and antimony. Nickel enters the environment mainly through the weathering of mineral and rocks and as a result of anthropogenic activities, principally from the burning of fossil fuels, and mining activities.

Nickel occurs in water as a relatively soluble salt associated with suspended solids and in combination with organic material. Under anaerobic conditions and in presence of sulphur, insoluble sulfides are formed. However, under anerobic conditions below pH 9.0, nickel will form compounds with hydroxide, carbonate, sulphate, and organic ligands.

Nickel is absent from most ground waters and normal concentrations in surface waters are of the order of a few µg/l. The World Health Organization has recommended a severe restriction on irrigation water with value of 2.0 mg/l of nickel.

## Lead

Lead is a relatively minor element in the earth's crust but is widely distributed in low concentration in uncontaminated sedimentary rocks and soil. In uncontaminated sea water its concentration is only 0.03 µg/1 but near the surface and near shore the concentration may be as much as ten times this value. Lead concentrations in fresh water are generally much higher. In a survey of 727 samples, lead was found in about 63 percent of the samples in concentrations ranging from 1 to 50 µg/1; only in three samples did the concentration exceed 50 µg/1.

High concentrations of lead result from atmospheric input of lead originating from its use in leaded gasoline or from smelting operations. Industrial and mine or smelter operations may contain relatively large amounts of lead. Many commonly used lead salts are water soluble. Lead acetate is used in printing and dyeing operations; lead chloride and sulfate are used in the manufacture of some explosives. In addition to other sources, the lead in drinking water may be due to the use of lead pipes or of plastic pipes stabilized with lead compounds.

Although the contributions of lead from food and from air are more significant, the World Health Organization has established 0.05 mg/litre as a guideline value for lead in drinking-water. Lead is toxic to aquatic organisms but the degree of toxicity varies greatly, depending on water quality characteristics as well as the species being considered.

## Zinc

Zinc is an abundant element in rocks and ores but it is present in natural water only as a minor constituent because of the lack of solubility of the free metal and its oxides. It is present only in trace quantities in most alkaline surface and ground waters, but more may be present in acid waters. The main industrial use of zinc is in galvanizing and it may enter drinking water from galvanized pipes. Another important use of zinc is in the preparation of alloys, including brass and bronze. Average zinc concentration in surface water is about 10 µg/litre, with a range from 0.2 µg/litre to 1 mg/litre.

Zinc is an essential element in human nutrition. The daily requirement is 4-10 mg depending on age and sex. Food provides the most important source of zinc. Long-term ingestion of quantities considerably in excess of these amounts does not result in adverse effects. The guideline value of zinc in drinking-water is, therefore, based on aesthetic considerations. Water containing zinc at concentrations in excess of 5.0 mg/litre has an undesirable astringent taste and may be opalescent, developing a greasy film on boiling. Although drinking-water seldom has a zinc concentration greater than 0.1 mg/litre, levels in tap-water can be considerably higher because of the zinc used in plumbing materials. The World Health Organization has proposed that the guideline value for zinc in drinking-water should be 5.0 mg/litre, based on taste considerations. Zinc may be toxic to aquatic organisms but the degree of toxicity varies greatly, depending on water quality characteristics as well as the species being considered.

## Cadmium

The chemistry of cadmium is similar to that of lead and zinc. Cadmium is found in nature largely in the form of the sulfide, and as an impurity of zinc - lead ores. The abundance of cadmium is much less than that of zinc. Cadmium may enter surface waters as a consequence of mining and smelting operations. Cadmium may be present in wastes from electroplating plants, pigment works, textile and chemical industries. Groundwater cadmium concentrations as great as 3.2 mg/litre have resulted from the seepage of cadmium from electroplating plants. Metal and plastic pipes constitute an additional possible source of cadmium in waters. In the absence of anthropogenic inputs, the cadmium concentration of surface water is probably below 1 µg/litre.

Cadmium is toxic to man. The reproductive organs may be affected after the administration of very small doses and cadmium is concentrated in the kidneys. There is some evidence that cadmium may be carcinogenic to experimental animals and it has been implicated in human prostrate carcinoma. A specific disease known as "itai - itai" has been observed in Japan where cadmium released from a mining complex resulted in the contamination of water and rice paddies. A guideline value of 5 µg/litre is recommended as the upper level of cadmium in drinking-water (WHO 1984).

Fish and certain invertebrates have been found to be sensitive to very low levels of cadmium in water. Salmonids and cladocerans are among the most sensitive organisms tested. In addition, due to bioaccumulation, certain edible organisms may become hazardous to the ultimate consumer. Therefore, the U.S. Environmental Protection Agency (1976) has recommended that cadmium concentrations should not exceed very low levels ranging from 0.4 µg Cd/l in soft water for the protection of cladocerans and salmonid fishes to 12 µg Cd/litre for the protection of less sensitive aquatic organisms in hard water.

Copper

Copper is a widely distributed trace element but, because most copper minerals are relatively insoluble and because copper is sorbed to solid phases, only low concentrations are normally present in natural waters. Equilibrium with copper oxide or hydroxy-carbonate minerals would limit the concentration of uncomplexed copper in aerated water to about 04 mg/litre at pH 7.0 and about one-tenth that value at pH 8.0. Because of the presence of sulfide, copper would be expected to be even less soluble in anoxic systems. The presence of higher concentrations of copper can usually be attributed to corrosion of copper pipes, industrial wastes or, particularly in reservoirs, the use of copper sulfate as an algicide.

Copper is an essential trace element in the nutrition of plants and animals including man. It is required for the function of several enzymes and is necessary in the biosynthesis of chlorophyll. Higher levels are toxic to organisms but the response varies greatly between species. Algae and molluscs are particularly sensitive to copper and the safe concentration for those organisms is less than 10 µg/litre in soft water.

The presence of copper in a water supply, although not considered as a health hazard, may interfere with the intended domestic uses of the water. Copper in public water supplies increases the corrosion of galvanized iron and steel fittings. At levels above 4 mg/litre, it also imparts a colour and undesirable bitter taste to water. Staining of laundry and plumbing fixtures occurs at copper concentrations above 1.0 mg/litre. Copper is extensively used in domestic plumbing systems, and levels in tap-water can therefore be considerable higher than the level present in water entering the distribution system. The guideline value is 1.0 mg/litre based on its laundry and other staining properties.

Sample Handling - Mn, Pb, Zn, Cd, Cu, Ni

Because manganese, lead, zinc, cadmium, copper and nickel may be lost from solution to the walls of sample containers, samples should be acidified by the addition of 1.5 ml of concentrates $HNO_3$ per litre of sample prior to storage in a plastic container. If the pH is not less than 2 after the addition of acid, more $HNO_3$ should be added. If analyses are to be made of the soluble metal fraction, samples should be filtered through 0.45 µm membrane filters as soon after collection as possible and then the filtrate should be acidified.

## Atomic Absorption Spectrophotometry (AAS)

Atomic absorption spectrophotometry is based on the principle that metallic elements in the ground state will absorb light of the same wavelength which they emit when excited. When radiation from a given excited element is passed through a flame containing ground state atoms of that element, the intensity of the transmitted radiation will decrease in proportion to the amount of ground state elements in the flame. The lamps used to furnish the light beam are called hollow cathode lamps and are made of or lined with the element of interest and filled with an inert gas, generally neon or argon. When subjected to a current, these lamps emit the spectrum of the desired element together with that of the filler gas. The metal atoms to be quantified are placed in the beam of light radiation by aspirating the sample into a flame. The element of interest in the sample is not excited by the influence of the flame, but merely dissociated from its chemical bonds and placed in an unexcited, un-ionized "ground" state. The element is then capable of absorbing radiation from the light source. The amount of radiation absorbed in the flame is proportional to the concentration of the element present. A monochromator isolates the characteristic radiation from the hollow cathode lamp and a photosensitive device measures the attenuated transmitted radiation.

While the simplest analysis procedure is direct aspiration of a liquid sample into the atomizer-burner assembly, there may be limitations of detectability or interferences that make further sample processing necessary to increase concentration or isolate the element of interest from interfering species. One of the more common approaches in the regard is the selective extraction of one or more elements into an immiscible solvent via complex formation. The extraction can be highly selective such as the extraction of aluminium or beryllium into methyl isobutyl ketone (MIBK) as the 8-hydroxyquinoline complex or fairly general as the extraction of the pyrrolidine dithiocarbonate complexes of cadmium, chromium, cobalt, copper, iron, lead and silver into MIBK.

## Specific Methods

(i) Alkali and Alkaline Earth Metals - Na, K, Ca, Mg:

The method of choice is atomic absorption spectrophotometry (AAS) by direct aspiration into an air-acetylene flame. (Standard Methods, 1989, APHA). An optional method for Ca and Mg is by EDTA titration (Standard Methods, 1989, APHA).

(ii) Trace Metals:

### Aluminum

- AAS by direct aspiration into a nitrous oxide - acetylene flame or for low concentrations, chelation with 8-hydroxyquinoline, extraction into methyl isobutyl ketone (MIBK) and aspiration into nitrous oxide-acetylene flame. (Standard Methods, 1989, APHA).

- Colorimetric method with Eriochrome cyanine R dye (Standard Methods, 1989, APHA) uses simple instrumentation.

- Colorimetric method with pyrocatechol violet is used as a highly sensitive flow injection or continuous-flow analysis technique (Standard Methods, 1989, APHA).

### Chromium

- AAS by direct aspiration into an air-acetylene flame. For low concentrations, chelation with ammonium pyrrolidine dithiocarbamate (APDC), extraction into MIBK and aspiration into an air-acetylene flame or use the graphite furnace AAS. (Standard Methods, 1989, APHA).

- Colorimetric method with diphenylcarbazide in acid solution. This is a preferred procedure for measuring hexavalent chromium in a natural or treated water intended to be potable (Standard Methods, 1989, APHA).

### Iron

- AAS by direct aspiration into an air-acetylene flame. For low concentrations, chelation with APDC, extraction into MIBK and aspiration into an air-acetylene flame or use the graphite furnace AAS (Standard Methods, 1989, APHA).

- Colorimetric method with 1,10-phenanthroline (Standard Methods, 1989, APHA).

### Mercury dissolved

- Cold vapour AAS is the preferred method for all samples. The organomercury compounds in the sample are oxidized to inorganic mercury Hg (II) compounds by heating with sulphuric acid, potassium permanganate and potassium persulphate. The mercury compounds are then reduced with stannous chloride in a hydroxylamine sulphate - sodium chloride solution to elemental mercury. The mercury is sparged from solution with a stream of air and passed through an absorption cell situated in the pathway of the mercury lamp (Standard Methods, 1989, APHA).

- Colorimetric dithizone method can be used with potable waters where the mercury levels are high (>2µg/L). (Standard Methods, 1989, APHA).

### Mercury total

- Hot permanganate - peroxodisulphate oxidation (Standard Methods, 1989, APHA).

  Following the procedure, total mercury can be determined in the same fashion as for dissolved mercury.

Manganese

- AAS by direct aspiration into an air-acetylene flame. For low concentrations, chelation with APDC, extraction into MIBK and aspiration into an air-acetylene flame or use the graphite furnace AAS (Standard Methods, 1989, APHA).

- Colorimetric persulphate method (Standard Methods 1989, APHA).

Lead

- AAS by direct aspiration into an air-acetylene flame. For low concentrations, chelation with APDC, extraction into MIBK and aspiration into an air-acetylene flame or use the graphite furnace AAS (Standard Methods, 1989, APHA).

- Colorimetric dithizone method (Standard Methods, 1989, APHA).

Zinc

- AAS by direct aspiration into an air-acetylene flame. For low concentrations (<10µg/L), chelation with APDC, extraction into MIBK and aspiration into an air-acetylene flame. (Standard Methods, 1989, APHA).

- Colorimetric Zincon Method (Standard Methods, 1989, APHA).

Cadmium

- AAS by direct aspiration into an air-acetylene flame. For low concentrations, chelation with APDC, extraction into MIBK and aspiration into an air acetylene flame or use the graphite furnace AAS (Standard Methods, 1989, APHA).

- Colorimetric dithizone method (Standard Methods, 1989, APHA).

Copper

- AAS by direct aspiration into an air-acetylene flame. For low concentrations, chelation with APDC, extraction into MIBK and aspiration into an air-acetylene flame or use the graphite furnace AAS (Standard Methods, 1989, APHA).

- Colorimetric neocuproine and bathocuproine methods (Standard Methods, 1989, APHA).

## 4.0 NON-METALLIC CONSTITUENTS

### Alkalinity

1. General

The alkalinity of a natural or treated water is the capacity of some of its components to accept protons (to bind an equivalent amount of a strong acid). Examples of such components are hydroxyl ions and anions of weak acids, e.g. bicarbonate, carbonate, phosphate, silicate. The equivalent amount of a strong acid needed to neutralise these ions gives the total alkalinity (T). Alkalinity is reported in mg/1 as $CaCO_3$.

The alkalinity of many natural and treated waters is due only to bicarbonates of calcium and magnesium. The pH of these waters does not exceed 8.3. Their total alkalinity is practically identical with their carbonate hardness. Waters having a pH range above 8.3 contain, besides bicarbonates, normal carbonates and, possibly hydroxides. The alkalinity fraction equivalent to the amount of acid needed to lower the pH value of the sample to 8.3 is called phenolphthalein alkalinity (P). The fraction is contributed by the hydroxide, if present, and half of the carbonate (the pH range of 8.3 is approximately that of a dilute bicarbonate solution.)

The determination of alkalinity is useful for dosage of chemicals required in the treatment of water supplies and wastewaters. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of a water for irrigation.

2. Methods

The alkalinity is determined by titration of the sample with a standard solution of a strong mineral acid (Standard Methods, 1989, APHA). The simple and rapid visual method using an indicator is satisfactory for control and routine applications. Electrometric titration is the method of choice for accurate determinations. It must also be used when the colour, turbidity or suspended matter in a sample interferes with the determination by the indicator method. Low alkalinities (below approximately 10 mg/1) are also best determined by electrometric titration.

Titration to the end point of pH 8.3 determines the phenolphthalein alkalinity; to the end point of pH 4.5 the total alkalinity. The pH to which the titration of total alkalinity should be taken lies between 4 and 5; theoretically, it depends on the amount of the alkalinity and free carbon dioxide. For most purposes the end point of pH 4.5 (indicated by methyl orange) gives sufficiently accurate results. For the most accurate determination, however, the pH should be; 5.1 at alkalinity 30 mg/1, 4.8 and 150 mg/1, and 4.5 at 500 mg/1. Methyl orange is suitable for the lower pH values, while a mixed indicator (e.g. prepared from bromocresol green and methyl red) can be used for higher pH values.

Wherever possible, the titration should be carried out at the point of sampling. If this is not possible, the sampling bottle must be completely filled and the alkalinity determined within 24 hours.

### Arsenic

1. General

Arsenic is poisonous and severe toxicity has been reported after ingestion of only 100 mg of the element. Chronic toxicity can result from a build up of lower intakes. Arsenic is not geologically uncommon and occurs in natural water as arsenate ($As0_4^{3-}$) and arsenite ($As0_2$-). Additionally, arsenic may occur from industrial discharges or insecticide application.

2. Sample Handling

Collect the sample in a polyethelyne bottle and acidify with concentrated sulfuric acid (2 ml/l) if it is to be stored. Nitric acid interferes in the determination.

3. Methods

Two analytical methods for inorganic arsenic are suggested:

- Colorimetric method with silver diethyldithiocarbamate: inorganic arsenic is reduced to arsine ($AsH_3$) by zinc in acid solution. arsine is passed through a scrubber container glass wool impregnated with lead acetate solution and into an absorber tube containing silver diethyldithiocarbamate dissolved in pyridine. Arsine reacts with the silver compound to form a soluble red complex which can be measured photometrically. (Standard Methods, 1989, APHA).

- Hydride Generation/AAS: Arsenic is instantaneously converted to arsine by sodium borohydride reagent in acid solution. The volatile hydride is then purged continuously by argon or nitrogen into an appropriate atomizer of an atomic absorption spectrometer and converted to the gas-phase atoms. The sodium borohydride reducing agent, by rapid generation of $AsH_3$

in the reaction cell, minimizes dilution of the hydrides by the carrier gas and permits rapid and sensitive measurements of arsenic (Standard Methods, 1989, APHA).

## Boron

1. General

In most natural waters boron is rarely found in concentrations greater than 1 mg/l, but even this low concentration can have deleterious effects on certain agricultural products including citrus fruits, walnuts, and beans. Water having boron concentrations in excess of 2 mg/l can adversely affect many of the more common crops. Groundwater may have greater concentrations of boron, particularly in areas where the water comes in contact with igneous rocks or other boron-containing strata. The boron content in water has been increasing due to the introduction of industrial waste. The use of boric acid and its salts in cleaning compounds also contributes to this increase.

Ingestion of boron at concentrations usually found in natural water will have no adverse effects on humans. Ingestion of large quantities of boron can affect the central nervous system, while extended consumption of water containing boron can lead to a condition known as borism.

2. Sample Handling

Many types of glass contain boron and consequently their use should be avoided. Samples should be stored in polyethylene bottles or alkali-resistant, boron-free glassware.

3. Methods

Three methods are suggested for the determination of boron in natural waters:

- Colorimetric curcumin method: this method is applicable for waters containing 0.10 to 1.00 mg/l B. A water sample is acidified and evaporated in the presence of curcumin forming a red-coloured product called rosocyanine. This is then taken up in ethanol and the red colour compared photometrically with standards.

