United Nations Environment Programme
Global Environment Monitoring System (GEMS) / Water Programme

Operational Guide

Version 3.1 (Third Edition Revised)

Operational Guide v. 3.1

Prepared and published by the United Nations Global Environment Monitoring System (GEMS)/Water Programme.

Electronic files of this document may be downloaded from the GEMS/Water website at http://www.gemswater.org/publications/index-e.html

UN GEMS/Water Programme Office
c/o National Water Research Institute
867 Lakeshore Road
Burlington, Ontario, L7R 4A6 CANADA
website: http://www.gemswater.org
tel: +1-905-336-4919
fax: +1-905-336-4582
email: gems@ec.gc.ca

ISBN 92-95039-01-7

The Operational Guide (third edition) was a collaboration between:

United Nations Environment Programme

United Nations Educational, Scientific and Cultural Organization

World Health Organization

World Meteorological Organization

FOREWORD

Established in 1978, the UNEP GEMS/Water Programme is the primary source for global water quality data. It is a multi-faceted water science centre oriented towards building knowledge on inland quality issues worldwide. Key activities include monitoring, assessment and capacity building. The twin goals of the programme are to improve water quality monitoring and assessment capacity in participating countries, and to determine the state and trends of regional and global water quality.

These goals are implemented through the GEMS/Water data bank, with water quality data from more than 100 countries, and over two million entries for lakes, reservoirs, rivers and groundwater systems. GEMS/Water activities add value to country-level data by creating global and regional water quality assessments. The programme also carries out assessments on a range of water quality issues and methodologies. GEMS/Water data have been used by many organizations, including the UN system and universities around the world. GEMS/Water is part of the Division of Early Warning and Assessment (DEWA), UNEP.

GEMS/Water receives data from national governments that have active water quality-monitoring programmes for rivers, lakes, reservoirs wetlands and groundwater. Thus, the cost for a country to participate in the programme is small. The use of electronic databases makes the transfer of data to GEMS/Water simple and cost-effective.

The value-added of GEMS/Water is that the programme produces water quality assessments at a different geographical scale than those undertaken by national governments. By compiling water quality data from countries around the world, GEMS/Water is able to provide global and large-scale perspectives and trends in water quality to the international community and, in particular, to the United Nations. The information can also be used to assess the effectiveness of multilateral agreements and international conventions.

The hydrological counterpart to GEMS/Water is the Global Runoff Data Centre (GRDC) located in Koblenz, Germany (see http://grdc.bafg.de/). By combining the GEMS/Water and GRDC datasets, we are able to calculate loads of nutrients, contaminants and suspended materials to near-shore marine environments or to large lakes.

INTRODUCTION

The purpose of this guide is to assist with the implementation of the UN GEMS/Water Programme at the national level, particularly in terms of programme design and implementation of participating water authorities.
It also aims to ensure as much harmonization of GEMS/Water operations as possible at the regional and global level.

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, "Sampling Frequencies and Methods," describes the minimum sample collection programme for different water bodies, i.e., rivers, lakes, and groundwater and for the different types of stations, i.e., baseline, trend and global river flux. It includes detailed methods for the sampling process, preservation of samples in the field, field quality assurance, and field measured variables.

Chapter III, "Analytical Methods," provides a brief description of the variables and their importance for water quality and outlines the prescribed methods of analysis. Detailed analytical methods are not presented in this document, but are available.

Chapter IV on the "Monitoring of Particulate Matter Quality" presents the importance of sampling 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: the measurement of phytoplankton biomass, community structure monitoring, and the analysis of biological tissues.

Chapter VII on "Analytical Quality Control" describes the scheme for intra- and inter- laboratory procedures for achieving the accuracy targets specified for the project.

Chapter VIII on "Quantitative 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 database systems of the GEMS/Water Programme Office are also presented.

Chapter X on "Data Analysis and Presentation" presents typical outputs for presentation of data.

CONTENTS

CHAPTER I: THE SELECTION OF GLOBAL NETWORK STATIONS

CONTENTS

Further information on the subject of this chapter may be obtained from "Water Quality Assessments: A Guide to the Use of Biota, Sediments, and Water in Environment Monitoring".

1.0 INTRODUCTION

Water quality monitoring, designed to provide reliable and usable data, is often expensive, 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 be to decide which data are needed and how they will be used. Sampling sites should 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 can support 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 should 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 groundwater constitutes 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 for GEMS/Water, to develop regional monitoring of groundwaters. In the interim, operation of the existing groundwater stations 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.

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 can take into consideration the following site specific criteria.

Station Type	Basic Selection Criteria	Type of Water
Baseline Station	• in small undisturbed basins • no source of pollutants • no direct human activities (including roads) • Avoid basin with a high proportion of metal-bearing rocks • at least 100 km from major air pollution source (i.e., cities, industries etc.)	• Headwater lakes • (water residence time: 0.5-2 years) • upstream river stretches • •
Trend Station	• in medium-sized basins, • moderate time frame response to pollution and changes in land-uses • Range of pollution inducing activities/or/single dominant activities (e.g. Industrial, municipal, agricultural, mining etc.)	• Lakes/Reservoirs • (water residence time: (1-3 years) • Rivers • 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 • most downstream station not influenced by tides • station must be representative of the cross-sectional characteristics of the river • 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 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. 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. Sven 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	
- low grade - e.g. cooling	National and local importance of factory.
- high grade - e.g. food and drink	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	
bathing boating amenity	Number of people, frequency of use, membership of clubs, distance from urban areas, access to alternative waters.
Navigation (risk of silting or aquatic vegetation)	Quality and value of goods transported, people employed.
Drainage (risk of silting or obstruction causing floods)	Potential damage, remedial costs, population affected.

2.4 Use of Data

The use 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 identify 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 affected 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.

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.

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.

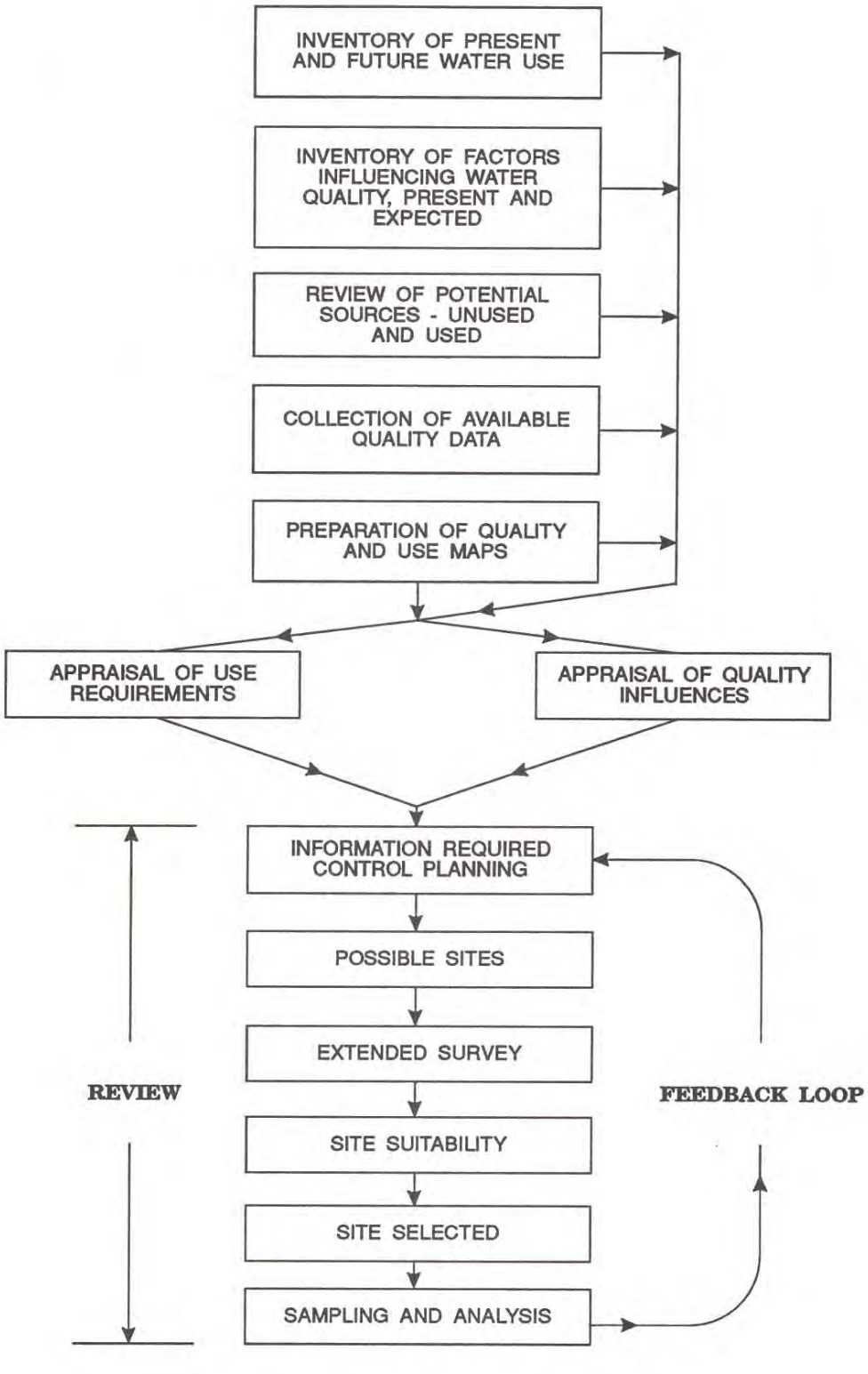


Figure 1: Scheme for selection of water sampling sites

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.

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 quantitative 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 access is to 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.

Bridges

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.

Boats

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 and 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.

Wading

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.

Bankside

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. 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:

Oligotrophic: 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.

Mesotrophic: 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.

Eutrophic: 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.

Dystrophic: 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^{o}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^{o}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 one 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 becomes 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 - micro organisms 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 ▪ Leakage from sewage systems ▪ Infiltration from stabilization ponds	▪ Artificial recharge with treated sewage ▪ Excessive distribution of sludge on farm lands
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 including cooling water by discharge into boreholes ▪ Accidental spillages during use, storage or transport ▪ Leakage from tanks and pipelines	▪ Disposal of industrial wastes by land irrigation
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: (m^3/sec), (m^3/sec)

(m^3/sec)

Outlets: (m^3/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:

49) Waater 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:

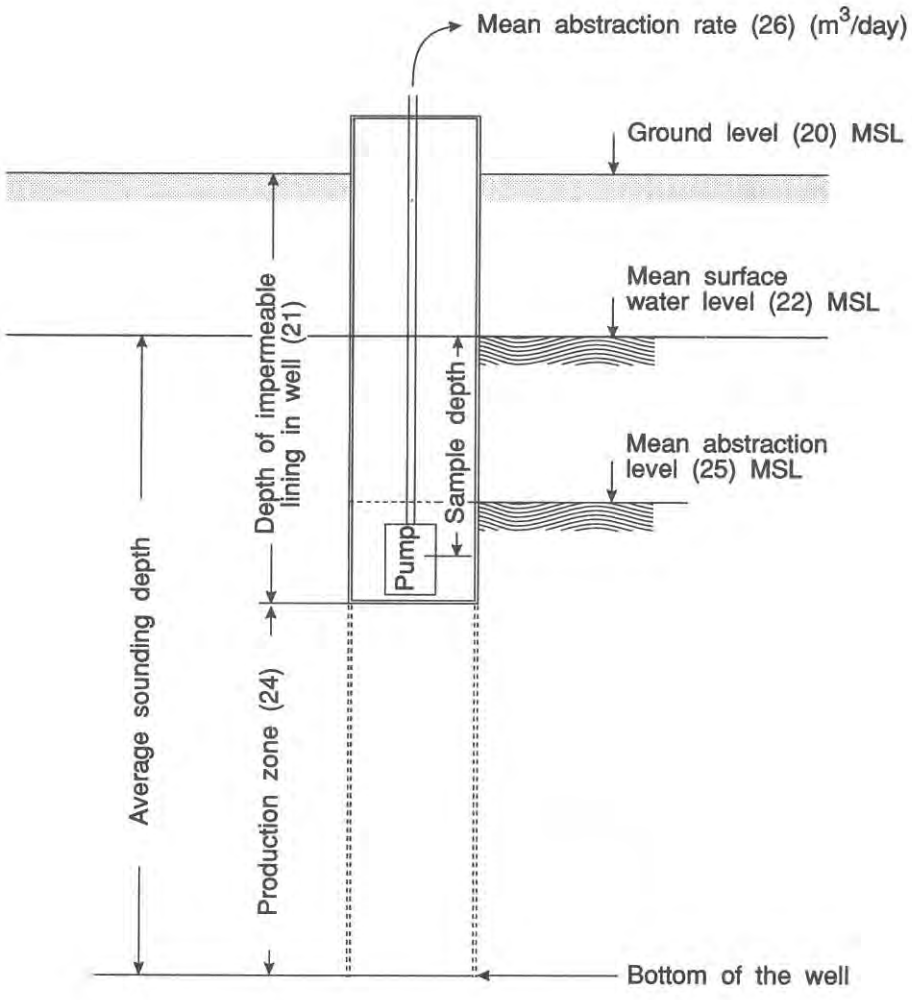
41) List of determinations carried out occasionally and methods used:

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

CHAPTER II: SAMPLING FREQUENCIES AND METHODS

CONTENTS

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 on the sampling practices and experiences of the National Water Research Institute of Environment Canada.

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 smoothes 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 Groundwater

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, and 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 stages:

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 **Optimum**: 24, i.e. fortnightly sampling, and weekly for total suspended solids	**Minimum**: 1 at turnover (sampling at lake outlet) **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) **Maximum**: 24 for small drainage area (ca: 10,000 km^2)	**EUROPHICATION ISSUE**: 12, including twice monthly during summer **OTHER ISSUES**: **Minimal**: 1 at turnover **Maximal**: 2, one at turnover, and one at maximum thermal stratification	**Minimum**: 1 for large, stable aquifers **Maximum**: 4 for small alluvial aquifers **Karstic Aquifers**: same as rivers
GLOBAL RIVER FLUX	**LARGE BASINS** (>200,000 km^2) (1) 6, for some particulate metals (2) 12, for all other variables **SMALL BASINS** (< 200,000 km^2) (1) 24, for basic monitoring variables (3), 12, for expanded nutrients, organic contaminants and some expanded metal monitoring (4) 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 aluminium, 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 Groundwater

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 Technique

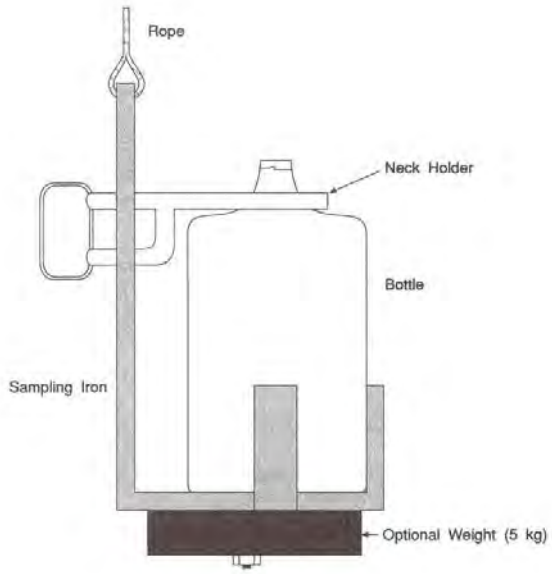
3.3.1 Grab Water Samplers

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 Sampler

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.



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.

Figure 1. Sampling Iron

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.

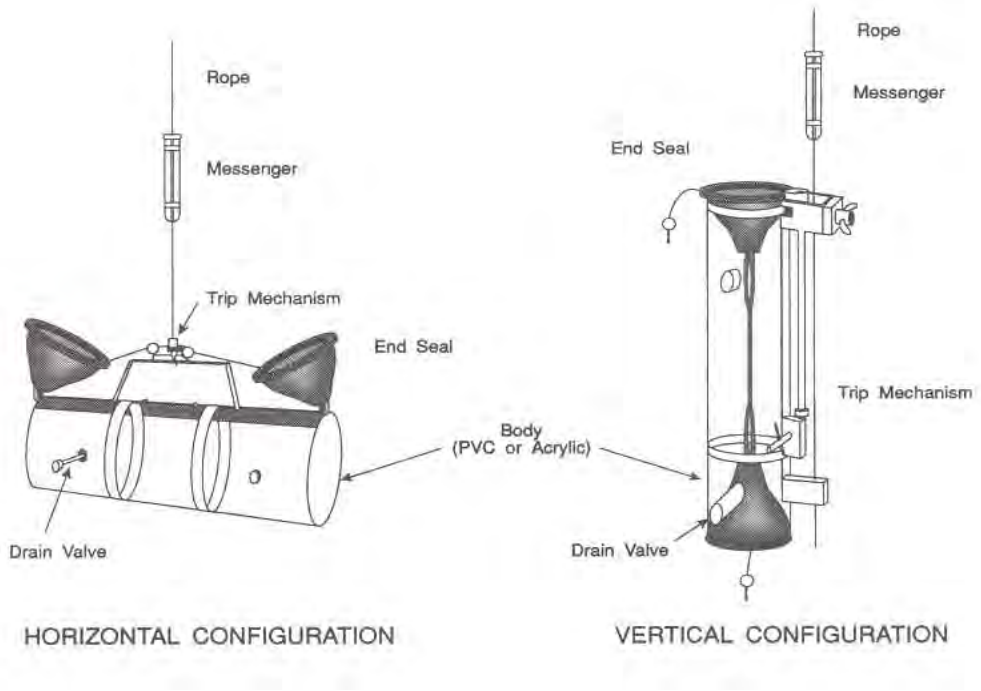


Figure 2. Van Dorn Bottle

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) Activate a metal or rubber messenger to "trip" the mechanism that closes the end seals of the sampler;
(e) Transfer the water sample from the Van Dorn bottle to individual sample containers via the drain valve.

The Kemmerer type 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:

1. 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;
2. Purge the pump and hoses with water from the station to be sampled before the actual water sampling begins;
3. Each pump should be operated according to the instruction manual for that particular pump;
4. 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.

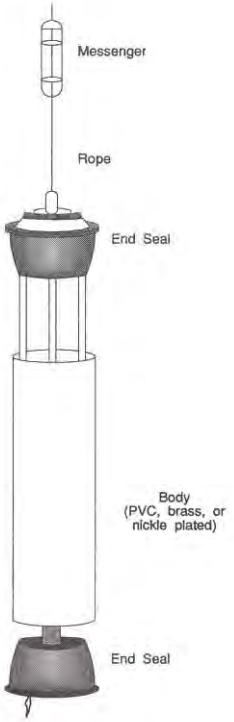


Figure 3. Kemmerer Sampler

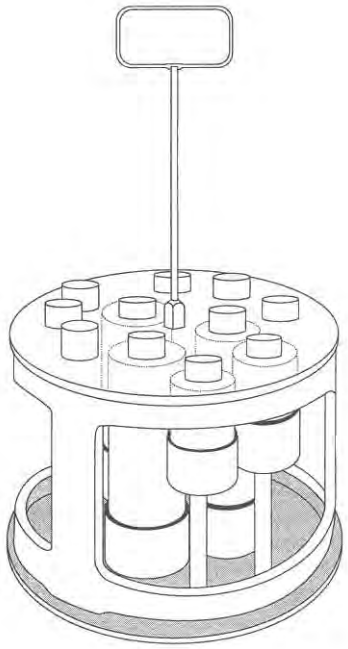


Figure 4. Multiple Sampler

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.

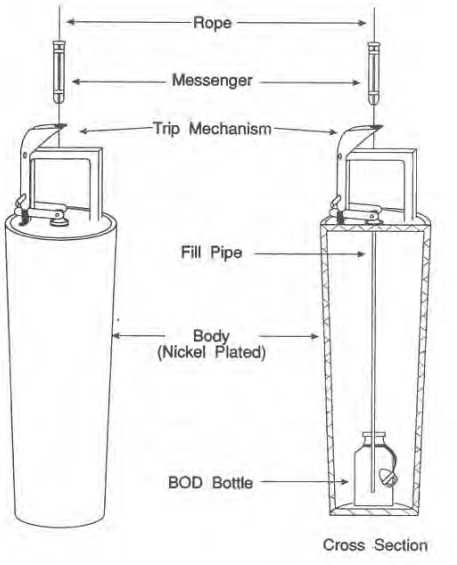


Figure 5. Dissolved Oxygen Sampler

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 KC1 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);
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.

Table 2. Washing Procedures and Containers Recommended for Water Samples

Variable(s) to be Analyzed	Recommended container*	Washing procedure
Alkalinity, Sodium, Calcium, Sulfate, Chloride, Nonfilterable residue, Fluoride, Potassium, Magnesium, Arsenic, pH	1000 ml polyethylene	Rinse: three times with tap water; once with chromic acid, three times with tap water; once with 1:1 nitric acid and then: three times, with distilled water, in that order
Nitrogen, ammonia Nitrogen, nitrate and nitrite Carbon, total organic Nitrogen, total	250 ml polyethylene	Rinse: three times with tap water; once with chromic acid three times with tap water and then: three times with water in that order
Phosphorus total	50 ml. Glass (sovirel)	
Aluminum, Lead, Cadmium, Manganese, Chromium, Nickel, Copper, Selenium, Iron, Zinc	500-1000 ml polyethylene (choice of size depends on the number of metals to be determined and the quantity of sample required)	Rinse: three times with tap water; once with chromic acid three times with tap water; once with 1:1 nitric acid and then:
Mercury	100 ml Glass (sovirel)	three times with ultrapure distilled water, in that order
Organochlorinated pesticides and PCB's	1000 ml glass (amber) with teflon-lined cap	Rinse: three times with tap water, once with chromic acid,
Pentachlorophenol	1000 ml glass (amber) with teflon-lined cap	three times with organic-free water,
Phenolics	1000 ml glass (amber) with teflon-lined cap	twice with washing acetone, once with special grade** acetone,
Phenoxy acid herbicides	1000 ml glass (amber) with teflon-lined cap	twice with pesticide grade hexane and dry (uncapped) in a hot air oven at 360^0C for at least 1 hour

* 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.

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 analogue 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 (ΦS/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 in situ 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-Φm 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-Φm 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.2.2

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.

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 re-entry of sedimented material into the water, owing to physical, chemical, or biological processes in natural situations, always exists. Also, with bottom-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.

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, 10gNa_2SO_4/1	extract immediately
Carbon/inorganic/organic	Polyethylene	Cool, 4^0C	24 h
Carbon, particulate	Plastic petri-dish	Filter using GF/C filter; Cool,4^0C	6 months
Chloride	Polyethylene	Cool, 4^0C	7 days
Chlorinated hydrocarbon	Glass	Cool, 4^0C	extract immediately
Chlorophyll	Plastic petri-dish	Filter on GF/C filter; freeze -20^0C	7 days
Chromium	Polyethylene	2 ml Conc. HNO_3/1 sample	6 months
COD	Polyethylene	Cool, 4^0C	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, 4^0C	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, 4^0C	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, 4^0C, 2 ml 40% H_2SO_4/1	24 h
Kjeldahl	Polyethylene	Cool, 4^0C	24 h
Nitrate + Nitrite	Polyethylene	Cool, 4^0C	24 h
Organic nitrogen	Polyethylene	Cool, 4^0C	24 h
Organic-particulate	Plastic petri-dish	Filter using GF/C filter, Cool, 4^0C	6 months
Organophosphorus	Glass	Cool, 4^0C, 10% HC1 to pH 4.4	No holding,extraction on site
pesticides			
Pentachlorophenol	Glass	H_2SO_4 to pH < 4, 0.5g $CuSO_4$/1 sample Cool,4^0C	24 h
pH	Polyethylene	None	6 h
Phenolics	Glass	H_3PO_4 to pH < 4, 1.0g $CuSO_4$/1 sample;Cool,4^0C	24 h
Phenoxy acid herbicides	Glass	Cool, 4^0C	extract immediately
Phosphorus			
Dissolved	Glass	Filter on site using 0.45 -µm filter	24 h
Inorganic	Glass	Cool, 4^0C	24 h
Total	Glass	Cool, 4^0C	1 month
Potassium	Polyethylene	Cool, 4^0C	7 days
Residue	Polyethylene	Cool, 4^0C	7 days
Selenium	Polyethylene	Cool, 4^0C	6 months
Silica	Polyethylene	Cool, 4^0C	7 days

Sodium	Polyethylene	Cool, 4^0C	7 days
Electrical conductivity	Polyethylene	Cool, 4^0C	24 h
Sulfate	Polyethylene	Cool, 4^0C	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).

CHAPTER III: ANALYTICAL METHODS

CONTENTS

1.0 INTRODUCTION

Revised List of GEMS/Water Variables

Monitoring has been 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 l. Revised List of GEMS/Water Variables

General Water Quality:	Organic Matter:	Particulate Matter:
Water discharge/level	Organic carbon, dissolved	Aluminium, particulate (GRF)
Total suspended solids (R)	Organic carbon, particulate	Arsenic, particulate (GRF)
Temperature	BOD	Cadmium, particulate (GRF)
pH	COD	Chromium, particulate (GRF)
Electrical conductivity	Chlorophyll *a* (R,L)	Copper, particulate (GRF)
Dissolved oxygen		Iron, particulate (GRF)
Transparency (L)		Lead, particulate (GRF)
	Microbial Pollution:	Manganese, particulate (GRF)
	Faecal coliforms	Mercury, particulate (GRF)
Dissolved Salts:	Total coliforms	Selenium, particulate (GRF)
Calcium		Zinc, particulate (GRF)
Magnesium		
Sodium	Inorganic contaminants:	Organic contaminants:
Potassium	Aluminium, dissolved	Aldicarb
Chloride	Aluminium, total	Aldrin
Fluoride (G.W.)	Arsenic, dissolved	Altrazine
Sulphate	Arsenic, total	Benzene
Alkalinity	Boron, dissolved	2, 4-D
	Boron, total	DDTs
	Cadmium, dissolved	Dieldrin
Ionic Balance:	Cadmium, total	Lindane
Sum of cations	Chromium, dissolved	Total hydrocarbons
Sum of anions	Chromium, total	Total chlorinated hydrocarbons
Sodium adsorption ratio	Copper, dissolved	Total polyaromatic hydrocarbons
	Copper, total	PCBs
Nutrients:	Iron, dissolved	Phenols
Nitrate plus nitrite	Iron, total	
Ammonia	Lead, dissolved	
Organic nitrogen, dissolved	Lead, total	
Organic nitrogen, particulate	Manganese, dissolved	
Total phosphorus, dissolved (R,L)	Manganese, total	
Total phosphorus, particulate	Mercury, dissolved	
Total phosphorus, unfiltered (R,L)	Mercury, total	
Silica reactive (R,L)	Nickel, dissolved	
	Nickel, total	
	Selenium, dissolved	
	Selenium, total	
	Zinc, dissolved	
	Zinc, total	

- 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 on (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, persistent 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 # 63Φm. 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 following section 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.

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 constituents
- organic constituents.

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	Anions	F
*Ca	0.04990	*SO_4	0.02082
*Mg	0.08224	*Cl	0.02820
b Sr	0.02282	a*HCO_3	0.01639
*Na	0.04348	a*CO_3	0.03333
*K	0.02558	*N-NO_3	0.07143
b N-NH_4	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.

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

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, temperatures 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 0.1^0C.

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 25^0C.

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 20^0C. Note that 1 m S/m = 10 ΦS/cm = 10 Φmho/cm. Freshly distilled water has a conductivity of 0.5 to 2 ΦS/cm whereas natural waters have conductivity values ranging from 50 to 1500 ΦS/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 ΦS/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 105^0C. If the suspended matter clogs the filter and prolongs filtration, the difference between the total solids content (also dried at 103 - 105^0C) and the total dissolved solids (filtrate dried to constant weight at 180^0C) 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 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 sulphate 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 sulphates 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 re-dissolved 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 Φm 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.

Aluminium

1. General

Although aluminium is among the most abundant elements in the earth's crust, it is present only in trace concentrations in natural waters. Because aluminium 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 aluminium 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 aluminium is to be determined, filter a portion of the unacidified sample through a 0.45-Φm 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 aluminium, because these materials will remove most of the soluble aluminium.

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 Φg/litre. The mean concentration was 14 Φg/litre. Sea water concentrations are substantially lower, with a reported range of 0.04-3 Φg/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 Φg/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 Φm membrane filters (pre-cleaned) 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% $K_2Cr_20_7$ 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 $K_2Cr_20_7$ 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 Φg/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 sulphides 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 Φg/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 Φg/1; only in three samples did the concentration exceed 50 Φg/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 sulphate 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 Φg/litre, with a range from 0.2 Φg/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 Φg/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 Φg/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 Φg Cd/l in soft water for the protection of cladocerans and salmonid fishes to 12 Φg 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 Φg/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 Φm 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 delectability 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:

Aluminium

– 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 (>2Φg/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 (<10Φg/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 polyethylene bottle and acidify with concentrated sulphuric 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 aluminium 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 Φg 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 4^0C. 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 Φg 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 Φg NH_3 -N/L and is useful for up to 500 Φg 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 Φg 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 4^0C 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 (-20^0C), or by the addition of 40 mg mercuric ion as $HgCl_2$ per litre of sample, with storage at 4^0C.