- Colorimetric azomethine-H method: This method is applicable in the range 0.04 to 4.0 mg/l B. A yellow complex is formed between azomethine-H and the boron dissolved in the water sample.

- Colorimetric carmine method: This method is applicable for boron concentrations in the range 1.0 to 10.0 mg/l. In the presence of boron, a solution of carmine or carminic acid in concentrated sulphuric acid changes from a bright red to a bluish red or blue, depending on the concentration of boron present.

## Chloride

1. General

Chloride anion is generally present in natural waters. A high concentration occurs in waters from chloride-containing geological formations. Otherwise, a high chloride content may indicate pollution by sewage or some industrial wastes or an intrusion of sea water or other saline water. A salty taste produced by chloride depends on the chemical composition of the water. A concentration of 250 mg/l may be detectable in some waters containing sodium ions. On the other hand, the typical salty taste may be absent in waters containing 1000 mg/1 chloride when calcium and magnesium ions are predominant. A high chloride content also has a deleterious effect on metallic pipes and structures, as well as on agricultural plants.

2. Sample Handling

Collect representative samples in clean, chemically resistant glass or plastic bottles. No special preservative is necessary if the sample is to be stored.

3. Methods

Three methods are suggested:

- The argentometric method is suitable for use in relatively clear waters where the $Cl^-$ concentration in the tested sample is from 0.15 to 10.0 mg/L. In this method, chloride is determined in a neutral or slightly alkaline solution by titration with standard silver nitrate, using potassium chromate as indicator. Silver chloride is quantitatively precipitated before red silver chromate is formed.

- In the mercuric nitrate method, chloride is titrated with mercuric nitrate, Hg $(NO_3)_2$, forming the soluble, slightly dissociated compound mercuric chloride. In the pH range 2.3 to 2.8, diphenylcarbazone, indicates the titration end point by formation of a purple complex with the excess mercuric ions. The end point is easier to detect than in the argentometric method.

- The potentiometric method is suitable for coloured or turbid samples in which colour-indicated end points are difficult to record. Chloride is determined by titration with silver nitrate solution using a glass and silver-silver chloride electrode system. The change of the potential between the two electrodes is detected. The end point of the titration is that instrument reading at which the greatest change in voltage has occurred for a small and constant increment of silver nitrate added.

## Fluoride

1. General

While fluoride is considered to be one of the major ions of sea water, its concentration in sea water, 1.3 mg/kg (Salinity = 35g/kg) is indicative of most natural water concentrations. In rare occasions, natural waters may contain fluoride concentrations up to 10 mg/l, generally in ground waters of arid regions. More commonly, fluoride is added to drinking water to assist in control of dental caries. Such additions require close control of fluoride concentrations (roughly 1.0 mg/l) as higher fluoride levels cause mottling of the teeth. The guideline value of 1.5 mg/l in drinking water has been proposed by WHO. The local application of this value must take into account the climate conditions and levels of water consumption.

Fluoride is frequently found in certain industrial processes and consequently in resulting waste waters. Significant industrial sources of fluoride are coke, glass and ceramic, electronics, and pesticide and fertilizer manufacturing, steel and aluminum processing, and glass and electroplating operations. Waste levels may range from several hundred to several thousand mg/l in raw streams. Notable is that conventional treatment (lime) seldom reduces fluoride concentration below 8 to 15 mg/l without dilution.

2. Sample Handling

Generally clean polyethylene bottles are preferred for collection and storage of samples for fluoride analysis provided long term evaporative loss is not encountered. Glass or pyrex bottles should be avoided but can be used provided low pH is not maintained, the containers have been properly cleaned and have not bee previously in contact with high fluoride concentration solutions. Pre-treatment with high levels of sodium thiosulphate should be avoided (less than 100 mg/l).

3. Methods

- In the reference method, fluoride is determined potentiometrically using a specific ion electrode in conjunction with a standard reference electrode and a pH meter that has an expanded scale capability. Specific ion meters are available that have a direct concentration scale for fluoride. The method is applicable to all natural waters and wastewaters having a fluoride concentration greater than 0.05 mg/L.

- The secondary colorimetric method is used with water samples in which the fluoride has been separated from other nonvolatile constituents by conversion to hydrofluoric or fluosilicic acid and subsequent distillation. The fluoride-containing distillate is reacted with alizarin fluorine blue-lanthanum reagent to form a blue complex measured photometrically at 620 nm. This method is applicable to potable, surface and saline waters as well as domestic and industrial wastewaters. The range of the procedure, which can be modified by using an adjustable colorimeter, is 0.1 to 2.0 mg $F^-$/L.

## Ammonia

1. General

Ammonia is formed by the deamination of organic nitrogen - containing compounds and by the hydrolysis of urea. Ammonia is readily available as a nutrient for plant uptake and, therefore may contribute greatly to increased biological productivity. It is easily oxidized to nitrite and nitrate in the presence of sufficient oxygen (nitrification). Under anaerobic conditions, organic nitrogen is converted into ionized $(NH_4^+)$ and un-ionized $(HN_3)$ ammonia. Un-ionized ammonia is toxic to fish at fairly low concentrations; however, it is in equilibrium with the less toxic $NH_4^+$ ion and, for the pH and temperature ranges of most natural waters, its relative concentration is quite low.

Ammonia concentrations vary from less than 10 µg ammonia nitrogen/L in some surface and groundwaters to more than 30 mg/L in wastewaters.

2. Sample Handling

If it is not possible to carry out the determination very soon after the sampling, then the best way is to refrigerate the sample at $4^0$C. Chemical preservation may be done by adding either 20 to 40 mg $HgCl_2$ or 1 ml $H_2SO_4$ to 1 litre of sample.

As regards sewage samples, any urea present is hydrolysed by the enzyme ureas which is normally present, and the reaction is usually complete after the sewage has settled and passed to the biological oxidation stage. Samples of crude sewage may need overnight storage in the laboratory before all the urea has been converted to free ammonia and the analysis of this becomes comparable with that of settled sewage.

3. Methods

Ammonia concentration and the presence of interferences are the two major factors determining the method of analysis. In general, the direct manual determination of low levels of ammonia is restricted to drinking waters, clean surface water and good quality nitrified wastewater. Where interferences are present and greater precision is required, a preliminary distillation step (Standard Methods, 1989) is required. Following distillation, the following test options are available:

- The titrimetric method is the reference for waste waters and can be used for polluted surface and ground waters where $NH_3$ -N concentrations are generally greater than 5 mg/L.

- The Nessler colorimetric method is sensitive to 20 µg $NH_3$ -N/L under optimum conditions and may be used for up to 5 mg $NH_3$ -N/L.

- The phenate colorimetric method has a sensitivity of 10 µg $NH_3$ -N/L and is useful for up to 500 µg $NH_3$ -N/L.

Two techniques measure ammonia without preliminary distillation. A direct colorimetric method using Nessler's reagent assumes limited interferences and can be employed as a rapid confirmatory test or for routine estimations. In the second colorimetric method, the sample is chlorinated in the presence of phosphate buffer, excess hypochlorite is destroyed and the chlorinated ammonia is determined with O-tolidine. This automated technique is applicable for measuring ammonia in surface waters in the range 1 to 150 µg $NH_3$-N/L. (Analytical Methods Manual, 1979).

## Total Kjeldahl And Organic Nitrogen

1. General

Total Kjeldahl nitrogen is defined as the sum of the free ammonia and organic nitrogen compounds which are converted to ammonium bisulphate during the digestion process. The method determines nitrogen in the trinegative state only and fails to account for nitrogen in the form of azide, azine, azo, hydrazone, nitrate, nitrite, nitrile, nitro, oxime and semi-carbazone.

Organic nitrogen is calculated as the difference between total Kjeldahl nitrogen and free ammonia. Organic nitrogen may also be determined directly by removal of the ammonia before the digestion step.

2. Sample Handling

Samples should be stored at $4^0$C and may be preserved by the addition of 2 mL of conc. $H_2SO_4$ per litre. Samples should be analyzed within 24 h of sampling because conversion of organic nitrogen to ammonia may occur.

3. Methods

The Kjeldahl method involves a digestion procedure in which sulphuric acid, potassium sulphate and mercuric sulphate (a catalyst) are added to a water sample so as to mineralize the organic nitrogen to ammonium bisulphate. The ammonia is then distilled from an alkaline medium and absorbed in boric acid. The ammonia can be determined by titration with standard sulphuric acid, using a mixed indicator. This method is applicable to surface waters, wastewaters and saline waters where total Kjeldahl nitrogen concentrations are greater than 0.5 mg/L N. Values less than this may be questionable and should be determined using an ultraviolet digestion procedure described in Analytical Methods Manual (1979).

A secondary method is based on the mineralization of organic matter in an acid medium followed by the determination of ammonia by indophenol blue spectrophotometry. (GEMS/Water Operational Guide, 1987).

## Nitrate

1. General

Nitrate, the most highly oxidized form of nitrogen compounds, is commonly present in rural waters, because it is the end produce of the aerobic decomposition of organic nitrogenous matter. Significant sources of nitrate are chemical fertilizers from cultivated land, drainage from livestock feed lots, as well as domestic and some industrial waters.

The determination of nitrate helps to follow the character and degree of oxidation in streams, in ground water penetrating through soil layers, in biological processes and advanced treatment of waste water. Unpolluted natural waters usually contain only minute amounts of nitrate. Excessive concentrations in drinking water are considered hazardous for infants; in their intestinal tract, nitrates are reduced to nitrites which may cause methaemoglobinaemia. In surface water, nitrate is a nutrient taken up by plants and converted into cell protein. The growth stimulation of plants, especially of algae, may cause objectionable eutrophication. The subsequent death and decay of plants produces secondary pollution.

2. Sample Handling

To prevent any change in the nitrogen balance through activity, the nitrate determination should be started promptly after sampling. If storage is necessary, samples should be kept at a temperature just above the freezing point, with or without preservatives such as $H_2SO_4$ (0.8 ml $H_2SO_4$, (density 1.84) per litre of sample) or $HgCl_2$, (40 mg mercury as mercuric chloride per litre of sample). If acid preservation is employed, the sample should be neutralized to about pH 7 immediately before the analysis is begun.

3. Methods

Nitrate determinations are rather difficult as a result of the relatively complex procedures required, the high probability of interfering constituents being present, and the limited concentration ranges offered by various methods - consequently, several methods are presented covering a wide range of $NO_3$ -N concentrations. It is up to the analyst to select the method most suitable for the sample types and the available laboratory equipment. The first method is used to determine the concentration of nitrate plus nitrite.

- The cadmium reduction method uses Cd granules or a granulated cadmium-copper catalyst to reduce nitrate to nitrite. The nitrite produced plus that originally present is reacted with sulphanilamide to form the diazo compound. The coupling reaction is carried out on the diazotized sample by the addition of N-(1-naphthyl)-ethylenediamine dihydrochloride to form the azo dye. The azo dye intensity, which is proportional to the nitrate concentrations is then measured spectrophotometrically. Separate nitrate and nitrite values can be obtained by carrying out the procedure without the cadmium reduction step. This method is used with surface, ground and wastewaters where $NO_3$ concentrations range from 0.005 to 2.0 mg/L N.

- The brucine colorimetric method measures the yellow complex formed upon the reaction of nitrate with brucine (GEMS/Water Operational Guide, 1987).

- The chromotropic acid method is a colorimetric technique based upon the yellow colour produced by the reaction of nitrate with chromotropic acid (1,8 - dihydroxynaphthalene -3,6- disulphonic acid) (GEMS/Water Operational Guide, 1987).

- Devarda's alloy method employs a reduction of nitrate to ammonia by nascent hydrogen using Devarda's aloy (59% Al, 39% Cu, 2% Zn). The resulting ammonia is distilled and measured by titration or colorimetrically with Nessler's reagent (GEMS/Water Operational Guide, 1987).

## Nitrite

1. General

Nitrite is formed in waters by oxidation of ammonium compounds or by reduction of nitrate. As an intermediate stage in the nitrogen cycle, it is unstable. Usual concentrations in natural waters are in the range of some tenths of mg/l. Higher amounts are present in sewage and industrial wastes, especially in biologically purified effluents, and in polluted streams. The nitrite concentration in collected samples can change very rapidly due to bacterial oxidative or reductive conversions.

2. Sample Handling

The determination should be made promptly on fresh samples to prevent bacterial conversion of the nitrite to nitrate or ammonia. In no case should acid preservation be used for samples to be analyzed for nitrite. Short-term preservation for 1 to 2 days is possible by deep-freezing (-20$^0$C), or by the addition of 40 mg mercuric ion as $HgCl_2$ per litre of sample, with storage at 4$^0$C.

3. Methods

In this Colorimetric method: nitrite reacts in strongly acid medium with sulfanilamide. The resulting diazo compound is coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride to form an intensely red-coloured azo-compound. The absorbence of the dye is proportional to the concentration of nitrite present. The method is applicable in the range of 0.01 to 1.0 mg/l nitrite nitrogen. Samples containing higher concentrations must be diluted.

## Phosphorus

### 1. General

Phosphate is released into natural waters by the weathering of rocks. Depending on the pH, orthophosphate may exist in any of three forms (i.e. $H_3PO_4$,$H_2PO_4^-$, $HPO_4^{2-}$); the predominant forms at pH 6-8 are $H_2PO_4^-$(10%) and $H_2PO_4^{2-}$(90%). The latter is the principal nutrient form. Orthophosphates are bioavailable. Once assimilated, they are converted to organic phosphorus and into condensed phosphates. Upon death of an organism, the condensed phosphates are released into the water. They are not available for biological uptake, however, until they are hydrolysed into orthophosphates by bacteria. The availability of phosphorus to biota depends on the uptake and release rates by biota, chemical speciation (e.g. organic or inorganic bound phosphorus) and the relative abundance and residence time of the dissolved phosphorus fraction.

Ground waters contain only very small amounts of phosphates, usually less than 0.1 mg/l. Exceptions are waters from phosphate-containing soil, or polluted by organic matter.

Orthophosphates are supplied as fertilizers. Condensed phosphates are used in the water treatment of some water supplies. They are major constituents of many cleaning preparations (detergents). Organophosphorus compounds produced in biological processes are regular constituents of sewage. Phosphorus compounds are carried into natural waters with waste waters and storm runoff. They may produce a secondary pollution, being essential nutrients. In waters where phosphorus is a growth-limiting nutrient it stimulates the growth of photosynthetic aquatic micro and macro-organisms sometimes in nuisance quantities.

Occurrence of different phosphorus compounds in waters and the analytical procedures for their determination result in the following classifications:

CLASSIFICATION OF PHOSPHORUS FRACTIONS

| Chemical Types | Physical States | | |
|---|---|---|---|
| | Total | Filtrable dissolved | Particulate |
| Total | a. Total dissolved and suspended phosphorus | e.Total filtrable (dissolved) phosphorus | i.Total particulate phosphorus |
| Orthophosphate | b.Total dissolved and suspended orthophosphate | f.Filtrable (dissolved) orthophosphate | j.Particulate orthophosphate |
| Acid hydrolysable phosphate | c.Total dissolved and suspended acid-hydrolysable | g.Filtrable (dissolved) acid hydrolysable phosphate | k.Particulate acid-hydrolysable phosphate |
| Organophosphorus | d.Total dissolved and suspended organophosphorus | h.Filtrable (dissolved) organophosphorus | l.Particulate organo-phosphorus |

In the revised GEMS/Water programme, only data on total phosphorus are required, i.e., unfiltered (a), dissolved (e), and particulate (i).

### 2. Sample Handling

If phosphorus forms are to be differentiated, filter sample immediately after collection. Preserve by freezing at or below -10°C. Add 40 mg $HgCl_2$/L to the sample, especially, for long-term storage. Do not add either acid or $CHCl_3$ as a preservative if phosphorus forms are to be determined. For total P analyses, add 1 ml conc HCl/L or freeze without any additions.

Do not store samples containing low P concentrations, unless in a frozen state, to prevent P absorption on the walls of the container. Rinse all glass sample bottles with hot, dilute HCl followed by several rinses with distilled water. Avoid all detergents containing phosphate for glass cleaning.

3. Methods

Phosphorus analyses involve two general procedural steps: (a) conversion of the phosphorus form to dissolved orthophosphate, and (b) colorimetric determination of the dissolved orthophosphate. The separation of phosphorus into its various forms is defined analytically but these differentiations are structural so as to assist data interpretation.

Filtration through a 0.45 µm membrane filter separates dissolved from suspended forms of phosphorus. However, this is not a true separation of dissolved and suspended phosphorus; it is merely a convenient and replicable analytical technique. Consequently, the term "filterable" is preferred to "soluble".

- Orthophosphate: Orthophosphate, or "reactive phosphorus" is phosphate that responds to colorimetric tests without preliminary hydrolysis or oxidative digestion of the sample. Orthophosphate occurs in both dissolved (filterable) and suspended forms. Two analytical methods are recommended based on the phosphorus concentration:

  (a) For P concentrations in the range 0.01 to 6.0 mg/L, the ascorbic acid method, a colorimetric technique is recommended. In this, ammonium molybdate and potassium antimonyl tartrate react in acid medium with orthophosphate to form a heteropoly acid-phosphomolybolic acid that is reduced to intensely coloured molybdenum blue by ascorbic acid.

  (b) For P concentrations < 20 µg/L, an extraction step, in which the molydenum blue complex from up to 200 ml of sample is extracted into a relatively small volume of hexanol, is used to increase the sensitivity of the analysis.