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 bio-available. 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) suspended 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 -10^0C. 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 Φm 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 Φg/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 Φg/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 Φg/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 Φg/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 aluminium 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 Φg/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 Φm membrane filter as soon after sample collection as possible. All samples should be stored at 4^0C, 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 Φg 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 20^0C 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 4^0C 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 4^0C 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 4^0C 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 ≤ 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^o to 4^0C, 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-Φm-pore-diam filter; nondissolved organic carbon (NDOC) - also referred to as particulate organic

carbon, the fraction of TOC retained by a 0.45-Φm 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 interferes. 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 4^0C 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 4^0C 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 4^0C. 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 Φg/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 woollen 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^{0}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 4^0C 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 4^0C 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 Φg/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 4^0C until analyzed. Teflon-lined bottle caps are recommended or pre-cleaned heavy aluminium 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).

6.0 REFERENCES

American Public Health Association (APHA), American Water Works Association & Water Pollution control Federation, 1989. Standard Methods for the examination of Water and Wastewater, 17th Edition, Washington, D.C.

U.S. - EPA, 1989. Method 1618: Organo-halide Pesticides, Organo-phosphorus Pesticides, and Phenoxy-acid Herbicides by Wide Bore Capillary Column Gas Chromatography with Selective Detectors. Office of Water Regulations and Standards, Industrial Technology Division. June 1989.

Chaput, D., 1986. On-line Trace Enrichment for Determination of Aldicarb Species in Water, Using Liquid Chromatography with Post-column Derivatization. J. Assoc. Off. Anal. Chem. V. 69: 985-989.

Lesage, S. 1989: Solid-Phase Sample Collection for the Analysis of Aldicarb Residues in Groundwater. LC-GC 7(3).

Krause, R.T., 1980. Multiresidue Method for Determining N-Methylcarbamate Insecticides in Crops, Using High Performance Liquid Chromatography. J. Assoc. Anal. Chem. V. 63, No. 5: 1114-1124.

Environment Canada (1979) Analytical Methods Manual. Inland Waters Directorate, Ottawa, Canada.

CHAPTER IV: MONITORING OF PARTICULATE MATTER QUALITY

CONTENTS

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. 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 l. 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 (^{0}C)		5. .....
6. ignition (^{0}C)		

C. ANALYTICAL RESULTS

			Treatments		
			Physical	Chemical	Analysis
1. Inorganic Pollutants:					
Arsenic	12.5	µg As g^{-1}	4;5 (50^{0}C)	1	
Cadmium	0.95	µg Cd g^{-1}	4;5 (106^{0}C)	1	
Chromium	215	µg Cr g^{-1}	4;5 (106^{0}C)	1	2
Copper	45	µg Cu g^{-1}	4;6 (550^{0}C)	1	2
Mercury	0.22	µg Hg g^{-1}	4;5 (50^{0}C)	1	
Nickel	135	µg Ni g^{-1}	4;6 (550^{0}C)	1	2
Lead	260	µg Pb g^{-1}	4;5 (50^{0}C)	1	2
Zinc	340	µg Zn g^{-1}	4;6 (550^{0}C)	1	2
2. Nutrients:					
Particulate organic carbon	5.3%				
Particulate nitrogen	0.58%				
Total part. phosphorous	1630	µg P g^{-1}			
3. Organic Pollutants:					
River unfiltered water:					
PCB:	0.60	µg.l^{-1}			
ΣDDT:	0.24	µg.l^{-1}			
Lindane:	0.30	µg.l^{-1}			
Total hydrocarbons:	7200	µg.l^{-1}			
Bottom Sediments:					
PCB:	170	µg.kg^{-1}			
ΣDDT:	23	µg.kg^{-1}			
Lindane:	240	µg.kg^{-1}			
Total hydrocarbons	37	µg.kg^{-1}			

4. Supporting Analyses:		
Aluminum:	105000	µg Al g^{-1}
Iron:	55000	µg Fe g^{-}
Grain size (median):	35	µm
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 - Extreme discharge statistics
	R2	- Suspended sediment (TSS)	- TSS variability - Relationship TSS = f(Q) - Annual sediment discharge
	R2 R4	- Inventory of major pollutant sources	- Location of pollutant sources - Types of pollutants - Approximate quantities discharged
	R4	- Sediment mapping	- Occurrence of fine sediment deposits
LAKES and RESERVOIRS	L4	- Bathymetric survey	- Deepest points - Bathymetric map
	L4	- Sediment survey	- Area of deposition - Occurrence of fine deposits
	L4	- Inventory of major pollutant sources	- Location of pollutant sources - Types of pollutants - 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; utrients (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, 3DDT; 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 another organic solvent free of chlorinated hydrocarbons. The storage glass vessels should be rinsed in the same manner, heated at 300^{0}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 pre-cleaned 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 Φm or 0.45 Φm 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 issolved 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 300^0C. The water rinsed filters should be kept in Petri dishes, the others in clean metal or glass containers sealed with aluminium 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

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., 20^0C for organochlorines and hydrocarbons; 50^0C 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(-20^0C). 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. 60^0C); 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 110^0C 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 90^0C 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 1100^0C; 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 pre-treatments (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 ($mg.g^{-1}$; $\Phi g.g^{-1}$; $ng.g^{-1}$) 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 m. 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) Aluminum 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 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 <63 m or <125 m 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 63Φm 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 in the layer z
Alb = concentration of the 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 $\Phi g.l^{-1}$. 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 $T=\ni t_i$ will be:

$$Mx = \sum_i Qs_{xi} t_i$$

$$where\ Qs_{xi} = TSS_i Q_i Cs_{xi}$$

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:

$$Mx = \sum_i Cs_{xi} Ms_i$$

$$where\ Ms_i = t_i \sum_j TSS_j Q_j$$

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.

6.0 REFERENCES

Adams, D.D. (1991). Sampling sediment pore water. In: A. Mudroch and S.S. Macknight (eds.). Handbook of Techniques for Aquatic Sediment Sampling, Chapter 7, pp. 171-202, CRC Press, Boca Ratan, Fl.

Agemian, H. and Chau, A.S.Y. (1976). Evaluation of extraction techniques for the determination of metals in aquatic sediments. The Analyst, Vol. 101, No. 1207:761-767.

American Public Health Association (1951) Standard methods for the examination of water and waste water (13th ed.). Amer. Publ. Health Ass., Washington, D.C.

Environment Canada (1979) Analytical Methods Manual. Inland Waters Directorate, Ottawa.

E.P.A. Methods for Chemical Analyses of Water and Wastes. Rept. E.P.A. -600/4-79-020.

Food and Agriculture Organization (1976) FAO Manual of Methods in Aquatic Environmental Research: part 3. Sampling and Analysis of Biological Materials. FAO Fisheries Technical Paper No. 158, 124 p.

Förstner, U. and Wittmann, G.T.W. (1979). Metal Pollution in the Aquatic Environment, Berlin, Heidelberg, New York. Springer Verlag. 400 p.

Golterman, H.L., Sly, P.G. and Thomas, R.L. (1983). Study of the Relationship Between Water Quality and Sediment Transport: A Guide for the Collection and Interpretation of Sediment Quality Data, Unesco, Paris, 231p.

Horowitz, A.J. (1985). A Primer on Trace Metal-Sediment Chemistry. U.S. Geol. Survey Water Supply Paper 2277, 67 p.

Horowitz, A.J. (1991). A primer on sediment-trace element chemistry, 2nd rev. ed., Lewis Publishers, Inc., Chelsea, Mi.

Horowitz, A.J., and Elrick, K.A. (1988). Interpretation of bed sediment trace metal data: methods for dealing with grain size effect. Special Technical Publication 976, Am. Soc. Testing and Materials, Philadelphia, PA.

Horowitz, A.J., Elrick, K.A. and Hooper, R.C. (1989). A Comparison of Instrumental Dewatering Methods for the Separation and Concentration of Suspended Sediment for Subsequent Trace Element Analysis. Hydrolog. Processes, 2, p. 163-184.

Martin, J.M. and Meybeck, M. (1979). Elemental Mass-Balance of Material Carried by Major World Rivers. Mar. Chem., 7, p. 173-206.

Meybeck, M. (1982). Carbon, Nitrogen, and Phosphorus Transport by World Rivers. American J. Science, 282, p. 401-450.

Meybeck, M., Friedrich, G., Thomas, R., and Chapman, D. (1991). River Monitoring in: D. Chapman (ed.) Water Quality Assessments, A Guide to the use of Biota, Sediment and Water in Environmental Monitoring. Chapter 6, Chapman Publ. London (in press).

Mudroch, A. and Bourbonniere, R.A. (1991). Sediment sample handling and processing in: A. Mudroch and S.D. MacKnight (eds.) Handbook of Techniques for Aquatic Sediment Sampling. Chapter 4, pp. 29-96. CRC Press Inc., Boca Ratan, Fl.

Mudroch, A. and Macknight, S.D. (1991). Bottom sediment sampling. In: A. Mudroch and S.D. Macknight (eds.). Handbook of Techniques for Aquatic Sediment Sampling. Chapter 4, pp. 29-96. CRC Press Inc. Boca Ratan, Fl.

Salomons, W. and Förstner, U. (1984). Metals in the Hydrological Cycle. Springer-Verlag, New York, 350 p.

Skougstad, M.W., Fishman, J.J., Friedman, L.C., Erdman, D.E. and Duncan S.S. Methods for Determination of Inorganic Substances in Water and Fluvial Sediments. Techniques of Water Resources Investigations of the United States Geological Survey, Book Ch.AI, 626 p., US Printing Office, Washington,DC.

Tessier, A., Campbell, P.G.C. and Bisson, M. (1979). Sequential extraction procedure for the speciation of particulate trace elements. Analytical Chemistry, V 51:844-850.

Thomas, R. and Meybeck, M. (1991). The use of particulate matter. In: D. Chapman (ed.). Water Quality Assessments, A Guide to the Use of Biota, Sediment and Water in Environmental Monitoring. Chapter 4, Chapman Publ., London (in press).

Thomas, R., Meybeck, M. and Beim, A. (1991b). Lake Monitoring. In: D. Chapman (ed.) Water Quality Assessments, A Guide to the Use of Biota, Sediment and Water in Environmental Monitoring. Chapter 7, Chapman Publ., London (in press).

Turekian, K.K. and Wedepohl, K.H. (1961). Distribution of the Elements in some Major Units of the earth's Crust, Bull. Geol. Soc. Amer., 72, p. 175-192.

WMO (1981) Measurement of River Sediment. WMO Operational Hydrology Report 16, World Meteorological Organization, Geneva, 61 p.

ACKNOWLEDGEMENTS

Corrections and suggestions from Arthur Horowitz (U.S. Geological Survey, Doraville, GA) and Alena Mudroch (National Water Research Institute, Burlington, Ontario) were greatly appreciated.

CHAPTER V: PRINCIPLES FOR PLANNING AND IMPLEMENTATION OF MICROBIOLOGICAL ANALYSES

CONTENTS

1.0 INTRODUCTION

When planning the microbiological monitoring of water courses and drinking water supplies, a number of issues should be considered to ensure that the methods and strategies adopted will produce valid and reliable results. Such 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 are 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 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
37^0C Count	0	0	2	0
22^0C 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 44^0C or 44.5^0C 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 37^0C 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 - 44^0C. 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 37^0C or 22^0C. 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 45^0C. 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	Wastewater	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 2	MF,MT	MF,MT	MT
Colony Count	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 identifiable 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

ISO 9308-1 Water quality - Detection and enumeration of coliform organisms, thermotolerant coliform organisms and presumptive Escherichia coli

	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.	
	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.

CHAPTER VI: BIOLOGICAL MONITORING

CONTENTS

1.0 INTRODUCTION

Biological monitoring of water quality is used in many countries as a complimentary approach to physical and chemical monitoring. Biological monitoring examines the effects on freshwater communities and individuals, measuring processes such as primary production by algae, community structure or contaminant levels in individual organisms.

1.1 Types of Biological Monitoring

Many sorts of biological techniques could be used to examine the impact of human activities on the aquatic environment. These techniques would range from molecular and genetic tests to full ecological surveys. Only three of the most widely used techniques will be described here; measurement of phytoplankton biomass by measurement of chlorophyll *a*; simple indices of biological diversity and the use of plant or animal tissues to monitor specific contaminants.

2.0 PHYTOPLANKTON BIOMASS - CHLOROPHYLL *a*

2.1 Rationale

Planktonic algae - phytoplankton - grow in the water column and can be used as indicators of water quality. Phytoplankton are responsive to natural conditions and human influences and community structure will differ markedly between different water bodies. Phytoplankton populations and biomass can be reduced by inputs of toxic substances but may be increased by artificial inputs of nitrates or phosphates (from human sewage or fertilizers). They may therefore indicate water quality but will also influence water quality - high populations of certain phytoplankton can produce unacceptable levels of toxins, change pH, colour or taste of water. Where artificially high nutrient concentrations are found in the water (eutrophication) the high phytoplankton populations will eventually die and their decomposition can lead to serious problems with oxygen depletion in the water. The changes in biomass can be monitored by measuring the concentration of the photosynthetic pigment chlorophyll *a* in the water.

2.2 Sampling

Samples should be taken with a bottle sampler. For nutrient-poor (high transparency) water up to 6 litres will be required. For eutrophic waters, 1-2 litres will usually be sufficient.

2.3 Principle

Three types of chlorophyll are found in phytoplankton: chlorophyll *a*, chlorophyll *b* and chlorophyll *c*. The chlorophylls are extracted from the cell with acetone. Each chlorophyll has a characteristic light absorption spectrum with particular peak absorbances. The acetone extract is analysed on a spectrophotometer at these peaks - the peak height indicates chlorophyll concentration. Chlorophyll starts to degrade immediately after the cell dies. This can lead to errors in estimating sample concentration since the degradation product of chlorophyll *a*, phaeophytin *a*, fluoresces in the same spectral region. The concentration of phaeophytin *a* must be measured and appropriate corrections made.

2.4 Apparatus

- Spectrophotometer with a spectral band width of between 0.5 and 2 nm;
- Cuvettes, 1 cm - longer path length cuvettes may be used (usually 4 cm or 10 cm);
- Centrifuge;
- Tissue grinder;
- Centrifuge tubes, 15 ml, graduated, screw tops;
- Filters, glass-fibre GF/C, 4.7 cm diameter;
- Filtration cup and pump;
- Forceps.

(All apparatus, as far as possible, should be acid and alkali free).

2.5 Reagents

- Magnesium Carbonate suspension 1.0 g $MgCO_3$ in 100 ml distilled water. Shake before use;
- Acetone solution - 90% acetone;
- Hydrochloric acid - 1N HCl.

2.6 Procedure

i) Concentrate the water sample by filtration (after recording initial water volume). Filter continuously, not allowing filter to dry during concentration of single sample. Add 0.2 ml $MgCO_3$ suspension to final few millilitres of water in filter cup as filtration ends. If extraction is delayed at this point, filters should be placed in individual labelled bags with forceps and stored at -20EC in darkness. Samples may be transported in this form.

ii) Place the filter in the tissue grinder, add 2-3 ml of 90% acetone and grind until the filter fibres are separated. Pour this acetone and ground filter into a centrifuge tube, rinse out the grinding tube with another 2 ml of 90% acetone and add this to the centrifuge tube.

Make up the total volume in the centrifuge tube to 10 ml with 90% acetone. Place top on tube, label and store in dark at 4EC for 10-12 hours. Transport of samples may take place at this stage.

iii) Centrifuge closed tubes for 15 minutes at 3,000 rpm to clarify samples. Decant the clear supernatant into a clean centrifuge tube and record the volume.

iv) Fill a cuvette with 90% acetone. Record absorbance on the spectrophotometer at 750 nm and 663 nm and 665nm. Zero on this blank if possible, otherwise record absorbances and subtract from sample readings.

v) Place sample in the cuvette and record absorbance at 750 nm and 663 nm (750a, 663a).

vi) Add 2 drops 1N HCl to sample in 1 cm cuvette (increase acid in proportion to volume in larger cuvettes). Agitate gently for 1 minute and record absorbance at 750 nm and 665 nm (750b , 665b).

vii) Repeat procedure for all samples. Some preliminary samples may need to be taken to assess the best sample volume.

2.7 Calculations

i) Subtract absorbances: 663a - 750a, - corrected 663a absorbance
665b - 750b, - corrected 665b absorbance

ii) Use these corrected 663a and 665b absorbances to calculate:

$$Chlorophyll\ a\,(mg/m^3) = \frac{26.73(663a - 665b)(Ve)}{(Vs)(l)}$$

$$Phaeophytin\ \ a\,(mg/m^3) = \frac{26.73(1.7(665b) - 663a)(Ve)}{(Vs)(l)}$$

where Ve= volume of acetone extract in litres
" Vs = volume of water sample, m^3
" 1 = path length of cuvette, cm

Chlorophyll *a* concentrations should be recorded. The ratio of chlorophyll *a* to phaeophytin *a* gives an indication of the effectiveness of sample preservation, as well as of the condition of the algal population.

3.0 COMMUNITY STRUCTURE MONITORING

Biological monitoring of communities of aquatic organisms is used to indicate the ecological effects of changes in water quality. Different species have different capacities to resist adverse conditions. At the most basic level, this can be translated into monitoring of the presence or absence of particular species which are sensitive to particular types of pollution. However, before species disappear altogether, more subtle effects may be seen in changes in community structure - monitoring will identify relative changes in abundance, together with species absence or presence as responses to changed conditions. Different species have different sensitivities to different pollutants - this would be very difficult to characterize for practical use - community structure indices give subtle indications of ecological response to total water quality. The usual approaches are either biotic indices or diversity indices. Biotic indices rely on good taxonomic and ecological information and are designed for use in specific environments. Diversity indices combine species richness with individual abundance to give general indications of community structure. It must be emphasized that indices give only crude approximations of the community condition. It is generally acknowledged to be preferable to use community data in their basic form for interpretation by expert biologists. Information is lost when the data are combined in an index which in turn is susceptible to over-simple interpretation. Indices have proven useful in the past in many areas but their use and interpretation must be subject to critical scrutiny.

Diversity indices can be used on any group of organisms, whether phytoplankton, zooplankton, benthic invertebrates or fish. A difficulty with all of these groups is that of separating responses to water quality from other factors which may influence the community, such as reproduction. Fish are easy to identify and their responses to stress is well known, in addition to being an important element in human use of water. However, they are able to move away from poor water quality and their capture may require expensive equipment. Phytoplankton and zooplankton are responsive to water quality but identification requires expertise. Benthic invertebrates are widely used and have several advantages. Invertebrates are relatively sedentary and therefore reflect water quality at a single geographical point. In addition, they have relatively long life cycles which allow their communities to integrate responses to water quality over long periods. Benthic invertebrates are easy to collect and can be easy to identify. The disadvantage with benthic invertebrates is that in some environments they may not be easy to collect - deep rivers, lakes and seasonally-flooded fast-flowing rivers may present problems. The techniques presented here give very basic guidelines for monitoring. It is probable that data will only be suitable for within-site comparison and time trend identification but it is hoped that these methods will provide a basis for the development of biological monitoring in the GEMS/Water Programme.

3.1 Programme Design and Site Selection

The programme design and site selection for biological monitoring are generally considered in parallel to those of chemical and physical monitoring. However, certain specific biological considerations can be addressed.

If no ecological information is available, it may be worth conducting a preliminary qualitative survey to determine which animals are present. Literature searches may provide some useful information.

Programme design consists of:

i) Identifying measurements to be taken;

ii) Selecting sites and frequency of sampling;

iii) Choosing methods of collection, storage and analysis; and

iv) Procedure for handling and presenting data.

Methods are given below for collection, analysis and data handling. Site selection is discussed elsewhere but should include considerations of the practibility of collection of biological samples. No fixed frequency can be recommended - thought should be given as to how the water quality would change in the course of a year - oxygen depletion, flow changes and dilution of pollution load, temperature and sediment load - and biological monitoring be designed to reflect such changes. Sampling should be sufficiently frequent to detect any natural seasonal trends in communities such as reproduction or mortality.

3.2 Habitat Characteristics

An important element in biological monitoring is the description of the physical setting for the invertebrate community. Special attention should be given to the following:

i) Substrate characteristics - stony, sandy, muddy;
ii) Flow characteristics;
iii) Channel morphology; and
iv) Vegetation - macrophytes in the water
- overhanging vegetation.

These characteristics, together with physical and chemical variables, are important in determining the invertebrate community structure and should be recorded. In addition, events such as short seasonal floods may have a strong influence on community structure. In some areas, high suspended sediment will result in a shifting bed - in this case, the use of benthic invertebrates may be reconsidered and plankton may be a more practical choice.

3.3 Sampling Theory and Planning

The number of units to be taken at each site should be estimated on the basis of preliminary surveys. A desired degree of precision can be calculated as follows:

$$D = \frac{1}{x}\sqrt{\frac{S^2}{n}}$$

where D = degree of precision
X = mean abundance
S = standard deviation
n = number of units

A degree of precision of 20% is generally acceptable for ecological surveys, so

$$n = \frac{S^2}{(0.2)^2 (X)^2}$$

The location of units at the sampling site depends to some extent on the purpose of the monitoring. The sample site should be divided into a grid (for example, a grid 3 m x 3 m would give 100 potential sampling units of 30 cm x 30 cm each) and the potential units numbered.

For time trends and routine sampling for relatively infrequent monitoring, equally spaced units can be sampled (for example, every third unit). For sampling of higher frequency (for example, for an environmental impact assessment), units should be chosen from the grid at random (the units' assigned numbers can be selected from a random number table). If the environment is non-uniform - perhaps composed of several biotopes - the grid should be divided according to the different areas, a number of units assigned to each area in proportion to the area fraction of the total grid, and the units selected randomly within each area.

3.4 Field Sampling

Preliminary surveys may rely upon qualitative sampling using a hand net. Data from such sampling are not quantitative but may be considered to be semi-quantitative if standard techniques are used. The net is commonly used in shallow rivers or streams with eroding substrata. The net is placed vertically on the bed, the mouth facing upstream. The operator stands upstream and kicks the substrate over a fixed area and for a fixed time, the dislodged invertebrates being caught in the net. Some stones should be examined for clinging animals. Data obtained in this way is used in semi-quantitative ways. In rivers with large stones, animals must be picked from rocks by hand and the substratum dislodged to allow animals to drift into the net. Lake shores may also be sampled in a kick-sampling way, dislodging substratum and making sweeps with the net across the disturbed area. This latter method is not reliable. All hand-net methods are subject to considerable problems of operator bias - strength of kicks, time of sampling, area of sampling - and have limited use.

Several techniques are available for quantitative sampling. In shallow water with a flow of > 10 cm/s a Surber sampler is commonly used. It is difficult to use if boulders or macrophytes dominate the river. The sampler consists of a hinged metal frame which opens to 90E. The vertical square is attached to a net and the angle between the squares has canvas screens to prevent animals from escaping around the sides of the frame. The open horizontal square is placed on the substrate, the mouth of the net facing upstream and the substrate within the square dislodged into the net. If the substrate is uneven, the gaps under the square should be filled before dislodging. Alternatively, a foam rubber strip can be fixed on the lower edge of the horizontal square to ensure that gaps are filled and that no animals escape. The sampled substrate can be taken for analysis. Nets on surber samples are usually nine meshes/cm - these will catch animals > 0.75 mm.

Deep rivers and lakes are more difficult to sample. The usual method of sampling is to use grabs or cores from a boat.

3.5 Sample Handling

If necessary, the sample may be washed free of sediment with a gentle water jet on a 500 mm sieve. The animals should be placed in water in a white dish or tray for sorting and removed with a pipette, placing in a labelled screw-top jar. Animals are easier to see when alive because of movement. Labels on jars should be recorded on data sheets with time and place of sampling.

The sample may be preserved before or after this sorting stage, depending on facilities available in the field. Samples should be fixed in buffered formalin for 24 hours then preserved in 70% alcohol. Buffered formalin is made by adding 2 g sodium tetraborate to 98 ml 40% formaldehyde. This solution is diluted 1 part formaldehyde: 9 parts filtered water for use. Unsorted samples may be placed in formalin after removing large debris and stored in this way until sorting.

3.6 Data

The general assumption behind the use of diversity indices is that as pollution increases, diversity decreases. This is true in certain cases but is by no means universal. Interpretation in the light of knowledge of local ecology is of great value.

Samples should be sorted and, where possible, identification performed. Ideally, taxonomic keys should be available but these may not have been produced for many areas. The method described below does not require detailed taxonomic knowledge. However, its accuracy will be enhanced if the animals are properly identified. In some situations, the number of species (or other taxa) alone may accurately reflect pollution impact but this takes no account of population changes and may not always be sufficiently sensitive.

3.7 The Shannon-Weiner Index

The Shannon-Weiner Index has been extensively used in analysing the changes in invertebrate communities as a result of water quality changes. It combines data on species (or taxa) richness with individual abundance. Diversity is taken to be a function of the number of species (or taxa) and the evenness of distribution of individuals between species. When sorting, animals should be classified according to particular taxa (species, genus, family). Ideally, to ensure consistency and comparability, all animals should be identified to the same taxonomic level. The animals sampled should be classified and counted.

The index is counted as follows:

$$H^1 = - \sum_{i=1}^{t} \left(\frac{n_i}{N} \right)$$

where t = numbers of groups in the sample (taxa)
n_i = number of individuals in the ith group
N = total number of individuals in the sample

4.0 BIOLOGICAL TISSUE ANALYSIS

The recommendation of standard methods for analysis of chemicals in biological tissues is difficult. A wide range of techniques and equipment is available and frequently the different techniques will be used for different organisms and for different chemical substances (for example, different digestion methods may be used for different metals). Of greatest importance is not the standardization of methods but the application

of quality control to method development and the use of standard reference materials. The range of types of biological material often means that modifications must be made to existing methods to meet the needs of new situations.

The methods presented here can be used as the basis for methods developed in the context of good quality control. It is assumed that the fundamentals of metal analysis are the same as for water and sediments. The analysis of synthetic organic substances is not described here.

As for non-biological samples, great emphasis is placed upon the avoidance of contamination, both in the laboratory environment and in apparatus used. Acid washing of all plastic and glass coming into contact with samples is essential and water for rinsing and analysis should be as pure as possible (preferably de-ionized and distilled in a glass-element still).

4.1 Selection of Organisms

Different organisms have very different ways of responding to metal contamination, some excluding or excreting certain metals while accumulating and detoxifying others. Organisms may be selected for metal monitoring for two primary reasons - either because they accumulate metal over time, giving an indication of residual trends in metal contamination, or because they are of importance as food organisms and the metal may be transferred to humans with consequent health effects. Fish fall into the latter category but have the disadvantage for an indicator of being mobile and therefore possibly subject to a range of influences. For the use of organisms as biological monitors of metal pollution, several criteria should be taken into account:

i) the organism should accumulate metals;

ii) the organism should be available in suitable places and quantities to allow regular and unbiased sampling at all required times;

iii) uptake and accumulation should be related to exposure - this may require a knowledge of the physiology of the organism; and

iv) the organism should not be expensive to collect.

In order for an organism to be used as an indicator of metal pollution at a particular monitoring site, it is preferable that it should be relatively sedentary, i.e., subject only to the contamination influences at that particular site. Bivalve molluscs have been widely used as indicators but many other animals and plants have been used in biological monitoring. The choice of organism must be made on a local scale, taking account of the above criteria. The knowledge of physiology should be stressed - in order to explain the observed levels of contaminants, some understanding of the behaviour of the contaminant in the organism is necessary. Taxonomic identification of sampled organisms is an obvious requirement.

4.2 Collection of Samples

Apparatus

- Gloves - polyethylene or latex (metal-free);
- Polyethylene or glass jars (acid-washed);
- Polyethylene bags (metal-free);
- Distilled water; and
- Insulated box, ice or solid CO_2.

Organisms should be collected avoiding contamination from metals or sediments and handled with polyethylene or latex gloves (ensuring that gloves are not dusted with zinc powder). Organisms may be rinsed with distilled water and placed in clean metal-free polyethylene bags or glass or plastic vessels (acid washing should ensure cleanliness). Jars or bags should be labelled and a record kept of sampling site and time. Samples should then be transported to the laboratory, either at between -2E and 4EC (refrigerated) or frozen at -20EC. Transport in insulated boxes is most practical, cooling with ice for refrigeration or solid CO_2 for frozen samples.

4.3 Treatment of Samples

- Distilled water;
- Clean plastic sheet/acid-washed plastic tray;

- PTFE/quartz/stainless steel knifes; and
- PTFE forceps.

Organisms which are to be digested whole for metal analysis may be rinsed thoroughly with a gentle jet of distilled water to remove adhering material before being placed in a clean vessel.

Bivalve mollusc tissue must be separated from the shell. Adhering material should first be scraped from the shell with a knife and the byssus removed. A knife should be inserted between the two shell halves and used to cut the adductor muscles. The shell can be opened and the tissue loosened with a knife. Water should be drained off and the tissue removed with forceps and placed in a clean vessel.

Methods using more elaborate dissection are indicated in the references. It may be decided to separate muscle tissue and liver for analysis individually, especially in the case of fish. In this event, great care must be taken to avoid contamination of the tissue of interest by other tissues, such as skin surface - meticulous dissection is therefore required.

If composite samples are required, the sample tissues should be homogenized in a glass/PTFE tissue grinder or a stainless steel homogenizer and suitable subsamples taken. Stainless steel instruments have been commonly used in preparing samples metal analyses, except for samples intended for manganese and nickel analysis, where contamination problems may arise.

4.4 Blanks and Reference Materials

The procedures for sample treatment outlined from this point on should be performed on blank samples and standard reference materials in parallel to the actual sample, as for non-biological samples. Blanks are subjected to the whole series of reagent and apparatus procedures, only lacking the biological material itself.

4.5 Dry Mass Determination

i) Oven drying

Apparatus: weighing bottles;
drying oven (105EC); and
balance (preferably top-pan with a sensitivity of ∀ 0.001 g).

The weighing bottle is first dried to constant mass in the oven and the final mass of bottle and stopper noted. 1-2 g of fresh sample is placed in the bottle and the stopper inserted. The bottle is weighed and then placed in the oven where the stopper is removed and the sample dried to constant mass. Each time the bottle is removed to check for constant mass, the stopper is inserted, the bottle removed from the oven, allowed to cool in a desiccator and weighed.

ii) Freeze drying

Apparatus: drying vessels (stoppered);
freeze dryer; and
balance.

For material containing large quantities of lipid, freeze drying may be preferable, performed in an equivalent manner to oven drying in suitable vessels.

Both oven drying and freeze drying may be performed in glass digestion vessels.

iii) Fresh sample

For mercury, arsenic, tin and selenium determinations, digestion of the fresh sample may be preferred. In this case, a sub-sample may be used for dry mass determination and the metal values from the wet-digested sample corrected accordingly.

4.6 Digestion - Basic Method

The times for digestion and quantities of acids will need to be adjusted according to the sample type. Only the simplest methods are presented here - more complex digestion procedures are outlined in the references. Preliminary digestions will be needed to determine suitable methods.

Reagents: distilled water; and
concentrated HNO_3 d_{20EC} 1.4g/ml

Apparatus: hot plate/oven 120EC - 150EC;
digestion vessels 25 ml or more, PTFE;
25 ml borosilicate glass volumetric flasks;
pipettes;
laminar flow hood/clean room for handling; and
fume cupboard for digestion.

Place the dried sample in the digestion vessel. The equivalent of 1 g fresh mass should be sufficient for a 25 ml vessel. The precise dry mass should be known. Add sufficient acid (about 20 ml HNO_3 for each gram dry mass of sample). Close the vessel and leave overnight for pre-digestion. Place in the oven or on the hot plate at 140EC for 3 hours. Remove from heat and allow to cool. Examine the digest. If the sample is clear, pale yellow, transfer to a 25 ml volumetric flask and make up to volume with distilled water. If the digest is dark or cloudy, return to the heat until it clears.

If cost is a problem, borosilicate glass digestion vessels may be used with reflux bulbs to digest at 120EC. If analysing for silver, the digest should be evaporated to dryness, cooled and the residue dissolved in concentrated HCl (~ 2.5 ml) and diluted to 25 ml.

4.7 Arsenic and Tin

Reagents: ashing slurry; 10 g MgO + 6 g $Mg(NO_3)_2$ in 100 ml H_2O; distilled water; and 50% HCl.

Apparatus: 100 ml borosilicate glass beakers;
muffle furnace; and
50 ml borosilicate glass volumetric flasks.

Take 1 - 10 g samples (fresh mass) after removing sub-samples for dry mass determination. Add to 15 ml of ashing slurry in the beakers. Dry ash this mixture in the muffle furnace at 500EC. Allow to cool and dissolve the residue in 25 ml of 50% HCl. Make up to 50 ml with distilled water.

4.8 Mercury and Selenium

Reagents: distilled water;
3:1 HNO_3/H_2SO_4; and
30% w/v H_2O_2

Apparatus: hotplate 50 - 80EC; and
Kjeldahl flasks.

Mercury may be best digested using the basic method with sealed PTFE digestion vessels. The following method is an alternative. Determine dry mass on a subsample and place 1 - 10 g of homogenised sample in a Kjeldahl flask with a condenser. Digest with 20 ml 3:1 HNO_3:H_2SO_4 at 50 - 60EC for 4 hours. Cool and add 10 ml 30% w/v H_2O_2, raise temperature to 80EC for 1 hour. Dilute to 50 ml in a volumetric flask.

5.0 REFERENCES

Cantle, J. E. 1982 Atomic Absorption Specrometry. Techniques and Instrumentation in Analytical Chemistry, Vol. 5, Elsevier Scientific Publishing Company, Amsterdam.

UNEP/FAO/IAEA 1982 Sampling of selected marine organisms and sample preparation for trace metal analysis. Reference methods for marine pollution studies, No. 7, UNEP, 1982.

UNEP/FAO/IAEA 1982 Determination of total mercury in selected marine organisms by flameless atomic absorption spectrophotometry. Reference methods for marine pollution studies, No. 8, UNEP, 1982.

UNEP/FAO/IAEA/IOC 1984 Determination of total cadmium, zinc, lead and copper in selected marine organisms by flameless atomic absorbtion spectrophotometry. Reference methods for marine pollution studies, No. 11, Rev. 1, UNEP, 1984.

CHAPTER VII: ANALYTICAL QUALITY CONTROL

CONTENTS

1.0 INTRODUCTION

1.1 The Need for Analytical Quality Control

The basic purpose of a water laboratory is to produce accurate and reliable data describing the quality characteristics of the water body under study. One of the essential components for assuring accurate and reliable analytical results is analytical quality control (AQC), which refers to routine application of procedures for controlling the measurement process.

Many laboratories are not convinced of the necessity for analytical quality control. They believe that use of standard methods is all that is needed to assure the accuracy of results. Unfortunately, interlaboratory studies do not support such optimism. A number of such studies have been performed, all giving clear evidence of the existence of analytical errors. Collaborative studies have also been conducted after the establishment of AQC procedures in the participating laboratories. Although analytical errors still occur, their magnitude has been considerably reduced, thus giving clear evidence that a systematic AQC programme improves data quality.

Since one of the objectives of the GEMS/Water is to improve the validity and comparability of water quality data, great emphasis should be devoted to the establishment of AQC programmes in all participating water laboratories.

1.2 Scope of the Present Report

Although a number of guidelines and recommendations on AQC are available for water laboratories, only a limited number of water laboratories have implemented a AQC programme on a routine basis. One reason could be that the existing guidelines contain procedures that are too complicated for the average laboratory. The existing guidelines may give global or regional AQC coordinators useful tools, but may be considered too general for national programmes and individual laboratories. The present chapter is intended, therefore, to give detailed and operational guidance to individual laboratories. In addition, this chapter outlines the programme involving routine use of commercially available QA materials and the periodic availability of samples for performance evaluation of laboratories participating in GEMS/Water.

2.0 ORGANIZATION OF AQC PROGRAMME FOR GEMS/Water LABORATORIES

2.1 Introduction

In order to assure good and reliable water laboratory results, the following is required:

(1) suitable laboratory facilities;

(2) up-to-date laboratory instruments, sampling equipment, glassware, and reagents;

(3) standardized analytical procedures covering the desired variables and ranges of concentration;

(4) a well-trained laboratory staff;

(5) well-maintained equipment and facilities;

(6) adequate filing and reporting systems; and

(7) a systematic analytical quality control programme.

The above items constitute, as a whole, the within-laboratory AQC activities. The present report deals mainly with item (7).

2.2 Reasons for AQC Programmes

Within-laboratory quality control is the most important component of any laboratory quality control programme. Experience indicates that 10-20% of the resources (manpower, instrument utilization, and consumables) of a laboratory should be devoted to this work. The range of 10-20%, however, should be considered a minimum, which is valid for the basic variables in higher concentrations. When it comes to more difficult variables and variables in very low concentration, the resources spent for AQC should be higher. Determination of low concentrations of heavy

metals and pesticides will often require that more than 20% of the resources are to be spent on analytical quality control work.

Laboratory managers may feel that they cannot afford to spend even 10-20% of their resources on within-laboratory AQC and a systematic programme is therefore not implemented. This reason for not implementing AQC should be rejected because the alternative is generation of data of unknown quality, which is of doubtful value for decision-making by programme managers.

Another reason often heard for not implementing AQC is that the needed information to begin AQC programmes, i.e., technical descriptions, manuals, or guidelines, are not available to the laboratory. This report references papers and books that should be available at or may be obtained by water laboratories. Such books may also be important as reference texts on analytical procedures.

A third reason for not implementing AQC procedures may be that the chief chemist and staff do not have the knowledge of statistical procedures needed for setting up an AQC programme. Although very detailed descriptions are available, even these require a certain knowledge of statistical methods. This situation underlines the need for training in the field of AQC. The benefit of such training programmes has been clearly demonstrated by courses in the Western Pacific region, Southeast Asia, and the Americas.

A final reason for not implementing AQC may be lack of understanding of the problem or a lack of motivation to solve the problem. Although technical literature gives many examples of poor analytical results obtained from laboratories not using AQC and demonstrates the improvements that can be obtained when AQC has been introduced, a continuous effort should be made to underline these facts.

2.3 The Global and Regional System

The principles of coordinating AQC within the framework of GEMS/Water is illustrated in Figure 1. The Global and Regional coordinators are now in full operation, and a number of activities have been implemented; among these, special attention should be given to the following:

- global guidelines on AQC were given in a chapter of the GEMS/Water Operational Guide in 1987;
- quality control (QC) samples were distributed globally in 1982-83, 1985 and 1988-89;
- global performance evaluation (PE) studies were performed in 1982-83 and 1990-91;
- regional PE studies were performed in Europe and the Western Pacific;
- regional AQC courses were conducted in Europe, Southeast Asia, the Western Pacific, and the Americas; and
- national courses have been organized with the assistance of regional AQC coordinators.

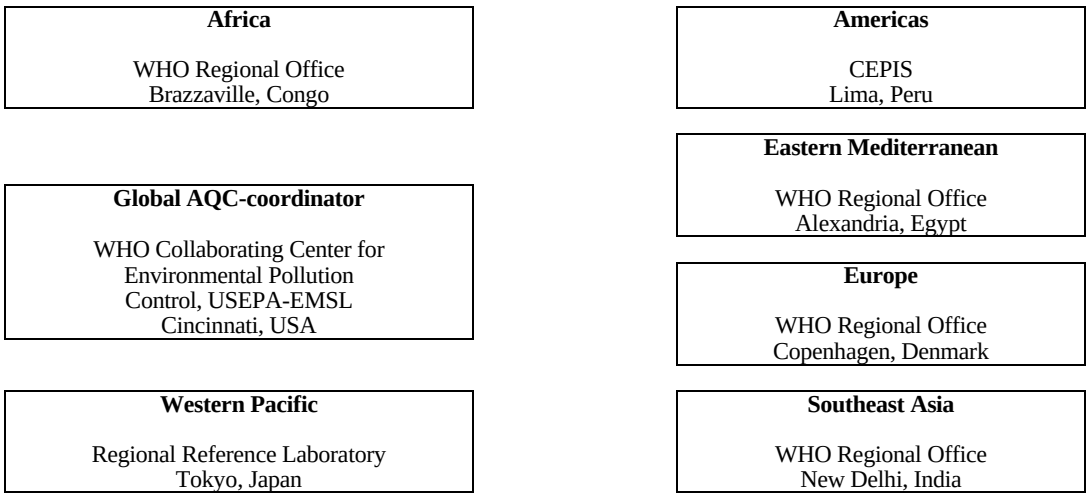


Figure 1. Global and Regional AQC coordinators in GEMS/Water

2.4 National Reference Laboratory Systems

In many countries, reference laboratories for water analysis have been formally established. Such systems have led to an improvement in the quality of the work carried out by local authorities.

It is recommended that reference laboratories be established in all countries participating in the GEMS/Water project. WHO global and regional coordinators can assist in establishing such national reference laboratories.

Figures 2 and 3 illustrate the possible organization of reference laboratories in countries with many water laboratories and in countries with a limited number of water laboratories, respectively.

The aim of a national reference laboratory is to assure reliable results from water laboratories in the country. This aim can be accomplished if the reference laboratory carries out the following tasks.

(1) assisting participating laboratories in setting up their own within-laboratory AQC programme;
(2) conducting interlaboratory performance evaluation studies to monitor the performance of the participants;
(3) testing of new methods and equipment, and giving recommendations and/or instructions regarding the choice of methods and equipment;
(4) training the staff of participating laboratories in use of an AQC programme, new analytical procedures, and new instruments; and
(5) cooperating with international organizations involved in water analysis.

The contents of items (3) to (5) will not be described further in this report, whereas items (1) and (2) will be described in subsequent sections.

The global and regional coordinating office for the GEMS/Water programme on analytical quality control are given in Table 1.

Table 1. GEMS/Water Global and Regional AQC - Coordinators and Reference Centres

Global AQC Coordinator

Quality Assurance Research Division
Environmental Monitoring Systems Laboratory
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268, USA

Regional AQC Coordinators and Reference Laboratories

AFRICA

Programme Manager 2
WHO Regional Office for Africa
P.O. Box No. 6
Brazzaville, Congo

AMERICAS

Director
CEPIS
Casilla Postal 4337
Lima 100, Peru

EASTERN MEDITERRANEAN

Chief
Environmental Health
WHO Regional Office for the
Eastern Mediterranean
P.O. Box 1517
Alexandria - 21511, Egypt

EUROPE

Director
Promotion of Environmental Health
WHO Regional Office for Europe
8, Scherfigsveg
DK - 2100 Copenhagen, Denmark

SOUTHEAST ASIA

Chief
Promotion of Environmental Health
WHO Regional Office for Southeast Asia
Indraprastha Estate
Mahatma Gandhi Road

WESTERN PACIFIC

Director
Department of Sanitary Engineering
The Institute of Public Health
6-1, Shirokanedai 4 chome
Minato-ku

New Delhi - 110002, India Tokyo 108, Japan

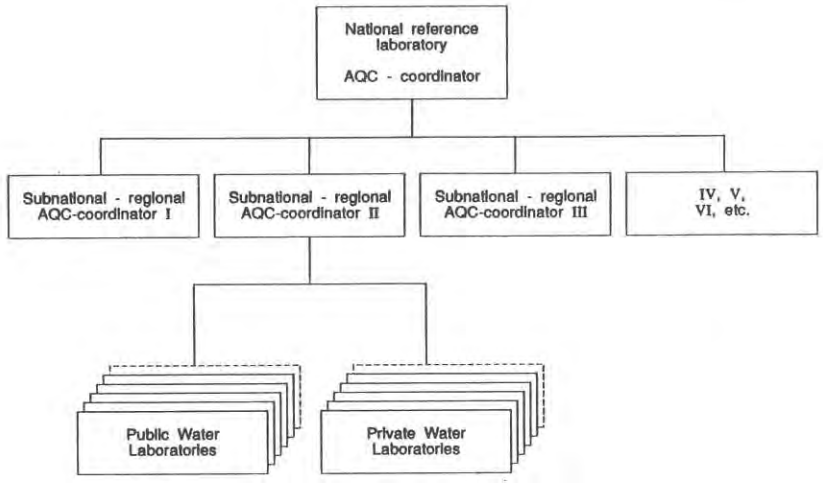


Figure 2: Organization of reference laboratories/AQC coordinators in federal countries with many water laboratories

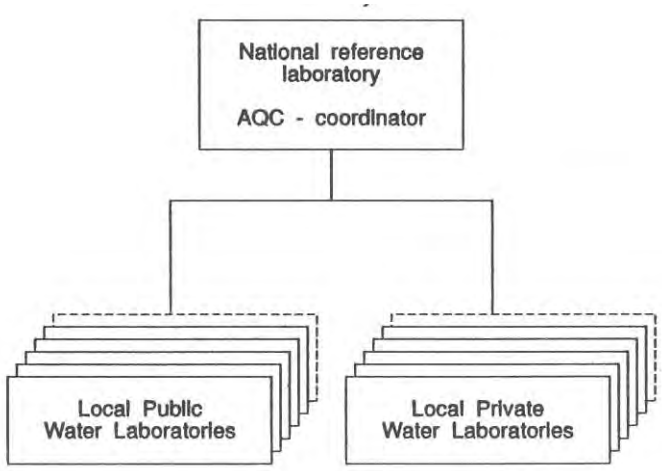


Figure 3: Organization of reference laboratories/AQC coordinators in smaller countries and other countries with a limited number of water laboratories

3.0 WITHIN-LABORATORY AQC PROGRAMME

The following items are recommended as the basis for a within-laboratory AQC programme and should be developed and used routinely at laboratories taking part in the GEMS/Water programme.

3.1 Calibration

(a) For each analyte, prepare a calibration curve which covers the entire working range of the method, where analyte means a constituent or characteristic of a sample which is measured or identified.

(b) Construct the curve using at least five (5) points, including one near the upper limit and one near the lower limit, of the concentration range.

(c) The difference (D) between the value observed for each calibration standard (X_{OBS}) and the value predicted for that standard using the fitted calibration curve (X_{PRED}), can be evaluated as follows:

1. After 20 to 25 initial values of $D = X_{OBS} - X_{PRED}$ are available, calculate their mean (D) and standard deviation (S_D).

2. If a subsequent D value is not within the interval $D \pm 3 S_D$, the system calibration is out-of-control and the system must be recalibrated before continuing routine analyses.

If the calibration curve was fitted by minimizing the sum-of-squares of the absolute deviations of each calibration point from the curve, then the D values should also be in absolute units. However, if percentage deviations were minimized, then the D's should also be percentages of the predicted value.

(d) If there is no obvious reason to require recalibration, instead of following steps (a) through (c) above, an existing calibration curve may be verified at the beginning of an analytical run by measuring two calibration standards, one in the lowest quarter of the total range of the existing calibration curve and one in the highest quarter of the range.

(e) Evaluate the difference $D = X_{OBS} - X_{PRED}$ for each calibration standard using the criteria developed in 3.1, Step c, above and recalibrate if results are not within the control limits. As in Step c, whether the D values are percentages or absolute units depends on how the calibration curve was fitted.

(f) Record the D values for all acceptable calibration analyses and after 20 to 25 additional results, revise the related control limits by recalculating D and S_D from the new data.

(g) It is important to preserve the sign of all D values.

3.2 Method Blank

(a) For every set or subset of 20 or fewer samples, analyze a method blank consisting of reagent water as a sample, which is carried through the complete routine method. A method blank should also be analyzed whenever there is a change in the reagent water system, or whenever a new source (newly-prepared reagent or solvent) is introduced into the analytical system.

(b) Carry each method blank through the entire procedure.

(c) Response to a non-zero method blank depends a great deal upon the method, but the associated routine data must certainly be corrected or discarded whenever a method blank produces a response above the detection limit. Every effort should be made to resolve or minimize system interferences.

3.3 Field Blank

A field blank is a blank solution which has been bottled in the laboratory, shipped with bottles to a sampling site, processed and preserved as a routine sample and returned with the routine samples to the laboratory for analysis.

(a) Analyze a field blank with each set of samples from a given source.

(b) Carry each field blank through the entire procedure.

(c) When interferences occur, discard the associated analytical results unless sufficient data from these blanks are available to justify correction of the results.

3.4 Precision

Precision is the closeness of agreement between the results of repeated analysis on the same sample.

(a) Develop necessary initial data by randomly selecting routine samples to be analyzed twice to provide duplicate analyses. Consider the following:

(1) Develop these data over a reasonable period of time to reflect day-to-day operations.

(2) Choose samples that are most representative of the interference potential of the sample type. If the laboratory handles multiple sample type with different precision characteristics, it will be necessary to establish and maintain separate background data and evaluation criteria for each sample type.

(3) Ultimately, the programme should include precision criteria appropriate for the entire concentration range of each analyte routinely analyzed, within each sample type if necessary.

(b) From each pair of duplicate analyses (X_1 and X_2) calculate their relative range value, (R):

$$R = \frac{|X_1 - X_2|}{(X_1 + X_2)/2}$$

Where ,$X_1 - X_2$, means the unsigned difference between X_1 and X_2.

(c) After 50 to 100 R values are available for a variable, order the R values by their related sample concentration estimates, organize the values into concentration ranges that seem to have a similar underlying R value and calculate the average R value (R) for each of these concentration ranges. Minimize the number of concentration ranges as much as practical.

(d) Calculate the upper limit (UCL) for each concentration range as recommended in Duncan (1974):UCL = 3.27 (R)

(e) Review the initial data for R values greater than the UCL value for the appropriate concentration range. If such values are found, they should be discarded and the related UCL value should be recalculated from the remaining R values within that concentration range.

(f) Within each set of 20 or fewer samples to be analyzed together, evaluate system precision by conducting duplicate analyses on one of the samples selected at random. If the relative range value, R, calculated from these duplicates is greater than the appropriate UCL value, system precision is judged to be out-of-control and analyses must stop until the problem has been corrected. Problems with these data may indicate the need for stricter adherence to accepted laboratory practices.

(g) Periodically (after 20 to 25 additional acceptable pairs of data are obtained within each concentration level for a sample type), update the table of critical relative range values by repeating step 3.4 (d) using the new data. Review the criteria being maintained and combine any which are very similar for related concentrations or sample types. If the criteria for adjacent concentration ranges are quite different, further subdivision by concentration may be necessary.

(h) Table 2 presents the results of carrying out steps 3.4 (c) and (d) for three different analytes to illustrate use of the UCL values. If duplicate chromium results of 31.2 and 33.7 were obtained, the system precision would be checked as follows:

$$R = \frac{|31.2 - 33.7|}{(31.2 + 33.7)/2} = \frac{|-2.5|}{64.9/2} = \frac{2.5}{32.45} = 0.0770$$

Since the appropriate UCL from Table 2 is 0.109 and the current R value is not greater, precision of the analytical system is judged to be within control.

3.5 Recovery Check Using Standard Solutions

(a) Analyses at least one standard through the complete method for every subset of 20 or fewer routine samples to be analyzed together.

(b) To provide a complete record of the calibration and recovery for each analytical run, one of these standard samples should be the last sample analyzed.

(c) Use concentrations that approximate those found in the related routine samples.

(d) Calculate percent recovery (P) as:

$$P = \frac{100\,(observed\ value)}{(true\ value)}$$

Table 2. Precision Estimates from Duplicate Analyses Within Specific Concentration Ranges For Three Analytes

Analytes	Concentration Range	Number of Sets of Duplicates	Average Concentration of Data	Average Relative Range(R)	R for Combined Concen-tration Range	Final UCL Results
BOD	1 to 10	21	5.85	0.1776	0.1381	0.452
5-day	10 to 25	30	17.6	0.1104		
	25 to 50	27	36.1	0.0924		
	50 to 150	29	102.	0.0638		
	150 to 300	17	197.	0.0564		
	300 to 1,000	12	520.	0.0232	0.0652	0.213
	1,000 up	3	3341.	0.0528		
Chromium	5 to 10	32	6.15	0.9612	0.0612	0.200
(µg/L)						
	10 to 25	15	16.7	0.0340		
	25 to 50	16	36.2	0.0319		
	50 to 150	15	85.1	0.0446	0.0334	0.109
	150 to 500	8	240.	0.0218		
	500 up	5	31780.	0.0240		
Copper	5 to 15	16	11.1	0.1234		
(µg/L)	15 to 25	23	19.1	0.0736	0.0940	0.307
	25 to 50	23	35.4	0.0338		
	50 to 100	26	65.9	0.0354		
	100 to 200	10	134.	0.0210	0.0313	0.102
	200 up	3	351.	0.0130		

(e) After 20 to 25 standards are analyzed over time, calculate the average percent recovery (P) and standard deviation (S_P) of the resulting P values.

(f) If subsequent standards for percent recovery are not within the intervalP $\pm$ 3 S_P, the analytical system should be checked for problems. If problems exist, correct them before continuing the analyses. Problems with these data often require greater care in sample processing prior to actual measurement.

(g) Runs of 8 or more successive points, either all above or all belowP , also indicate the system is out-of-control. Use of a ShewhartX -chart is recommended to facilitate evaluation of percent recovery results.

(h) An example of the calculation of percent recovery and development of a ShewhartX -chart is given in Table 3 and Figure 4.

(i) Record recovery of all acceptable check standards and after 20 to 25 additional results, revise the related control limits by recalculatingP and S_P from the new data. As in 3.4, step g, the criteria subdivisions by sample type and concentration range should be periodically reviewed to judge their appropriateness.

3.6 Accuracy Check Using Recovery of Spikes

(a) Do essentially the same thing for recovery as was done in 3.5, except that a concentrate spike is added to a randomly-selected routine environmental sample from the current analytical run rather than to distilled water, and P values for the recovery data are calculated as:

$$P = \frac{100\,[X - (\frac{BV}{V+v})]}{T}, where:$$

X = the analytical results from the spiked sample,
B = the background concentration naturally present in the sample,
T = the known concentration of the spike,
V = the volume of sample used, and
v = the volume of spike added.

(b) In spiking samples, make sure that:

(i) Sufficient spike is added to at least double the background concentration or to reach a concentration for which the calibration curve has been established. If the background concentration is higher than the midpoint of the standard curve, the background water should be diluted into the lower half of the calibration range and reanalyzed before spiking.

(ii) The volume of a spike should generally be kept to a minimum and not exceed 5 percent of the sample volume. In organic analyses, the volume of a spike should be 150 mL/litre or less so that the solubility of the standard in the water will not be affected.

(c) Resulting P values must fall within $\bar{P} \pm 3\,S_P$ calculated from previous related spike recovery data. If not, the system is out-of-control, and the source of the problem must be identified and corrected before continuing the analyses. Problems with these data often indicate sample matrix interferences.

(d) As in 3.5 step (g), runs of 8 or more results on the same side of $\bar{P}$ indicate the system is out-of-control and use of a Shewhart $\bar{X}$-chart is recommended to facilitate evaluation of results.

(e) By simply calculating $\bar{P}$ as specified in 3.6 step (a) instead of as specified in 3.5 step (d), percent recoveries of a spike can be treated as shown in the sample given in Table 3 and Figure 4. The relevant calculations are:

$$\bar{P} = (\sum_{i=1}^{n} P_i)/n = 2104/21 = 100.2$$

$$S_P = \sqrt{\frac{1}{n-1}(\sum_{i=1}^{n} P_i^2 - (\sum_{i=1}^{n} P_i)^2/n)}$$

$$= \sqrt{\frac{1}{20}\,(211{,}504 - \frac{2104^2}{21})}$$

$$= \sqrt{\frac{1}{20}(703.24)} \quad = \sqrt{35.163} \quad = 5.93$$

$$\overline{P} + \_ \, 3 S_P = 100.2 + \_ \, 17.8 = 82.4 \text{ to } 118.0$$

Therefore, percent recovery values between 82.4% and 118% for total PO_4-P standards within the concentration range of 0.34 to 4.9, would indicate that the accuracy of the analytical system is under control. The related ShewhartX -chart is illustrated in Figure 4.

(f) Periodically review and update the recovery criteria similarly to 3.5 step (i)

3.7 Summary of Within-Laboratory AQC Programme

The recommended analytical quality control programme is summarized as:

(a) Five standards to develop a calibration curve in concentrations covering the working range, as necessary OR measurement of two calibration standards to verify the existing calibration curve.

(b) One method blank per run.

(c) One field blank per set of samples.

(d) One duplicate for precision check (at least one every 20 routine samples).

(e) One standard sample for recovery and calibration check (at least one every 20 routine samples). A standard should be the last sample analyzed, in each run.

(f) One spiked sample for recovery check in the presence of a sample matrix (at least one every 20 routine samples).

(g) Total: Seven to ten AQC analyses may be required for runs of up to 20 routine samples, 10 to 13 AQC analyses may be required for runs of 21 to 40 routine samples, etc.

(h) Items (a) to (f) should be the standard practice in any laboratory.

3.8 Minimal AQC Programme

For very small operations or small sample loads, the described AQC programme may not be practical or necessary for all analytes. Whenever AQC must be reduced below the level recommended, the following minimal AQC programme should be maintained:

(a) Continue calibration or calibration checks as in 3.1.

(b) Analyze one field blank per set of samples to check for contamination. If the analyte is detected, a method blank should be run to find out
whether the contamination problem is in the laboratory or the field.

(c) Analyze one spiked sample at the end of each analytical run to check for recovery or precision problems. If the percent recovery is outside the control limits, analyze a standard to further define the likely source of the problem. Successful recovery of the standard

would suggest either a matrix problem or a precision problem. A precision problem would randomly produce unsuccessful recovery, probably caused by poor or inconsistent analytical technique.

3.9 Correction of Problems

Extreme, unexpected or questionable results are normally detected and reported by the analyst, or are noted by the supervisor in the review of results. When a deviation is noted, the complete sequence of sampling, sample preservation, holding times, analysis, and quality control should be investigated. The documented within-laboratory analytical quality control programme will provide the primary means to perform the review.

(a) Sampling

Review the records of the sample collection. Check the preservation technique, the record of sample handling, the time in transit, and the conditions of the samples upon arrival at the laboratory.

(b) Analytical method

Confirm that the method is appropriate to the application and verify that the method is being performed properly.

(c) Calculations

Check calculations for a transposition of numbers or mathematical error. Verify that results are reported in the proper units (i.e., milligrams/litre versus milligram/kilogram versus micrograms/litre and so forth).

(d) Reagents

Check AQC results on reagent water. Check reagents for changes in bottle and lot, and confirm that the expiration dates have not been exceeded.

(e) Titrating solutions

If wet chemistry methods are used, check the normality of the titrating solutions such as: sodium thiosulfate, ferrous ammonium sulfate, potassium dichromate, sulfuric acid, etc., by comparison against a primary standard.

Table 3. Analysis* of Total Phosphate-Phosphorus Standards;
in mg/L Total PO_4-P

Point	Known	Obtained	Percent Recovery P_i	P_i^2
1	0.34	0.33	97	9,409
2	0.34	0.34	100	10,000
3	0.40	0.40	100	10,000
4	0.49	0.49	100	10,000
5	0.49	0.49	100	10,000
6	0.50	0.47	94	8,836
7	0.50	0.53	106	11,236
8	0.50	0.56	112	12,544
9	0.52	0.59	113	12,769
10	0.66	0.70	106	11,236
11	0.66	0.60	91	8,281
12	0.67	0.65	97	9,409
13	0.68	0.65	96	9,216
14	0.83	0.80	96	9,216
15	1.3	1.2	92	8,464
16	1.3	1.3	100	10,000
17	1.6	1.7	106	11,236
18	2.3	2.3	100	10,000
19	2.3	2.4	104	10,816
20	3.3	3.3	100	10,000
21	4.9	4.6	94	8,836
		TOTALS	2104	211,504

* Using a colorimetric method with persulfate digestion.