- Acid-Hyrolyzable (Inorganic) Phosphate: This fraction generally includes condensed phosphates such as pyro-, tripoly-, and higher-molecular weight species such as hexametaphosphate. In addition, some natural waters contain organic phosphate compounds that are hydrolysed to orthophosphate under the test conditions. In the procedure, acid hydrolysis at boiling-water temperature converts dissolved and particulate condensed phosphates to dissolved orthophosphate which is then measured colorimetrically as in "orthophosphate" method.

- Total Phosphorus: This fraction includes orthophosphate, acid-hydrolysable and organic phosphorus. Because phosphorus may occur in combination with organic phosphorus, a rigorous digestion step is required to oxidize the organic matter and liberate phosphorus as dissolved orthophosphate. Various digestion procedures are suggested: The perchloric acid method, the most drastic and time-consuming, is recommended only for particularly difficult samples such as sediments. The nitric-sulphuric acid method is recommended for most samples. However, the simplest method by far is the persulphate oxidation technique. Following digestion, the dissolved orthophosphate is measured colorimetrically.

The total phosphorus as well as the dissolved (filterable) and suspended fractions may each be divided analytically into orthophosphate, acid-hydrolysable and organic phosphorus. Note that the determinations are usually conducted only on the unfiltered and filtered samples. Suspended fractions are calculated by difference.

## Dissolved Oxygen

1. General

The oxygen dissolved in surface waters is largely derived from the atmosphere and from the photosynthetic activity of algae and higher aquatic plants. In the surface waters of productive lakes, photosynthesis may produce supersaturation by day, and respiration may result in a concentration well below saturation by night. Oxygen is only moderately soluble in water. Concentrations of dissolved oxygen will vary daily and seasonally and depend on the species of phytoplankton present, light penetration, nutrient availability, temperature, salinity, water movement, partial pressure of atmospheric oxygen in contact with the water, thickness of the surface film and biodepletion rates (by aquatic organisms and oxidation and decomposition processes).

In the bottom waters of lakes and reservoirs, the concentration of dissolved oxygen can be decreased by oxidation of inorganic wastes and nutrients and by processes that consume organic matter. The rate and extent of decomposition is a function of the type of matter available and the composition and numbers of bacteria. If these processes exceed oxygen supply, the water can become anaerobic. Under such conditions, aquatic organisms can be affected both from the effects of low dissolved oxygen and from the chemical changes in the water column; eg., increased solubility of trace elements from the bottom sediments.

The dissolved oxygen concentration is important for the evaluation of surface-water quality and waste-treatment process control. It is essential for aerobic respiration and is an indicator of the biological activity (i.e. photosynthesis) in a body of water. Dissolved oxygen can be associated with the corrosivity and septicity of water.

2. Sample Handling

Collect samples very carefully so as to avoid contact with air or any agitation. Procedures and equipment have been developed for sampling waters under pressure and unconfined waters such as streams, rivers and reservoirs (Standard Methods, 1989, APHA). Ideally, a sample should be taken in which a several-fold displacement of the liquid in the sampling bottle occurs without agitation producing air bubbles. If chemical preservatives are to be used, they should be added immediately after sample collection as changes in the dissolved oxygen may occur rapidly. Record sample temperature to the nearest degree Celsius and, if very accurate records are required, note the barometric pressure.

3. Methods

Two methods are prescribed:

- The iodometric test (Winkler method) is the most precise and reliable titrimetric procedure for dissolved oxygen analysis. The sample is treated with manganous sulphate and a strongly alkaline iodide reagent. The manganous hydroxide formed reacts with the dissolved oxygen in the sample to form a brown precipitate, manganic hydroxide. Upon acidification, in the presence of iodide, iodine is liberated to an amount equivalent to the dissolved oxygen originally present. The iodine is then titrated with sodium thiosulphate. Modifications to the Winkler titration include the addition of sodium azide and treating the sample with acid permanganate to eliminate interferences from nitrate and ferrous iron respectively.

- The membrane-electrode method is based on the diffusion of molecular oxygen across a membrane and its reduction on the electrode surface. This method is particularly useful in strong wastes which interfere with the idometric methods or its modifications. It is well suited for field testing, especially for use in situ, and for continuous monitoring.

## Selenium

1. General

The chemistry of selenium is similar in many respects to that of sulphur, but selenium is a much less common element. The selenium concentrations usually found in water are of the order of a few micrograms per litre, but may reach 50-300 µg/l in seleniferous areas and have been reported to reach 1 mg/l in drainage water from seleniferous irrigated soil. Well water containing 9 mg of selenium per litre has been reported.

Little is known about the oxidation state of selenium in water. Selenium appears in the soil as basic ferric selenite, calcium selenate, and as elemental selenium. Although the solubility of elemental selenium is limited, selenium may be present in water in the elemental form as well as the selenate ($SeO_4^{2-}$), selenite ($SeO_3^{2-}$), and selenide ($Se^{2-}$) anions. In addition, many organic compounds of selenium are known. The geochemical control of selenium concentrations in water is not understood, but adsorption by sediments and suspended materials appears to be of importance.

Selenium is an essential, beneficial element required by animals in trace amounts but toxic to them when ingested at higher levels. The World Health Organization has placed a tentative limit of 0.01 mg/l on the selenium content of drinking water. In man, symptoms of selenium toxicity are similar to those of arsenic poisoning. Selenium poisoning in animals has occurred when grazing has taken place exclusively in areas where the vegetation contains toxic levels of selenium, due to highly seleniferous soils. In general, such soils are found in arid or semiarid areas of limited agricultural activity. Selenium deficiency in animals occurs in many areas of the world and causes large losses in animal production.

2. Sample Handling

Selenium in concentrations of around 1 µg/l has been found to be adsorbed on Pyrex glass and on polyethylene containers. Collect the sample in a polyethylene bottle and acidify by the addition of 1.5 ml of concentrated $HNO_3$ per litre if the sample is to be stored.

3. Methods

Two general methods are recommended:

- The AAS method is applicable to surface, ground and saline water and industrial wastewater and measures selenium in the concentration range 2 to 20 µg/L. The procedure involves the destruction of all organoselenides with acidic persulphate, the reduction of all selenium forms to selenite with a potassium iodide-stammous chloride mixture and a further reduction of selenite to hydrogen selenide via the generation of hydrogen with aluminum or zinc in acid. The $H_2Se$ is then stripped from solution with argon and carried into the hydrogen flame of an AAS for measurement of Se. A refinement of this method uses a tube furnace in the AAS and can achieve a detection level of 0.1 µg/L (Analytical Methods Manual, 1979).

- The colorimetric method uses diaminobenzidine or 2,3-diaminonapthalene to react with selenite and produce a brightly coloured and strongly fluorescent piazselenol compound. Piazselenol is then extracted into toluene (GEMS Manual) or cyclohexane and measured colorimetrically or fluorometrically. (GEMS/Water Operational Guide, 1987).

## Reactive Silica

1. General

Silicon ranks next to oxygen in abundance in the earth's crust. It appears as the oxide (silica) in quartz and sand and is combined with metals in the form of many complex silicate minerals, particularly igneous rocks. The chemical reactions involved in the decomposition of silicates are highly complex. In general they can be represented as hydrolysis reactions in which the silicate lattice is altered. In most of these reactions, clay minerals are formed and excess silica is released. This results in the presence of silica in natural water, both as suspended particles in a colloidal or polymeric state, and as silicic acids or silicate ions. In addition to silicon in mineral matter, particulate silicon is also present in the cell walls of diatoms. The actual form of silica in a sample is not generally known. It is customary to report the concentration of silicon present in a water sample in terms of the oxide, silica ($SiO_2$).

The concentration of silica in most natural waters is in the range 1 to 30 mg/l but concentrations as high as 100 mg/l are not uncommon. Concentrations over 100 mg/l are relatively rare, although concentrations exceeding 1000 mg/l are found in some brackish water and brines, and in particular, geothermal waters associated with volcanic activity.

Silica in water is undesirable for a number of industrial uses because it forms silica and silicate scales on various items of equipment and these scales are difficult to remove. Silica is particularly undesirable in boiler feed water; a pure silica deposit can be formed on high-pressure steam-turbine blades. Silica removal is most commonly accomplished by deionization using strongly basic anion-exchange resins or by distillation. Some older plants use precipitation with magnesium oxide in either the hot or cold lime softening process.

2. Sample Handling

All samples should be stored in plastic bottles to prevent leaching of silica from glass. Samples for reactive silica should be filtered through a 0.45 µm membrane filter as soon after sample collection as possible. All samples should be stored at 4°C, without preservatives and they should be analyzed within one week of collection.

3. Methods

For all methods, batches of chemicals low in silica should be used. All reagents should be stored in plastic containers as a precaution against high blank values. Deionized water often contains traces of soluble silica; distilled water for reagents used in the determination of silica is to be preferred.

Two colorimetric methods are based on the reaction of silica with molybdate in acid solution:

- In the molybdosilicate method, ammonium molybdate reacts with silica at pH 1.2 to form molybdosilicic acid, a yellow compound whose colour intensity is proportional to the concentration of "molybdate-reactive" silica. The minimum detection concentration is approximately 1 mg $SiO_2$/L.

- For increased sensitivity (detection level 20 µg $SiO_2$/L), the yellow molybdosilicic acid in previous method is reduced by means of aminonaphtholsulphonic acid to heteropoly blue which is more intense than the yellow colour. An automated adaptation of the heteropoly blue method utilizes a continuous-flow analyzer and is suitable for potable, surface, domestic and other waters containing 0 to 20 mg $SiO_2$/L.

## Sulphate

1. General

Sulphate is an abundant ion in the earth's crust and high concentrations may be present in winter due to leaching of gypsum, sodium sulphate, and some shales. As a result of oxidation of pyrites, mine drainage may contain high concentrations of sulphate. Sulphate also results from sulphur-containing organic compounds and sulphate is present in many industrial waste discharges. Sulphate concentrations in natural water range from a few mg to several thousand mg per litre. Sulphate exerts a cathartic action in the presence of magnesium or sodium ions. The taste threshold is in the range of from 400 mg/1 to 1000 mg/1 depending on the taste sensitivity of the consumer. The World Health Organization has established a guideline level of 400 mg/1 in drinking water based on taste considerations.

2. Sample Handling

Samples may be stored in either plastic or glass containers. It is recommended that samples be refrigerated and stored for not more than 7 days. This reduces the possibility of bacterial reduction of sulphate to sulphide in polluted samples. Reduction of the pH to less than 8.0 inhibits oxidation of sulphite to sulphate by dissolved oxygen.

3. Methods

Four methods are presented for a range of sulphate concentrations and laboratory operating conditions:

- The gravimetric method with residue ignition is suitable for $SO_4^{2-}$ concentrations above 10 mg/L. Here, sulphate is precipitated in a HCl solution as barium sulphate by the addition of barium chloride. The precipitation is carried out near the boiling temperature, and after a period of digestion, the precipitate is filtered, washed with water until free of $Cl^-$, ignited and weighed as $BaSO_4$.

- The turbidimetric method measures $SO_4^{2-}$ in the range 1 to 40 mg/L. Sulphate ion is precipitated in an acid medium with barium chloride so as to form barium sulphate crystals of uniform size. Light absorbance of the $BaSO_4$ suspension is measured by a photometer and the $SO_4^{2-}$ concentration is determined by comparison of the reading with a standard curve.

- The titrimetric method is applicable to surface and ground waters containing 5 to 150 mg $SO_4^{2-}$/L. Sulphate ion is titrated in an alcoholic solution under controlled acid conditions with a standard barium chloride solution. Thorin is used as the indicator.

- The automated methylthymol blue method is applicable to potable, surface and saline waters as well as domestic and industrial wastewaters over a range from about 10 to 300 mg $SO_4^{2-}$/L. In this procedure, barium sulphate is formed by reaction of the $SO_4^{2-}$ with barium chloride at a low pH. At high pH, excess barium reacts with methylthymol blue to produce a blue chelate. The uncomplexed methylthymol blue is gray and can be used to quantify the concentration of $SO_4^{2-}$.

## Sodium Adsorption Ratio (SAR)

Excess sodium in irrigation water relative to calcium and magnesium or relative to the total salt content can adversely affect soil structure and reduce the rate at which water moves into and through the soil (infiltration, permeability), as well as reducing the soil aeration. When calcium is the predominant cation of the soil exchange complex, the soil tends to have a granular structure that is easily workable and permeable. However, when adsorbed sodium exceeds 10-15% of the total cations, the clay becomes dispersed when wetted, and the soil becomes puddled when wet, lowering permeability and forming a hard permeable crust when dry.

The magnitude of the effect of excess sodium can be related to the relative proportion of sodium ions and calcium plus magnesium ions in the irrigation water. The Sodium Adsorption Ratio (SAR) can be calculated as follows:

$$SAR = \frac{Na^+}{\sqrt{\frac{Ca^{2+} + Mg^{2+}}{2}}}$$

Where concentrations of $Na^+$, $Ca^{2+}$, and $Mg^{2+}$ are expressed in milliequivalents per litre, as totals.

When the SAR approaches 10, the probability of soil permeability problems increases. However the potential permeability effects of SAR can be counteracted by high salt concentrations.

## 5.0 ORGANIC CONSTITUENTS

### Biochemical Oxygen Demand (BOD)

1. General

The biochemical oxygen demand (BOD) is an empirical test, in which standardized laboratory procedures are used to estimate the relative oxygen requirements of waste waters, effluents and polluted waters. Micro-organisms utilize the atmospheric oxygen dissolved in the water for biochemical oxidation of polluting matter, which is their source of carbon. The biochemical oxygen demand is used as an approximate measure of the amount of biochemically degradable organic matter in a sample.

The BOD determined by the dilution method has come to be used as an approximate measure of the amount of biochemically degradable organic matter in a sample. For this purpose the dilution test, applied skilfully to samples in which nitrification does not occur, remains probably the most suitable single test, though in some cases manometric methods may warrant consideration. The analyst should also consider whether the information required could be obtained some other way. For example, the chemical oxygen test will effect virtually complete oxidation of most organic substances and thus indicate the amount of oxygen required for complete oxidation of the sample. In other circumstances, and particularly in research work, determination of the organic carbon content may be more appropriate. In any case, results obtained by the BOD test should never be considered in isolation but only in the context of local conditions and the results of other tests.

Complete oxidation of a given waste may require a period of incubation too long for practical purposes. For this reason, the 5-day period has been accepted as standard. However, for certain industrial wastes, and for waters polluted by them, it may be advisable to determine the oxidation curve obtained. Calculations of ultimate biochemical oxygen demand from 5-day BOD values (e.g. based on calculations using exponential first order rate expressions) are not correct. Conversion of data from one incubation period to another can only be made if the course of the oxidation curve has been determined for the individual case by a series of BOD-tests carried out in different incubation periods.

2. Sample Handling

Samples for BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. Minimize reduction of BOD by analyzing sample promptly or by cooling it to near-freezing temperature during storage. However, even at low temperature, keep holding time to a minimum. Warm chilled samples to 20°C before analysis.

- Grab samples - If analysis is begun within 2 hrs of collection, cold storage is unnecessary. If analysis is not started within 2 hours of samples collection, keep sample at or below 4°C from the time of collection. Begin analysis within 6 hours of collection; when this is not possible because the sampling site is distant from the laboratory, store at or below 4°C and report length and temperature of storage with the results. In no case start analysis more than 24 hours after grab sample collection. When samples are to be used for regulatory purposes make every effort to deliver samples for analysis within 6 hours of collection.

- Composite samples - Keep samples at or below 4°C during compositing. Limit compositing period to 24 hours. Use the same criteria as for storage of grab samples, starting the measurement of holding time from end of compositing period. State storage time and conditions as part of the results.

3. Methods

The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 days. Dissolved oxygen (DO) is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined immediately after the dilution is made, all oxygen uptake, including that occurring during the first 15 minutes is included in the BOD measurement.

Interferences and inadequacies with BOD test:

- If required, adjust sample pH to between 6.5 and 8.5 with sufficient alkali or acid.

- If the sample is sterile, introduce a biological population capable of oxidizing the organic matter in the wastewater (i.e. seeding);

- If the sample is supersaturated with dissolved oxygen, reduce DO concentration to saturation level before testing;

- If sample contains any residual chlorine, allow sample to stand for 1 to 2 hours before testing or sodium bisulphite to remove higher levels of chlorine and chlorine-containing compounds.

Recommended dilution rates and formulations for dilution water make-up for the BOD test are provided in many standard analytical texts (e.g., Standard Methods 1989, APHA.

## Chemical Oxygen Demand (COD)

### 1. General

The chemical oxygen demand (COD) is used as a measure of the oxygen equivalent of the organic matter content of a sample that is susceptible to oxidation by a strong chemical oxidant. It is an important, rapidly measured variable for characterizing streams, sewage, industrial waste and treatment plant effluents. For samples from a specific source, COD can be related empirically to BOD, organic carbon, or organic matter. The test is useful for monitoring and control after correlation has been established. The dichromate reflux method is preferred over procedures using other oxidants because of superior oxidizing ability, applicability to a wide variety of samples, and ease of manipulation. Oxidation of most organic compounds is 95 to 100% of the theoretical value. Pyridine and related compounds resist oxidation and volatile organic compounds are oxidized only to the extent that they remain in contact with the oxidant. Ammonia, present either in the waste or liberated from nitrogen-containing organic matter, is not oxidized in the absence of significant concentration of free chloride ions.

### 2. Sample Handling

Preferably collect samples in glass bottles. Test unstable samples without delay. If delay before analysis is unavoidable, preserve sample by acidification to pH $\leq 2$ using concentrated $H_2SO_4$. Blend samples containing settleable solids with a homogenizer to permit representative sampling. Make preliminary dilutions for wastes containing a high COD to reduce the error inherent in measuring small sample volumes.

### 3. Methods

The dichromate method is the reference procedure for COD determinations. In this, a sample is refluxed in strongly acid solution with a known excess of potassium dichromate. Most types or organic matter are oxidized in the boiling mixture of chromic and sulphuric acid. After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulphate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent.

## Organic Carbon

### 1. General

The concentration of organic carbon present in surface water is generally less than 10 mg/1, except where a high concentration of municipal or industrial waste is present. Higher levels of organic carbon may be encountered in highly coloured water, and water collected from swamps may have organic carbon concentrations exceeding 100 mg/1. For municipal wastewater treatment plants, influent total organic carbon concentrations may reach several hundred mg/1, but effluent concentrations from a secondary treatment facility are typically less than 50 mg of organic carbon per litre.

### 2. Sample Handling

Collect and store samples in bottles made of glass, preferably brown. Plastic containers are acceptable after tests have demonstrated the absence of extractable carbonaceous substances. Samples that cannot be examined promptly should be protected from decomposition or oxidation by preservation at 0° to 4°C, minimal exposure to light and atmosphere, or acidification with sulfuric acid to a pH not over 2. Under any conditions, minimize storage time. Maximum storage time should not exceed 7 days and, depending on the type of sample, even shorter storage may be indicated.

### 3. Methods

To determine the quantity of organically bound carbon, the organic molecules must be broken down to single carbon units and converted to a single molecular form that can be measured quantitatively. TOC methods utilize heat and oxygen, ultraviolet irradiation, chemical oxidants, or combinations of these oxidants to convert organic carbon to carbon dioxide ($CO_2$). The $CO_2$ may be titrated chemically.

The methods and instruments used in measuring organic carbon analyze fractions of total carbon (TC) and measure of dissolved or particulate organic carbon by two or more determinations. These fractions of total carbon are defined as: inorganic carbon (IC)- the carbonate, bicarbonate, and dissolved $CO_2$; total organic carbon (TOC)- all carbon atoms covalently bonded in organic molecules; dissolved organic carbon (DOC) - the fraction of TOC that passes through a 0.45-µm-pore-diam filter; nondissolved organic carbon (NDOC) - also referred to as particulate organic carbon, the fraction of TOC retained by a 0.45-µm filter; purgeable organic carbon (POC) - also referred to as volatile organic carbon, the fraction of TOC removed from an aqueous solution by gas stripping under specified conditions; and nonpurgeable organic carbon (NPOC) - the fraction of TOC not removed by gas stripping.

In most water samples, the IC fraction is many times greater than the TOC fraction. Eliminating or compensating for IC interferences requires multiple determinations to measure true TOC. IC interference can be eliminated by acidifying samples to pH 2 or less to convert IC species to $CO_2$. Subsequently, purging the sample with a purified gas removes the $CO_2$ by volatilization. Sample purging also removes POC so that the organic carbon measurement made after eliminating IC interferences is actually a NPOC determination; determine POC to measure true TOC. In many surface and ground waters the POC contribution to TOC is negligible. Therefore, in practice, the NPOC determination is substituted for TOC.

## Chlorophyll *a*

1. General

The concentration of photosynthetic pigments is used extensively to estimate phytoplankton biomass. All green plants contain chlorophyll *a*, which constitutes approximately 1 to 2% of the dry weight of planktonic algae. Other pigments that occur in phytoplankton include chlorophylls *b* and *c*, xanthophylls, phycobilins, and carotenes. The important chlorophyll degradation products found in the aquatic environment are the chlorophyllides, pheophoribides, and pheophytins. The presence or absence of the various photosynthetic pigments is used, among other features, to separate the major algal groups.

2. Sample Handling

Collect sample in polyethylene bottle. Add 0.1 to 0.2 ml of magnesium carbonate suspension; sample can be stored in a cool dark place for a maximum of about 8 h. It is desirable, however, that samples be filtered at the time of collection; the filter can be stored frozen until analysis. Filters, however, should not be stored more than several days; then they should be extracted without delay or a lower result will be obtained.

3. Methods

Basically, the water sample is filtered and the residue extracted with acetone for spectrophotometric determinations at the specified wavelengths. Chlorophyll values are calculated by SCOR/UNESCO equations. For detailed method, please refer to Chapter VI of this Guide.

## Analysis of Trace Organics

Analytical methods for trace organic constituents in water generally involve isolation and concentration of the organics from a sample by solvent or gas extraction, separation of the components, and identification and quantification of the compounds with a detector. Various extraction techniques are available allowing the analysis of ultratrace (parts-per-trillion) levels of organic pollutants.

With closed-loop stripping analysis (CLSA), volatile organic-compounds of intermediate molecular weight are stripped from water by a recirculating stream of air. The organics are removed from the gas phase by an activated carbon filter and then extracted into carbon disulphide for analysis. In the purge and trap procedure, also suitable for volatile compounds, an inert gas is bubbled through the sample to concentrate the organics. The collector gas is then concentrated in a sorbent trap from which the organic compounds are desorbed for measurement.

A gas chromatograph (GC) used to separate the individual organic compounds, consists of a mobile phase (carrier gas) and a stationary phase (column packing or capillary column coating). When the sample solution is introduced into the column, the organic compounds are vaporized and transported through the column by the carrier gas. Travel times for individual compounds vary depending on differences in partition coefficients between the mobile and stationary phases.

Various detectors are available for use with GC systems:

(1) The electrolytic conductivity detector is a sensitive and element-specific device used in the analysis of purgeable halocarbons, pesticides, herbicides, pharmaceuticals and nitrosamines.

(2) The electron capture detector is utilized for testing organic compounds having high electron affinities, such as chlorinated pesticides, drugs and their metabolites. It is highly sensitive toward molecules that contain electronegative groups: halogens, peroxides, quinones and nitro groups but relatively insensitive toward functional groups such as amines, alcohols and hydrocarbons.

(3) The flame ionization detector is widely used because of its overall sensitivity to most organic compounds, its large linear response range, its reliability and ease of operation and its fast response.

(4) The photoionization detector has high sensitivity, low noise, a large linear response range, is non-destructive and can be used as a universal or selective detector.

(5) The mass spectrometer can detect a wide variety of compounds, and can deduce organic compound structures from fragmentation patterns, or mass spectra. The quadruple mass spectrometer has wide application in water and wastewater analysis.

## Total Hydrocarbons

1. General

Total hydrocarbons can be determined as a second step in oil and grease analyses. Oil and grease represent a group of substances with similar physical characteristics that are measured quantitatively on the basis of their common solubility in trichlorotrifluorethane. The methodology for oil and grease analysis is suitable for both biological lipids and mineral hydrocarbons.

Certain constituents measured by the oil and grease analysis may influence waste-water treatment systems. If present in excessive amounts, they may interfere with aerobic and anaerobic biological processes and lead to decreased wastewater treatment efficiency. When discharged in wastewater or treated effluents, they may cause surface films and shoreline deposits leading to environmental degradation. A knowledge of the quantity of oil and grease present is helpful in proper design and operation of wastewater treatment systems and also may call attention to certain treatment difficulties.

2. Sample Handling

Collect a representative sample in an wide-mouth glass bottle that has been rinsed with the solvent to remove any detergent film, and acidify in the sample bottle. Collect a separate sample for an oil and grease determination and do not subdivide in the laboratory. When information is required about average grease concentration over an extended period, examine individual portions collected at prescribed time intervals to eliminate losses of grease on sampling equipment during collection of a composite sample.

In sampling sludges, take every possible precaution to obtain a representative sample. When analysis cannot be made immediately, preserve samples with 1 mL conc. HCl/80 g sample. Never preserve samples with $CHCl_3$ or sodium benzoate.

3. Methods

Oil and grease analysis, which is usually the first step in the determination of hydrocarbons, involves an initial extraction of the liquid sample by trichlorotrifluoroethane. The extracted oil and grease is then measured by one of three methods:

- the partition-gravimetric method;
- the partition-infrared method is designed for samples containing volatile hydrocarbons and is sensitive to low levels of oil and grease (i.e. <10 mg/L);
- the Soxhlet method is used when relatively polar, heavy petroleum fractions are present or when there are high levels of nonvolatile greases which could exceed the solubility limit of the extracting solvent.

## Total Chlorinated Hydrocarbons

1. General

Total chlorinated hydrocarbons is a measure of the halogenated organic material in a water sample. Dissolved organic halogens (DOX) or adsorbable organic halides (AOX) compounds are indicative of synthetic chemical contamination and include but are not limited to: the trihalomethanes (THMs); organic solvents such as trichloroethene, tetrachloroethene, and other halogenated alkanes and alkenes; chlorinated and brominated pesticides and herbicides; polychlorinated biphenyls (PCBs); chlorinated aromatics such as hexachlorobenzene and 2,4-dichlorophenol; and high-molecular-weight, partially chlorinated aquatic humic substances. Compound-specific methods such as gas chromatography typically are more sensitive than AOX measurements.

AOX analysis is an inexpensive and useful method for screening large numbers of samples before specific (and often more complex) analyses; for extensive field surveying for pollution by certain classes of synthetic organic compounds in natural waters; for mapping the extent of organohalide contamination in groundwater; for monitoring the breakthrough of some synthetic organic compounds in water treatment processes; and for estimating the level of formation of chlorinated organic by-products after disinfection with chlorine. When used as a screening tool, a large positive (i.e., above background measurements) AOX test result indicates the need for identifying and quantifying specific substances. In saline or brackish waters the high inorganic halogen concentration interfere. The possibility of overestimating AOX concentration because of inorganic halide interference always should be considered when interpreting results.

2. Sample Handling

Collect composite samples over a one hour period and store in amber glass bottles. If amber bottles are not available, polyethylene bottles can be used, but must be stored in the dark. Acidify samples taken downstream of a biological treatment plant to pH 1.5-2.0 with nitric acid. Completely fill the bottles with sample and seal. For bleach plant effluents containing residual chlorine, add sodium sulphite crystals. If samples cannot be analyzed promptly, refrigerate at 4°C with minimal exposure to light. Storage time and temperature must be reported in all cases.

3. Methods

The method involves the adsorption of halogenated organic material on granular activated carbon (GAC). Inorganic halides that also adsorb on the carbon are removed by washing with a nitrate solution. The GAC with adsorbed organic material is then pyrolyzed in a combustion furnace and the resulting halides, including chloride, bromide and iodide are determined by microcoulometric titration and reported as chloride. Fluorinated organics are not detectable.

The method is described in (Standard Methods, (1989), APHA).

## Phenols

1. General

Phenols defined as hydroxy derivatives of benzene and its condensed nuclei, may occur in domestic and industrial wastewaters, natural waters, and potable water supplies. Chlorination of such waters may produce odorous and objectionable-tasting chlorophenols. Phenol removal processes in water treatment include superchlorination, chlorine dioxide or chloramine treatment, ozonation, and activated carbon adsorption.

2. Sample Handling

Phenols in concentrations usually encountered in wastewaters are subject to biological and chemical oxidation. Preserve and store samples at 4°C or lower unless analyzed within 4 hours after collection. Acidify with 2 mL conc $H_2SO_4$/L. Samples may be stored for 4 weeks at 4°C. Preserved and stored samples should be analyzed within 28 days after collection.

3. Methods

The colorimetric method is suitable for measuring total phenolic compounds in the concentration range 1 to 250 µg/L using phenol ($C_6H_5OH$) as a standard. Steam-distillable phenols react with 4-aminoantipyrine at pH 7.9 ± 0.1 in the presence of potassium ferricyanide to form a coloured antipyrine dye. This dye is extracted from aqueous solution with chloroform and the absorbance is measured at 460 nm. For individual phenolic compounds, gas chromatographic and gas chromatographic/mass spectrometric methods are available (Standard Methods, 1989, APHA).

## Benzene

1. General

Benzene is a monocyclic aromatic compound ($C_6H_6$) used as an intermediate in chemical and pharmaceutical manufacturing, including the preparation of styrene, cyclohexane, detergents and pesticides. It is used as a thinner for lacquers and paints, a degreasing and cleaning agent, an solvent in the rubber industry and a fuel additive. Benzene is also used in dyes, explosives, flavours and perfumes and photographic materials.

Benzene may be released into the aquatic environment from both point and nonpoint sources. Sources include spills and releases during manufacturing use, evaporation and combustion of fuel. As it is volatile, benzene will readily evaporate from surface waters, hence concentrations in the water column will genrally be low. Although very little is known about its environmental fate, volatilization with subsequent atmospheric oxidation is considered to be its primary fate. Some biodegradation may occur over an extended period of time. Toxicological studies have linked benzene to adverse human health effects.

2. Methods

The purge and trap gas chromatographic method is applicable to purgeable aromatics like benzene. Detection can be by a photoionization unit or by mass spectrometry (Standard Methods, 1989, APHA).

## Organochlorine Pesticides

The organochlorine pesticides commonly occur in waters that have been affected by agricultural discharges. Several of the pesticides are bioaccumulative and relatively stable, as well as toxic or carcinogenic; thus they require dose monitoring.

Aldrin: The original uses of aldrin were as a pesticide for control of soil, fruit and vegetable pests, as well as for specific control of grasshoppers, locusts and termites. Aldrin is applied to soil and foliage by injection or aerial spraying. Leaching of aldrin is thought to be minimal, with soil erosion and sediment transport the major pathways for entering the aquatic environment. Various studies have reported aldrin concentrations in surface waters ranging from 0.1 to 85 mg/L. Biotransformation, volatilization, bioaccumulation and photolysis may all play significant roles in removing aldrin from the water column. Little information is available on environmental residue levels of aldrin, probably because it is rapidly transformed to dieldrin in the environment.

Dieldrin: Dieldrin has seen wide application as a pesticide for control of soil, fruit and vegetable pests, as well for control of grasshoppers, locusts and termites. It has also been used to mothproof woolen garments. Dieldrin enters the environment through manufacturing emissions and applications. The pathways for general environmental contamination by dieldrin include atmospheric dispersion, wind and water erosion of soil and transport while sorbed onto soil particles in the silt of streams, estuaries and also can be transported as residues in plants and animals, especially in fish and wildfowl.

Lindane: Benzene hexachloride (BHC) is the common name used to describe the mixed stereoisomers of 1,2,3,4,5,6-hexachlorocyclohexane (HCH). The γ-isomer, called lindane, is the only hexachlorocyclohexane isomer possessing significant insecticidal activity. BHC (technical grade) is a mixture of the eight possible isomers that constitute the different spatial arrangements of the six chlorine atoms on the *trans* form of the cyclohexane ring. Its composition approximates 65% α-isomer; 11% β; 13-14% γ; 8-9% δ; and 1% ε. The lowest melting point compound, melting at 112.8°C, is designated as the γ-isomer. Because γ-BHC (lindane) is the active ingredient in technical-grade BHC, technical-grade BHC now has limited use commercially except as the raw material from which the purified γ-isomer is extracted.

γ-BHC (lindane) has been used to control insects in domestic and commercial settings, in numerous agricultural and silvicultural applications and in dips, sprays and dusts for livestock and domestic pets. Direct and indirect application of lindane, agricultural runoff and industrial discharges are the principal sources of lindane in surface waters. Long-range transport and, consequently, atmospheric deposition appear to be the mechanisms by which lindane and its isomers occur in the surface waters of isolated areas. Other sources include the pulp and paper industry, pesticide packaging and manufacturing plants, farm buildings and warehouse spraying and the seed dressing industry.

Lindane is relatively stable in the water column. Sorption to suspend sediment and biota and volatilization do not appear to be important removal mechanisms for this compound. Lindane can be biologically transformed, particularly in anaerobic sediments, to penta - and tetrachlorocyclohexanes. Bioaccumulation in aquatic organisms can occur although lindane appears to be rapidly eliminated once continuous exposure ceases.

DDT: (1,1,1-trichloro-2,2-bis(4-chlorophenyl)ethane) was the first of a series of chlorinated hydrocarbons manufactured as insecticides. DDT was first synthesized in 1874; its use began in 1942 and 1943 when its effectiveness as an insecticide was demonstrated during World War II. DDT has been used extensively throughout the world for public health and agricultural programs because of its efficiency as a broad-spectrum insecticide and its low cost to manufacture.

DDT has several derivatives or metabolites. Those most frequently found in nature are DDD (TDE), 1,1'-dichloro-2,2-bis-(4-chlorophenyl)ethane, and DDE, 1,1'-dichloro-2,2-bis-(chlorophenyl)ethylene, both of which are toxic, persistent in the environment and have widespread occurrence.

DDT may enter the aquatic environment through its manufacture and application. The pathways for general environmental contamination by DDT include atmospheric dispersion, wind and water erosion of soil and transport while sorbed onto soil particles in the silt of streams, estuaries and oceans.

Because of the persistent nature of DDT, coupled with its hydrophobic properties and solubility in lipids, this pesticide is concentrated by aquatic organisms at all trophic levels. It enters the food web, and is biomagnified. Bioconcentration factors for DDT as high as $10^6$ have been reported for several species in aquatic systems.