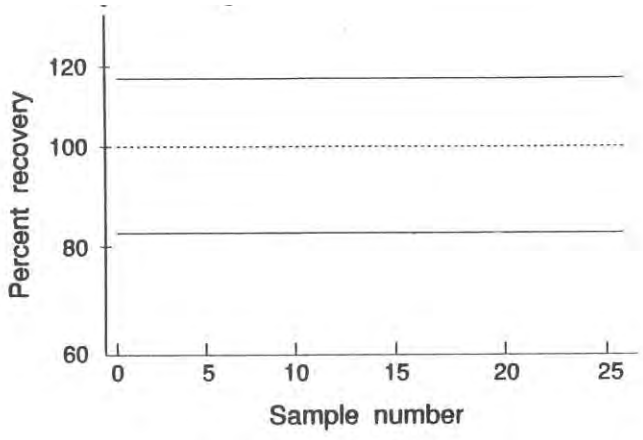


Figure 4. Shewhart control chart for percent recovery data

(f) Instruments

Since mechanical and electronic devices malfunction or go out of proper adjustment through use, make the following checks weekly or more often, depending on usage.

1. Check the balance for accuracy using reference weights that are kept exclusively for this purpose and not used in routine weighing.

2. Check the spectrophotometer for linearity and wavelength using reference glass filters available from the instrument manufacturer and other sources.

3. Check the pH meter using fresh reference buffer solutions. If the source of these buffer solutions is in question, recheck with buffers from a different source.

4. Check the atomic absorption lamps for adequate light output using a standard and blank to verify sufficient differences in signal.

5. Check the dissolved oxygen meter, turbidity meter, and conductivity meter against known standards.

6. Consult the operating manuals of the instruments for additional advice on instrument checks.

(g) Confirmation of correction of a problem

Analyze or reanalyze samples to confirm the source and correction of problems. Confirm recoveries with analyses of known reference samples.

3.10 Improved Laboratory Practices

Trouble-shooting may indicate a practice which should be adopted to improve the laboratory operation, such as:

(a) Sampling

Maintain a bound field logbook for recording field measurements, time, temperature, sampling location, weather conditions and any other relevant information.

(b) Data transcription errors

Enter analytical results directly into laboratory notebooks. Re-check all data entered in reports or returned in computerized data summaries, against the original results in the laboratory notebooks.

(c) Standards

Standard solutions used for calibration of instruments may degrade from light, improper storage, accidental contamination, or age. Standard solutions should be compared frequently by parallel analysis against standards or reference check samples obtained from an outside source of good reputation.

New standards should be prepared frequently or purchased in ready-to-use form. The frequency of comparison checks and preparation or purchase of standards should be based on knowledge of the stability of the standard solutions. Most standards should be prepared or replace at least every six (6) months.

(d) Reagents

Maintain records of when chemicals are received and first opened. Record dates and details of preparation of reagents, including estimates of shelf life.

Label and date all reagent containers. Develop a plan for reorder of chemicals based upon their estimated shelf life.

Analysts should carry reagent blanks through the entire sampling and analytical procedure. In colorimetry, the reagent blank should be compared with the reagent water to detect any unusual response.

As a standard curve is developed, the points on the curve should be used to develop a regression line for the analysis.

(e) Reference materials

Reference materials are of two types. The first type is high purity chemicals in neat form for preparation of exact known concentrations in solution. These are designed for use as calibration standards. The second type is quality control samples or other non-calibrative samples of pure chemicals in water or in other matrices, also in known concentrations but for use as checks on calibration, instrumentation, technique, analyst, etc. Such chemicals or materials are available for a fee from US's National Institute of Standards and Technology, Canada's National Research Council, Community Bureau of Reference (Europe), National Institute for Environmental Studies (Japan), other governmental sources and some commercial firms. Quality control samples and calibration standards formerly available for free from the U.S. Environmental Protection Agency are now available in expanded series and types through selected commercial sources, where they are identified as "EPA Certified" Reference Materials. A list of these sources is available from the Quality Assurance Research Division, EMSL-Cincinnati, U.S. Environmental Protection Agency, Cincinnati, OH 45268-1525. Listings of other sources are available in National Oceanic and Atmospheric Administration (NOAA) and REMCO reference catalogues.

(f) Laboratory reagent water

Laboratory reagent water may become contaminated by improper operation or maintenance of a distillation or deionization unit. High-quality water will deteriorate upon storage. Aside from raw water contamination due to system failure, the most common contaminants are chlorine, ammonia, carbon dioxide, bacteria, and trace metals. Ammonia and carbon dioxide are absorbed from the air and chlorine is a carry-over problem. Trace metals can occur from failure of tin plating in the still lines or storage tank, from units installed with copper lines, brass fittings, or from plumbing solder used in connections. Bacterial growth can occur in any stored water system. Algal growth can develop in transparent plastic or glass storage containers exposed to light. An inline specific conductance meter is recommended for continuous monitoring of water quality. Ideally, reagent water is prepared fresh just before use and is not stored. Problems with the reagent water will often be seen as erratic test results or excessive variability among analyses of method blanks.

(g) Dishwashing

A common source of error is contamination from improper dishwashing and rinsing. Such errors often produce erratic results or excessive variability among analyses of method blanks. One way of solving the problem is to maintain separate sets of glassware and sample bottles for different types of analyses, such as: general inorganic, trace metals, or trace organics. The cleaning agent and the dishwashing and rinsing procedure should be tailored to the type of analysis to be carried out.

(h) Other sources of contamination

Do not store water samples containing trace pollution, with water or wastewater samples which are highly-polluted. Do not store samples in the same refrigerator with standards or stock solutions. Protect samples and standards from high humidity, dust, fumes, tobacco smoke, insecticides or other contaminants in ambient air. Laboratories should be air-conditioned, if possible, to avoid many contamination and moisture problems. Such contamination will be indicated as a difference in the field and method blanks.

3.11 Performance Review

Analysts should maintain a permanent record of the quality control checks which are performed. The laboratory supervisor should meet frequently with the analysts to review the results of the quality control checks and the correction of any problems which are detected. Deficiencies should be documented in the record book indicating the analytical method, instruments and analysts involved, the problem, the probable source of error, the action taken, and results of the correction. The true benefits of a quality control programme can be realized and overall data quality improved only after the deficiencies have been discovered, corrected, and confirmed as corrected.

4.0 GEMS/Water QUALITY CONTROL SAMPLES

4.1 Purpose

Quality control samples are reference samples of known concentrations designed for use in a within-laboratory AQC program, wherein they are used to check calibration, method, analyst or instrumentation. They are not intended as substitutes for the local standards, replicates or spiked samples analyzed routinely in the quality control programme of each laboratory. Quality control samples can be spiked into reagent-grade and natural water for determination of recoveries, or by comparison of recoveries from these waters can generate separate measures of method bias and possible interference from the natural water.

4.2 Distribution of Samples

QC samples have been distributed to GEMS/Water laboratories for free, through 1990. Participating laboratories were provided with a standard series of quality control samples in sealed ampuls for the six types of samples specified in Table 4. These samples covered most of the variables of primary interest to GEMS/Water. Each sample type was furnished with instructions on the handling and preparation of samples in the laboratory and a statement of true values. It was recommended that the true values be restricted to the laboratory director or laboratory quality control officer until the analyses had been completed. If possible, it was also recommended that the samples be disguised as routine samples. This assured a more normal or routine handling of these sample by laboratory personnel and thus provided a truer measure of the performance of the laboratory.

Table 4. GEMS/Water QC Samples Previously Distributed to Laboratories*

TYPE AND NUMBER OF SAMPLES	VARIABLES AVAILABLE
Trace Metal Analyses (1)	aluminum, arsenic, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, vanadium, and zinc; 1 level each
Mineral Analyses (3)	sodium, potassium, calcium, magnesium, pH, sulfate, chloride, fluoride, total alkalinity, total hardness, total dissolved solids, and specific conductance; 1 level each
Nutrient Analyses (2)	nitrate-N, ammonia-N, total Kjeldahl-N, orthophosphate-P, and total P; 1 level each BOD, COD, and TOC; 2 levels each
Demand Analyses (2)	aldrin, dieldrin, DDT, DDE, DDD, and heptachlor in acetone; 1 level each
Chlorinated Hydrocarbon Pesticides - I Analyses (1)	2 levels each
Non-filterable, Total filterable, Volatile, residue analyses (2)	
*Total: 10 or 11 ampules per set	

Since "EPA certified" quality control samples are now (1991) only available for a fee through commercial suppliers, arrangements for funding further distribution of QC samples are being explored.

4.3 Proposed Sample Use

It is up to the individual laboratory to decide which quality control samples are tested, how they are applied or whether the constituents and their

concentrations are made known to the analyst. Guidance for relevant within-laboratory checks are contained in Section 3 above.

4.4 Follow-up Activities

Participating laboratories are not to routinely report the results of the analyses of quality control samples. If the analysis of the quality control samples uncovers quality control problems unsolvable by the laboratory in question, the WHO regional AQC coordinator should be asked to provide the necessary technical advice and assistance to the extent possible.

Successful completion of within-laboratory control checks is considered essential prior to participation in the second stage of a global AQC study, that is, the analysis of unknown samples in a formal performance evaluation study.

5.0 GEMS/Water PERFORMANCE EVALUATION STUDY

5.1 Purpose

Quality control samples are provided with known values and performance limits to assist individual laboratories in their internal AQC programme. Performance evaluation studies involving analyses of unknown samples, provide a basis for evaluating the performance of individual laboratories and provide a basis for estimating the combined analytical precision and recovery of the laboratories participating in the GEMS/Water monitoring network.

5.2 Distribution

Laboratories participating in GEMS/Water should take part in these performance evaluation studies. They will be notified of the time schedule by WHO-Geneva or their WHO Regional Office. There are six types of samples included in each package as listed in Table 5. Instructions on sample preparation and analysis are included with each sample type.

Table 5. Scope of the 1991 GEMS/Water Laboratory Performance Evaluation Study

TYPE AND NUMBER OF SAMPLES	VARIABLES AVAILABLES
Trace Metal Analyses (2)	aluminum, arsenic, beryllium, cadmium, chromium, cobalt, copper, iron, lead, manganese, mercury, nickel, selenium, vanadium, and zinc; 1 level each
Mineral Analyses (8)	sodium, potassium, calcium, magnesium, pH, sulfate, chloride, fluoride, total alkalinity, total hardness, total dissolved solids, and specific conductance; 1 level each
Nutrient Analyses (4)	nitrate-N, ammonia-N, total Kjeldahl-N, orthophosphate-P, and total P; 1 level each
Demand Analyses (2)	BOD, COD, and TOC
Chlorinated Hydrocarbon Pesticides - I Analyses (2)	aldrin, dieldrin, DDT, DDE, DDD, and heptachlor in acetone
Non-filterable, Total filterable, Volatile, residue analyses (2)	total suspended solids
Total: 20 ampuls per laboratory	

Since 1982, the USEPA's Environmental Monitoring Systems Laboratory at Cincinnati has periodically conducted a formal performance evaluation study for GEMS/Water laboratories at WHO's request. Samples are provided as unknowns to the laboratories. Results are coded for

confidentiality and evaluated against acceptance limits that have been demonstrated achievable for the analytes tested. Results are reported back to each laboratory for its information and the coded results are summarized and reported to WHO-Geneva and the Regional Offices to provide an overall measure of the performance of GEMS/Water laboratories.

Future Performance Evaluation Studies

In 1991, EMSL-Cincinnati is conducting a second WHO performance evaluation study. The analytes shown in Table 5 cover most of the basic analytes routinely measured and reported for GEMS/Water. WHO-Geneva hopes to continue these studies periodically into the future.

5.3 Reporting

The analytical results for each performance evaluation sample are entered on the appropriate report form and mailed to the relevant WHO regional AQC coordinator (see list provided in Table 1).

Instructions for reporting results are provided with the samples.

5.4 Evaluation

For the purpose of the evaluation report, laboratories are identified only by a numerical code. Each network laboratory will know its own code but no others. The list of codes is kept confidential, known only to EMSL-Cincinnati and the GEMS/Water coordinator at WHO.

After the reporting deadline, the EMSL-Cincinnati will tabulate all data received, and prepare individual evaluation reports on the results achieved by each laboratory when compared to statistically based limits recommended by Britton (16). An example of such an evaluation report is provided in Table 6. This type of report will be received by each laboratory giving details for its own results. The results of the laboratory will be inserted in the column marked "Reported value" and their compliance with respect to the limits will be indicated in the column marked "Evaluation". The GEMS/Water global AQC study is based on the USEPA programme for evaluation of laboratories analyzing water and wastewater.

In addition, a report summarizing all results will be prepared by the EMSL-Cincinnati. It is envisioned that on the basis of this report a group of experts will review the analytical quality control component for GEMS/Water and advise on future activities.

5.5 Follow-up

Problems with results outside the acceptance limits in the performance evaluation study may be resolved as part of a three-step sequence:

1. Performance evaluation completed. If results are within the acceptance limits then no further action is required beyond the normal routine AQC.

2. If some results are outside acceptance limits then the WHO regional AQC coordinator can work with the laboratory to identify and correct the problem.

3. When the problems have apparently been corrected, additional quality control (samples with known values) will be provided through the WHO regional AQC coordinator to confirm the resolution of the problems.

NOTE: The results of the first performance evaluation study are contained in References 15 and 16 of the Bibliography.

Table 6. Example of a GEMS/Water Performance evaluation Study Report

Example of Performance Evaluation Report

Laboratory Code Number..... Date .....

Analytes	Sample Number	Report Value	True Value	Acceptance Limits[a]	Warning Limits[b]	Performance Evaluation[c]
		Trace Metals in Micrograms Per litre				
ALUMINUM	1		473.	359.-641.	394.-606.	
	2		60.2	30.0 -136.	43.4 -123.	
ARSENIC	1		120.	73.6 -164.	84.8 -152.	
	2		17.5	9.24 -24.4	11.1 -22.5	
BERYLLIUM	1		473.	392. -549.	412. -529.	
	2		22.5	16.9 -29.2	18.4 -27.6	
CADMIUM	1		32.5	22.7 -36.5	24.4 -34.8	
	2		2.60	.573 -4.35	1.05 -3.88	
COBALT	1		171.	141. -201.	149. -194.	
	2		13.7	9.34 -17.7	10.4 -16.6	
CHROMIUM	1		76.5	53.8 -96.2	59.0 -91.0	
	2		9.18	5.50 -13.1	6.44 -12.1	
COPPER	1		130.	106. -152.	111. -146.	
	2		11.4	6.70 -17.4	8.02 -16.1	
IRON	1		275.	222. -330.	235. -317.	
	2		15.4	3.55 -30.9	6.93 -27.5	
MERCURY	1		6.11	4.08 -8.22	4.61 -7.69	
	2		.797	.182 -1.43	.337 -1.27	
MANGANESE	1		189.	152. -225.	161. -216.	
	2		18.2	10.7 -25.2	12.5 -23.4	
NICKEL	1		150.	114. -181.	122. -173.	
	2		15.0	6.37 -24.4	8.60 -22.1	
LEAD	1		210.	167. -252.	177. -242.	
	2		27.1	17.6 -39.6	20.3 -36.9	
SELENIUM	1		35.0	17.8 -48.3	21.7 -44.5	
	2		4.77	1.89 -7.13	2.55 -6.47	
VANADIUM	1		367.	259. -476.	287. -448.	
	2		72.4	35.2 -107.	44.5 -97.6	
ZINC	1		140.	115. -164.	121. -158.	
	2		14.0	4.18 -25.6	6.84 -23.0	

(a) A 99 percent prediction interval (ref. 16).

(b) A 95 percent prediction interval (ref. 16).

(c) ACCEPTABLE, i.e., within the warning limits.

CHECK FOR ERROR, i.e., within the acceptance limits, but beyond warning limits. A value receiving this evaluation does not require follow-up.

NOT ACCEPTABLE, i.e., beyond acceptance limits. UNUSABLE DATA, i.e., the response cannot be quantitatively judged.

Example of Performance Evaluation Report

Laboratory Code Number..... Date.....

Analytes	Sample Number	Report Value	True Value	Acceptance Limits[a]	Warning Limits[b]	Performance Evaluation[c]
		Minerals in milligrams per litre (except as noted)				
pH (in pH Units)	3		5.45	5.32 -5.56	5.35 -5.53	
	4		6.45	6.31 -6.60	6.35 -6.56	
Spec Conduct.	1		136.	118. -153.	122. -148.	
µmhos 25EC	2		568.	487. -641.	506. -622.	
TDS at 180EC	1		78.0	47.4 -119.	56.2 -110.	
	2		357.	278. -424.	296. -406.	
Total Hardness (as	1		29.3	23.4 -34.5	24.8 -33.1	
$CaCO_3$)	2		142.	130. -150.	133. -148.	
Calcium	1		8.28	6.66 -9.82	7.06 -9.43	
	2		38.5	33.2 -43.3	34.4 -42.0	
Magnesium	1		2.10	1.48 -2.62	1.63 -2.48	
	2		11.1	8.95 -12.9	9.44 -12.4	
Sodium	1		7.8	6.64 -9.11	6.95 -8.80	
	2		43.8	38.0 -49.9	39.5 -48.4	
Potassium	1		2.4	1.82 -3.01	1.97 -2.86	
	2		8.8	7.21 -10.6	7.63 -10.1	
Total Alkalinity (as	1		18.4	13.6 -23.4	14.8 -22.2	
$CaCO_3$)	2		84.9	76.5 -88.3	78.0 -86.9	
Chloride	1		24.1	20.9 -27.6	21.8 -26.8	
	2		83.8	76.6 -92.0	78.5 -90.1	
Fluoride	1		.147	.0958-.215	.111 -.200	
	2		1.05	.897 -1.21	.935 -1.17	
Sulfate	1		11.2	7.41 -14.1	8.25 -13.3	
	2		89.0	75.0 -99.6	78.0 -96.6	
		Demands in milligrams per litre				
COD	1		40.2	26.6 -49.3	29.4 -46.5	
	2		92.	72.6 -107.	76.9 -102.	
TOC	1		15.8	11.0 -20.5	12.2 -19.2	
	2		36.1	26.6 -47.7	28.8 -42.4	
5-DAY BOD	1		26.7	15.9 -37.5	18.6 -34.9	
	2		61.1	37.4 -85.0	43.2 -79.2	

(a) A 99 percent prediction interval (ref. 16).

(b) A 95 percent prediction interval (ref. 16).

(c) ACCEPTABLE, i.e., within the warning limits.

CHECK FOR ERROR, i.e., within the acceptance limits, but beyond warning limits. A value receiving this evaluation does not require follow-up.

NOT ACCEPTABLE, i.e., beyond acceptance limits. UNUSABLE DATA, i.e., the response cannot be quantitatively judged.

Example of Performance Evaluation Report

Laboratory Code Number..... Date.....

Analytes	Sample Number	Report Value	True Value	Acceptance Limits[a]	Warning Limits[b]	Performance Evaluation[c]
		Minerals in milligrams per litre (except as noted)				
Ammonia - Nitrogen	1		.663	.544 -.779	.573 -.750	
	2		2.51	2.15 -2.87	2.24 -2.78	
Nitrate -	1		4.3	3.79 -4.75	3.91 -4.63	
Nitrogen	2		.352	.294 -.408	.308 -.393	
Orthophosphate	1		2.19	1.98 -2.38	2.03 -2.33	
	2		3.69	3.36 -4.01	3.44 -3.93	
Kjeldahl - Nitrogen	3		7.69	6.30 -8.96	6.63 -8.63	
	4		13.3	10.9 -15.3	11.5 -14.7	
Total	3		.515	.455 -.597	.473 -.579	
Phosphorus	4		.911	.820 -1.04	.847 -1.01	
		Pesticides in micrograms per litre				
Aldrin	1		.118	.0348-.147	.0489-.133	
	2		.591	.207 -.733	.274-.666	
Dieldrin	1		.186	.104 -.270	.125 -.1249	
	2		.698	.365 -1.03	.449 -.948	
DDD	1		.212	.0914-.316	.120 -.288	
	2		.397	.190 -.569	.238 -.521	
DDE	1		.131	.0523 -.205	.0715 -.185	
	2		.505	.286 -.671	.334 -.623	
DDT	1		.290	.155 -.440	.191 -.404	
	2		.958	.445 -1.36	.559 -1.23	
Heptachlor	1		.065	.0217-.0983	.0314-.0886	
	2		.323	.119 -.449	.161 -.408	
Heptachlor	1		.335	.201 -.421	.229 -.399	
Epoxide	2		.805	.341 -1.20	.453 -1.09	
		Non-filterable residue in milligrams per litre				
Non-filterable Residue	1		31.6	24.3 -38.9	26.1 -37.1	
	2		44.2	36.3 -52.1	38.3 -50.1	

(a) A 99 percent prediction interval (ref. 16).

(b) A 95 percent prediction interval (ref. 16).

(c) ACCEPTABLE, i.e., within the warning limits.

CHECK FOR ERROR, i.e., within the acceptance limits, but beyond warning limits. A value receiving this evaluation does not require follow-up.

NOT ACCEPTABLE, i.e., beyond acceptance limits.

UNUSABLE DATA, i.e., the response cannot be quantitatively judged.

6.0 REFERENCES

1. UNEP/WHO (1985) GEMS/Water Operational Guide Chapter IV; analytical quality control, Geneva, World Health Organization (WHO/EFP/85.4)

2. WHO (1982) Global study on analytical quality control, 1982/1983. Annex III: Recommended quality control programme, Geneva, World Health Organization (WHO 82.30).

3. CEPIS (1979) Guide for the evaluation of water, pp. 80-85 (Technical Document No. 4).

4. NEERI (1979) Basic principles of statistics for analytical quality control.

   NEERI (1979) Laboratory manuals for analytical quality control,: lead, P, DDT, residue, chromium, iron, mercury, fluoride, and ammonia.

   NEERI (1979) Analytical quality control exercises.

   NEERI (1979) Analytical quality control (training programme).

5. US EPA (1979) Handbook for analytical quality control in water and waste water laboratory, US Environmental Protection Agency (EPA 600/4-79-019).

6. [Handbook on within-laboratory quality control in water laboratory], Denmark, Water Quality Institute (Project No. 180-21-16) (in Danish).

7. WHO REGIONAL OFFICE FOR EUROPE (1974) Manual on analyses for water pollution control: analytical errors, Copenhagen, World Health Organization.

8. KATEMAN, G & PIPES, F.W. (1981) Quality control in analytical chemistry, Wiley Interscience Chemical Analysis, Vol. 60.

9. DUNCAN, A.J. (1974) Quality control and industrial statistics, Illinois.

10. YOUDEN, W.J. & STEINER (1975) Statistical manual of the AQC.

11. WATER RESEARCH CENTRE (1978) In: Cheeseman, R.V. & Wilson, A.L., ed. Manual on analytical quality control for the water industry, Medmenham, U.K. (TR 66).

12. WATER RESEARCH CENTRE (1976) Accuracy required of analytical results for water quality data banks, Medmenham, U.K. (TR 34).

13. NATIONAL AGENCY OF ENVIRONMENTAL PROTECTION (1983) Interlaboratory analytical quality control in water chemistry. An international comparison, Horsholm, Reference Laboratory for Chemical Water Analysis (den 7, January).

14. IUPAC (1982) In: Egan, H. & West, T.S., ed. Collaborative interlaboratory studies in chemical analyses, Oxford, New York, Pergamon Press.

15. WINTER, J.A. (1985) Quality assurance support to the GEMS/Water programme, Water Quality Bulletin, Vol. 10, No. 4, pp. 181-185 and 216.

16. BRITTON, P.W. (1986) Laboratory performance evaluation studies and their relationships to the global environmental monitoring system in water (GEMS/Water), World Health Statistical Quarterly, Vol. 39, No. 1, pp. 46-57.

CHAPTER VIII: QUANTITATIVE HYDROLOGICAL MEASUREMENTS

CONTENTS

1.0 INTRODUCTION

This chapter discusses the role of hydrological measurements in water quality monitoring, lists the hydrological data requirements, indicates the recommended hydrological measurement techniques and describes the application of hydrological measurements in the framework of the water quality monitoring network. Detailed information on water quantity and quality monitoring is given in the following WMO publications:

- Guide to Hydrological Practices [1]*;
- Manual on Stream Gauging [2];
- Manual on Water Quality Monitoring [3];
- Manual on Operational Methods for the Measurement of Sediment Transport [4].

Chapters from these publications with material relevant to this document are listed in Table 1.

Table 1. Relevant chapters of WMO Guide and Manuals

Source	Chapter	Title
[1]*	10	Water levels (stage)
	11	Discharge measurement
	12	Stream gauging (hydrometric stations)
	13	Sediment discharge
	14	Ice on rivers, lakes and reservoirs
	17	Surface water quality
[2]	4	Measurement of stage
	5	Measurement of discharge by conventional current meter methods
	6	New methods
	8	Measurement of discharge by miscellaneous methods
[3]	2	General water sampling conditions
	10	Sediment sampling procedures
[4]	1	Measurement of suspended sediment
	2	Measurement of bed load
	3	Measurement of total sediment discharge
	6	Data processing

2.0 ROLE OF HYDROLOGICAL MEASUREMENTS IN WATER QUALITY MONITORING

Hydrological measurements are required in the framework of water quality monitoring for several purposes, namely to provide for:

- the estimation of average instantaneous values of the water quality constituents in the river, groundwater body or lake at the time of sampling (instantaneous flow rate or volume);
- the computation of mass flow or mass balance of the water quality constituents of interest (historical time series of flow data);
- the estimation of errors in water quality data originating from errors in hydrological measurements which will be compounded with the other errors;
- inputs to water quality models (historical time series of flow data).

The fifth edition of the WMO Guide to Hydrological Practices is expected to be published in 1992/93 and these chapter titles relate to that edition. For these reasons it is of utmost importance that hydrological measurements and water quality sampling are carried out in a fully co-coordinated manner.

3.0 DATA REQUIREMENTS

Two basic types of hydrological data are required for water quality monitoring:

- Water quantity data such as water level, velocity, flow and the occurrence of ice on or in the water;
- Sediment load (Suspended sediment and bed load**), which are in the realm of water quality, but are traditionally measured by hydrologists.

Basic hydrological data can, in turn, be divided into two subgroups: hydrological measurements carried out at the time of sampling (sub-section 3.1) and historical time series data for the whole record period (sub-section 3.2).

3.1 Quantitative Hydrological Measurements at the Time of Water Quality Sampling

For rivers having stable stage-discharge relationships and relatively small water level variations it is generally sufficient to have a water level reading and the usual observations on ice conditions at the time when the sampling is done. If the stage-discharge relationship exhibits hysteresis (i.e. a loop related to increasing and decreasing stages) careful readings before and after the sampling will be necessary, in addition to those taken at the time of sampling to determine the status of the river (rising or falling). The number of readings before and after the sampling, and the time interval between readings, will be determined at each station in terms of the hysteresis characteristics of the stage-discharge relationships. If the stage-discharge relationship is unstable, that is: if the river bed changes shape with time and flow, a discharge measurement at the time of sampling becomes necessary.

It should be noted that in the case of single point sampling, it is not absolutely necessary to take the sample from the same river section as the water level and/or discharge measurement. However, when it is possible to do so, this should be preferred.

If multiple point sampling over the cross-section is necessary, the hydrological measurements and sampling should be carried out in the same cross section. The measurements and observations are the same as in the case of one single point sampling, with the difference that flow measurement is mandatory in this case. During the discharge measurements, the velocity should be measured in all points used as sampling points.***

In the case of lakes and reservoirs, if the sampling takes place on out- and inflowing rivers, the required measurements are the same; except at the time of sampling, it is advisable to carry out observations on lake levels and waves (sub-section 3.2) at a few intervals, before and after, depending upon lake and other local conditions. If the measurements are carried out within the lake proper, the following hydrological measurements should be carried out at the time of sampling, as well as a few intervals before and after, for those parameters that are not continuously gauged:

- water levels at all gauges on the lake;
- ice conditions at all observation points;
- wave characteristics, wind set up, and seiches.

In addition, if temperature sampling and current metering programs are carried out on a routine basis in the lake (reservoir), it is necessary to co-ordinate these programmes with those for water quality sampling, so that the sampling is done simultaneously with the current and temperature measurements. In the case of a reservoir, the operation of the intakes and discharge facilities, at the time of sampling, should also be noted.

** Because of current (1991) difficulties in measuring bed load by means of a globally acceptable instrument, for the time being, bed load sediment discharge is not considered as part of the GEMS/Water project.

*** Sampling and velocity measurements should be carried out as close in time as is practically possible. Velocity at a point in a river varies rapidly in time, but most measurement techniques obtain an average velocity over a period of 1-2 minutes. Water quality may also vary with the velocity. By sampling a volume of 1 litre or more within a minute of the velocity measurement this variation is reduced

significantly.

In the case of samples taken from groundwater, the water level in the well should be noted at the time the sample is taken. If the well does not have a level recorder, or if the water levels are measured at longer intervals than one day, water levels should also be measured at a few time intervals before and after taking the sample. The time intervals should be established on the basis of local conditions, particularly expected rate of variation of water level. If, at the time of sampling, pumping from the well is taking place for exploratory or operational purposes, the well discharge and levels in auxiliary wells around the well sampled should be noted at the time of sampling, and at a few time intervals before and after sampling. The depth from which the sample is taken should always be noted. If the sample is taken from water pumped from the well this should also be noted, and the pumping rate, or rate of withdrawal from the well, at the time of sampling, should be noted.