2. Sample Handling (Aldrin, Dieldrin, Lindane, DDT)

Collect grab samples in 1-L amber glass bottles fitted with a screw lined cap. If amber bottles are not available, protect samples from light. Wash and rinse bottle and cap liner with acetone or methylene chloride, and dry before use. Follow conventional sampling practices but do not rinse bottle with sample. Collect composite samples in refrigerated glass containers. Optionally, use automatic sampling equipment as free as possible of plastic tubing and other potential sources of contamination; incorporate glass sample containers for collecting a minimum of 250 mL. Refrigerate sample containers at 4°C and protect from light during compositing. If the sampler includes a peristaltic pump, use a minimum length of compressible silicone rubber tubing, but before use, thoroughly rinse it with methanol and rinse repeatedly with distilled water to minimize contamination. Use an integrating flow meter to collect flow-proportional composites. Fill sample bottles and, if residual chlorine is present, add 80 mg sodium thiosulphate per litre of sample and mix well. Ice all samples or refrigerate at 4°C from time of collection until extraction. Extract samples within 7 days of collection and analyze completely within 40 days of extraction.

3. Methods (Aldrin, Dieldrin, Lindane, DDT)

The method for organochlorine pesticides is based on liquid-liquid extraction of water samples using a mixed solvent, diethyl ether/hexane or methylene chloride/hexane, followed by electron capture gas chromatography.

## Polychlorinated Biphenyls (PCBs)

1. General

Polychlorinated biphenyls (PCBs) have been widely used in industrial applications because they have excellent thermal stability, strong resistance to both acid and base hydrolysis, general inertness, solubility in organic solvents, excellent di-electric properties, resistance to oxidation and reduction and nonflammability. They are also good lubricants and have high film strength.

The empirical formula for PCBs is $C_{12}H_{10-n}Cl_n$ where n may be any value from 1 to 10. There are 209 theoretically possible chlorinated biphenyl congeners of which 194 have more than two chlorine atoms. PCBs with 5 or more chlorine atoms per molecule are referred to as "higher chlorobiphenyls" and are relatively more persistent in the environment than "lower chlorobiphenyls".

PCB congeners have a low solubility in water and high octanol-water partition coefficients, bioaccumulation potential and resistance to degradation. Removal from the water column is primarily accomplished by sorption onto suspended and bottom sediments, particularly sediments of small particle size and those enriched in organic matter. PCBs are very stable and persistent in the environment with photochemical transformation perhaps the only important degradation pathway in the water column. Microbial transformation in bottom sediments is generally limited to lower chlorinated congeners under aerobic conditions, although recent studies have indicated that several penta - and hexachlorobiphenyls can be dechlorinated by anaerobic bacteria. PCBs are soluble in the lipids of biological systems and therefore tend to accumulate in fatty tissues, especially the higher chlorinated, planar PCB congeners.

2. Sample Handling

Refer to organochlorine pesticides.

3. Methods

The water sample is extracted by an organic solvent, after which the solvent extract is cleaned up and concentrated to an appropriate volume for direct GC analysis. Separation, detection and measurement is accomplished by electron-capture gas chromatography.

## Polynuclear Aromatic Hydrocarbons (PAHs)

1. General

Polynuclear aromatic hydrocarbons (PAHs) are generated by processes that involve the incomplete combustion of organic material. They are thus produced in the burning of fuels and refuse, and from thermal power stations and internal combustion engines. Materials containing polynuclear aromatic hydrocarbons may also directly enter the aquatic environment via the release of crude oil and petroleum products during exploration, production, transport and natural seepage, and the release of PAHs from materials used in water, such as creosoted pilings, piers and containment facilities. Atmospheric deposition is believed to be a significant route of entry of PAHs into the aquatic environment, and is responsible for much of the background concentration of PAHs. Water and land-based discharges may also contribute significant amounts of PAHs.

Concentrations of PAHs in aquatic ecosystems are generally highest in sediments, intermediate in aquatic biota and lowest in the water column. Levels can be quite variable as well, in part reflecting the degree of urban and industrial development in a watershed and the specific use of the water. Removal processes include volatilization of low-molecular weight PAHs and photolysis of PAHs dissolved in the water column. Those compounds accumulated in the bottom sediments will also undergo some biodegradation and biotransformation. Both low- and high- molecular weight PAHs accumulate in the tissues of aquatic organisms fairly rapidly; however, metabolism and separation of PAH compounds can also occur quickly.

2. Sample Handling

Refer to organochlorine pesticides. PAHs are light-sensitive, necessitating the storage of samples, extracts and standards in amber or foil-wrapped bottles so as to minimize photolytic decomposition.

3. Methods

The water sample is extracted by an organic solvent, after which the solvent is cleaned up and concentrated to an appropriate volume for direct GC analysis. Separation, detection and measurement is by gas chromatography and either a mass spectrometer or flame ionization detector, (Standard Methods 1989 APHA), also presents a high-performance liquid chromatographic (HPLC) method using ultraviolet and fluorescence detection.

## Atrazine

1. General

Atrazine, 2- chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine, is a herbicide used for the pre- and post-emergence control of annual broadleaf and grassy weeds. Commercial uses include the control of grassy weeds in corn, sorghum, sugar cane and pineapple, and various turf and forestry applications. It is also applied as a soil sterilant on noncroplands such as airfields, parking lots and industrial sites. Atrazine may enter the aquatic environment during production, spillage, use and disposal. The majority of atrazine loss via surface runoff occurs immediately following application and during rainstorm runoff events.

The principal mode of biological action of atrazine appears to be the blockage of photosynthesis. Because of potentially detrimental effects to algae and aquatic vascular plants (and therefore fish and aquatic invertebrates), the concentration of atrazine in freshwater should not exceed 2 µg/L for the protection of aquatic life.

2. Sample Handling

Water samples for atrazine testing should be collected in long-necked, glass bottles (1 L) and kept in the dark at 4°C until analyzed. Teflon-lined bottle caps are recommended or pre-cleaned heavy aluminum foil can be used to prevent the sample from contacting the bottle cap. Samples should be analyzed as soon as possible after collection.

3. Methods

Neutral herbicides such as atrazine are analyzed by the liquid-liquid extraction gas chromatographic method. In this, the neutral herbicides are isolated from the water by acidification of the sample followed by solvent extraction with dichloromethane. Co-extracted acidic components are then separated from the neutral analytes by back extraction with alkaline solution. Other interferences are removed by column chromatography on Florisil prior to GC analysis. An electron capture detector can be used to measure all parameters; however, increased specificity and sensitivity to atrazine is obtained by employing a nitrogen phosphorus detector.

## 2,4-D

2,4 - dichlorophenoxyacetic acid, or 2,4-D, is used as a systemic herbicide to control broadleaf weeds in cereal cropland and on industrial property, lawns, turfs, pastures and non crop land. It is also used in grain farming to eliminate competing weeds, in forestry and in clearing right-of-ways for public utilities. Aquatic uses include the control of rooted macrophytes and floating and submerged weeds.

2,4-D enters the aquatic environment from herbicide manufacturing and packaging plants, from municipal effluents, via atmospheric deposition, and from direct application to surface waters. Important removal processes in water include photochemical degradation and microbial decomposition under aerobic conditions. Microbial degradation in soils also occurs and is favoured by moist, warm conditions and a high organic content.

2. Sample Handling

Collect samples in 1 L amber glass bottles with lined caps. If amber bottles are not available, protect samples from light.

3. Methods

A gas chromatographic method employing derivatization and GC with an electron capture detector is recommended. Because chlorinated phenoxy acid herbicides like 2,4-D may occur in water in various forms (e.g. acid, salt, ester) a hydrolysis step is included to permit measurement of the active part of the compound. Chlorinated phenoxy acids and their esters are extracted from the acidified water sample with ethyl ether. The extracts are hydrolysed and extraneous material is removed by a solvent wash. The acids are converted to methyl esters and are further cleaned up on a microadsorption column. The methyl esters are determined by gas chromatography.

## Aldicarb

1. General

Aldicarb is an oxime carbamate pesticide used primarily for beets, potatoes, tobacco, onions, peanuts and ornamentals. Carbamate pesticides are synthetic relatives of the alkaloid physostigmine from the calabar bean. They comprise a diverse group of organic chemicals based on carbamic acid ($H_2NCOOH$). Carbamate toxicity to insects is due to inhibition of acetylcholinesterase at certain synaptic junctions in the nervous system. Aldicarb is one of the most acutely toxic registered pesticides with an average lethal dose of 0.6 mg/kg of body weight.

The environmental fates of carbamates vary widely; each compound's lifetime in a specific situation depends upon various physical and chemical parameters. Although some information is available on their persistence in terrestrial systems, relatively little information is available on their persistence in aqueous systems. In general, as a class, the carbamates are not considered to be long-term contaminants in the environment; they do not persist as long as many of the organochlorine pesticides under similar circumstances.

The major processes governing the fate of carbamates in the aquatic environment appear to be alkaline hydrolysis, photolysis and biodegradation, although rates of removal from the water column vary dramatically with the specific carbamate. Sorption does not appear to play a significant role in removing carbamates from the water column. Because they are water-soluble, it is expected that only a small fraction of the carbamates present in aqueous systems would be associated with sediments. Bioaccumulation of carbamates is not expected to be significant in the aquatic environment because of their generally weak lipophilic character and relatively rapid degradation.

2. Sample Handling

It is recommended that the sample be frozen immediately after collection and prior to analysis. Because this is not always feasible, Lesage (1989) proposed the use of Supelco C8 reversed-phase cartridges to collect and ship the aldicarb samples. An advantage to this treatment is that sample preconcentration is also possible.

3. Methods

Aldicarb is metabolized to the toxic metabolites, aldicarb sulfoxide and sulfone; therefore, any practical residue analysis should consider the total bioactive complex either by summation of individual compound analyses or through conversion of the residues to a common material. Gas chromatographic methods have encountered difficulties in differentiating the parent aldicarb and metabolic products and have been subject to rather restrictive analytical procedures.

A successful method that can measure low levels of aldicarb residues employs on-line pre-concentration and high performance liquid chromatography (HPLC). In this technique, the aldicarb residues are separated on a reverse phase HPLC column using an acetonitrite-water gradient mobile phase. Separation is followed by post-column hydrolysis to yield methylamine, and formation of a fluorophore with o-phthalaldehyde and 2-mercaptoethanol prior to fluorescence detection (Chaput, 1986). Improvements to the pre-concentration step involve the use of solid-phase extraction cartridges which also act as excellent sample collection and shipping devices (Lesage, 1989).

## Organophosphorus Pesticides

1. General

Organophosphorus compounds enjoy an ever increasing share of the synthetic organic insecticide market. This is based on several factors: (i) their broad spectrum of applicability to numerous pests on a variety of crops (ii) an advantageous cost-performance analysis; and (iii) a reduced level of resistance by various insect strains compared to other types of organic insecticides. Three compounds, - parathion, methyl parathion and malathion, account for a majority of the annual volume in organophosphorus sales in North America. Organophosphorus insecticides function by a common mechanism, that of cholinesterase inhibition in the nervous system.

Most organophosphorus pesticides (diazinon excluded) are readily hydrolysed in water. This is important in that the insecticide can be detoxified within a plant prior to the product going to market. Various pathways to the aquatic environment exist and include aerial spraying, the direct application to water bodies and most importantly, leaching and surface runoff from treated terrestrial ecosystems. Effective removal mechanisms involve sorption to sediments, volatilization from shallow water bodies and soils, microbial degradation and chemical hydrolysis.

Malathion, parathion and methyl parathion are rapidly degraded in the environment such that significant bioaccumulation in aquatic organisms is not expected.

2. Sample Handling

Water samples should be collected in 1.2-L glass bottles and stored at $4^0C$ or just above the freezing point to retard degradation of some organophosphorous pesticides. A clean piece of aluminum foil should cover the mouth of the sample bottle before the plastic cap is tightened. Preferably, extraction should be done in the field, and the extracts sent to the laboratories for analysis. Avoid exposure to sunlight.

3. Methods

Gas chromatographic methods are used to measure specific organophosphorus pesticides (e.g., malathion, parathion, etc.). Although an electron capture detector is suitable in the analysis, superior sensitivity and detection is available through the use of flame photometric detector (FPD) and nitrogen-phosphorus detectors (NPD). Standardized methods are available from Analytical Methods Manual (1991, V. 3) and from the U.S. EPA (Method 1618).

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UNEP/WHO/UNESCO/WMO PROGRAMME ON GLOBAL WATER QUALITY MONITORING AND ASSESSMENT

GEMS/WATER OPERATIONAL GUIDE

# CHAPTER IV: MONITORING OF PARTICULATE MATTER QUALITY

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# 1.0 INTRODUCTION

The monitoring of particulate matter has been recognized as a major component of the GEMS/Water programme. Although it can be very useful in water quality surveys, routine monitoring of particulate matter in rivers and lakes is still rare. The following recommendations are mainly based on Thomas and Meybeck (1991) and take into account the re-orientation of the programme during GEMS/Water Phase Two. More information on trace metals in rivers may be found in Horowitz (1991).

Monitoring of particulate matter differs from water monitoring itself, therefore special attention has been given in this chapter to sampling and to additional analyses which are to be made on the suspended or deposited material. The analysis of the dissolved elements does not fundamentally differ from analysis recommended in Chapter III of this Guide. Therefore, only the special laboratory operations relevant to the dissolution of the particulate matter are presented here. The final part describes the methods of data reporting and discussion of results.

The present chapter reviews two levels of monitoring: a basic study, and then the complete monitoring of the particulate matter. This has been done in recognition of the different technical and financial capability of the countries participating in the GEMS/Water programme.

# 2.0 IMPORTANCE OF PARTICULATE MATTER IN WATER QUALITY SURVEYS

## 2.1 Types of particulate matter

According to their means of transportation, three major types of particulate matter can be distinguished in rivers and lakes:

(i) Suspended matter particles are maintained in suspension by the water turbulence without contact with the bed of the water body. The total suspended matter in rivers usually ranges from a few $mg.l^{-1}$ to a few $g.l^{-1}$; however higher contents have been measured in some rivers or during hydrological events such as floods. In lakes, the suspended material is usually less than 10 $mg.l^{-1}$ and consists mostly of organic lacustrine detritus and very fine terrigenous material. In rivers the suspended material originates mainly from land erosion and has a relatively fine grain size (e.g., clay and silt fractions) in most rivers.

(ii) The Bedload is the part of the particulate matter which remains in almost constant contact with the riverbed and is moved by rolling, sliding or skipping. The bedload consists of coarse particles (coarse sand, gravel, pebbles) which move along the river bed much more slowly than the velocity of the flowing water.

(iii) Deposited matter (or bottom sediments) results from the decrease of energy level in the water body. Coarse material is deposited first. In the centre of lakes, the sediments occur generally as fine particles from the silt and clay-size fractions, while in rivers the deposited material is more heterogeneous with alternate fine and coarse layers.

More details on origins, transport and occurrence of particulate material can be found in Golterman et al. 1983.

### Dissolved and particulate matter

The distinction between dissolved and particulate matter is mainly technical, for there is no physical discontinuity between the dissolved and solid states which are linked by the colloidal state. Therefore, the ratio of dissolved to particulate matter for a given sample will depend on the separation method. At present, the most commonly used means of separation is filtration through 0.4 or 0.45 µm pore-sized filters. The use of continuous-flow centrifugation is rapidly expanding and provides much greater quantities of particulate matter than filters which clog rapidly (Horowitz et al 1989). Due to the difficulties and cost of appropriate separation methods (e.g., centrigation), it is recommended within GEMS/Water to use deposited sediments, except for determination of river fluxes where suspended matter will have to be analyzed.

## 2.2 Particulate Matter and Environmental Quality

Particulate matter should be considered in environmental quality studies for their role as:

(i) pollutant carrier: heavy metals and organic micro-pollutants are carried preferentially on the particulate matter. The percentage of heavy metals carried by the suspended matter ranges from 20% to 99% depending on the amount and type of particulate matter. Therefore it is important that suspended matter be taken into account in flux assessments.
(ii) pollutant reservoir: when deposited, the contaminated particulate matter constitutes a potential pollutant reservoir which may contaminate the biota through direct contact (e.g., benthic organisms and filter feeders) or by releasing pollutants into the water column. Deposited material is generally analyzed together with biota in ecotoxicological surveys.
(iii) pollutant indicator: as pollutants are generally concentrated in the particulate phase, this material can be used to detect environmental contamination even when concentrations in the water are very low. This is the most common use of river deposited sediment.