3.2 Time Series of Hydrological Data for Mass Flow Computations

In the case of rivers, the time series data required for mass flow computations will consist of daily flows for the period of computation. However, where the variation of the flow over the course of a day is large, and there is also a large variation (one order of magnitude) of the water quality parameter being measured, it will be necessary to provide flows at shorter time intervals.

For the computation of mass flow into and out of lake, reservoir and groundwater systems, the following time series will be required:

- flow data of the rivers flowing into and out of the systems, as in the case of mass flow computations of rivers;
- lake (reservoir) water levels and a storage volume relationship; and,
- groundwater levels.

The time interval for this data will depend on the complexity and response time of the system. Other time series data required in this case, such as precipitation, lake evaporation (or meteorological data for its estimation), infiltration and human controlled inputs and outputs should be supplied by the organizations in charge of monitoring these elements, in co-operation with the hydrological service. In most cases daily values of these parameters will be sufficient.

3.3 Suspended Sediment Data

Suspended sediment data required will usually be in the form of daily sediment discharge, as estimated by the Hydrological Service (see Section 3.1) and suspended sediment grain size distribution. However, where significant pollutants are attached to suspended sediment, it will be necessary to provide detailed data on the suspended sediment concentration and flow velocity at sufficient points. In those cases where the Hydrological Service does not have sufficient data, a list of suspended sediment concentration values obtained during the period of concern will be required.

4.0 RECOMMENDED HYDROLOGICAL MEASUREMENT TECHNIQUES

In general, the recommended hydrological measurement techniques are those given in the "Guide to Hydrological Practices" [1], and the "Manual on Stream Gauging" [2]. The techniques described there are only briefly introduced here. Some additional techniques applicable in special cases, not described in the above publications, are also mentioned. However, since they do not represent widely used techniques, for a full description the user of this handbook will have to use the references indicated.

4.1 Rivers

Compatibility of the water quality sampling data and the discharge estimate is essential if data quality is to be maintained throughout the analysis.

Hydrometric gauging stations used in the GEMS/Water Network should be located in the same section as the one in which the water quality sampling is taking place, or as close as possible. When the water quality in the river cross section is non-homogeneous and, consequently, multiple point sampling across the section is required, it is not appropriate to have the discharge measurements and the water quality sampling taking place in two different sections.

As stated in Section 3, in the case of rivers, the hydrological data required for use in the water quality monitoring network are levels, velocities,

water discharges, ice conditions, temperature and suspended sediment.

Water levels should be measured using the equipment described in the WMO Guide [1] and the WMO Manual [2], or using a digital step gauge or an acoustic level meter [2]. The measurement techniques used should be those described in the WMO Guide [1].

Velocity and discharge measurements should be carried out wherever possible by using current meters ([1] and [2]) or ultrasonic methods [2]. The execution of the measurements should have minimum influence on the water quality characteristics. In particular, the bed should not be disturbed and water quality samples should be taken upstream of the measuring point.

Float discharge measurements ([1] and [2]) and measurement weirs are not recommended as float measurements are not sufficiently accurate for use in water quality analyses and measurement weirs can modify the normal water quality conditions at the site.

Ice measurements on rivers should be carried out using the techniques recommended by WMO [1]. Ice measurements should be carried but in such a manner as to avoid interference with water quality (reaeration through ice holes, sediment stirring in sampling for anchor ice, etc).

Water temperatures in rivers should be measured using the techniques recommended by WMO ([2] and [3]). Since large cross-sectional and longitudinal water temperature variation may be indicative of anomalous water quality conditions, and since water temperature is one characteristic that can be readily measured, it is recommended that exploratory temperature surveys be carried out whenever such anomalous water quality conditions are suspected. Water surface temperatures can also be measured by remote sensing. However, the surface temperature seldom represents the water temperatures further below the surface and the temperature profile cannot be obtained by the remote sensing technique. For inland waters, the very poor spatial resolution of current microwave radiometer scanning from satellites will inhibit the measurement of water temperature.

Suspended sediment measurements should be carried out as recommended by WMO ([1], [3] and [4]). In rivers with uniform cross section distribution of suspended sediment (well mixed), it is acceptable to take one single measurement. In such cross sections, a correction coefficient, determined on the basis of multiple-point cross-sectional measurements could be applied to reduce the error due to one point sampling (sub-section 5.1). In rivers with non-uniform cross section distribution of suspended sediment, multiple point and/or multiple depth integrated sampling should be carried out. In addition to analyzing suspended sediment, it is recommended that sampling and analysis of deposited sediments be carried out ([3] and [4]). Whenever possible, the withdrawal of undisturbed core samples should be attempted, as such cores can provide a historical record of water quality. For more information on the analysis of suspended and deposited sediments see Chapter IV of this Guide.

4.2 Lakes

In the case of lakes, the measurement techniques for sampling stations located on outflowing rivers should be similar to those used for rivers and described in section 4.1. For the inflowing rivers the influence of backwater effects caused by high lake levels should be taken into account if necessary.

Wind set up and seiches on lakes and reservoirs should be measured by setting up at least four level gauges provided with stilling wells [1], two located at opposite sides of the lake in the direction of the dominant winds and independent of the shape of the lake, and two located perpendicular to that axis. Wave characteristics on the lake should be measured using a wave buoy, or visually, at least twice a day.

Current measurements in lakes and reservoirs should include velocity and direction, and be co-ordinated with water quality and bottom sediment sampling. Aerial photography and satellite imagery can be used, in some cases, to delineate areas where sharp variations occur. When locating sampling points on lakes, one should give consideration to possible sharp variations of water quality from one point to another.

Temperature measurements in lakes and reservoirs are also very significant indicators of water quality variations, and should be co-ordinated with both current metering and water quality sampling. The techniques of temperature measurements are discussed in section 4.1.

In the case of reservoirs, the operation of certain structures, such as bottom outlets, can artificially create circulation currents and density currents in the reservoir. This should be carefully considered in planning current metering and water quality sampling programmes.

Sediment sampling from lakes should be carried out using similar techniques as those for rivers (Section 4.1). The significance of obtaining undisturbed bottom sediment samples for historical variations is again emphasised.

As indicated in sub-section 3.2, in addition to the measurements on lakes and reservoirs proper, the analysis of water quality data also requires a series of measurements related to the mass and energy balance of the lake or reservoir. These consists mainly of measurements of precipitation, evaporation and infiltration. These measurements should be carried out in accordance with WMO [1].

4.3 Groundwater

A great deal of hydrogeological information will be necessary to plan a sampling strategy for a groundwater system [3].

Measurement techniques for flow into and out of a groundwater system via river flow are as described in sub-section 4.1. Of particular importance here is spring flow and the techniques to measure flow at such sites are well covered in that section.

Information on water levels, hydraulic gradients, velocity and direction of water movement is necessary for water quality modelling of groundwater systems. The WMO [3] recommends that an inventory of wells, boreholes and springs fed by the aquifer should be drawn up and details of land use should be recorded.

Groundwater samples are taken from drainage water, open wells and drilled wells. Wells should be sampled only after they have been pumped long enough to ensure that a fresh sample has been obtained [5].

As stated above, the coincidence of water quality data and the above hydrogeological parameters in space and time is essential in water quality modelling of groundwater systems. The installation of observation wells and methods of measuring groundwater levels are described in the WMO Guide [1]. The volumetric method of deriving discharge can be used to determine flow from an aquifer [2]. Detailed logging of extractions (pumping rates and durations) is also necessary to establish the water balance of the system.

Information on velocity and direction of flow within the aquifer can be obtained from dye studies or from the analysis of the data from a well planned inventory system. Caution must be exercised in the analysis of water quality samples from systems where dye studies have been carried out.

Note: GEMS/Water is concerned only with the water quality of rivers, lakes and groundwater systems. However, if sampling stations are installed on open sewers or other artificial channels, the flow measurement techniques used in these cases should be those recommended by EPA, [6], Chapter 7, Flow Measurements.

5.0 MASS FLOW COMPUTATION TECHNIQUES AND ERROR ANALYSES

Water quality analyses are carried out in the framework of the Global Water Quality Monitoring Network with the purpose of establishing instantaneous average values of the water quality parameters, and mass quantities of dissolved or suspended materials (mass flow carried by the water through river sections or through lakes, reservoirs or groundwater systems over definite periods of time). This section deals with the computation of measured instantaneous mass flow values and of mass quantities of materials over definite periods of time, on the basis of actual water quality analyses and flow measurements.

5.1 Mass Flow Computation

In estimating instantaneous flows and/or volumes of materials over definite time intervals, one can encounter three basic situations:

(a) measurements are available for the instant or period of time under consideration. In this case the computations can be carried out using simple, direct methods;

(b) measurements are not available for the given instant but available at other times during the time interval. In this case, the computations require interpolation in time;

(c) measurements are not available at all at the section of interest but available at other points of the region. In this case, the computation requires interpolation in time and space.

Interpolation in time and/or space is discussed in sub-section 5.2.

The mass flow, or load, on rivers is the product of local discharge (l^3/t) and concentration (mg/l). If the values are more of less equally distributed over the cross section, use can be made of the local mean values.

Thus:

$$Q_M = c\,Q \qquad \mathbf{1}$$

where:

Q_M = mass flow
c = concentration
Q = discharge

Pay attention to the correct dimensions!

If the distribution of the velocity and the concentration show large variation over the cross section, then an integration procedure should be applied:

$$Q_M = \int_o^B \int_O^H C_i\,V_i\,dy\,dz = \sum_{i=1}^{n} c_i\,Q_i \qquad \mathbf{2}$$

where:

B = the river width
H = the river depth
c_i = concentration in vertical i
v_i = velocity in vertical i
n = the number of elements into which the cross section is divided.

An approximation can be made using an empirical coefficient K_n:

$$Q_M = K_n\,c\,Q \qquad \mathbf{3}$$

This coefficient (K_n) should be based on earlier, more detailed examinations. It should be noted that K_n may vary with Q. The WMO Guide [1] contains a graph for use in the computation of sediment discharge and additional information on mass flow calculations can be obtained from WMO [4].

In general, lakes and groundwater systems require a similar approach as is used in rivers. Usually, the analyses are carried out by computing the mass flow of rivers flowing into and out of the system with the stored water quality changing accordingly. Data on any human controlled inputs or extractions from the systems will be necessary for mass and energy balance computations. Water quality models using conservation of mass and energy techniques for lake, reservoir and groundwater systems are readily available. Complications arise when the three systems are combined and checks using a mass balance technique are recommended in such situations. On large lakes the influence of local precipitation may be of importance, and this should be included in the computations.

In order to obtain the mass flow of a water quality parameter in a defined period of time, values of the concentration at discrete intervals and flow data for the same interval are necessary. In natural streams, a pollutant concentration-discharge relationship may be able to be established. Equation (2) can be used to determine the mass in the required time interval, by integrating with respect to time.

5.2 Interpolation Techniques

If, for the site and the time considered no local data are available, then these should be derived from data at adjacent locations and/or times. This requires interpolation in space or time, and some errors are introduced. When the water quality determinations are carried out at rather large time intervals (weekly, bi-weekly or even larger intervals), the computation of the mass flow for a definite time period is usually carried out by assuming that the concentration varies in a linear manner. This assumption is acceptable only for rivers with very small variation of concentration with time of the given substance (rarely the case). Other methods of interpolation that may be used include:

- techniques based on simple or multiple regression;
- techniques based on conceptual models.

Interpolation techniques in space have to be applied when an attempt is made to compute the mass flow from an area in which water quality information is only available for some of the basins. Interpolation techniques that can be used in such instances include:

- water quality maps;
- multiple regression analysis (statistical models);
- conceptual models.

Extrapolations are not recommended because of error amplification.

5.3 Error Analysis

The errors of estimate of the mass flow data result from errors in the discharge and concentration data respectively.

The standard error of estimate of the mass flow, σ_M can be derived from those of its two basic components, as follows:

$$\sigma_M = Q_M \sqrt{\left(\frac{\sigma_c}{c}\right)^2 + \left(\frac{\sigma_Q}{Q}\right)^2} \qquad \textbf{4}$$

where σ_c and σ_Q are the standard errors of estimate of concentration (c) and discharge (Q) respectively. Both can be composed of several components, depending on the procedure used for their calculation.

6.0 DATA REPORTING

Hydrological data are required for processing water quality data at various stages of data storage, publication, and interpretation. When water quality data processing takes place outside the hydrological service carrying out the hydrological measurements, it is necessary to report data in more detail than would be otherwise required. This is the assumption made in the following sub-sections. In those instances when hydrological and water quality data are processed by one organization, adjustments in data reporting will be made accordingly. The suggested format of hydrological data reporting is to support the data reporting of water quality and will not necessarily enter in the reports on water quality.

6.1 Hydrological Data Obtained at the Time of Sampling

The hydrological data obtained at the time of sampling that should be reported for water quality data processing should include:

- water level and water level trends;
- water surface slope and water surface slope trends (if available);
- ice conditions and water temperature;
- water transparency (if available) and visual water colour observations;
- water flow and estimated error;
- if multiple point sampling is carried out, water velocities in the various points of the cross section;
- suspended sediment data; average concentration, grain size distribution (if available);
- bed load data (if available);
- observations on river bottom vegetation and conditions.

6.2 Hydrological Data for Mass Balance Computations

As shown in section 5, hydrological data are necessary for interpolation of water quality data, as inputs in mass balance computations, and for interpolation of mass flows at ungauged stations. Therefore the hydrological data reporting for mass flow computations should include:

- daily flows at water quality monitoring stations and estimated errors;
- measured flow volumes (averages) and error estimates at gauged sites at stations of interest, for mass flow computations.

In the case of lakes, reservoirs and groundwater systems, the specific data to be reported will depend upon the mass balance computation inputs.

6.3 Statistical Parameters for Summary Reporting

These parameters should parallel the statistical parameters selected for summary reporting of water quality data (Chapter IX and X of this Guide). Considering that reporting will be carried out periodically (probably annually), the statistical hydrological data should include:

- mean, minimum and maximum instantaneous flows and dates of occurrence for the period reported;
- mean, minimum and maximum instantaneous flows and dates of occurrence for the period of record;
- seasonal (monthly) mean, minimum, and maximum flows and time of occurrence for the period reported;
- seasonal (monthly) mean, minimum and maximum flows and time of occurrence for the period of record;
- statistically significant trends and periodicities (except for annual periodicities) where detected, for the period of record;
- estimated errors (confidence limits) for the above data.

7.0 REFERENCES

[1] WMO Guide to Hydrological Practices, 2 Volumes, Fourth Edition (1981) Fifth Edition (in Preparation), WMO No. 168, Geneva

[2] WMO Manual on Stream Gauging, 2 Volumes, Operational Hydrology Report No. 13, WMO No. 519, Geneva, 1980.

[3] WMO Manual on Water Quality Monitoring - Planning and Implementation of Sampling and Field Testing, Operational Hydrology Report No. 27, WMO No.680, Geneva, 1988.

[4] WMO Manual on Operational Methods for the Measurement of Sediment Transport, Operational Hydrology Report No. 29, WMO No. 686, Geneva 1989.

[5] WHO Water Quality Surveys, IHD/WHO Working Group on the Quality of Water, Paris, 1978

[6] E.P.A. Handbook for Monitoring Industrial Waste Water, Washington, D.C., 1973.

CHAPTER IX: DATA REPORTING AND PROCESSING

CONTENTS

1.0 INTRODUCTION

This chapter provides an introduction to this data system and describes the procedures for submitting water quality data and for retrieving information through the GLOWDAT system.

1.1 System Development

GLOWDAT is based upon proven data storage/retrieval techniques which have been enhanced by modern database technology. Principles and formats used in a number of existing computerized systems were examined in the light of the GEMS/Water requirements. In particular, many of the conventions used in NAQUADAT (The National Water Quality Data Bank of Canada) have been adapted by the GLOWDAT system. The database was originally developed using the System 2000 data base management system and has since been converted to the Oracle data base management system.

1.2 Data Flow

Samples collected at the monitoring site are analyzed in the local laboratory and the data entered into the coded data forms which are then sent to the National Centre. The National Centre assembles the data forms, checks the forms, adds coded hydrometric information as required and forwards the information via the Regional Centre or directly to GEMS/Water. The detailed hydrological information required for the Global River Flux Station are to be sent via the Global Runoff Data Centre (GRDC) at the Federal Institute of Hydrology in Koblenz, Germany, which operates under the World Meteorological Organization (WMO). The primary means of transmitting data to WHO/CC is the mandatory source data form. Countries may submit the corresponding data set on computer readable media (i.e. magnetic tape, disk, CD) or through electronic mail. Formatting instructions are given in Appendix I. Submission of data on forms only is adequate to meet the requirements of the system.

Specifications for the magnetic tape reels are: 9-track, 1600/6250 BPI, unlabelled/labelled, EBCDIC, ASCII, with a logical and physical record of 80 characters. Other tape specifications can be accepted by special arrangements with WHO/CC.

Files submitted on diskettes should be in ASCII format as per Appendix I on either diskettes or CD.

Files can be sent by electronic mail to gems@ec.gc.ca

The data received are processed by the Global Data Centre which provides Regional Centres with comprehensive reports. Statistically treated data summaries are forwarded regularly to WHO and then to UNEP Secretariat in Nairobi. Data summary reports have been published on a tri-annual basis (1979-81, 82-84, 85-87, etc.)

1.3 Accuracy

The successful operation of a computer-based information system depends on accurate, validated data being input correctly. For this reason, stringent validation and verification controls are required at all levels - local, national, regional and global. Similarly, the coding of data for storage must be done in a consistent manner if results are to be meaningful. It is mandatory that the conventions outlined in this manual for the coding of data be followed exactly.

1.4 Access

National participation in GEMS/Water implies acceptance of sharing water quality data with other participating countries.

2.0 INPUT OF DATA

The procedures for entering data into GLOWDAT have been designed to be simple and non-redundant. The following information is required with every analysis:

(1) sampling location (place and depth);
(2) time of sampling (year, month and day);
(3) variable measured (code);
(4) analytical result and physical value of instantaneous discharge (where applicable).

In order to enter this information into the computer system in as simple a manner as possible, two forms are required:

(1) Station Form - containing details about the monitoring site. This form must be completed only once for each sampling location and submitted to GEMS/Water before any data can be processed. All data are subsequently linked to the relevant station information by means of the station number.

(2) Data Form - containing the analytical results for a particular sample. There is one data form for each original water sample with space to enter the results of the analyses performed on that sample. The data form may also be used to change or delete data where necessary.

The Station Form and the Data Form are designed to be easily filled in and to permit direct data entry of results from these forms. Information entered on the forms should be printed carefully, one figure per box. The small printed numbers on the forms are data entry instructions and should be ignored when entering results or codes onto the forms. Instructions for the data entry of these forms are provided in Appendix I.

Decimals shall be coded using one box for the decimal point. The variables must be recorded in the units indicated in Appendix IV.

2.1 Station Form

The Station Form must be coded once for each sampling location. The basic form is shown in Figure 1 and a completed form serving as a sample is shown in Figure 2.

The following are instructions for coding the required information on the Station Form. Items 1-12 and 28-29 are to be completed for every station; items 13-17, 18-21 or 22-27 are to be completed according to the respective water type. It is mandatory that at least one item in the item groups 13-17, 18-21 or 22-27 be entered, and that items 1-6 and 28-29 be completed.

Average or mean values should be calculated using values obtained over the last five-year period or any available period of record.

(1) Station Number - the station number is a 6-digit numeric code consisting of the two subfields:

(a) Country code - the first 3 digits represent the country. The country codes to be used are given in Appendix III in numeric sequence, and also in alphabetic sequence by country name.

(b) Sequential Number - the last 3 digits represent a sequential number starting with 001. This number is assigned by the National Centre and is unique for each station within that country.

(2) Octant - A one digit numeric code indicating the octant of the globe.

This is in accordance with an established WMO convention. The code is selected from the following table.

Octant Code	Greenwich Longitude			Hemisphere
0	0°	-	90°W	North
1	190°	-	180° W	North
2	180°	-	90° E	North
3	90°	-	0° E	North
5	0°	-	90° W	South
6	90°	-	180° W	South
7	180°	-	90° E	South
8	90°	-	0° E	South

(3) Latitude - consists of the following subfields:

(a) Deg. - a two digit field for degrees;
(b) Min. - two digits for minutes;
(c) Sec. - two digits for seconds.

Where precise locations cannot be provided enter latitude to the nearest degree or minute only, ensuring that any such entry does not fall outside the physical boundaries of that country.

(4) Longitude - consists of the following subfields:

(a) Deg. - a three digit field for degrees;
(b) Min. - two digits for minutes;
(c) Sec. - two digits for seconds.

Where precise locations cannot be provided enter longitude to the nearest degree or minute only, ensuring that any such entry does not fall outside the physical boundaries of that country.

(5) Mean Surface Water Level - enter the mean level of the water surface above mean sea level, in metres, to one decimal place. For well stations reference is to be static water level.

(6) Average Sounding Depth - enter the average depth of the water at the station, in metres, to one decimal place. At river stations, the average river depth should be entered. For well stations enter the depth from the static well level to the bottom of the well.

(7) Date Station Opened - enter the date the station was established as a GEMS/Water monitoring site. The date consists of year (2 digits), month (2 digits), and day (2 digits).

(8) Regional Centre - enter the code for the responsible WHO regional centre if available (see Appendix II).

(9) Responsible Collection Agency - enter the code for the responsibility agency if available.

(10) WMO Station Code - enter the international hydrological observing station identification number as issued by WMO if it is available.

(11) Station Type - enter the type of station this represents. The valid types are Baseline, Trend, GRF (for Global River Flux) stations.

(12) Geographical Region - enter the code for geographical region of the world. The valid codes are listed in Appendix II.

Lake/Reservoir Stations Only

(13) Max. Depth - enter the maximum depth of the lake or reservoir, in meters, to one decimal place.

(14) Area - enter the area of the lake or reservoir, in km^2, to one decimal place.

(15) Volume - enter the volume of the lake or reservoir, in km^3 , to one decimal place.

(16) Retention - enter the retention time of water in the lake or reservoir, in years, to one decimal place.

(17) Area of Watershed - enter the area of the watershed for the lake or reservoir, in km^2.

The location of the decimal point in items 13-17 above may be adjusted as required, but wherever a decimal is used it must be clearly entered into one box on the form.

River Stations Only

(18) River Width - enter the width of the river at the station during average discharge conditions, in metres, to one decimal.

The location of the decimal point in item 18 above may be adjusted as required, but wherever a decimal is used it must be clearly entered into one box on the form.

(19) Discharge - enter the average river discharge at the station, in m^3/sec based on 3-5 years of data.

(20) Upstream Basin Area - enter the upstream river basin area, in km^2.

(21) Basin Area Upstream of Tidal Limit - enter the area of the basin upstream of the tidal limit, in km^2. The tidal limit is the limit of saline intrusion under average conditions.

Fig. 1

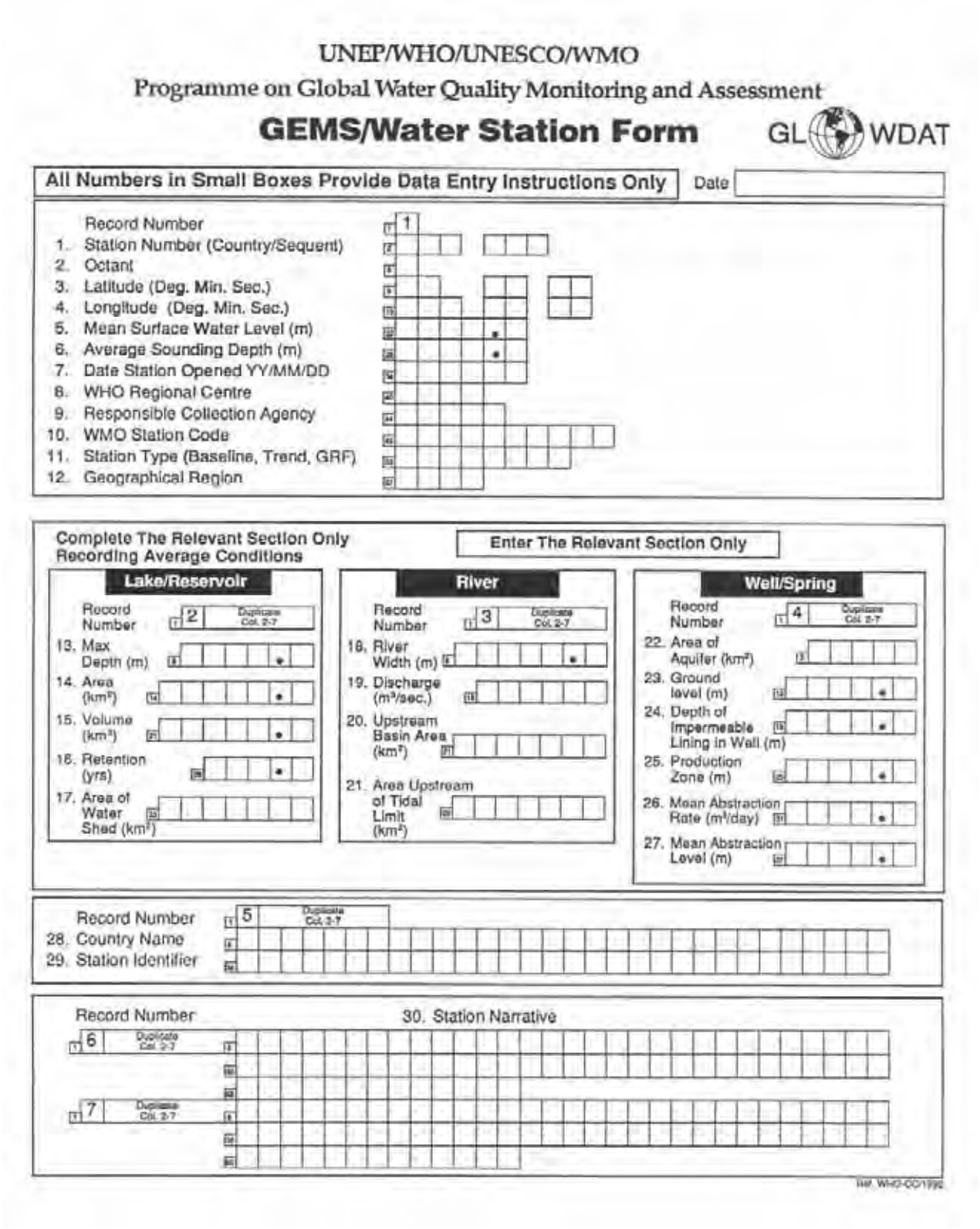

UNEP/WHO/UNESCO/WMO
Programme on Global Water Quality Monitoring and Assessment
GEMS/Water Station Form
GLOWDAT
All Numbers in Small Boxes Provide Data Entry Instructions Only
Date
Record Number
1. Station Number (Country/Sequent)
2. Octant
3. Latitude (Deg. Min. Sec.)
4. Longitude (Deg. Min. Sec.)
5. Mean Surface Water Level (m)
6. Average Sounding Depth (m)
7. Date Station Opened YY/MM/DD
8. WHO Regional Centre
9. Responsible Collection Agency
10. WMO Station Code
11. Station Type (Baseline, Trend, GRF)
12. Geographical Region
Complete The Relevant Section Only
Recording Average Conditions
Enter The Relevant Section Only
Lake/Reservoir
Record Number
13. Max Depth (m)
14. Area (km²)
15. Volume (km³)
16. Retention (yrs)
17. Area of Water Shed (km²)
River
Record Number
18. River Width (m)
19. Discharge (m³/sec.)
20. Upstream Basin Area (km²)
21. Area Upstream of Tidal Limit (km²)
Well/Spring
Record Number
22. Area of Aquifer (km²)
23. Ground level (m)
24. Depth of Impermeable Lining in Wall (m)
25. Production Zone (m)
26. Mean Abstraction Rate (m³/day)
27. Mean Abstraction Level (m)
Record Number
28. Country Name
29. Station Identifier
Record Number
30. Station Narrative

Fig. 2

UNEP/WHO/UNESCO/WMO

Programme on Global Water Quality Monitoring and Assessment

GEMS/Water Station Form

GLOWDAT

All Numbers in Small Boxes Provide Data Entry Instructions Only Date 92-02-29

	Record Number	1
1.	Station Number (Country/Sequent)	039 001
2.	Octant	1
3.	Latitude (Deg. Min. Sec.)	67 27 30
4.	Longitude (Deg. Min. Sec.)	133 42 00
5.	Mean Surface Water Level (m)	15.0
6.	Average Sounding Depth (m)	25.0
7.	Date Station Opened YY/MM/DD	600601
8.	WHO Regional Centre	AMRA
9.	Responsible Collection Agency	03903
10.	WMO Station Code	
11.	Station Type (Baseline,.Trend, GRF)	BASELINE
12.	Geographical Region	NA

Complete The Relevant Section Only Recording Average Conditions — **Enter The Relevant Section Only**

Lake/Reservoir

Record Number	2 (Duplicate Col. 2-7)
13. Max Depth (m)	
14. Area (km²)	
15. Volume (km³)	
16. Retention (yrs)	
17. Area of Water Shed (km²)	

River

Record Number	3 (Duplicate Col. 2-7)
18. River Width (m)	1300.0
19. Discharge (m³/sec.)	10300
20. Upstream Basin Area (km²)	1655000
21. Area Upstream of Tidal Limit (km²)	

Well/Spring

Record Number	4 (Duplicate Col. 2-7)
22. Area of Aquifer (km²)	
23. Ground level (m)	
24. Depth of Impermeable Lining in Well (m)	
25. Production Zone (m)	
26. Mean Abstraction Rate (m³/day)	
27. Mean Abstraction Level (m)	

Record Number	5 (Duplicate Col. 2-7)
28. Country Name	CANADA
29. Station Identifier	MACKENZIE RIVER

Record Number 30. Station Narrative

6 (Duplicate Col. 2-7): AT ARCTIC RED RIVER, N.W.T., 1. 2 KM UPSTREAM FROM I.H.D. STATION.