Table 1. Type of information relevant to particulate matter analysis and interpretation (with fictitious example)

A. STATION DESCRIPTION

| | | | |
|---|---|---|---|
| Water body: | River Phison | Sample code: | 007 |
| Station code/name: | Paradise Bridge | Sample depth: | cm |
| River discharge: | 120.0 $m^3/s$ | Type of sample (suspended/deposited): | |
| Sampling date: | 01-04-1991 | Type of sampler(hand/grab/core): | |

B. SAMPLE TREATMENT

| Physical Treatment | Chemical Treatment | Analytical Method |
|---|---|---|
| 1. no treatment: unfiltered water | 1. acid (name) | 1. organic C analyzer |
| 2. filtration | 2. solvent extraction(name) | 2. atomic absorption spectrometry |
| 3. ultracentrifugation | 3. ....... | 3. flameless atomic absorption spectrometry |
| 4. sieving | 4. | 4. gas chromatography |
| 5. drying (°C) | | 5. ....... |
| 6. ignition (°C) | | |

C. ANALYTICAL RESULTS

| | | | Treatments: Physical | Chemical | Analysis |
|---|---|---|---|---|---|
| 1. Inorganic Pollutants: | | | | | |
| Arsenic | 12.5 | $\mu g$ As $g^{-1}$ | 4;5 (50°C) | 1 | |
| Cadmium | 0.95 | $\mu g$ Cd $g^{-1}$ | 4;5 (106°C) | 1 | |
| Chromium | 215 | $\mu g$ Cr $g^{-1}$ | 4;5 (106°C) | 1 | 2 |
| Copper | 45 | $\mu g$ Cu $g^{-1}$ | 4;6 (550°C) | 1 | 2 |
| Mercury | 0.22 | $\mu g$ Hg $g^{-1}$ | 4;5 (50°C) | 1 | |
| Nickel | 135 | $\mu g$ Ni $g^{-1}$ | 4;6 (550°C) | 1 | 2 |
| Lead | 260 | $\mu g$ Pb $g^{-1}$ | 4;5 (50°C) | 1 | |
| Zinc | 340 | $\mu g$ Zn $g^{-1}$ | 4;6 (550°C) | 1 | 2 |
| 2. Nutrients: | | | | | |
| Particulate organic carbon | 5.3% | | | | |
| Particulate nitrogen | 0.58% | | | | |
| Total part. phosphorous | 1630 $\mu g$ P $g^{-1}$ | | | | |
| 3. Organic Pollutants: | | | | | |
| River unfiltered water: | | | | | |
| PCB: | 0.60 | $\mu g.l^{-1}$ | | | |
| ΣDDT: | 0.24 | $\mu g.l^{-1}$ | | | |
| Lindane: | 0.30 | $\mu g.l^{-1}$ | | | |
| Total hydrocarbons: | 7200 | $\mu g.l^{-1}$ | | | |
| Bottom Sediments: | | | | | |
| PCB: | 170 | $\mu g.kg^{-1}$ | | | |
| ΣDDT: | 23 | $\mu g.kg^{-1}$ | | | |
| Lindane: | 37 | $\mu g.kg^{-1}$ | | | |
| Total hydrocarbons: | 240 | $\mu g.kg^{-1}$ | | | |
| 4. Supporting Analyses: | | | | | |
| Aluminum: | 105000 | $\mu g$ Al $g^{-1}$ | | | |
| Iron: | 55000 | $\mu g$ Fe $g^{-1}$ | | | |
| Grain size (median): | 35 | $\mu m$ | | | |
| Quartz content: | 7.5 | % | | | |

D. MISCELLANEOUS INFORMATION

| | | |
|---|---|---|
| Water content (bottom sediment): | 23 | % wet weight |
| Total Suspended Solids (river samples): | | $mg.l^{-1}$ |

(iv) record of pollution: the sediment deposited in lakes and rivers can often provide complete records of environmental changes, through time, including pollution. Lake sediments, which are less subject to re-entrainment, are now widely studied for that purpose. The changes of concentrations of nutrients and organic matter of water bodies can also be studied through these deposits.

## 2.3 Information Relevant to Particulate Matter Quality

In addition to the list of variables taken into account within GEMS/Water, additional types of information are often required to support interpretation of particulate matter data: (e.g., aluminum, carbonate or quartz contents, granulometry) or for the computation of fluxes(e.g., rates of deposition). Four categories of information type and variables relevant to particulate matter are listed in Table 1.

It must be noted that the list of variables presented in Table 1 is not exhaustive. Many other substances may be harmful to man and biota, but the analysis of the substances listed will give a first assessment of particulate matter quality. Microbiological analyses, despite their importance, are not considered, for the moment, in the monitoring of particulate matter.

## 2.4 Origin of Particulate Matter

The natural particles found in water bodies consist mainly of land erosion material including rock debris, various residual minerals such as clays, feldspars and quartz, and terrestrial organic detritus. Particulate matter may also derive from the atmosphere (volcanic ashes, marine aerosols, wind-erosion products), and autochthonous material produced within the water body itself (e.g., organic matter and sometimes calcium carbonate). This particulate material may contain naturally occurring toxic elements such as lead, arsenic, cadmium and mercury; nutrients (nitrogen, phosphorus); organic carbon; etc.; the concentration of these elements constitute what will be referred to as the natural background. This "background" will vary both geographically and temporally according to geological, climatic, and vegetation characteristics. In some regions, the background concentration of one given element may be high enough to cause detrimental effects on biota or man.

Various human activities have two major effects on particulate matter:

i) They modify the quantities and composition of natural particulate matter; and

ii) add synthetic substances not occurring naturally in the environment (xenobiotic compounds) which may be harmful to man and the biota. The synthetic substances may be discharged as particulates from various industrial, urban and agricultural activities or discharged in solution and be readily taken up by particulates through various processes (e.g., adsorption).

## 2.5 Behaviour of Chemical Compounds Bound to Particulate Matter

Particulate pollutants and nutrients can be partitioned into different chemical forms (speciation), likely to occur in the suspended sediments. These forms depend on the origin of the substances bound to the particulate matter and on environmental conditions (e.g., such as Ph, redox potential etc). The major forms under which pollutants and nutrients occur in particulate matter are the following:

- adsorbed onto particles;
- bound to organic material, which consists mainly of organic debris and humic substances;
- bound to carbonates;
- occluded in Fe and Mn oxides, which occur commonly as particle coatings;
- bound to sulfides;
- including in the mineral matrix (specific minerals, silicates and other nonalterable minerals).

In unpolluted conditions the majority of mineral compounds (trace metals, mineral phosphorus, arsenic) are found in the three last categories. When the concentrations of these variables increase, additional inputs are mainly adsorbed onto particulates and bound to organic substances. The great majority of synthetic organic compounds will be found in the adsorbed fraction.

The adsorption capacity of particulate matter is inversely proportional to its grain size: the finest fractions (colloids and clays) and the organic matter will have the highest concentrations of trace metals and of organic pollutants.

As the environmental conditions change, the various forms of pollutants associated with the particulate matter are likely to be altered, and may be released in various amounts into solution where they may become available to the biota.

### 2.6 Development of a Programme for Monitoring of Particulate Matter Quality

#### 2.6.1 Objectives

The objectives of a monitoring programme of particulate matter quality are:

(i) to assess the present levels of pollutants found in the particulate matter and their variations in time and in space;
(ii) to determine the direct or potential bio-availability of these substances during the transport of particulate matter through rivers,lakes and reservoirs;
(iii) to determine the fluxes of these substances to major water bodies (lakes, reservoirs, regional seas and oceans);
(iv) to establish the trends of these levels and fluxes.

These objectives are listed in an increasing order of complexity with each step involving additional measurements (i.e., supporting analyses). The present level of contamination can be assessed with the analyses of only a few samples per year. Flux determination requires continuous or very frequent measurements of the suspended matter and water discharge coupled with frequent chemical analyses of the particulate matter.

Establishment of trend levels and fluxes is usually done by studying the sediments deposited on the bottom of a lake or river since the beginning of human activities in the area surrounding the water body. This implies chronological studies of the sediment which are generally based on sophisticated radionuclide measurements or palynological determinations. As a result, the type of information one could obtain through the study of particulate matter in rivers and lakes is highly variable and will vary accordingly with the type of studies. A summary is presented in table 2.

Table 2. Major objectives of particulate matter studies

| | | RIVERS | | LAKES AND RESERVOIRS |
|---|---|---|---|---|
| SUSPENDED MATTER | R1 - | Present level of pollution of particulate matter | L1 - | Present level of pollution of particulate matter |
| | R2 - | Pollutant and nutrient fluxes to seas or lakes | L2 - | Present eutrophication level |
| | | | L3 - | Present rate of vertical settling of pollutants and nutrients |
| BOTTOM DEPOSITS | R3 - | Present level of pollution of particulate matter | | |
| | R4 - | Pollution record in some cases | L4 - | Pollution record since the beginning of industrialization |

R3 and L4 are the most common objectives of particulate matter studies.

2.6.2 Studies Recommended Within the GEMS/Water Programme

Before establishing a new monitoring network, or extending an existing one, preliminary studies are recommended to collect information on the present characteristics of the water bodies of interest. These studies are needed for the selection of sampling sites, and for establishing sampling periods, and appropriate sampling devices, as well as for the interpretation of results. Table 3 summarizes the information needed for various types of studies.

- The study of deposited sediments is much easier to realize due to sampling facilities in both rivers and lakes. These activities (see R3 and L4) are highly recommended within the GEMS/Water programme.

- At international boundaries, at river mouths in great lakes and oceans, it is also recommended that fluxes of pollutants, organic matter, and nutrients, are taken into account (see R2 on table 2) as much as possible.

- The monitoring activities are summarized in Table 4.

Table 3. Preliminary surveys and information required for various particulate matter monitoring objectives

| | OBJECTIVES | PRELIMINARY SURVEY | INFORMATION NEEDED |
|---|---|---|---|
| RIVERS | R2 | - Water discharge (Q) | - River regime<br>- Extreme discharge statistics |
| | R2 | - Suspended sediment (TSS) | - TSS variability<br>- Relationship TSS = f(Q)<br>- Annual sediment discharge |
| | R2<br>R4 | - Inventory of major pollutant sources | - Location of pollutant sources<br>- Types of pollutants<br>- Approximate quantities discharged |
| | R4 | - Sediment mapping | - Occurence of fine sediment deposits |
| LAKES and RESERVOIRS | L4 | - Bathymetric survey | - Deepest points<br>- Bathymetric map |
| | L4 | - Sediment survey | - Area of deposition<br>- Occurence of fine deposits |
| | L4 | - Inventory of major pollutant sources | - Location of pollutant sources<br>- Types of pollutants<br>- Approximate quantities discharged |

R2: Pollution and nutrient fluxes to seas or lakes
R4: Pollution record in some cases
L4: Pollution record since the beginning of industrialization

Table 4. Recommended monitoring of particulate matter within GEMS/Water

| | Type of stations | Type of particulate matter | Sampler (3) (4) | Chemical compounds analysed | Sampling frequency |
|---|---|---|---|---|---|
| RIVERS | Baseline | sediment | hand | trace metals; organic pollutants (1) | 1/5 years |
| | Trend | sediment | grab | trace metals; organic pollutants; nutrients (2) | 2-4/year |
| | Global river flux | suspended matter | bottle + centrifugation | As,Cd,Cr,Cu,Pb,Hg,Se,Zn | 4/year |
| | | unfiltered water | bottle or bucket | total hydrocarbons; total PAH; total chlorinated hydrocarbons, ΣDDT; Endrin Aldrin; PCBs; atrazine, phenol | 12/year |
| LAKES & RESERVOIRS | Baseline | surficial sediment (lake center) | grab or corer | trace metals; organic pollutants (1) | 1/5 years |
| | Trend | sediment (vertical profile at lake center) | corer | (2) | 1/10 years |

(1) particularly the most volatile and persistent compounds (Hg, As, Pb, PCB, DDT)
(2) list defined after preliminary surveys and pollutant inventories
(3) must be precleaned (see 3.1)
(4) see also Mudroch and Macknight (1991) for selection of sampling equipment.

## 3.0 FIELD WORK

### 3.1 Sample contamination

Many of the variables selected for the GEMS/Water programme are present in particulate matter at a very low level ($10^{-6}g.g^{-1}$ to $10^{-9}g.g^{-1}$). Therefore any contamination of the particulate matter during sampling, sample recovery, storage or pretreatment prior to analysis may cause erroneous results. The precautions to be taken in order to avoid contamination will depend on the type of substances studied.

Precautions concerning sampling and storage operations are given for the following classes of micropollutants:

(i) Inorganic micropollutants (arsenic and heavy metals). The sampler should be made of plastic or be plastic-coated or of stainless steel. Rubber should be avoided. If a plastic sampler is not available, the sample should be retrieved as quickly as possible from the sampler, the part of the sediment in direct contact with the sampler should be discarded. The sampler should be previously washed with diluted analytical-grade nitric acid (5%) and rinsed with double distilled water. The water and sediment storage vessels should also be plastic and precleaned.

ii) Organic micropollutants (organochlorine compounds, hydrocarbons, etc.). The sampler should be metallic, preferably in stainless steel and rinsed with hexane or an other organic solvent free of chlorinated hydrocarbons. The storage glass vessels should be rinsed in the same manner, heated at 300°C for 4 hours to remove organic matter, and sealed with gaskets made of rinsed aluminum foil. The filter set and glass fibre filters should also be rinsed with hexane. Plastic devices should be avoided throughout organic micropollutants survey from the sampling operations to the laboratory analysis.

iii) Organic carbon and nutrients. The sampling devices and filter apparatus can be made of metal or plastic that have been cleaned and rinsed by the usual laboratory procedure. For phosphorus analyses, however, either washing with non-phosphate detergent or extra rinsing is necessary. Water and sediment storage vessels could be of glass.

The sample selected for analysis of bottom sediment should be collected from the inner part of the sediment sample material which has not been in direct contact with the walls of the sampler and kept in appropriate vessels (plastic bags for trace metals, glass vessels for toxic organics).

In order to prevent any cross-contamination, the samples selected for the determination of inorganic substances should be completely separated from the organic ones throughout the survey, i.e., from sampling operation to analysis.

3.2 Sampling Sites and Samplers

Lakes and reservoirs

In most cases samples of deposited sediments can be taken at the geographic centre of the lake, which also is usually near the deepest part of the lake. If the deepest point is located far from the centre of the lake or if there are many lacustrine basins, several base stations may be adequately described by one single station. For the study of pollution record, a gravity corer is appropriate. For surficial sediments, the Ekman-Birge grab is generally sufficient if lifted up slowly.

Rivers

(i) For the sampling of suspended matter, the river section should be as homogeneous as possible in order to avoid multiplication of sampling verticals and number of samples along one vertical. The quality of suspended material across a section is much less variable than its quantity, although the latter may influence the former due to variations in grain-size. 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. Large sampling bottles and precleaned buckets (see 3.1) can be used for this purpose.

(ii) River deposits should be sampled in shoals where the water velocity is at a minimum. In large rivers, the use of a grab will be required. Shipek-and-Ponar type grab are well suited, but they may require the use of a winch.

3.3 Separation of Particulate Matter from the Dissolved Phase

3.3.1 Suspended Matter

For separation of river suspended matter from the dissolved phase, sample filtration is recommended when small quantities are required (100 mg). If multiple analyses are to be performed, then a larger quantity (10 to 200 litres of water) is needed; it may require the use of a continuous flow centrifugation technique (Horowitz et al, 1989).

Although some toxic elements bound to the colloidal fraction may pass through the 0.4 µm or 0.45 µm pore size filter, this type of separation technique is widely used for the analysis of inorganic pollutants and is recommended in the GEMS/Water programme.

The water samples should be filtered as soon as possible after collection. When circumstances do not permit water filtration within 24 hours, the time elapsed between collection and filtering should be recorded on the analytical data sheet.

Filtration is normally carried out using a glass filtration kit under suction. Hand vacuum pumps easy to handle in the field are now commercially available. The sample should be thoroughly shaken before being poured into the funnel to ensure its homogeneity.

Special care must be taken when separating dissolved from particulate matter. According to the type of substances to be analyzed, two different types of filters may be used:

(i) Inorganic filters (polycarbonate, cellulose, acetate) are recommended for inorganic substances. Filters which have the lowest blank values for trace elements of interest should be used.

(ii) Glass-fibre filters are recommended for organics, particulate organic carbon and chlorophyll measurements. Glass-fibre filters may absorb dissolved chlorinated hydrocarbons.

For metal analysis, filters should always be cleaned in a dilute solution of analytical-grade acid, followed by a rinse with double distilled water; filters used for organic analysis should be rinsed with a solvent and heated at 300°C. The water rinsed filters should be kept in Petri dishes, the others in clean metal or glass containers sealed with aluminum foil or a screw cap. All filters should be pre-weighed before use. Filters may have to be changed several times during filtration. Parallel filtration material (e.g., ceramic, plastic) can be used to accelerate the filtration procedure. Once all the water has passed through, filters are removed with tweezers and placed in an appropriate container with proper precautions to avoid contamination. For blank assessments, chemical analysis should also be performed on five unused filters, similar to those used for filtration, for blank assessment.

3.3.2 Rivers and Lakes Surficial Sediments

Surficial sediment can be directly scooped with a precleaned plastic or metallic scoop (depending on compounds see 3.1) at the surface of the grab.

3.3.3 Lake Cores

Retrieval of sediment from cores should be done carefully in order to avoid the destruction of the sediment - water interface and mixing of different sediment layers. The following procedure is recommended:

(i) The overlying water is carefully siphoned off until one centimetre of water remains above the sediment-water interface, and is then transferred to a bottle and filtered;

(ii) The upper layer of the sediment ("floating material", "fluid-mud") is siphoned off, and kept as representative of the top layer of the core;

(iii) The core is sealed carefully at the bottom and at the top, then brought to the laboratory in a vertical position (tilting should be avoided as much as possible);

(iv) Usually the sediment is contained in an inner tube. The sediment should be forced out of the tube centimetre by centimetre, by a piston, and sliced; no leakage of sediment should be allowed during this operation;

(v) The slicing operation should be performed shortly after sampling on the fresh sediment. The particle material can be separated from interstitial water by pressure filtration or by centrifugation of each sediment slice. (Adams 1991).

(vi) Aliquots of known volumes of fresh sediment should be taken for the determination of water content and density, especially in the upper layers.

3.4 Additional Field Measurements and Storage Precautions

Lakes and Reservoirs:

The water content and density (i.e., mass of dry material per unit volume) of deposited sediments are basic information required for computation of deposition rates and should be determined on each sliced level of a core.

Rivers:

In order to compute the pollutant and/or nutrient fluxes in rivers, it is mandatory to have a continuous record of the river discharge. It is strongly recommended that intensive surveys be carried out to determine the quantity of particulate matter carried by the river. This should lead to intensive suspended matter sampling (WMO 1981).

Storage:

All samples should be dried before storage. Drying temperatures will vary with the types of pollutant or nutrient: (e.g., 20°C for organochlorines and hydrocarbons; 50°C for nutrients, total organic carbon and volatile mineral compounds such as Hg, Pb.). Prior to analysis, it is recommended that samples used for determining trace metals and nutrients be stored in plastic bags in a refrigerator. Samples for the determination of hydrocarbons and other organics should be placed in glass containers, sealed with aluminum foil, and stored in a freezer(-20°C). Sample handling and storage is described in Mudroch and Bourbonniere (1991).

4.0 LABORATORY WORK

4.1 Sample Pretreatment

Usually particulate matter must be dissolved before analysis. Solubilization or extraction may be either complete, or partial, with one or more of the several physico-chemical species present.

In the GEMS/Water programme it is recommended that at the first level of the survey the total amounts of pollutants and nutrients should be determined after appropriate pretreatment. The analysis of sediment deposited in lakes should be done on dry material. For inorganic pollutants analyzed at "trend", "baseline", and "global flux" stations in rivers it is recommended that the analysis of total pollutants and nutrients in the suspended particulate matter be undertaken on dry material obtained after filtration or ultra centrifugation. For toxic organic substances, the analysis can be performed on unfiltered water since the common use of organic solvents normally permits a complete extraction.

For the analysis of the total content of As and trace metals, the most common procedures of total sediment digestion are the following:

(i) Hydrofluoric acid decomposition: Few extraction procedures using hydrofluoric acid extraction are described in the literature. For example: 100 mg of powdered sediment sample were digested with a mixture of 6 ml of hydrofluoric acid, 4 ml of nitric acid and 1 ml of perchloric acid in a Teflon bomb (Agemian and Chau 1976). In a procedure described by Tessier et al (1979) 1 g of dry sediment was first digested in a platinum crucible with a mixture of perchloric acid (2 ml) and hydrofluoric acid

(10 ml) to near dryness; subsequently a second addition of perchloric acid (1 ml) and hydrofluoric acid (10 ml) was made and again the mixture was evaporated to dryness. Finally, perchloric acid (1 ml) alone was added and the sample was evaporated until the appearance of white fumes. The residue was dissolved in hydrochloric acid (12 N) and diluted to 25 ml. The resulting solution was then analyzed by flame atomic absorption spectrometry for trace metals. The use of perchloric acid in sediment extraction requires special caution because the possibility of vigorous oxidation of organic matter in the sediment which may result in an explosion. Therefore all extraction procedures using perchloric acid have to be carried out in a fume hood specially designed for the use of perchloric acid. Hydrofluoric acid is difficult to handle and dangerous to store. This digestion provides a true "total" value; however, it is no longer used by many environmental agencies because the digestion recovers metals bound in the crystal lattice structure of the sediment and which are not environmentally available.

(ii) Hydrochloric-nitric acid (aqua regia): Commonly used for all trace metals except mercury. This digestion provides "total" values but excludes metals bound into the crystal lattice of the sediment. These values will generally exceed the amount of the trace metal that is likely to become environmentally available. The procedure is as follows: 50 mg of the sample material are transferred to a 50 ml beaker. A mixture of concentrated $HNO_3$-HCl (1:3) is added and the sample is heated on a hot plate for 30 min. at moderate temperature (ca. 60°C); after cooling at room temperature the sample is diluted with distilled water to 50 ml.

Alternatively, Teflon-bombs are used for digestion of sediment samples to be analyzed for Cd, Hg and As: 100 mg of powdered sediments are placed in the Teflon bomb and 5 ml of aqua regia is added. The sealed bomb is heated at 110°C for 2 hours in an oven.

(iii) 0.5N Hydrochloric acid: Used to determine concentrations of trace metals that are loosely bound to mineral sediment and which are most likely to enter into environmentally significant chemical and biological interactions. The procedure is: heat sample and acid in a beaker, covered with a watch glass, on a hot plate at 90°C for 30 minutes. After cooling, filter through a W42 filter paper and quantitatively dilute with distilled water up to 50 ml. volume. This method does not extract metals from organic matter (compounds composed of organic nitrogen, sulphur, oxygen) and should be used only when organic matter is less than 30% of the sample by weight. (Organic matter can be estimated as: Particulate Organic Carbon x 1.7). For samples having >30% organic matter, use the agua regia method.

(iv) Lithium metaborate fusion (with simultaneous determination of silica): 50 mg of sample material are placed in a platinum or graphite crucible and mixed with approximately 200 ml of $LiBO_3$ before heating for 15 minutes at a temperature of 1100°C; the molten matter is cooled to room temperature. 25 ml of 10% nitric acid are added and the entire mass dissolved using a magnetic stirrer. The sample is transferred to a volumetric flask and diluted to 50 ml.

4.2 Analyses

Analytical methods are outlined in Chapter III of this Guide and in the references. Some of the methods that can be easily used in routine monitoring programme are briefly summarized.

Organic matter and nutrients: Particulate organic carbon (POC). Commercial instruments are available for POC determination on dried particulate matter. The determination is done through wet oxidation of the organic matter followed by $CO_2$ transfer and its subsequent measurement.

Total phosphorus: The sample is digested with sulfuric acid and with potassium peroxysulfate.

Total nitrogen: The total nitrogen (organic N and inorganic $HN_4^+$, if this latter has not been previously removed) is determined by the classic Kjeldahl method.

Arsenic and trace metals. The sample solubilised after pretreatment is analyzed by Hydride Generation Atomic Absorption Spectrometry. Flameless Atomic Absorption Spectrometry is recommended for Hg estimation. Other detailed procedures can be found in FAO (FAO, 1976) and in the USGS manual (Skougstad et al 1979) and in Salomons and Förstner (1984).

Organochlorine compounds: Dried filters are ground in a precleaned mortar or pulverized in a precleaned blender. In the case of blender grinding, solvent can be added to start the extraction. The common extraction solvent is acetonitrile. If the filters are ground dry, the extraction can be carried out with a solvent extractor. The extract is diluted with precleaned water in a ratio of 5 parts of water per 1 part of extract. The water-acetonitrile solution is then extracted with hexane free of chlorinated hydrocarbons. The hexane extract is purified by microcolumn chromatography on Florisil. The cleaned-up extract is then evaporated to a convenient volume for analysis. This can be done with a rotary evaporator followed by a Kuderna Danish concentrator. The final extract will be analyzed by gas chromatography. The complete analytical procedure is described in the FAO Manual (FAO, 1976).

It is important that the whole pretreatment and analytical procedures be checked for contamination by running blanks concurrently with the analyses.

## 4.3 Analytical Quality Control

Sample collection and pretreatment procedures should be standardized as much as possible during the whole survey. Comparability of analysis can be ensured through analytical quality control: intra-laboratory and inter-laboratory comparisons. The accuracy of the analyses can be checked within individual laboratories by analyzing standard reference materials of known concentrations. Group intercalibration exercises are done through analysis of homogeneous samples of unknown concentration. It is preferable to use reference samples having a matrix similar to that of the substances to be monitored. It is also preferable to prepare these samples starting from field samples containing particulate matter already contaminated rather than to prepare samples artificially spiked with pollutants. This will avoid differences in pretreatment between artificial and natural samples.

# 5.0 DATA EVALUATION

## 5.1 Data Reporting

All general recommendations made in Chapter I of the Guide and Chapter IX also apply to particulate matter. When reporting data on particulate matter, it is recommended that the following information be included (Table 1):

(i) the full description of sample collection procedures including: location, type of sample, quantity sampled, number of samples, type of filtration apparatus and filters used;

(ii) full description of the sample pretreatments (acid digestion, partial leaching, organic solvent, extraction, etc.);

(iii) analytical method used.

For the GEMS/Water programme, all concentrations should be reported as mass pollutant per dry mass of particulate matter ($mg.g^{-1}$; $\mu g.g^{-1}$; $ng.g^{-1}$) for inorganic pollutants and nutrients and as mass of pollutant per litre of unfiltered water for organic pollutants (see table 1). For sediment cores, each level analysed should be considered as a separate sample and reported on a separate reporting form.

## 5.2 Discussion of Results

The discussion of results should take into account various factors: dilution of pollutants by non-contaminated material such as quartz or carbonates; correction for size fraction; and evaluation of natural background values (in the case of naturally-occurring elements) are among the most pertinent.

### Effect of particle size distribution

The grain size distribution influences the quality of particulate matter. It is important to note that:

(i) The finest particles (e.g., clay minerals) generally have the highest contents of pollutants due to their adsorption capacity.

(ii) The coarser particles (consisting of rock fragments, quartz carbonate minerals or other inert minerals) usually have low concentrations of metals, nutrients and organic pollutants. This coarse material will generally dilute the pollutants; this is called the grain-size or matrix effect. However, coarse floating material or organic matter, may also be highly contaminated.

Therefore, it is common to remove the coarse fraction which is larger than 175 µm and perform chemical analysis on the component smaller than 175 µm. However, the remaining fraction will still contain appreciable quantities of inert particles in the sand fraction (usually quartz) or even in the silt fraction. River suspended matter and lake sediments are usually dominated by the clay and silt fractions.

### Standardization of Results

Trace metals are generally associated with the clay and, to a less extent, the silt fraction. This is due to adsorption processes associated with clay mineralogy, iron and manganese coatings, carbonate precipitates, and with particulate organic carbon. Because this tends to be associated with grain size (matrix effect), it is usual to **normalize** the metal concentration data using either a geochemical correction or a more simple matrix correction.

(i) Quartz correction: This is used by geochemists to normalize against the quartz component of the sample on the grounds that pollutants are considered to be associated with the complementary fraction of quartz. This is not widely used in environmental analysis because of the difficulty of determining quartz.

The quartz correction is calculated as: $\frac{\text{Observed concentration x 100}}{\text{100 - \% of Quartz}}$

(ii) Carbonates and other variables: Corrections can also be made for carbonates and other variables if they are found in appreciable quantity in the particulate matter. The corrected concentrations are usually reported as quartz-free or carbonate-free contents.

(iii) Aluminium correction: The effect of variable amounts of clay minerals can be minimized by standardizing the pollutant content to the aluminum content of the sample. This element is related to the amount of clay material, although it is also part of other minerals and is a very inert element in the aquatic environment. This correction is valid for the trace metals which generally have a linear relationship with the aluminum content. The result are expressed as the ratio of the concentration of metal to the concentration of aluminum in the sample (see an example below for the Sediment-Enrichment Factor).

(iv) Particle-size correction: Studies have shown that trace metal data tend to be associated with the <63µm or <125µm fraction of the sediment (suspended or deposited sediment). Consequently, analysis of a sample containing much sand will "dilute" the actual concentration of the metal. Therefore, the concentration value is pro-rated according to the percentage of <63µm (or <125µm) material in the sediment sample, providing that the <63µm (<125µm) material is at least 30-40% of the total sample. If it is less, the pro-rated value may be in error. This is the most common matrix correction used for environmental purposes. If agencies cannot investigate whether the 63µm or 125 boundary should be used, use the 63µm value. The percent <63 µm value can be determined by wet seiving a dispersed sediment sample of known weight through a 63µm tared screen and weighing the screen and content after drying.

This correction is calculated as:

$$\text{Corrected value } (\mu g/g) = \frac{\text{Trace metal concentration } (\mu g/g)}{\text{Percent of sample } <63\mu m \text{ (or } <125\mu m)}$$

Estimate of background values

Another important problem when discussing the analytical results is the evaluation of natural background levels of the substances being determined. This is the case for organic carbon, nutrients, the heavy metals and arsenic, but not for the organic micro-pollutants of interest listed in table 1 which are not likely to occur naturally in the sediments.

River and lake sediments deposited before the beginning of the industrial era are commonly used for the assessment of background natural values. While post-depositional migrations of heavy metals and nutrients are possible in the sediments, the bottom deposits generally provide valuable records of past contamination levels. For instance, an increase of nitrogen and phosphorus in the upper part of the bottom sediments has been clearly verified in many lakes and related to accelerated eutrophication. Higher levels of heavy metals have also often been encountered in polluted lakes, sometimes only as a result of atmospheric inputs.

(i) River particulate matter. For trace metals and arsenic associated with river particulates comparisons may be made with the suspended material sampled in the upper part of the drainage basin where there is usually less pollution. The result of the particulate matter analysis can also be compared to the average composition of rocks in the basin, if their chemical composition is known. If these comparisons are not possible, the world average contents of clays or of river particulate matter (Table 5) can be used for comparison.

Table 5. Average of some components of river particulate matter

| | Rivers and lake material | | Average Shales(3) |
|---|---|---|---|
| | Common range in lake sediment (1) | Average in river suspended matter (2) | |
| As $\mu g.g^{-1}$ | -- | 8 | 13 |
| Cd $\mu g.g^{-1}$ | 0.1 - 1.5 | 0.3 | 0.3 |
| Cr $\mu g.g^{-1}$ | 20 - 90 | 120 | 90 |
| Cu $\mu g.g^{-1}$ | 20 - 90 | 50 | 45 |
| Hg $\mu g.g^{-1}$ | 0.15- 1.5 | | 0.4 |
| Ni $\mu g.g^{-1}$ | 30 -250 | 80 | 68 |
| Pb $\mu g.g^{-1}$ | 10 -100 | 40 | 20 |
| Zn $\mu g.g^{-1}$ | 50 -250 | 240 | 95 |
| POC $g.g^{-1}$(4) | 0.005 - 0.2 | 0.01 | |
| TSS $mg.l^{-1}$(4) | | 500 | |

(1) Förstner & Whitman (1981)
(2) modified from Martin & Meybeck (1979)
(3) Turekian & Wedepohl (1961)
(4) POC: Particulate Organic Carbon, TSS: Total Suspended Solid, Meybeck (1982)

(ii) Lake sediment. The impact of pollution on lake sediments can be easily studied by the analysis of the elements of interest from the top centimetre down to the deposition layer corresponding to the last one or two hundred years. These measurements must be substantiated by core dating, either by radiochronology or palynological determination. The sediment layer below this horizon will be used as a basis for the determination of natural background values.

The pollution level of heavy metals can be estimated by the Sediment Enrichment factor (SEF) defined as:

$$SEF = \frac{\frac{Cz}{Alz} - \frac{Cb}{Al}}{\frac{Cb}{Alb}}$$

where Cz = concentration of the element in the layer z
Cb = concentration of the element in the bottom sediment layers (corresponding to preindustrial age)
Alz = concentration of the aluminum in the layer z
Alb = concentration of the aluminum in the bottom layers

5.3 Pollution Fluxes in Rivers

Determination of pollutant fluxes in rivers is needed for the assessment of pollutant inputs to lakes, regional seas or oceans and when studying pollutant mass balances within a drainage basin. When assessing the input of a river to another water body, the sampling stations should be chosen as close as possible to the confluence. The water should be well mixed in the river cross section in order to minimize the number of sampling points.

The sampling frequency is important due to variations in the total suspended solid content (TSS usually expressed in $mg. l^{-1}$) and in the content of the element x in the particulate matter (Csx usually expressed in $g. kg^{-1}$ or $mg.k^{-1}$). The amount of elements per unit volume of unfiltered water (Cvx) is easily obtained as CVx = TSS.Csx and is generally expressed in $mg.l^{-1}$ or $\mu g.l^{-1}$. In most surveys the analyses of suspended material will not be carried out more than 12 times a year. As both the amount of suspended solids (TSS) and its elemental content (Csx) are likely to vary between sampling periods, interpolation of the data will be needed; particularly during floods where TSS is highly variable.

Two different types of interpolation are proposed:

(i) Constant flux assumption: The flux $Qs_{xi}$ of pollutant x discharged by the river with the particulate matter is constant during a representative period (ti) around the time i of sampling. The total mass of pollutant (Mx) discharged during the time interval $T=\Sigma t_i$ will be:

$$Mx = \Sigma_i Qs_{xi} t_i$$

$$\text{where } Qs_{xi} = TSS_i Q_i Cs_{xi}$$

$TSS_i$ = total suspended matter at the time of sampling;
$Cs_{xi}$ = concentration of pollutant x in the particulate matter;
$Q_i$ = the water discharge at the time of sampling
$Qs_{xi}$ is computed for each sample. The length of the representative period ti can be variable according to the water discharge variations. This assumption is particularly valid for point sources releasing a relatively constant flux of pollutants.

(ii) Constant concentration assumption. The concentration $Cs_{xi}$ is constant during a given period $t_i$ around the time of sampling. The amount of suspended matter discharged during this period ($Ms_i$) should be measured with the maximum accuracy, for instance, by daily measurements of suspended matter ($TSS_j$). The total mass pollutant discharged will be:

$$Mx = \Sigma_i Cs_{xi} Ms_i$$

$$\text{where } Ms_i = t_i \Sigma_j TSS_j Q_j$$

This second method takes into consideration the variations in the total suspended matter, which can be up to three orders of magnitude in rivers, i.e., much more than the variations of Csx which is usually within one order of magnitude.