7 (Duplicate Col. 2-7): NAQUADAT STATION 00NW10LA0003. WSC FLOW STATION 10LA003.

Ref. WHO-CC/1992

Well/Spring Stations Only

(22) Area of Aquifer - enter the area of the aquifer, in km^2.

(23) Ground Level - enter the level of the ground above mean sea level, in metres, to one decimal place.

(24) Depth of Impermeable Lining in Well - enter the depth of the impermeable lining in the well (length of the well casing) from the surface of the earth, in metres, to one decimal place.

(25) Production Zone - enter the thickness of the layer, in meters, to one decimal through which water can enter the well. This will normally be the zone from the bottom end of the well casing to the bottom of the well.

(26) Mean Abstraction Rate - enter the mean rate of abstraction of water, in m^3/day, to one decimal place.

(27) Mean Abstraction Level - enter the water level above mean sea level during a period of normal abstraction.

The location of the decimal point in items 23-27 above may be adjusted as required, but wherever a decimal is used it must be clearly entered into one box on the form.

All Stations

(28) Country name - enter the name of the country in which the station is located.

(29) Station Identifier - enter the unique station identification, for example:

- Lake Ontario, Stn 001
- Thames River, at London Bridge
- Well a1-2Z3, Rgn 2

(30) Station Narrative - enter a narrative description of the sampling location or other special conditions. For well/spring stations include the geographical characteristics of the aquifer. For rivers enter a description of the corresponding flow measurement station and its location relative to the sampling site.

2.2 Data Form (General Information)

The Data form is used to enter the analytical results for a sample into the database. The form has been designed so as to permit the entry of all the analytical results required by the GEMS/Water program. The Data Form is shown in Figure 3 and a completed sample form is illustrated in Figure 4.

The top section of the Data Form identifies the station, the time, depth of sampling and whether the water sample has been integrated (composite sample). Also included are spaces to write the station name and type for clerical reference. The largest part of the form is reserved for the results of analytical tests performed on the sample. Specifically the data form contains:

(a) the abbreviated name of the variable to be measured and the units of the results, (this is for the convenience of the analyst; it is not entered into the computer system);

(b) the GLOWDAT variable code which defines the methods and units used;

(c) a flag which may be used to qualify the analytical result;

(d) the actual measured value including the relevant decimal point.

The National Centre may complete the code columns before reproducing the forms for laboratory use. The variables should be selected from those listed in Appendix IV. Additional code assignments for methods not in the list may be requested from the WHO/CC Global Data Centre. The data form may be used not only to add new data but also to change or to delete data previously submitted for entry into the system.

The laboratory analyst can record results directly on the Data Form adjacent to the appropriate variable code numbers. These results, together with the station number, time and depth at the top of the form, complete the information required for each sample.

2.3 Data Form (Detailed Instructions)

The following are detailed instructions for entering the required information into the Data Form. Items 1-6 must be completed for every sample.

(1) Addition, Change, Deletion - enter an A if the data listed on the form are to be added to the data base. Enter a C if data currently in the system are to be changed. Enter a D if data currently in the system are to be deleted. When changing data, the new value replaces the old value for that variable. Note that a form can be used for only a single purpose; separate forms must be used to change or delete data already entered into the system.

(2) Station Number - enter the assigned station number ensuring that it corresponds to the appropriate station form.

(3) Date Sample Taken - enter the date the sample was collected. The date code consists of year (2 digits), month (2 digits), and day (2 digits).

(4) Time Sample Taken - enter the time of the day the sample was collected in local standard time. The time consists of hour (2 digits, 00-23) and minute (2 digits, 00-59). For a sample integrated in time, the time entered shall be the beginning time of the integration period.

(5) Sample Depth - enter the depth below the water surface at which the sample was taken, in metres, to one decimal place. For a sample integrated vertically the depth entered will be the lowest depth.

(6) Integrated Sample - enter a V if the sample is integrated vertically, an H if the sample is integrated horizontally, or a T if the sample is integrated in time. If the sample is not integrated leave the item blank.

The remainder of the Data Form is used to record analytical results. The name of the variable and the units are preprinted on the form for laboratory use. The GLOWDAT variable code, a 5-digit code which represents both the variable and the analytical method, must be entered on the form according to the method in use. Appropriate variable codes are given in Appendix IV. Only approved variable codes may be used.

FLAG - A flag may optionally be used to qualify any analytical result. The flag is a one-character code to signify one of the following conditions:

L - Value was less than detection limit (value entered is the minimum detection limit).

G - Value was greater than measurement limit (value entered is the maximum measurable value).

The analytical Value or result of a test is entered in the boxes corresponding to the description and code of the variable. It is essential that the decimal point, if entered, be inserted into a unique box (see Figure 5) and that the units are correct.

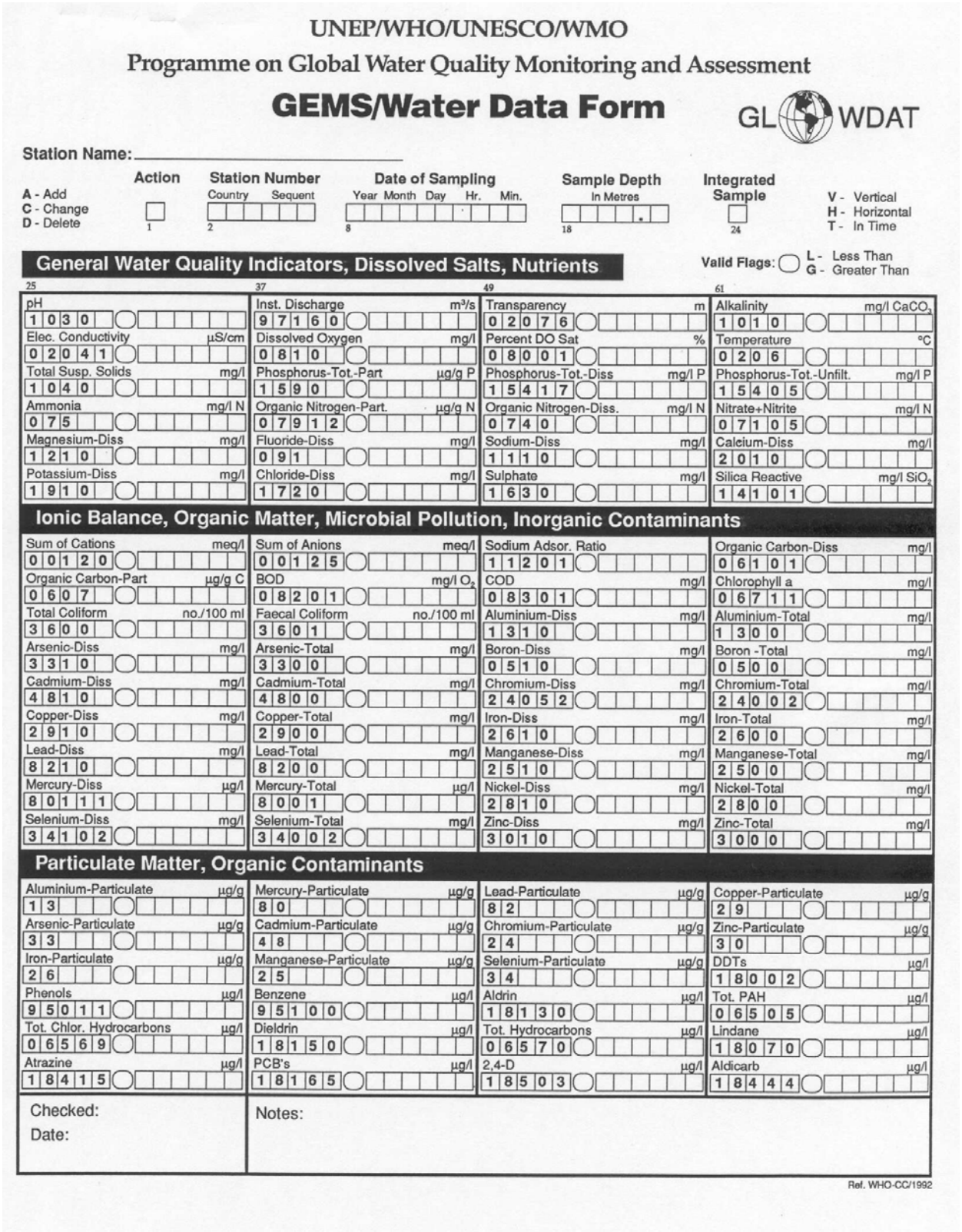
3.0 OUTPUT OF RESULTS

Once water quality data have been received and processed at the WHO/CC Global Data Centre, a variety of reports and statistics are available:

(1) Quality control error listing
(2) Inventories of stations (Figure 5), data and variables (Figure 6)
(3) Detailed data listing (Figure 7)
(4) Summary data listings (Figure 8 and 9)
(5) Loading report (Figure 10)
(6) Data reporting status (Figure 11)
(7) Mean summary by year (Figure 12)
(8) Percentile summary by year (Figure 13)
(9) Percentile summary by year/period of record (Figure 14)
(10) Other reports by arrangement with Global Data Centre (see also Chapter X).

Information output in these reports, while normally all-inclusive, may be selected by the user. The Station Inventory, for example, may include every monitoring station which has been entered, or may be restricted to those within a particular country.

Fig. 3



UNEP/WHO/UNESCO/WMO

Programme on Global Water Quality Monitoring and Assessment

GEMS/Water Data Form

GLOBAL WDAT

Station Name: _____

Action	Station Number	Date of Sampling	Sample Depth	Integrated Sample
A - Add C - Change D - Delete	Country Sequent	Year Month Day Hr. Min.	In Metres	
1	2	8	18	24

V - Vertical
H - Horizontal
T - In Time

Valid Flags: L - Less Than, G - Greater Than

General Water Quality Indicators, Dissolved Salts, Nutrients

25	37	49	61
pH 1030	Inst. Discharge m³/s 97160	Transparency m 02076	Alkalinity mg/l $CaCO_3$ 1010
Elec. Conductivity µS/cm 02041	Dissolved Oxygen mg/l 0810	Percent DO Sat % 08001	Temperature °C 0206
Total Susp. Solids mg/l 1040	Phosphorus-Tot.-Part µg/g P 1590	Phosphorus-Tot.-Diss mg/l P 15417	Phosphorus-Tot.-Unfilt. mg/l P 15405
Ammonia mg/l N 075	Organic Nitrogen-Part. µg/g N 07912	Organic Nitrogen-Diss. mg/l N 0740	Nitrate+Nitrite mg/l N 07105
Magnesium-Diss mg/l 1210	Fluoride-Diss mg/l 091	Sodium-Diss mg/l 1110	Calcium-Diss mg/l 2010
Potassium-Diss mg/l 1910	Chloride-Diss mg/l 17220	Sulphate mg/l 1630	Silica Reactive mg/l SiO_2 14101

Ionic Balance, Organic Matter, Microbial Pollution, Inorganic Contaminants

Sum of Cations meq/l 00120	Sum of Anions meq/l 00125	Sodium Adsor. Ratio 11201	Organic Carbon-Diss mg/l 06101
Organic Carbon-Part µg/g C 0607	BOD mg/l O_2 08201	COD mg/l 08301	Chlorophyll a mg/l 06711
Total Coliform no./100 ml 3600	Faecal Coliform no./100 ml 3601	Aluminium-Diss mg/l 1310	Aluminium-Total mg/l 1300
Arsenic-Diss mg/l 3310	Arsenic-Total mg/l 3300	Boron-Diss mg/l 0510	Boron -Total mg/l 0500
Cadmium-Diss mg/l 4810	Cadmium-Total mg/l 4800	Chromium-Diss mg/l 24052	Chromium-Total mg/l 24002
Copper-Diss mg/l 2910	Copper-Total mg/l 2900	Iron-Diss mg/l 2610	Iron-Total mg/l 2600
Lead-Diss mg/l 8210	Lead-Total mg/l 8200	Manganese-Diss mg/l 2510	Manganese-Total mg/l 2500
Mercury-Diss µg/l 80111	Mercury-Total µg/l 8001	Nickel-Diss mg/l 2810	Nickel-Total mg/l 2800
Selenium-Diss mg/l 34102	Selenium-Total mg/l 34002	Zinc-Diss mg/l 3010	Zinc-Total mg/l 3000

Particulate Matter, Organic Contaminants

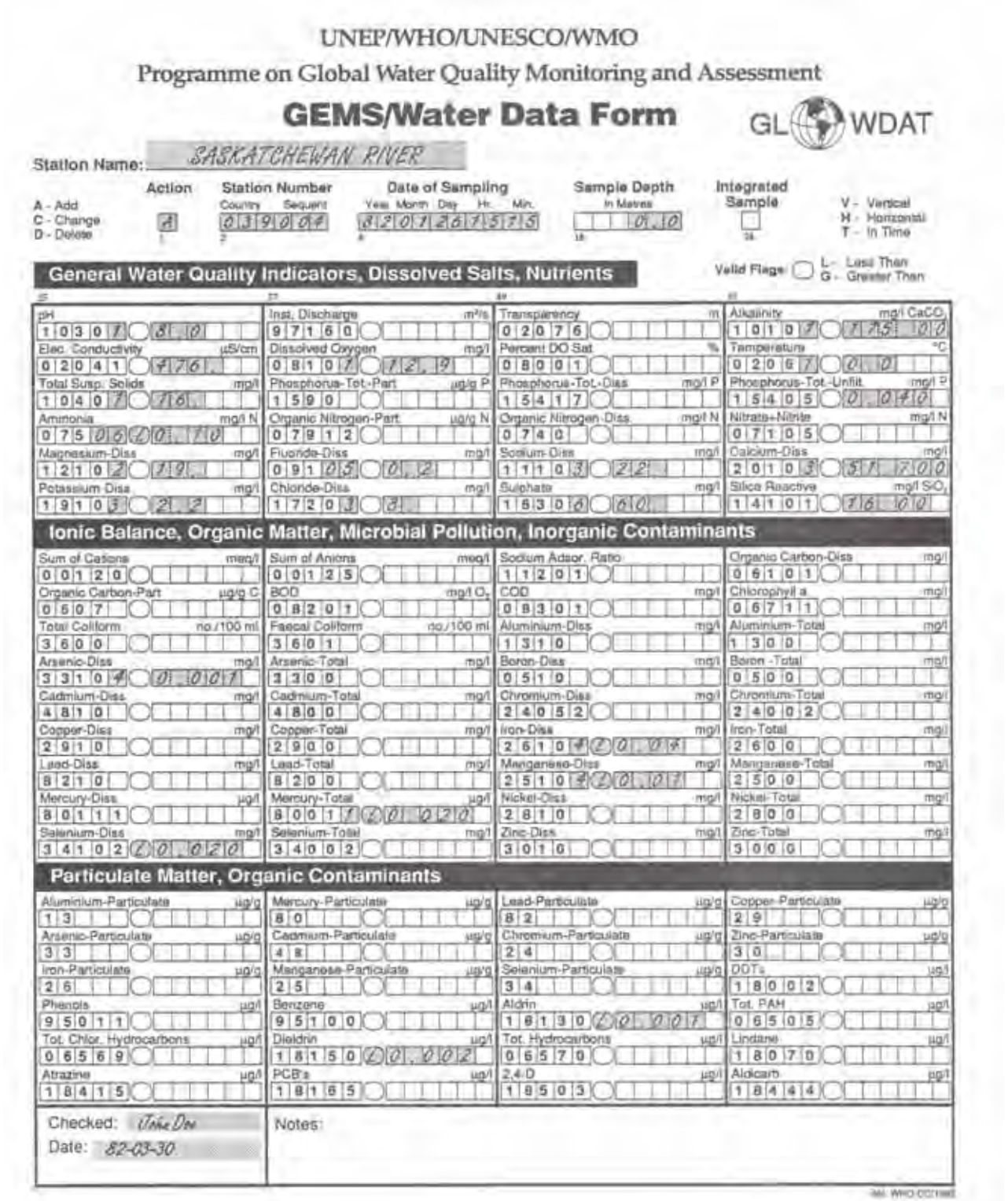
Aluminium-Particulate µg/g 13	Mercury-Particulate µg/g 80	Lead-Particulate µg/g 82	Copper-Particulate µg/g 29
Arsenic-Particulate µg/g 33	Cadmium-Particulate µg/g 48	Chromium-Particulate µg/g 24	Zinc-Particulate µg/g 30
Iron-Particulate µg/g 26	Manganese-Particulate µg/g 25	Selenium-Particulate µg/g 34	DDTs µg/l 18002
Phenols µg/l 95011	Benzene µg/l 95100	Aldrin µg/l 18130	Tot. PAH µg/l 06505
Tot. Chlor. Hydrocarbons µg/l 06569	Dieldrin µg/l 18150	Tot. Hydrocarbons µg/l 06570	Lindane µg/l 18070
Atrazine µg/l 18415	PCB's µg/l 18165	2,4-D µg/l 18503	Aldicarb µg/l 18444

Checked:
Date:

Notes:

Ref. WHO-CC/1992

Fig. 4



UNEP/WHO/UNESCO/WMO

Programme on Global Water Quality Monitoring and Assessment

GEMS/Water Data Form

GLOWDAT

Station Name: SASKATCHEWAN RIVER

Action: A - Add, C - Change, D - Delete → A

Station Number: Country 039 Sequent 0005

Date of Sampling: Year Month Day Hr. Min. → 82 07 26 15 15

Sample Depth in Metres: 0.10

Integrated Sample: ☐

V - Vertical, H - Horizontal, T - In Time

Valid Flags: ☐ L - Less Than, G - Greater Than

General Water Quality Indicators, Dissolved Salts, Nutrients

pH 1030 1 8.0	Inst. Discharge m³/s 9716 0	Transparency m 0207 6	Alkalinity mg/l CaCO₃ 1010 1 175.00
Elec. Conductivity µS/cm 0204 1 176.	Dissolved Oxygen mg/l 0810 1 12.9	Percent DO Sat. % 0800 1	Temperature °C 0206 7 0.0
Total Susp. Solids mg/l 1040 1 716.	Phosphorus-Tot.-Part µg/g P 1590	Phosphorus-Tot.-Diss mg/l P 1541 7	Phosphorus-Tot.-Unfilt. mg/l P 1540 5 0.0700
Ammonia mg/l N 0755 06 0.710	Organic Nitrogen-Part. µg/g N 0781 2	Organic Nitrogen-Diss. mg/l N 0740	Nitrate+Nitrite mg/l N 0710 5
Magnesium-Diss mg/l 1210 2 19.1	Fluoride-Diss mg/l 0910 5 0.2	Sodium-Diss mg/l 1110 3 21.2	Calcium-Diss mg/l 2010 3 51.700
Potassium-Diss mg/l 1910 3 2.2	Chloride-Diss mg/l 1720 3 8	Sulphate mg/l 1630 4 60	Silica Reactive mg/l SiO_2 1410 1 16.00

Ionic Balance, Organic Matter, Microbial Pollution, Inorganic Contaminants

Sum of Cations meq/l 0012 0	Sum of Anions meq/l 0012 5	Sodium Adsor. Ratio 1120 1	Organic Carbon-Diss mg/l 0610 1
Organic Carbon-Part µg/g C 0607	BOD mg/l O_2 0820 1	COD mg/l 0830 1	Chlorophyll a mg/l 0671 1
Total Coliform no./100 ml 3600	Faecal Coliform no./100 ml 3601	Aluminium-Diss mg/l 1310	Aluminium-Total mg/l 1300
Arsenic-Diss mg/l 3310 4 0.0001	Arsenic-Total mg/l 3300	Boron-Diss mg/l 0510	Boron -Total mg/l 0500
Cadmium-Diss mg/l 4810	Cadmium-Total mg/l 4800	Chromium-Diss mg/l 2405 2	Chromium-Total mg/l 2400 2
Copper-Diss mg/l 2910	Copper-Total mg/l 2900	Iron-Diss mg/l 2610 4 0.04	Iron-Total mg/l 2600
Lead-Diss mg/l 8210	Lead-Total mg/l 8200	Manganese-Diss mg/l 2510 4 0.07	Manganese-Total mg/l 2500
Mercury-Diss µg/l 8011 1 0.020	Mercury-Total µg/l 8001 1 0.020	Nickel-Diss mg/l 2810	Nickel-Total mg/l 2800
Selenium-Diss mg/l 3410 2 0.020	Selenium-Total mg/l 3400 2	Zinc-Diss mg/l 3010	Zinc-Total mg/l 3000

Particulate Matter, Organic Contaminants

Aluminium-Particulate µg/g 13	Mercury-Particulate µg/g 80	Lead-Particulate µg/g 82	Copper-Particulate µg/g 29
Arsenic-Particulate µg/g 33	Cadmium-Particulate µg/g 48	Chromium-Particulate µg/g 24	Zinc-Particulate µg/g 30
Iron-Particulate µg/g 26	Manganese-Particulate µg/g 25	Selenium-Particulate µg/g 34	DDTs µg/l 1800 2
Phenols µg/l 9501 1	Benzene µg/l 9510 0	Aldrin µg/l 1613 0 0.007	Tot. PAH µg/l 0650 5
Tot. Chlor. Hydrocarbons µg/l 0656 9	Dieldrin µg/l 1815 0 0.002	Tot. Hydrocarbons µg/l 0657 0	Lindane µg/l 1807 0
Atrazine µg/l 1841 5	PCB's µg/l 1816 5	2,4-D µg/l 1950 3	Aldicarb µg/l 1844 4

Checked: Mike Day

Date: 82-03-30

Notes:

3.1 Quality Control Error Listing

As one stage in the verification process each analytical result submitted to GLOWDAT will be tested against pre-assigned limits for reasonableness. In addition, a series of logical checks will be performed. These computer tests are designed primarily to pick up gross data translation errors and do not relieve the local laboratory or the National and Regional Centre of their responsibility for validating data before submitting them to the computer system.

The Quality Control Error Listings are produced whenever errors are detected by the quality control logic during input of data to the computer system. Minor errors such as data entry errors will be corrected where possible at the WHO/CC Global Data Centre using the mandatory source data forms which are to be mailed separately from any computer readable media submitted. Major errors are referred back to the Regions or National Centres for correction immediately.

3.2 Inventories of Station, Data and Variables

3.2.1 Station Inventory - a listing which provides a complete tabulation of information about any or all of the monitoring sites in the global network. This tabulation contains all the indicative and descriptive information stored in GLOWDAT about each monitoring site. This information was originally submitted on the Station Forms and provides a current inventory of network stations. A sample tabulation is provided in Figure 5.

3.2.2 Data Inventory - a computer listing which can be conditioned to show the number and types of variables measured at a station, in a country, a region or the entire network. An example is provided in Figure 6.

3.2.3 Variable Inventory - a listing which provides a complete tabulation of all the variable names together with a description of the GLOWDAT codes corresponding to particular analytical methods, the appropriate units and references for each method (Appendix IV).

3.3 Detailed Data Listing

The Detailed Data Listing provides a chronological record of monitoring data from a particular station for a specified time period. Each report will normally include all variables from the beginning of the calendar year.

On request, time periods may be specified, variables may be selected and ordered on the page and the report can be generated for classes of stations (e.g., all river stations in a country). An example of the Detailed Data Listing is given in Figure 7.

3.4 Summary Data Listing

(A) The Summary Data Listing provides a statistical overview of the data collected at a particular station during a specified time interval. It provides, for each variable measured, the abbreviated name, the code, the units, the number of 'less than detectable limit' values (L-Values), the number of 'greater than measurable limit' values (G-Values), and the number of unflagged values. The statistical information that is normally provided includes the unflagged values, the G-Values and L-Values. The value used for the G and L flagged values is the value that was entered on the data sheet. An example of the Summary Data Listing is shown in Figure 8.

(B) A further statistical summary by variable is exemplified in Figure 9.

3.5 Mass Loading Report

The values displayed on the mass loading report are calculated by multiplying the instantaneous concentration by the instantaneous discharge values and then reporting the results, in kg/sec. The format of the report is the same as the detailed listing. It is produced for river stations only. A sample report is shown as Figure 10.

3.6 Data Reporting Status

This report provides the status of the data contained in the data base. For each station, the report gives the minimum and maximum sampling date along with the number of variable values. A sample of this report is shown in Figure 11.

3.7 Mean Summary by Year

This report provides the mean and number of observations by year for the variable and stations requested. A sample of this report is shown in Figure 12.

3.8 Percentile Summary by Year

This report provides the 1st, 10th, 25th, 50th, 75th, 90th and 99th percentile by year for the stations selected. A sample of this report is shown in Figure 13.

3.9 Percentile Summary2

This report provides the number of observations, minimum and maximum values, median, the 25th and 75th percentiles for both the year requested and the total period of record. A sample of this report is shown in Figure 14.

It is expected that other forms of output may become desirable during the course of the monitoring program. The flexible nature of GLOWDAT makes it possible to implement new reports. Requests for variations on the established data output can be made if necessary.