These methods can be improved if relationships are established between the pollutant flux $Qs_{xi}$ and the water discharge $Q_i$, or between the contamination level $Cs_{xi}$ and the amount of suspended material TSSi. These relationships, if they exist, allow for estimates of $Qs_x$ and $Cs_x$ to be made between two consecutive sampling periods.

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UNEP/WHO/UNESCO/WMO PROGRAMME ON GLOBAL WATER QUALITY MONITORING AND ASSESSMENT

GEMS/WATER OPERATIONAL GUIDE

# CHAPTER V: PRINCIPLES FOR PLANNING AND IMPLEMENTATION OF MICROBIOLOGICAL ANALYSES

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## 1.0 INTRODUCTION

When planning the microbiological monitoring of water courses and drinking water supplies, a number of considerations must be taken in order to ensure that the methods and strategies adopted will produce valid results. These considerations which will be discussed below include: selection of parameters; selection of methods for analysis; organisation of laboratory support; sampling and sample transport; and quality assurance. Detailed methods are not provided, but a list of recommended reading covering detailed laboratory requirements and analytical and sampling methods is provided. The principles described below will be useful during the planning and evaluation of microbiological monitoring.

## 2.0 INDICATOR ORGANISMS

One of the most significant risk associated with water and wastewater worldwide and of special importance in many developing countries is that of infectious disease related to contamination by faecal material: Although it is now possible to undertake analysis for specific pathogens (disease-causing organisms), some of these methods are costly to perform or slow in providing a result. As it is not practical to attempt the routine isolation of specific pathogens in water, the analysis of waters and wastewaters for microbiological parameters is normally undertaken by assessment of hygienic quality. For this purpose, the isolation and enumeration of organisms which serve as indicators of the presence of faecal contamination is undertaken. The capacity to identify the pathogens themselves should be developed in reference laboratories for the purpose of investigations and control of outbreaks of disease.

Various indicators may be used for the assessment of microbiological water quality and also to assess the efficiency of drinking water wastewater treatment systems. Microbiological indicators which are not necessarily associated with faecal pollution may also be used for this purpose. The recommended applications of the most commonly applied indicator organisms is presented in Table 1.

Only two indicators are recommended within the GEMS/Water programme: total coliforms and thermotolerant ("faecal") coliforms. As far as risk to human health due to recreational contact with contaminated waters is concerned, it is recognized that faecal streptococci provide one of the most useful indicators of disease risk. It is therefore likely that faecal streptococci will be increasingly used in the analysis of recreational waters and that standards for inland and marine recreational water quality will reflect this trend. It is recommended that agencies concerned with recreational water quality and human health should include faecal streptococci as part of their analytical capability.

Table 1. Recommended applications of different indicator micro-organisms.

| | Indicators of Disease Risk | | Indicators of Treatment Process Efficiency | |
|---|---|---|---|---|
| | Drinking Water | Recreational Water | Drinking Water | Waste Water |
| Thermotolerant (faecal) coliforms | 4 | 4 | 4 | 4 |
| Total coliforms | 2 | 2 | 3 | 2 |
| Faecal Streptococci (enterococci) | 2 | 3 | 3 | 2 |
| 37°C Count | 0 | 0 | 2 | 0 |
| 22°C Colony Count | 0 | 0 | 3 | 0 |

Legend: 0 = no importance; 1 = little value; 2 = moderate value; 3 = important; 4 = essential.
Source: World Health Organization. 1988, *Training course manual for water and wastewater laboratory technicians*, (WHO/PEP/88.11), WHO, Geneva.

## 3.0 CHARACTERISTICS OF INDICATOR ORGANISMS

The definition of each of the important indicator groups is given below:

### 3.1 Thermotolerant (Faecal) Coliforms

This group *nearly always* indicates the presence of faecal pollution. Usually, a very high proportion (greater than 95 percent) of faecal or thermotolerant coliforms isolated from water are actually the gut organism *Escherichia coli*. However, it is often judged impractical or unnecessary to undertake the further biochemical testing required to confirm the presence of *E. coli*. Thermotolerant coliforms grow in or on media containing lactose at 44°C or 44.5°C with the production of acid and gas. They are usually detected by the incorporation of pH indicators in the medium.

It has been suggested that in some tropical environments, bacteria of other than faecal origin may form a proportion of the bacteria exhibiting the characteristics of thermotolerant coliforms. Nevertheless, there is as yet no reason to question the use of thermotolerant coliforms as the most generally useful indicator of faecal contamination.

### 3.2 Total Coliforms

This group may or may not indicate the presence of faecal pollution. It includes the thermololerant coliforms and other organisms including some which multiply on plant surfaces. Furthermore it is possible for some members of the group to multiply in the aquatic environment. In these cases, a high result for the total coliform group may be associated with a low or zero count for thermotolerant coliforms. Such results do not necessarily indicate the presence of faecal pollution. Most of the group however are bacteria which may be found in the gut. Total coliforms grow in or on media containing lactose at 35 or 37°C with the production of acid and gas. Like thermotolerant coliforms, they are usually detected by the incorporation of a pH indicator in the medium.

### 3.3 Faecal Streptococci (enterococci)

This group *usually* indicates the presence of faecal pollution. However, in some situations, particularly when there is a high level of organic matter, one or two members of the group may multiply in water. Also, faecal streptococci tend to persist longer in the environment than either faecal or total coliforms. Thus it is possible to get a higher than expected count of faecal streptococci compared with levels of faecal and/or total coliforms. In these cases, it may be assumed that *either* there has been some degree of organic pollution, or the source of faecal pollution was remote (in time or distance). Faecal streptococci grow in or on media containing sodium azide at 37 - 44°C. They are usually detected by the reduction of a dye or the hydrolysis of aesculin.

### 3.4 Colony Counts

These indicators have little or no hygienic significance and simply include all those micro-organisms (bacteria, yeasts and moulds) which are capable of growth on or in solid agar media at 37°C or 22°C. The groups therefore *exclude* organisms with complex nutritional requirements and, where growth is on the surface of an agar medium, organisms which do not grow in the presence of oxygen. Furthermore, the isolation technique usually involves the mixing of low volumes of water with comparatively high volumes of molten agar media at 45°C. The consequent heat shock can result in the death of a large proportion of organisms present in the sample.

## 4.0 ANALYTICAL METHODS: PRINCIPLES AND GENERAL DESCRIPTIONS

### 4.1 Principal Isolation Techniques

The principal techniques used in the isolation of indicator organisms from water are:

Membrane Filtration (MF)
Multiple Tube or Most Probable Number (MT or MPN)
Colony Count by Pour Plate (PP)
Colony Count by Spread Plate (SP)
Presence/absence tests

These techniques have various applications which are summarised in Table 2.

Table 2. Recommended application of different isolation techniques in various water and wastewater situations.

| | Drinking Water | Recreational Water | Waste-Water | Sewage Water |
|---|---|---|---|---|
| Thermotolerant (faecal) coliforms | MF,MT | MF,MT | MF,MT,SP | MT,SP |
| Total coliforms | MF,MT | MF,MT | MF,MT,SP | MT,SP |
| Faecal streptococci (enterococci) | MF,MT | MF,MT | MF,MT | MT |
| Colony counts | PP | N/A | N/A | N/A |

MF = Membrane Filtration, MT = Multiple Tube, SP = Spread Plate, PP = Pour Plate, N/A = Not Applicable.

Source: Jamie Bartram and David Wheeler, *Microbiological Methods (laboratory Analysis)* in *GEMS/Water Handbook for Water Quality Monitoring in Developing Countries*, Draft, University of Tampere, Finland, 1991.

Colony counts are only of value if they are performed regularly and reliable records are built up over many months. Then, if substantial changes occur at a particular point there may be a cause for concern. Bacteria which form spores, (e.g., species of *Bacillus*) are readily recovered as part of the colony count population and thus such counts may be used as a guide to the efficiency of disinfection procedures if these organisms are naturally present in the water prior to disinfection.

Presence/absence tests are more commonly used in developed countries. They are not quantitative and are therefore only appropriate for monitoring of waters from which positive results are uncommon. Such methods are of little use in situations where contamination is common and the purpose of analysis is to determine the degree of contamination. Presence/absence tests are not recommended for use in analysis of surface waters, or of untreated or partially treated drinking water supplies in less-developed countries.

### 4.2 Membrane Filtration

A volume of the sample, or dilution of the sample is added aseptically to a sterilised filtration apparatus containing a sterile membrane filter. The filter should have a nominal pore size of 0.2 or 0.45 µm. The sample is then drawn through the membrane filter by application of a vacuum. Any indicator organisms present in the sample are retained by the filter which is then transferred to a culture medium in a petri dish. The culture medium is selective for the indicator micro-organisms of interest and assists in their identification. Following a period of resuscitation, during which the bacteria adapt to the new conditions, the petri dish is transferred to the appropriate selective temperature and is incubated. After a suitable time visually identifable colonies will have formed and are counted. Results are expressed in numbers of 'colony forming units' (cfu) per 100 ml of original sample.

Membrane filtration cannot be applied to semi-solid samples such as sludge or to waters with a high level of turbidity which would quickly block the filter. Low volumes of sample (i.e. less than 10 ml) must be dispersed by an adequate volume of sterile diluent before filtration in order to ensure that the sample is filtered evenly across the entire surface of the membrane filter.

When the site has not been sampled previously or if the current degree of contamination is unknown, it is advisable to test two or more different volumes in order to ensure that the number of colonies on at least one of the membranes is in the optimum range for counting (30 - 300 colonies per membrane).

### 4.3 Multiple Tube Technique

This technique is also referred to as the Most Probable Number (MPN). Unlike the MF method, it relies on an indirect estimate of the density of microbes in the water sample. Statistical tables are used to determine the most probable number of microorganisms present in the sample. This technique must be used for very turbid or semi-solid samples which cannot be filtered and are not therefore suitable for analysis by membrane filtration. Analysis by the multiple tube method is inappropriate for areas without laboratory support or which depend on portable testing equipment. Furthermore the multiple tube method is time-consuming to perform and has greater requirements for equipment, glassware and consumables than membrane filtration.

The multiple tube method is based on the separate analysis of a number of volumes of the sample. Each volume is mixed with a liquid culture medium and incubated. The tubes are normally incubated immediately. By comparing the pattern of positive results (defined in terms of growth as indicated by visible turbidity and/or colour change in the medium and/or production of gas, detection of which may be facilitated by a small inverted tube) with statistical tables, the density of microorganisms in the original sample may be obtained. The tables provide an estimate of the "most probable number" (MPN) of indicator bacteria per 100 ml of original sample.

As with the MF method it is useful to have some idea of the degree of contamination likely to be present in a sample which enables selection of the most appropriate combination of sample volumes for processing. Where previous data is unavailable, the selection is made according to the type of water sample.

## 5.0 ORGANIZATION OF SAMPLING AND ANALYSIS FOR MICROBIOLOGICAL PARAMETERS

### 5.1 Analytical Facilities

Deterioration of sample quality during transport is a serious problem with samples for microbiological analysis. This can be minimised by ensuring prompt analysis. As a general rule, all analyses should be undertaken in a laboratory as close as possible to the site of sampling. In general, the development of the laboratory network which will undertake analysis will depend on the balance between the constraints associated with the costs of equipment and sampling (both of which are largely related to the number and frequency of samples to be analyzed) and savings associated with sample transport.

It is not always possible to establish a laboratory network which will enable all samples to be transported to a central or regional laboratory within a few hours of being taken. Furthermore, the analysis of microbiological samples collected from remote or inaccessible sites for indicator bacteria is associated with a number of problems. These include sample deterioration during transport; cost of sample transport; inadequacy of sample storage and preservation techniques for prolonged transport; and increased personnel costs due to repeat sampling journeys.

For these reasons, testing of water quality on-site using portable equipment may be preferable under certain circumstances. Portable testing equipment has been shown to be effective and may assist in overcoming logistical and financial constraints. Portable test kits vary widely in technical specifications, such as the range of analyses which can be performed, robustness, degree of independence from central laboratory support obtained, portability and requirements for consumables. Under certain circumstances, portable kits may also be used at a fixed site in place of a conventional laboratory.

Central or national laboratories have a number of important functions, including the provision of analytical quality control for regional and local laboratories and of training for analytical staff of regional and local laboratories. Certain more sophisticated analyses which cannot be decentralised due to the high capital cost of equipment purchase are also best performed in such laboratories.

### 5.2 Sample Collection and Transport

An important factor to be considered when planning for microbiological monitoring of water or of drinking water supply systems is sample transport. Sample preservation is especially difficult for microbiological samples, and this is more of a problem when sampling in remote or inaccessible areas.

Where samples are to be transported prior to analysis, adequate storage conditions are required during transport. For this reason, maximum storage times and conditions which are achievable under prevailing conditions must be determined. All samples should be received in the laboratory within the times and under the conditions which have been agreed and samples which do not fulfil these requirements should be discarded. Typically, samples should be taken into sterile, glass bottles reserved specifically for the purpose and transported in a cool, dark environment. Analysis should be completed within six hours of collection.

Where drinking water is to be analyzed and chlorination is practised, the chlorine residual should be tested on-site and microbiological analysis undertaken on a fresh sample. If the sample is to be transported prior to analysis, then the chlorine must be neutralised, for instance employing sodium thiosulphate.

## 6.0 QUALITY CONTROL AND QUALITY ASSURANCE

Quality control requires the generation of data to assess and monitor how good an analytical method is and how well it is operating. This is normally described in terms of within-day and day-to-day precision.

In contrast, 'quality assurance' represents all those steps taken by a laboratory to assure those who receive the data that it is producing valid results. Quality assurance includes quality control, but also encompasses other aspects. For example individuals should be demonstrated to be competent to carry out their functions (such as particular analyses); analytical methods and procedures for sample handling should be established and documented; and equipment calibration procedures should be defined and implemented at determined intervals. Quality assurance should also consider other aspects of laboratory function, such as management lines of responsibility and systems for data retrieval.

### 6.1 Quality Control

Quality control is considered in greater detail in Chapter VII. However, there are a number of special features associated with microbiological analyses which merit special attention here.

All analytical methods should be subject to internal quality control. This is undertaken by estimating the within-day and day-to-day precision of the method (precision is the spread of results around the mean result, whereas accuracy is the spread of results around the true result). These measurements of precision are normally made by undertaking replicate measurements on aliquots from the same sample.

Quality control for microbiological analyses is less straightforward than that for chemical parameters. This is because it is very difficult to prepare and store aliquots of a single sample which will not change significantly with time. It is therefore almost impossible to monitor within-day and day-to-day variation in precision. Validation of methods and quality control of equipment and consumables is therefore especially important for microbiological analyses.

These problems of quality control for microbiological analysis are exacerbated where on-site testing is adopted since this usually leads to the performance of analyses in smaller numbers at a greater number of sites. Training of the personnel responsible for on-site analysis should therefore receive significant attention.

On-site analysis will typically be undertaken under more exacting conditions and may also be performed by relatively unspecialised staff. Therefore, quality control is most difficult to undertake under conditions where it is most important. Three approaches listed below may help overcome this problem.

### 6.1.1 Supervision

Adequate supervision of all aspects of field work should be ensured and this should encompass water quality testing. Supervision of staff in the field (i.e., under the conditions in which they will normally perform analyses) can contribute to ensuring adequate analytical standards.

### 6.1.2 Sterile Sample Analysis

Occasional 'samples' of sterile water should be processed by all staff undertaking on-site analysis. If positive results are obtained then the analyst should recognize that there must be inadequacies in their own technique and re-assess their work accordingly.

### 6.1.3 Equipment Review

Because a commitment to water quality testing with portable equipment normally results in a greater number of testing sites and therefore quantity of equipment and this equipment will be used under more demanding circumstances then would otherwise be encountered, regular review of the equipment is important.

## 7.0 FURTHER READING ON MICROBIOLOGICAL TESTING

Two texts are likely to be of particular interest to those involved in monitoring for the GEMS/Water programme. These are the GEMS handbook, which includes detailed analytical procedures and the World Health Organization publication *Guidelines for Drinking Water Quality*. The latter is divided into three volumes and publication of revised editions is anticipated in 1992-3.

For those concerned with implementation of water quality monitoring in the context of less-developed countries, a forthcoming publication entitled *GEMS-Water Handbook for Water Quality Monitoring in Developing Countries* should be of particular interest.

International Standards

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| ISO 9308-1 | Water quality - Detection and enumeration of coliform organisms, thermotolerant coliform organisms and presumptive Escherichia coli<br>Part 1: Membrane filtration method |
| ISO 9308-2 | Part 2: Multiple tube (most probable number) method |
| ISO 7899-1 | Water quality - Detection and enumeration of faecal streptococci.<br>Part 1: Method by enrichment in a liquid medium |
| ISO 7899-2 | Part 2: Method by membrane filtration |
| ISO 8199 | Water quality - General guide to the enumeration of microorganisms by culture. |
| ISO 6222 | Water quality - Enumeration of viable microorganisms - Colony count by inoculation in or on a solid medium. |

WHO (1984). *Guidelines for Drinking Water Quality. Volumes 1, 2 and 3.* WHO, Geneva.

APHA (1985). Standard Methods for the Examination of Water and Wastewater, 16th Edition. APHA, Washington.

Anon (1983). The Bacteriological Examination of Drinking Water Supplies 1982. HMSO, London.