Fig. 5

GLOBAL WATER QUALITY MONITORING - STATION INVENTORY
****

STATION NAME - KAPTAI LAKE
COUNTRY - **BANGLADESH**
DATE OPENED -
REGIONAL CENTRE - ***SEAA***
COLLECTION AGENCY - 13602
WMO CODE -
STATION TYPE - IMPACT

STATION NUMBER - 136001
OCTANT - 2
LATITUDE - 22/29/30
LONGITUDE - 092/13/45
WATER LEVEL (M)- 9999.9
AVG. DEPTH (M) - 9999.9
WATER TYPE - LAKE

RETENTION (YRS) - 1.0
AREA OF WATERSHED (KM**2) -

MAX. DEPTH (M) -
AREA (KM**2) - 800.0
VOLUME (KM**3) -

NARRATIVE
IN OUTLET DOWNSTREAM OF DAM

STATION NAME - LOWER GANGES RIVER (PADHA)
COUNTRY - **BANGLADESH**
DATE OPENED -
REGIONAL CENTRE - ***SEAA***
COLLECTION AGENCY - 13601
WMO CODE -
STATION TYPE - BASELINE

STATION NUMBER - 136002
OCTANT - 3
LATITUDE - 24/05/00
LONGITUDE - 089/02/00
WATER LEVEL (M)- 9999.9
AVG. DEPTH (M) - 9999.9
WATER TYPE - RIVER

UPSTREAM BASIN AREA (KM**2) - 846900
AREA UPSTREAM OF TIDAL LIMIT (KM**2)-

RIVER WIDTH (M) - 980.0
DISCHARGE(M**3/SEC)- 50000

NARRATIVE
750 M UPSTREAM HARDINGE BRIDGE

STATION NAME - BRAHMAPUTRA RIVER
COUNTRY - **BANGLADESH**
DATE OPENED -
REGIONAL CENTRE - ***SEAA***
COLLECTION AGENCY - 13601
WMO CODE -
STATION TYPE - IMPACT

STATION NUMBER - 136003
OCTANT - 3
LATITUDE - 25/11/00
LONGITUDE - 089/40/00
WATER LEVEL (M)- 9999.9
AVG. DEPTH (M) - 9999.9
WATER TYPE - RIVER

UPSTREAM BASIN AREA (KM**2) - 536000
AREA UPSTREAM OF TIDAL LIMIT (KM**2)-

RIVER WIDTH (M) - 4500.0
DISCHARGE(M**3/SEC)- 19000

NARRATIVE
NEAR BAHADURABAD FERRYGHAT

STATION NAME - MEGHNA RIVER
COUNTRY - **BANGLADESH**
DATE OPENED - 1979-07-01
REGIONAL CENTRE - ***SEAA***
COLLECTION AGENCY - 13603
WMO CODE -
STATION TYPE -

STATION NUMBER - 136004
OCTANT - 2
LATITUDE - 24/02/15
LONGITUDE - 090/59/30
WATER LEVEL (M)- 7.0
AVG. DEPTH (M) - 30.0
WATER TYPE - RIVER

UPSTREAM BASIN AREA (KM**2) - 64750
AREA UPSTREAM OF TIDAL LIMIT (KM**2)- 1295

RIVER WIDTH (M) - 850.4
DISCHARGE(M**3/SEC)- 14413

NARRATIVE
NEAR ASHUGANG FERTILIZER FACTORY 100 METER UPSTREAM OF THE FACTORY
DISCHARGE POINT

Fig. 6

GLOWDAT GLOBAL WATER QUALITY MONITORING - DATA INVENTORY

STATION - SASKATCHEWAN RIVER STATION NO. 039004 DEPTH(M) 5.0
COUNTRY - CANADA ELEVATION(M) 258.0
LOCATION- OCT. 1 LAT. 53/50/30 LONG. 101/20/06 WATER TYPE RIVER
REGIONAL CENTRE - AMRA

CODE	VARIABLE	1979	1980	1981	1982
		JFMAMJJASOND	JFMAMJJASOND	JFMAMJJASOND	JFMAMJJASOND
02041	ELEC COND	11111.111111	111.11111111	111111111111	111.111...11
02061	TEMP	11111.111111	111.11111111	111111111111	111.111...11
05105	B DISS	11111.111111	111.11111111	111111111111	111.111...11
06510	PAH	1...1.111111	111.11111111	111111111111	111.111.....
06532	PHENOLS	111.1..11111	111.11111111	111111111111	111.111...11
06606	CN	11111.111111	111.11111111	111111111111	111.111...11
06711	CHLORA A	111...111111	111.....	.....	.....
07105	N03NO2	11111.111111	111.11111111	111111111111	111.111...11
07506	NH3	.....	.....	...11.111111	111.111...11
08101	DISS O2	.....	111.11111111	111111111111	111.111...11
08201	B.O.D.	111.....	.....	.....	.....
09105	F DISS	11111.111111	111.11111111	111111111111	111.111...11
10101	ALK TOT	11111.111111	111.11111111	111111111111	111.111...11
10301	PH	11111.111111	111.11111111	111111111111	111.111...11
10401	SUSP SOL - 105	11111.111111	111.11111111	111111111111	111.111...11
11103	NA DISS	11111.111111	111.11111111	111111111111	111.111...11
12102	MG DISS	11111.111111	111.11111111	111111111111	111.111...11
14101	SI REAC	11111.111111	111.11111111	111111111111	.11.111...11
15103	P DISS	11111.111111	111.11111111	111111111111	111.111...11
15255	P ORTHO DISS	.....	.....	...111111111	111.111...11
15405	P TOTAL	11111.111111	111.11111111	111111111111	111.111...11
15901	P PART	.....	.....	11.....1....	......1...11
16306	SULPHATE	11111.111111	111.11111111	111111111111	111.111...11
17203	CL DISS	11111.111111	111.11111111	111111111111	111.111...11
18000	P,P-DDT	11111.111111	.11.11111111	111111111111	111.111...11
18005	O,P-DDT	11111.111111	.11.11111111	111111111111	111.111...11
18010	P,P-DDD	11111.111111	.11.11111111	111111111111	111.111...11
18020	P,P-DDE	11111.111111	.11.11111111	111111111111	111.111...11
18075	ALPHA-BHC	11111.111111	.11.11111111	111111111111	111.111...11
18125	MIREX	11111.111111	.11.11111111	111111111111	111.111...11
18130	ALDRIN	11111.111111	.11.11111111	111111111111	111.111...11
18140	ENDRIN	11111.111111	.11.11111111	111111111111	111.111...11
18150	DIELDRIN	11111.111111	.11.11111111	111111111111	111.111...11
19103	K DISS	11111.111111	111.11111111	111111111111	111.111...11
20103	CA DISS	11111.111111	111.11111111	111111111111	111.111...11
25104	MN DISS	......1.....	11111111	111111111111	111.111...11
26104	FE DISS	......1.....	11111111	111111111111	111.111...11

Fig. 7

GLOWDAT GLOBAL WATER QUALITY MONITORING - DATA LISTING

STATION - SASKATCHEWAN RIVER STATION NO. 039004 DEPTH(M) 5.0
COUNTRY - CANADA ELEVATION(M) 258.0
LOCATION- OCT. 1 LAT. 53/50/30 LONG. 101/20/06 WATER TYPE RIVER
REGIONAL CENTRE - AMRA

DATE	TIME	DEPTH	ELEC COND	TEMP	B DISS	PAH	PHENOLS	CN	NO3NO2	NH3	DISS O2	F DISS
			02041	02061	05105	06510	06532	06606	07105	07506	08101	09105
YR-MO-DY		METRES	USIE/CM	DEG C	MG/L B	UG/L	MG/L	MG/L CN	MG/L N	MG/L N	MG/L O2	MG/L F
82-01-26	1515	.0	476.	.0	.1	1.000L	.001	.003	.23	.10L	12.9	.2
82-02-23	1430	.0	437.	.0	.1	1.000L	.002	.001	.35	.13	11.8	.2
82-03-23	1330	.0	425.	.0	.1	1.000L	.001L	.004	.37	.20	14.2	.2
82-05-26	1420	.0	288.	17.0	.0	1.000L	.002	.001	.01	.10L	11.4	.1
82-06-15	1615	.0	283.	17.5	.1	1.000L	.002	.002	.11	.10L	9.2	.1
82-07-13	1500	.0	385.	20.0	.1	1.000L	.001	.003	.09	.10L	7.2	.1
82-11-23	1430	.0	395.	.0	.1	--	.002	.002	.02	.10L	13.8	.2
82-12-08	1500	.0	379.	.5	.1	--	.001	.001L	.03	.10	13.0	.1
83-01-25	1430	.0	448.	.0	.1	--	.002	.002	.21	.20	10.6	.1
83-03-02	1820	.0	414.	.0	.1	--	.005	.002	.33	.10L	9.4	.2
83-03-30	1445	.0	403.	1.0	.1	--	.002	.004	.31	.10L	10.3	.1
83-05-26	1441	.0	301.	8.0	.1	--	.004	.003	.01	.10L	10.2	.1
83-06-14	1400	.0	340.	15.0	.1	--	.007	.002	.01L	.10L	7.5	.1
83-07-19	1450	.0	360.	22.0	.1	--	.007	.003	.04	.10L	7.5	.1
83-08-23	1620	.0	313.	17.0	.1	--	.006	.005	.05	.10L	8.4	.2
83-09-20	1837	.0	338.	7.0	.1	--	.003	.004	.06	.10L	10.6	.1
83-10-18	1534	.0	345.	4.0	.1	--	.002	.003	.08	.10L	12.0	.1
83-12-06	1350	.0	360.	.2	.1	--	--	.002	.06	.10L	13.5	.1

DATE	TIME	DEPTH	PH	SUSP SOL 105 DEG	NA DISS	MG DISS	SI REAC	P DISS	P ORTHO DISS	P TOTAL	P PART	SULPHATE
			10301	10401	11103	12102	14101	15103	15255	15405	15901	16306
YR-MO-DY		METRES	PH UNITS	MG/L	MG/L NA	MG/L MG	MG/L	MG/L P	MG/L P	MG/L P	MG/L P	MG/L SO4
82-01-26	1515	.0	8.0	16.	22.	19.	--	.016	.010	.043	--	60.
82-02-23	1430	.0	8.1	12.	15.	17.	3.60	.005	.003L	.010	--	58.
82-03-23	1330	.0	7.8	10.	18.	13.	3.80	.015	.014	.030	--	56.
82-05-26	1420	.0	8.4	50.	12.	12.	.40	.009	.003L	.060	--	34.
82-06-15	1615	.0	8.1	66.	13.	11.	1.20	.014	.003L	.070	--	36.
82-07-13	1500	.0	7.8	175.	16.	13.	2.00	.010	.003L	.130	.120	48.
82-11-23	1430	.0	8.1	11.	17.	17.	.80	.010	.003L	.023	.013	59.
82-12-08	1500	.0	8.0	11.	17.	16.	.80	.009	.003L	.026	.017	52.
83-01-25	1430	.0	8.1	21.	20.	18.	2.50	.013	.006	.031	.018	56.
83-03-02	1820	.0	8.0	16.	16.	17.	3.20	.018	.009	.040	.022	52.
83-03-30	1445	.0	8.0	5.	16.	16.	3.20	--	--	.025	--	46.

Fig. 8

GLOBAL WATER QUALITY MONITORING - STATISTICAL SUMMARY BY STATION

STATION - SASKATCHEWAN RIVER STATION NO. 039004 DEPTH(M) 5.0
COUNTRY - CANADA ELEVATION(M) 258.0
LOCATION - OCT. 1 LAT. 53/50/30 LONG. 101/20/06 WATER TYPE RIVER
REGIONAL CENTRE - AMRA

PERIOD REQUESTED FROM - 79-01-01 TO 89-12-31
PERIOD OF RECORD FROM - 79-01-17 TO 88-03-16

STATISTICS INCLUDE ALL FLAGGED DATA AS REPORTED

	ELEC COND 02041 USIE/CM	TEMP 02061 DEG C	B DISS 05105 MG/L B	PAH 06510 UG/L	PHENOLS 06532 MG/L	CN 06606 MG/L CN	CHLORO A 06711 MG/L	NO3NO2 07105 MG/L N	NH3 07506 MG/L N
NO. OF L-FLAGGED VALUES	0	0	0	37	9	2	2	7	39
NO. OF G-FLAGGED VALUES	0	0	0	0	0	0	0	0	0
NO. OF UNFLAGGED VALUES	90	91	92	0	51	61	10	56	17
MEAN	374.	11.5	.1	1.000	.002	.003	.0043	.12	.10
MINIMUM	240.	.0	.0	1.000	.001	.001	.0010	.01	.05
DATE OF MINIMUM	79-04-25	81-12-15	80-05-07	81-07-29	80-02-13	81-10-21	79-01-17	83-06-14	86-06-17
10TH PERCENTILE	301.	.0	.0	1.000	.001	.001	.0010	.01	.05
MEDIAN	370.	10.4	.1	1.000	.002	.003	.0040	.06	.10
90TH PERCENTILE	448.	25.0	.1	1.000	.005	.005	.0074	.32	.11
MAXIMUM	498.	25.0	.1	1.000	.007	.009	.0110	.41	.20
DATE OF MAXIMUM	88-02-16	88-03-16	80-02-13	80-11-26	81-06-16	81-07-29	80-03-26	84-03-20	84-03-20
STANDARD DEVIATION	56.	10.5	.0	.000	.002	.002	.0033	.12	.03

	F DISS 09105 MG/L F	F DISS 09106 MG/L F	ALK TOT 10101 MG/L	PH 10301 PH UNITS	SUSP SOL 105 DEG 10401 MG/L	FIX SUSP SOLIDS 10501 MG/L	NA DISS 11103 MG/L NA	MG DISS 12102 MG/L MG	AL DISS 13102 MG/L AL
NO. OF L-FLAGGED VALUES	0	0	0	0	1	0	0	0	36
NO. OF G-FLAGGED VALUES	0	0	0	0	0	0	0	0	0
NO. OF UNFLAGGED VALUES	52	14	63	91	91	24	89	91	0
MEAN	.1	.1	133.09	7.9	45.	41.	16.	15.	.100
MINIMUM	.1	.1	7.50	7.1	1.	5.	10.	10.	.100
DATE OF MINIMUM	83-03-30	85-08-19	84-08-15	80-02-13	79-02-21	84-11-21	85-05-14	84-05-08	85-06-18
10TH PERCENTILE	.1	.1	110.00	7.5	7.	8.	12.	12.	.100
MEDIAN	.1	.1	130.00	7.9	24.	33.	16.	14.	.100
90TH PERCENTILE	.2	.2	164.00	8.2	108.	69.	20.	18.	.100
MAXIMUM	.2	.2	176.00	8.4	175.	190.	23.	20.	.100
DATE OF MAXIMUM	79-09-20	86-02-25	79-01-17	82-05-26	82-07-13	85-04-24	80-01-24	79-01-17	86-02-25
STANDARD DEVIATION	.0	.0	25.72	.3	43.	39.	3.	2.	.000

Fig. 9

GLOWDAT GLOBAL WATER QUALITY MONITORING - STATISTICAL SUMMARY BY VARIABLE

VARIABLE 02041 ELEC COND USIE/CM

FOR RIVER STATIONS PERIOD REQUESTED FROM 80-01-01 TO 90-12-31

REGIONAL CENTRE AMRA

STATISTICS INCLUDE ALL FLAGGED DATA
INCLUDING DATA FLAGGED AS LESS THAN DETECTION LIMIT

COUNTRY NAME	STATION NAME	VALUES TOTAL	VALUES UNFLD	MEAN	MINIMUM	10TH PERCENT	MEDIAN	90TH PERCENT	MAXIMUM	S.D.
ARGENTINA	RIO DE LA PLATA BUENOS AIRES	125	125	181.	10.	127.	170.	251.	307.	49.
	RIO PARAGUAY Y PUERTO BERME JO	27	27	104.	10.	13.	95.	183.	401.	85.
	RIO PARANA CORRIENTES	75	75	33.	3.	4.	31.	58.	77.	22.
	RIO PARANA PUERTO LIBERTAD	30	30	48.	22.	25.	51.	70.	78.	16.
	RIO PARANA ROSARIO	14	14	147.	114.	116.	144.	174.	220.	29.
BRAZIL	RIB. SERRA AZUL-FAZ SOBRADINHO	40	40	32.	21.	25.	30.	41.	56.	7.
	RIO CAPIBARIBE	38	38	702.	111.	147.	700.	1154.	1350.	326.
	RIO GUANDU-TOMADA D'AGUA	87	87	70.	31.	52.	63.	78.	514.	60.
	RIO JACUI.JA 042	20	20	45.	32.	34.	42.	60.	90.	13.
	RIO PARAIBA DO SUL-APARECIDA	59	59	55.	25.	45.	55.	65.	75.	9.
	RIO PARAIBA DO SUL-BARRA MANSA	94	94	61.	42.	46.	57.	70.	270.	25.
	RIO SAO FRANCISCO-PETROLANDIA	47	47	77.	11.	18.	64.	97.	650.	89.
	RIO VELHAS - HONORIO BICALHO	48	48	42.	19.	30.	42.	56.	63.	10.
CANADA	CHURCHILL RIVER	50	50	84.	57.	60.	77.	111.	139.	22.
	FRASER RIVER	69	69	126.	5.	79.	124.	160.	358.	36.
	GREAT BEAR RIVER	29	29	157.	90.	109.	156.	180.	206.	25.
	MACKENZIE RIVER	65	65	264.	160.	217.	256.	310.	352.	39.
	NELSON RIVER	15	15	271.	168.	179.	248.	341.	401.	66.
	ROSEAU RIVER	59	59	468.	250.	310.	410.	664.	990.	164.
	SAINT JOHN RIVER	33	33	63.	30.	41.	64.	91.	90.	14.
	SASKATCHEWAN RIVER	79	79	376.	274.	313.	369.	448.	498.	54.
	SKEENA RIVER	20	20	96.	58.	59.	91.	130.	136.	20.
	SLAVE RIVER	30	30	205.	160.	166.	200.	236.	263.	26.
	ST. LAWRENCE RIVER	27	27	291.	176.	248.	301.	315.	320.	32.
	STIKINE RIVER	15	15	115.	90.	94.	113.	134.	151.	17.
CHILE	RIO MAIPO EN EL MANZANO	114	114	1003.	585.	709.	1003.	1318.	1461.	215.
	RIO MAPOCHO EN LOS ALMENDROS	117	117	247.	137.	166.	232.	327.	676.	75.
COLOMBIA	RIO CAUCA JUANCHITO	39	39	105.	73.	80.	104.	127.	181.	21.
	RIO MEDELLIN MACHADO	12	12	129.	0.	0.	95.	293.	338.	140.
ECUADOR	RIO DAULE	10	10	53.	13.	13.	17.	131.	145.	56.
	RIO SAN PEDRO	42	42	99.	29.	33.	47.	333.	539.	129.
GUATEMALA	RIO LOS PLATANOS	6	6	363.	150.		385.		510.	128.
	RIO PIXCAYA	13	13	149.	130.	132.	145.	166.	178.	13.
	RIO TXEPELA	3	3	68.	40.				85.	

Fig. 10

GLOWDAT GLOBAL WATER QUALITY MONITORING - INSTANTANEOUS MASS LOADINGS

STATION - MISSISSIPPI RIVER STATION NO. 028001 DEPTH(M) 14.0
COUNTRY - UNITED STATES ELEVATION(M) 21.0
LOCATION- OCT. 1 LAT. 32/18/45 LONG. 90/54/25 WATER TYPE RIVER
REGIONAL CENTRE - AMRA

NOTE - 1) MASS LOADINGS ARE CALCULATED BY MULTIPYLING INSTANTANEOUS CONCENTRATION BY INSTANTANEOUS DISCHARGE
2) CALCULATIONS USE L-FLAGGED DATA AS ZERO VALUES AND G-FLAGGED DATA AS REPORTED

DATE	TIME	DEPTH	LI DISS	TOC	N KJEL	NO3NO2	DISS O2	F DISS	MG DISS	CL DISS	ALDRIN
YR-MO-DY		METRES	03101 KG/SEC	06001 KG/SEC	07004 KG/SEC	07105 KG/SEC	08102 KG/SEC	09106 KG/SEC	12102 KG/SEC	17203 KG/SEC	18130 KG/SEC
79-01-03	1500	.0	--	--	3.56E+01	2.61E+01	2.71E+02	2.38E+00	1.90E+02	3.33E+02	--
79-02-07	1230	.0	--	7.81E+01	1.82E+01	2.60E+01	3.44E+02	2.60E+00	1.82E+02	3.38E+02	--
79-03-06	1300	.0	--	2.32E+02	3.64E+01	3.31E+01	3.98E+02	3.31E+00	2.32E+02	4.64E+02	0.00E+00
79-04-03	1230	.0	--	--	2.78E+01	7.53E+01	3.65E+02	3.96E+00	3.57E+02	7.53E+02	0.00E+00
79-05-01	1200	.0	--	5.64E+02	3.29E+01	8.93E+01	3.76E+02	4.70E+00	4.23E+02	6.11E+02	0.00E+00
79-06-05	1300	.0	--	1.58E+02	1.58E+01	3.69E+01	1.74E+02	5.27E+00	2.90E+02	5.00E+02	0.00E+00
79-07-03	1130	.0	--	--	1.23E+01	2.64E+01	1.14E+02	3.52E+00	2.29E+02	3.87E+02	--
79-08-07	1200	.0	--	1.69E+02	1.48E+01	2.75E+01	1.27E+02	4.23E+00	1.90E+02	4.02E+02	--
79-09-25	1330	.0	--	--	--	--	1.49E+02	--	--	--	--
79-10-02	1100	.0	--	--	1.23E+01	2.00E+01	1.51E+02	4.00E+00	1.84E+02	2.25E+02	--
79-11-06	1330	.0	--	3.25E+01	4.33E+00	1.02E+01	8.87E+01	2.16E+00	1.51E+02	1.95E+02	--
79-12-11	1200	.0	--	1.54E+02	1.79E+01	3.33E+01	2.82E+02	5.13E+00	2.56E+02	5.89E+02	--
80-01-08	1130	.0	--	--	2.43E+01	3.09E+01	2.56E+02	4.42E+00	2.43E+02	3.09E+02	--
80-02-05	1100	.0	--	1.31E+02	1.64E+01	2.29E+01	2.11E+02	3.27E+00	1.80E+02	2.46E+02	--
80-04-04	1300	.0	--	--	1.44E+01	5.04E+01	3.42E+02	7.19E+00	3.24E+02	6.11E+02	--
80-04-28	1300	.0	--	1.69E+02	2.36E+01	5.06E+01	2.59E+02	6.74E+00	3.37E+02	5.39E+02	--
80-06-03	1300	.0	--	3.51E+01	7.02E+00	1.76E+01	1.47E+02	3.51E+00	1.58E+02	3.69E+02	--
80-06-27	1100	.0	--	--	1.64E+01	4.43E+01	1.33E+02	4.93E+00	2.14E+02	4.60E+02	--
80-07-29	1300	.0	--	6.44E+01	5.52E+00	1.29E+01	6.17E+01	1.84E+00	1.20E+02	1.66E+02	--
80-08-26	1300	.0	--	5.98E+01	2.39E+00	1.11E+01	9.20E+01	3.59E+00	1.55E+02	2.39E+02	--
80-10-08	1100	.0	--	--	4.28E+00	1.03E+01	6.76E+01	2.57E+00	1.28E+02	1.54E+02	--
80-11-03	1300	.0	--	4.13E+01	4.13E+00	6.61E+00	7.02E+01	1.38E+00	1.03E+02	1.24E+02	--
80-12-01	1330	.0	--	4.50E+01	5.40E+00	8.20E+00	1.13E+02	1.80E+00	1.17E+02	1.98E+02	--
81-01-13	1200	.0	--	--	2.49E+00	6.98E+00	6.73E+01	9.97E-01	8.97E+01	1.20E+02	--
81-02-03	1400	.0	--	2.72E+01	4.35E+00	5.44E+00	6.52E+01	1.63E+00	5.98E+01	1.20E+02	--
81-02-25	1500	.0	--	4.45E+01	7.79E+00	1.11E+01	1.14E+02	2.23E+00	1.11E+02	2.56E+02	--
81-03-25	1100	.0	--	--	6.62E+00	1.80E+01	8.99E+01	1.09E+00	1.14E+02	1.89E+02	--
81-04-28	1200	.0	--	1.58E+02	2.46E+01	3.69E+01	1.28E+02	3.52E+00	2.46E+02	3.17E+02	--
81-05-28	1200	.0	--	0.00E+00	2.41E+01	5.06E+01	1.64E+02	4.81E+00	2.65E+02	3.37E+02	--
81-06-24	1200	.0	--	--	1.49E+01	3.47E+01	1.54E+02	4.96E+00	2.23E+02	3.23E+02	--
81-07-29	1100	.0	--	1.03E+02	8.04E+00	2.65E+01	9.42E+01	2.95E+00	1.91E+02	2.21E+02	--
81-09-22	1200	.0	--	3.65E+01	4.56E+00	1.28E+01	7.30E+01	2.74E+00	1.37E+02	1.82E+02	--

Fig. 11

GLOBAL WATER QUALITY MONITORING – DATA REPORTING STATUS 2003-09-08

REGIONAL CENTRE EURA

COUNTRY NAME	STATION	STATION NAME	FIRST DATE SAMPLED	LAST DATE SAMPLED	NUMBER OF DATA POINTS
AUSTRIA	062001	ABWINDEN/ASTEN-DONAU R.	1995-01-11	1995-12-13	132
	062002	WOLFSTAHAL-DONAU RIVER	1995-01-12	1995-12-14	168
	062003	SPIELFELD-MUR. RIVER	1995-02-07	1996-01-25	40
	062004	LAVAMUND-DRAU RIVER	1995-02-29	1005-11-29	44
	062005	KUFSTEIN/ERL-INN RIVER	1995-01-23	1995-11-27	104
	062006	OBERNDORF-SALZACH RIVER	1995-02-16	1996-01-23	124
BELGIUM	051001	ESCAUT RIVER AT BLEHARIES	1978-01-19	1992-12-02	4609
	051002	MEUSE RIVER AT VISE			0
	051003	MEUSE RIVER AT HASTIERE			0
	051004	NICRAMOUT RESERVOIR			0
	051006	WATERLOO			0
	051007	WARNETON – LYS RIVER	1978-01-18	1992-12-03	4166
	051008	LEERS/NORD – ESPIERRE RIVER	1978-02-14	1992-12-04	3675
	051009	DOEL – SCHELDT RIVER	1978-02-08	1992-12-14	6750
	051010	BLEHARIES – SCHELDT RIVER	1979-02-01	1980-11-05	152
	051011	ERQUELINNES – SAMBRE RIVER	1978-01-19	1992-11-25	4014
	051012	HEER/AGIMONT – MEUSE RIVER	1978-01-25	1992-12-18	3750
	051013	LANAYE/TERNAAIEN – MEUSE RIVER	1978-01-04	1992-12-08	6460
	051014	MARTELANCE – SURE RIVER	1978-01-26	1992-12-18	3763
	051015	ZELZATE – GHENT/TERNEUZEN	1978-03-06	1992-12-17	4529
DENMARK	008001	NABY – SUSA RIVER	1979-01-17	1980-12-15	125
	008002	NR BROBY – ODENSE RIVER	1980-06-19	1996-12-19	734
	008003	TVILUM BRO – GUDENA RIVER	1979-02-07	1996-12-09	933
	008004	AHLERGARD – DKJERNA RIVER	1979-01-22	1980-12-16	315
	008005	HOLLOSE MOLLE – SUSA RIVER	1990-01-04	1996-12-17	810
	008006	AHLERGARD – SKJERNA RIVER	1990-01-04	1996-12-11	418
FINLAND	065001	TORNIONJOKI RIVER STN 14100	1979-03-08	19998-09-09	1263
	065002	KYMIJOKI STN 5610	1979-03-06	1998-08-31	2630
	065003	KALKKINEN STN 4800	1979-01-31	1998-08-11	2317
	065005	YLI-KITKA LAKE STN 144	1979-03-26	1998-08-25	2545
	065006	LAKE INARI 151	1988-03-15	1998-07-21	2260
	065007	RAASAKA – IIJOKI RIVER	1993-01-15	1995-12-15	179
	065008	ISOHAARA 14000 – KEMIJOKI RIVER	1993-01-15	1995-12-15	209
	065009	KOJO 35 PORI-TRE-KOKRMAENJOKI	1993-01-15	1995-12-15	268

Fig. 12

GLOWDAT GLOBAL WATER QUALITY MONITORING - STATION MEANS BY YEAR

VARIABLE 02061 TEMP DEG C
02062 TEMP DEG C

STATISTICS INCLUDE ALL FLAGGED DATA AS REPORTED

STATION NAME	STATION NUMBER	1979 NUMBER	1979 MEAN	1980 NUMBER	1980 MEAN	1981 NUMBER	1981 MEAN
MACKENZIE RIVER	039001	2	12.8	9	8.0	10	4.8
NELSON RIVER	039002	-	-	-	-	-	-
ST. LAWRENCE RIVER	039003	-	-	-	-	3	12.7
SASKATCHEWAN RIVER	039004	11	5.6	11	6.3	12	7.8
SLAVE RIVER	039005	4	15.0	7	13.1	5	10.6
ROSEAU RIVER	039006	12	7.1	12	6.8	12	8.9
FRASER RIVER	039007	5	9.5	11	9.3	4	4.0
LAKE HURON	039008	-	-	-	-	-	-
GREAT BEAR RIVER	039009	3	5.2	8	3.1	5	2.7
LAKE ONTARIO MID LAKE	039010	54	6.0	22	3.7	456	7.1
SUPERIOR MID LAKE	039011	-	-	-	-	-	-
SAINT JOHN RIVER	039012	1	18.0	5	9.1	-	-

Fig. 13

GLOBAL WATER QUALITY MONITORING - STATISTICAL SUMMARY BY STATION

STATION - FRASER RIVER
COUNTRY - CANADA
LOCATION - OCT. 1 LAT. 49/23/15 LONG. 121/27/00
REGIONAL CENTRE - AMRA

STATION NO. 039007

DEPTH(M) 10.0
ELEVATION(M) 45.0
WATER TYPE RIVER

STATISTICS INCLUDE ALL FLAGGED DATA AS REPORTED

YEAR 1985

PARAMETER	UNITS	CODE	OBS	1%	10%	25%	50%	75%	90%	99%
ELEC COND	USIE/CM	02041	19	30.	106.	152.	155.	162.	165.	54.
TEMP	DEG C	03061	19	-.1	.0	.5	2.0	7.0	11.0	3.0
NO3NO2	MG/L N	07105	19	.01	.07	.10	.11	.12	.13	.03
F DISS	MG/L F	09105	19	.0	.0	.0	.1	.1	.1	.0
ALK TOT	MG/L	10101	19	8.62	43.50	59.60	60.70	63.20	64.30	13.69
PH	PH UNITS	10301	19	1.4	7.3	7.7	7.8	7.9	8.0	1.7
SUSP SOL - 105	MG/L	10401	12	2.	14.	20.	35.	69.	83.	12.
FIX SUSP SOLIDS	MG/L	10501	12	1.	11.	17.	29.	63.	71.	10.
NA DISS	MG/L NA	11103	19	0.	2.	4.	5.	5.	6.	1.
SI REAC	MG/L	14101	19	.40	4.60	6.40	6.50	6.70	6.90	1.49
P TOTAL	MG/L P	15405	19	.002	.013	.014	.025	.058	.096	.021
SULPHATE	M/L SO4	16306	19	1.	8.	10.	11.	12.	12.	3.
CL DISS	MG/L CL	17203	19	0.	2.	3.	4.	5.	5.	1.
K DISS	MG/L K	19103	19	.1	.6	.8	.8	.9	1.0	.2
CA DISS	MG/L CA	20101	19	3.040	15.600	19.800	20.600	21.600	21.900	4.599
MN TOTAL	MG/L MN	25004	18	.00	.01	.01	.02	.05	.08	.02
FE TOTAL	MG/L FE	26004	18	.00	.16	.27	.78	2.16	3.32	.71
CU TOTAL	MG/L CU	29005	18	.000	.002	.002	.004	.005	.009	.002
ZN TOTAL	MG/L ZN	30005	18	.000	.002	.002	.005	.011	.015	.004
CD TOTAL	MG/L CD	48002	18	.000	.001	.001	.001	.001	.001	.000
HG TOTAL	UG/L HG	80011	12	.003	.020	.020	.020	.020	.041	.007
PB TOTAL	MG/L PB	82002	18	.000	.001	.001	.001	.001	.003	.002
TEMP AIR	DEG C	97060	18	-.6	1.5	5.0	7.0	10.0	14.9	4.8

Fig. 14

GLOBAL WATER QUALITY MONITORING - STATISTICAL SUMMARY BY STATION

STATION - FRASER RIVER STATION NO. 039007 DEPTH(M) 10.0
COUNTRY - CANADA ELEVATION(M) 45.0
LOCATION - OCT. 1 LAT. 49/23/15 LONG. 121/27/00 WATER TYPE RIVER
REGIONAL CENTRE - AMRA

STATISTICS INCLUDE ALL FLAGGED DATA AS REPORTED

			YEAR 1985					PERIOD OF RECORD 79-07-17 TO 85-10-28					
PARAMETER	UNITS	CODE	OBS	MIN	MAX	MEDIAN	25%	75%	OBS	MIN	MAX	MEDIAN	25%	75%
ELEC COND	USIE/CM	02041	19	102.	258.	155.	152.	162.	74	5.	258.	125.	106.	152.
TEMP	DEG C	02061	19	-.5	17.0	2.0	.5	7.0	87	-.5	21.9	7.5	3.0	12.5
CN	MG/L CN	06606	0	----	----	----	----	----	1	.001	.001	----	----	----
NO3NO2	MG/L N	07105	19	.04	.13	.11	.10	.12	87	.00	.21	.09	.05	.12
F DISS	MG/L F	09105	19	.0	.1	.1	.0	.1	62	.0	.2	.1	.0	.1
F DISS	MG/L F	09106	0	----	----	----	----	----	25	.0	.1	.1	.1	.1
ALK TOT	MG/L	10101	19	43.10	65.20	61.60	59.60	63.20	87	24.00	65.20	51.30	45.20	58.40
PH	PH UNITS	10301	19	7.1	8.2	7.9	7.7	7.9	74	7.0	8.2	7.8	7.7	7.9
SUSP SOL 105	MG/L	10401	12	12.	85.	35.	20.	69.	70	2.	475.	37.	18.	75.
FIX SUSP SOLIDS	MG/L	10501	12	9.	72.	29.	17.	63.	47	2.	287.	32.	17.	67.
NA DISS	MG/L NA	11103	19	2.	6.	5.	4.	5.	87	1.	6.	3.	2.	4.
SI REAC	MG/L	14101	19	4.00	7.10	6.50	6.40	6.70	87	3.90	7.30	5.80	4.80	6.50
P TOTAL	MG/L P	15405	19	.011	.100	.028	.014	.058	61	.011	.502	.052	.020	.096
SULPHATE	MG/L SO4	16306	19	6.	13.	11.	10.	12.	87	4.	13.	8.	6.	10.
CL DISS	MG/L CL	17203	19	1.	5.	4.	3.	5.	87	1.	5.	2.	1.	3.
K DISS	MG/L K	19103	19	.6	1.0	.8	.8	.9	87	.4	1.0	.7	.6	.8
CA DISS	MG/L CA	20101	19	15.200	21.900	21.000	19.800	21.600	87	9.800	22.200	17.700	15.600	19.400
MN TOTAL	MG/L MN	25004	18	.01	.08	.02	.01	.05	59	.01	.30	.04	.02	.08
FE TOTAL	MG/L FE	26004	18	.02	3.54	.78	.27	2.16	59	.02	13.00	1.35	.61	3.25
CU TOTAL	MG/L CU	29005	18	.001	.008	.004	.002	.005	59	.001	.020	.004	.003	.007
ZN TOTAL	MG/L ZN	30005	18	.001	.021	.005	.002	.011	59	.001	.033	.005	.002	.010
CD TOTAL	MG/L CD	48002	18	.001	.001	.001	.001	.001	59	.001	.001	.001	.001	.001
HG TOTAL	UG/L HG	80011	12	.020	.050	.020	.020	.020	48	.020	.050	.020	.020	.020
PB TOTAL	MG/L PB	82002	18	.001	.009	.001	.001	.001	59	.001	.009	.001	.001	.002
TEMP-AIR	DEG C	97060	18	-3.0	24.0	7.0	5.0	10.0	61	-3.0	25.0	10.0	6.5	16.0
INST DIS CHG	M3/S	97160	0	----	----	----	----	----	36	538.0	8610.0	2095.0	1217.5	4392.5

APPENDIX I - Data Entry Instructions

General Instructions

1. Each form provides information for more than one line of input.
2. The small boxes indicate the record columns for data entry.
3. Enter all decimals as shown on the forms.
4. Each field must begin in the record column designated, and use one column for each box provided. For example, mean surface water level on the station form:

			1	0	.	2
22						

will be entered onto the file as ‘blank blank 1 0 . 2' beginning in column 22 and ending in column 27.

Similarly latitude:

	0	5		1	5		2	0
9								

will be entered as '0 5 1 5 2 0' starting in column 9 and ending in column 14.

Station Form

1. A record is provided for each line of input. The record number will be entered into column 1 of the appropriate line.
2. Only those records with coded data need be entered. For example, there must only be one of the records numbered 2, 3 and 4. Similarly, record 5, 6 and 7 may not all be required.
3. Duplicate columns 2-7 inclusive from Record No. 1 into each subsequent line prepared from the station form.

Data Form

1. Indicative information in columns 1-24 inclusive must be repeated in each line prepared from that data form.
2. Column 1 of each line will always contain an alphabetic character (A, C or D).
3. Duplicate columns 1-24 inclusive from Record No. 1 into each subsequent line prepared from the data form.
4. The order in which data sets are entered into the file is irrelevant.

APPENDIX II - Regional Centres and Geographical Regions

Regional Centre Codes		WHO Regional Centres
AFRA	Africa	AFRO/WHO P.O. Box No. 6 Brazzaville Congo Attention: PM2
AMRA	South and Central America	PAHO/WHO 525 Twenty-third Street, NW Washington, DC 20037 U.S.A. Attn: Environmental Health Program
EMRA	Eastern Mediterranean	EMRO/WHO P.O. Box 1517 Alexandria - 21511 Egypt Attn: Chief, Environmental Health
EURA	Europe	WHO/EURO 8 Scherfigsvei DK - 2100 Copenhagen Denmark Attn: Director, Promotion of Environmental Health
SEAA	South-East Asia	SEARO/WHO World Health House Indraprastha Estate Mahatma Gandhi Road New Delhi - 110002 India Attn: Chief, Environmental Health
WPRA	Western Pacific	PEPAS c/o The WHO Programme Coordinator P.O. Box 12550 50782 Kuala Lumpur Malaysia Attn: Director

Geographical Region Codes

AFRI	Africa	EURO	Europe
MIDD	Middle-East	NA	North America
ASIA	Asia	CASA	Central and South America
OCEA	Oceania	CARI	the Caribbean

APPENDIX III - Country Codes

Numerical Order

COUNTRY CODE	DATE OF UN ADMISSION	COUNTRY NAME
001	OCT. 24,1945	ARGENTINA
002	OCT. 24,1945	BRAZIL
003	OCT. 24,1945	BELARUS (BYELORUSSIAN SOVIET SOCIALIST REPUBLIC)
004	OCT. 24,1945	CHILE
005	OCT. 24,1945	CHINA
006	OCT. 24,1945	CUBA
007	JAN. 19,1993	CZECH REPUBLIC
008	OCT. 24,1945	DENMARK
009	OCT. 24,1945	DOMINICAN REPUBLIC
010	OCT. 24,1945	EGYPT
011	OCT. 24,1945	EL SALVADOR
012	OCT. 24,1945	FRANCE
013	OCT. 24,1945	HAITI
014	OCT. 24,1945	IRAN, ISLAMIC REPUBLIC OF
015	OCT. 24,1945	LEBANON
016	OCT. 24,1945	LUXEMBOURG, GRAND DUCHY OF
017	OCT. 24,1945	NEW ZEALAND
018	OCT. 24,1945	NICARAGUA
019	OCT. 24,1945	PARAGUAY
020	OCT. 24,1945	PHILIPPINES
021	OCT. 24,1945	POLAND
022	OCT. 24,1945	SAUDI ARABIA
023	OCT. 24,1945	SYRIAN ARAB REPUBLIC
024	OCT. 24,1945	TURKEY
025	OCT. 24,1945	UKRAINE
026	OCT. 24,1945	RUSSIAN FEDERATION
027	OCT. 24,1945	UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND
028	OCT. 24,1945	UNITED STATES OF AMERICA
029	OCT. 24,1945	YUGOSLAVIA
030	OCT. 25,1945	GREECE
031	OCT. 30,1945	INDIA
032	OCT. 31,1945	PERU
033	NOV. 01,1945	AUSTRALIA
034	NOV. 02,1945	COSTA RICA
035	NOV. 02,1945	LIBERIA
036	NOV. 05,1945	COLUMBIA
037	NOV. 07,1945	MEXICO
038	NOV. 07,1945	SOUTH AFRICA
039	NOV. 09,1945	CANADA
040	NOV. 13,1945	ETHIOPIA
041	NOV. 13,1945	PANAMA
042	NOV. 14,1945	BOLIVIA
043	NOV. 15,1945	VENEZEULA
044	NOV. 21,1945	GUATEMALA
045	NOV. 27,1945	NORWAY
046	DEC. 10,1945	NETHERLANDS
047	DEC. 17,1945	HONDURAS
048	DEC. 18,1945	URUGUAY
049	DEC. 21,1945	ECUADOR
050	DEC. 21,1945	IRAQ
051	DEC. 27,1945	BELGIUM
052	NOV. 19,1946	AFGHANISTAN
053	NOV. 19,1946	SWEDEN
054	DEC. 16,1946	THAILAND
055	NOV. 19,1946	ICELAND
056	SEP. 30,1947	PAKISTAN
057	SEP. 30,1947	YEMEN
058	APR. 19,1948	MYANMAR
059	MAY. 11,1949	ISRAEL
060	SEP. 28,1950	INDONESIA
061	DEC. 14,1955	ALBANIA
062	DEC. 14,1955	AUSTRIA
063	DEC. 14,1955	BULGARIA
064	DEC. 14,1955	CAMBODIA (DEMOCRATIC KAMPUCHEA)
065	DEC. 14,1955	FINLAND
066	DEC. 14,1955	HUNGARY
067	DEC. 14,1955	IRELAND

068	DEC. 14,1955	ITALY
069	DEC. 14,1955	JORDAN
070	DEC. 14,1955	LAO PEOPLE'S DEMOCRATIC REPUBLIC
071	DEC. 14,1955	LIBYAN ARAB JAMAHIRIYA
072	DEC. 14,1955	NEPAL
073	DEC. 14,1955	PORTUGAL
074	DEC. 14,1955	ROMANIA
075	DEC. 14,1955	SPAIN
076	DEC. 14,1955	SRI LANKA
077	NOV. 12,1956	MOROCCO (MAROC)
078	NOV. 12,1956	SUDAN
079	NOV. 12,1956	TUNISIA
080	DEC. 18,1956	JAPAN
081	MAR. 08,1957	GHANA
082	SEP. 17,1957	MALAYSIA
083	DEC. 12,1958	GUINEA
084	OCT. 07,1960	NIGERIA
085	SEP. 20,1960	BENIN
086	SEP. 20,1960	CENTRAL AFRICAN REPUBLIC
087	SEP. 20,1960	CHAD
088	SEP. 20,1960	CONGO
089	SEP. 20,1960	CYPRUS
090	SEP. 20,1960	GABON
091	SEP. 20,1960	COTE D'IVOIRE
092	SEP. 20,1960	MADAGASCAR
093	SEP. 20,1960	NIGER
094	SEP. 20,1960	SOMALIA
095	SEP. 20,1960	TOGO
096	SEP. 20,1960	CAMEROON
097	SEP. 20,1960	BURKINA FASO
098	SEP. 20,1960	DEMOCRATIC REPUBLIC OF THE CONGO
099	SEP. 28,1960	MALI
100	SEP. 28,1960	SENEGAL
101	SEP. 27,1961	SIERRA LEONE
102	OCT. 27,1961	MAURITANIA
103	OCT. 27,1961	MONGOLIA
104	DEC. 14,1961	UNITED REPUBLIC OF TANZANIA
105	SEP. 18,1962	BURUNDI
106	SEP. 18,1962	JAMAICA
107	SEP. 18,1962	RWANDA
108	SEP. 18,1962	TRINIDAD AND TOBAGO
109	OCT. 08,1962	ALGERIA
110	OCT. 25,1962	UGANDA
111	MAY. 14,1963	KUWAIT
112	DEC. 16,1963	KENYA
113	DEC. 01,1964	MALAWI
114	DEC. 01,1964	MALTA
115	DEC. 01,1964	ZAMBIA
116	SEP. 21,1965	GAMBIA
117	SEP. 21,1965	MALDIVES
118	SEP. 21,1965	SINGAPORE
119	SEP. 20,1966	GUYANA
120	OCT. 17,1966	BOTSWANA
121	OCT. 17,1966	LESOTHO
122	DEC. 09,1966	BARBADOS
123	APR. 23, 1990	NAMIBIA
124	APR. 24,1968	MAURITIUS
125	SEP. 24,1968	SWAZILAND
126	NOV. 12,1968	EQUATORIAL GUINEA
127	OCT. 13,1970	FIJI
128	SEP. 21,1971	BAHRAIN
129	SEP. 21,1971	BHUTAN
130	SEP. 21,1971	QATAR
131	OCT. 07,1971	OMAN
132	DEC. 09,1971	UNITED ARAB EMIRATES
133	SEP. 18,1973	BAHAMAS
134	SEP. 18, 1990	LIECHTENSTEIN
135	SEP. 18,1973	GERMANY
136	SEP. 17,1974	BANGLADESH
137	SEP. 17,1974	GRENADA
138	SEP. 17,1974	GUINEA-BISSAU
139	SEP. 16,1975	CAPE VERDE
140	SEP. 16,1975	MOZAMBIQUE
141	SEP. 16,1975	SAO TOME AND PRINCIPE
142	OCT. 10,1975	PAPUA NEW GUINEA
143	NOV. 12,1975	COMOROS

144	DEC. 04,1975	SURINAME
145	SEP. 21,1976	SEYCHELLES
146	DEC. 01,1976	ANGOLA
147	DEC. 15,1976	SAMOA
148	SEP. 20,1977	DJIBOUTI
149	SEP. 20,1977	VIET NAM
150	SEP. 20, 1977	KOREA, REPUBLIC OF (SOUTH KOREA)
151	SEP. 17, 1991	MONACO
152	MAY 28, 1993	HONG KONG
153		GUAM
154	SEP. 19,1978	SOLOMON ISLANDS
155	DEC. 18,1978	DOMINICA
156	SEP. 18,1979	SAINT LUCIA
157	AUG. 25,1980	ZIMBABWE
158	SEP. 16,1980	SAINT VINCENT AND THE GRENADINES
159	SEP. 15,1981	VANUATU
160	SEP. 25,1981	BELIZE
161	NOV. 11,1981	ANTIGUA AND BARBUDA
162	SEP. 23,1983	SAINT KITTS AND NEVIS
163	SEP. 21,1984	BRUNEI DARUSSALAM
164	SEP. 17, 1991	DEMOCRATIC PEOPLE'S REPULBIC OF KOREA (NORTH KOREA)
165	SEP. 17, 1991	ESTONIA
166	SEP. 17, 1991	LATVIA
167	SEP. 17, 1991	MARSHALL ISLANDS
168	SEP. 17, 1991	MICRONESIA, FEDERATED STATES OF
169	MAR. 02, 1992	ARMENIA
170	SEP. 17, 1991	LITHUANIA
171	MAR. 02, 1992	AZERBAIJAN
172	MAR. 02, 1992	KAZAKHSTAN
173	MAR. 02, 1992	KYRGYZSTAN
174	MAR.02, 1992	REPUBLIC OF MOLDOVA
175	MAR. 02, 1992	SAN MARINO
176	MAR. 02, 1992	TAJIKISTAN
177	MAR. 02, 1992	TURKMENISTAN
178	MAR. 02, 1992	UZBEKISTAN
179	MAY 22, 1992	BOSNIA AND HERZEGOVINA
180	MAY 22, 1992	CROATIA
181	MAY 22, 1992	SLOVENIA
182	JUL. 31, 1992	GEORGIA
183	JAN. 19, 1993	SLOVAKIA
184	APR. 8, 1993	THE FORMER YUGOSLAV REPUBLIC OF MACEDONIA
185	MAY 28, 1993	ERITREA
186	JUL. 28, 1993	ANDORRA
187	DEC. 15, 1994	PALAU
188	SEP. 14, 1999	KIRIBATI
189	SEP. 14, 1999	NAURU
190	SEP. 14, 1999	TONGA
191	SEP. 5, 2000	TUVALU
192	NOV. 01, 2000	SERBIA AND MONTENEGRO
193	SEP. 27, 2002	TIMOR-LESTE
200	SEP. 10, 2002	SWITZERLAND

APPENDIX III - Country Codes

Alphabetical Order

COUNTRY CODE	COUNTRY
052	AFGHANISTAN
061	ALBANIA
109	ALGERIA
186	ANDORRA
146	ANGOLA
161	ANTIGUA AND BARBUDA
001	ARGENTINA
169	ARMENIA
033	AUSTRALIA
062	AUSTRIA
171	AZERBAIJAN
133	BAHAMAS
128	BAHRAIN
136	BANGLADESH
122	BARBADOS
051	BELGIUM
160	BELIZE
085	BENIN
129	BHUTAN
042	BOLIVIA
177	BOSNIA AND HERZEGOVINA
120	BOTSWANA
002	BRAZIL
163	BRUNEI DARUSSALAM
063	BULGARIA
097	BURKINA FASO
105	BURUNDI
003	BYELORUSSIAN SOVIET SOCIALIST REPUBLIC
096	CAMEROON
039	CANADA
139	CAPE VERDE
086	CENTRAL AFRICAN REPUBLIC
087	CHAD
004	CHILE
005	CHINA
036	COLUMBIA
143	COMOROS
088	CONGO
034	COSTA RICA
091	COTE D'IVOIRE
180	CROATIA
006	CUBA
089	CYPRUS
007	CZECH REPUBLIC
064	DEMOCRATIC KAMPUCHEA
164	DEMOCRATIC PEOPLE'S REPUBLIC OF KOREA (NORTH KOREA)
123	NAMIBIA
008	DENMARK
148	DJIBOUTI
155	DOMINICA
009	DOMINICAN REPUBLIC
049	ECUADOR
010	EGYPT
011	EL SALVADOR
126	EQUATORIAL GUINEA
185	ERITREA
165	ESTONIA
040	ETHIOPIA
127	FIJI
065	FINLAND
012	FRANCE
090	GABON
116	GAMBIA
182	GEORGIA
135	GERMANY, FEDERAL REPUBLIC OF
081	GHANA
030	GREECE
137	GRENADA

153	GUAM
044	GUATEMALA
083	GUINEA
138	GUINEA-BISSAU
119	GUYANA
013	HAITI
047	HONDURAS
152	HONG KONG
066	HUNGARY
055	ICELAND
031	INDIA
060	INDONESIA
014	ISLAMIC REPUBLIC OF IRAN
050	IRAQ
067	IRELAND
059	ISRAEL
068	ITALY
106	JAMAICA
080	JAPAN
069	JORDAN
172	KAZAKHSTAN
112	KENYA
188	KIRIBATI
150	KOREA, REPUBLIC OF
111	KUWAIT
173	KYRGYZSTAN
070	LAO PEOPLES'S DEMOCRATIC REPUBLIC
166	LATVIA
015	LEBANON
121	LESOTHO
035	LIBERIA
071	LIBYAN ARAB JAMAHIRIYA
134	LIECHTENSTEIN
170	LITHUANIA
016	LUXEMBOURG
092	MADAGASCAR
113	MALAWI
082	MALAYSIA
117	MALDIVES
099	MALI
114	MALTA
167	MARSHALL ISLANDS
102	MAURITANIA
124	MAURITIUS
037	MEXICO
168	MICRONESIA, FEDERATED STATES OF
151	MONACO
103	MONGOLIA
077	MOROCCO
140	MOZAMBIQUE
058	MYANMAR
123	NAMIBIA
189	NAURU
072	NEPAL
046	NETHERLANDS
017	NEW ZEALAND
018	NICARAGUA
093	NIGER
084	NIGERIA
045	NORWAY
131	OMAN
056	PAKISTAN
187	PALAU
041	PANAMA
142	PAPUA NEW GUINEA
019	PARAGUAY
032	PERU
020	PHILIPPINES
021	POLAND
073	PORTUGAL
130	QATAR
174	REPUBLIC OF MOLDOVA
074	ROMANIA
107	RWANDA
162	SAINT KITTS AND NEVIS
156	SAINT LUCIA

158	SAINT VINCENT AND THE GRENADINES
147	SAMOA
175	SAN MARINO
141	SAO TOME AND PRINCIPE
022	SAUDI ARABIA
100	SENEGAL
192	SERBIA AND MONTENEGRO
145	SEYCHELLES
101	SIERRA LEONE
118	SINGAPORE
182	SLOVAKIA
181	SLOVENIA
154	SOLOMON ISLANDS
094	SOMALIA
038	SOUTH AFRICA
075	SPAIN
076	SRI LANKA
078	SUDAN
144	SURINAME
125	SWAZILAND
053	SWEDEN
200	SWITZERLAND
023	SYRIAN ARAB REPUBLIC
176	TAJIKISTAN
054	THAILAND
184	THE FORMER YUGOSLAV REPUBLIC OF MACEDONIA
193	TIMOR-LESTE
095	TOGO
190	TONGA
108	TRINIDAD AND TOBAGO
079	TUNISIA
024	TURKEY
177	TURKMENISTAN
191	TUVALU
110	UGANDA
025	UKRAINE
178	UZBEKISTAN
026	RUSSIAN FEDERATION
132	UNITED ARAB EMIRATES
027	UNITED KINGDOM OF GREAT BRITAIN AND NORTHERN IRELAND
104	UNITED REPUBLIC OF TANZANIA
028	UNITED STATES OF AMERICA
048	URUGUAY
159	VANUATU
043	VENEZEULA
149	VIET NAM
057	YEMEN
029	YUGOSLAVIA
098	DEMOCRATIC REPUBLIC OF THE CONGO
115	ZAMBIA
157	ZIMBABWE

APPENDIX IV – Selection of Method Codes

ANALYTICAL METHOD CODES
(NUMERICAL ORDER)

	CODE	ALPHADESCRIPTION	NO. DEC.	ABBREVIATION	UNITS	METHOD
	00120	SUM OF CATIONS	3	SUM OF CATIONS	meq/L	CALCULATED
	00125	SUM OF ANIONS	3	SUM OF ANIONS	meq/L	CALCULATED
	00130	SUM OF CATIONS + ANIONS	3	SUM OF CATIONS + ANIONS	meq/L	CALCULATED
	00190	INTEGRATED SAMPLE Code is for internal use only	0	INTEG SAMPLE	N/A	VERTICAL(V),HORIZONTAL(H), TIME(T)
*	01000	HYDROGEN SULPHIDE	2	H_2S	mg/L	
¤	02003	ABSORBANCE @ 340 nm	1	A340	Abs*1000	SPECTROPHOTOMETRIC ABSORBANCE READING
¤	02004	ABSORBANCE @ 440 nm	1	A440	Abs*1000	SPECTROPHOTOMETRIC ABSORBANCE READING
¤	02005	ABSORBANCE @ 740 nm	1	A740	Abs*1000	SPECTROPHOTOMETRIC ABSORBANCE READING
¤	02006	ABSORBANCE CO-EFFICIENT @ 340 nm	1	G340	M	CALCULATED FROM 440&740 NM ABSORBANCES
¤	02007	ABSORBANCE CO-EFFICIENT @ 440 nm	1	G440	M	CALCULATED FROM 340&740 NM ABSORBANCES
	02011	COLOUR APPARENT	1	COLOUR APPARENT	Rel. Units	VISUAL COMPARISON
	02040	ELECTRICAL CONDUCTANCE	0	ELEC. COND.	µs/cm	ELECTROMETER
	02041	ELECTRICAL CONDUCTIVITY	0	ELEC COND	µs/cm	CONDUCTIVITY METER
	02049	ELECTRICAL CONDUCTANCE	0	ELEC COND	µs/cm	RADIOMETER CDM 83
	02050	TOTAL DISSOLVED SOLIDS	0	TDS	mg/L	CALIBRATED CONDUCTIVITY METER @25°c
	02055	SALINITY	0	SALINITY	ppt	TDS-SALINITY-CONDUCTIVITY METER @ 25°C
	02061	TEMPERATURE	1	TEMP	Deg. C	MERCURY THERMOMETER
	02062	TEMPERATURE	1	TEMP	Deg. C	BATTERY THERMOMETER
	02070	CLARITY	1	CLARITY	m	HORIZONTAL BLACK DISC
	02071	TURBIDITY	1	TURBIDITY	JTU	VISUAL
	02073	TURBIDITY	1	TURBIDITY	JTU	PHOTOMETRY
	02074	TURBIDITY	1	TURBIDITY	NTU	NEPHELOMETRIC - HACH
	02076	TRANSPARENCY	1	TRANS	Metre	30 CM SECCHI DISC
*	03001	LITHIUM - TOTAL	1	Li TOTAL	mg/L Li	AAS - DIRECT ASPIRATION
*	03101	LITHIUM - DISSOLVED	1	Li DISS	mg/L Li	AAS - DIRECT ASPIRATION
	05001	BORON - TOTAL	1	B TOTAL	mg/L B	AAS
	05002	BORON - TOTAL	1	B TOTAL	mg/L B	COLOURIMETRY
	05009	BORON - TOTAL	1	B TOTAL	mg/L B	ICP 1502
	05011	BORON - TOTAL	1	B TOTAL	mg/L B	ICP 1503
	05090	BORON - TOTAL	1	B TOTAL	mg/L B	ICP - MS
	05101	BORON - DISSOLVED	1	B DISS	mg/L B	POTENTIOMETRIC - Mannitol
	05102	BORON - DISSOLVED	1	B DISS	mg/L B	CURCUMIN METHOD
	05105	BORON - DISSOLVED	1	B DISS	mg/L B	COLOURIMETRY
	05107	BORON - DISSOLVED	1	B DISS	mg/L B	ICP 1516
	05109	BORON - DISSOLVED	1	B DISS	mg/L B	ICP 1502
	05111	BORON - DISSOLVED	1	B DISS	µg/L B	ICP 1516
	05190	BORON - DISSOLVED	1	B DISS	mg/L B	ICP - MS

*	06001	CARBON - TOTAL ORGANIC	0	TOC	mg/L C	INFRARED ANALYSIS - DUAL CHANNEL
	06076	CARBON ORGANIC - PARTICULATE	3	ORG. CARBON-PART	µg/g	CHN ANALYZER
	06077	CARBON ORGANIC - PARTICULATE	3	ORG. CARBON-PART	µg/g	FLAME IONIZATION
	06101	CARBON ORGANIC - DISSOLVED	1	ORG. CARBON-DISS	mg/L	INFRARED ANALYSIS
	06201	BICARBONATE	0	BICARBONATE	mg/L HCO_3	CALCULATED
	06301	CARBONATE	0	CARBONATE	mg/L CO_3	CALCULATED
*	06402	CO_2 - DISSOLVED	0	CO_2 DISS	mg/L	
	06505	POLYAROMATIC HYDROCARBONS	2	PAH	µg/L	GC - MS
*	06510	POLY AROMATIC HYDROCARBONS	3	PAH	µg/L	FLUORESCENCE SPECTROPHOTOMETRY
	06521	OIL AND GREASE	0	OIL AND GREASE	mg/L	PETROLEUM ETHER EXTRACTION
*	06532	PHENOLS	3	PHENOLS	mg/L	COLOURIMETRY
	06570	HYDROCARBONS - TOTAL	1	HYDROCAR.-TOTAL	µg/L	IR INTENSITY SPECTROSCOPY
*	06606	CYANIDE	3	CN	mg/L CN	COLOURIMETRY
	06711	CHLOROPHYLL A	4	CHLORO A	mg/L	SCOR - UNESCO (COLOURIMETRY)
*	07001	NITROGEN KJELDAHL ORGANIC	1	N KJEL	mg/L N	KJELDAHL METHOD
*	07004	NITROGEN KJELDAHL ORGANIC	1	N KJEL	mg/L N	COLOURIMETRY
	07105	NITROGEN,NITRATE + NITRITE	2	NO_3NO_2	mg/L N	COLOURIMETRY
*	07207	NITRITE	2	NO_2-N	mg/L N	COLOURIMETRY (SULFANILAMIDE)
	07210	NITRITE	3	NO_2-N	mg/L N	COLOURIMETRIC (CLEVE'S ACID)
	07300	NITRATE	3	NO_3-N	mg/L N	AUTOMATED HYDRAZINE REDUCTION
	07302	NITROGEN (NO_3-N + NO_2-N)	2	NO_3NO_2	mg/L N	CALCULATED (CODES 07321 + 07210)
	07303	NITROGEN (NO_3-N + NO_2-N)	1	NO_3NO_2	mg/L N	CALCULATED (CODES 07320 + 07210)
*	07306	NITRATE	2	NO_3-N	mg/L N	BRUCINE METHOD
*	07309	NITRATE	2	NO_3-N	mg/L N	CHROMOTROPIC ACID
*	07313	NITRATE	2	NO_3-N	mg/L N	CADMIUM REDUCTION
*	07314	NITRATE	2	NO_3-N	mg/L N	DEVARDA'S ALLOY METHOD
	07316	NITRATE + NITRITE	2	NO_3NO_2	mg/L N	ION CHROMATOGRAPHY
	07320	NITRATE	1	NO_3-N	mg/L N	ION SPECIFIC ELECTRODE
	07321	NITRATE	2	NO_3-N	mg/L N	ION CHROMATOGRAPHY
	07401	NITROGEN ORGANIC DISSOLVED	1	ORG. NIT.-DISS	mg/L	KJELDAHL WITH REMOVAL OF NH_3
	07403	NITROGEN ORGANIC DISSOLVED	1	ORG. NIT.-DISS	mg/L	DIFFERENCE CALCULATION
	07506	AMMONIA	2	NH_3	mg/L N	ION SELECTIVE ELECTRODE
	07507	NITROGEN TOTAL AMMONIA	2	NH_4-N	mg/L N	COLOURIMETRIC (SALICYLATE)
	07550	NITROGEN TOTAL AMMONIA	2	NH_4-N	mg/L N	NESSLERIZATION & DISTILLATION
	07551	AMMONIA	2	NH_3	mg/L N	DIRECT NESSLERIZATION
	07553	AMMONIA	2	NH_3	mg/L N	DISTILLATION AND TITRATION
	07554	AMMONIA	2	NH_3	mg/L N	DISTILLATION + NESSLERIZATION
	07555	AMMONIA	2	NH_3	mg/L N	ALPHA - NAPHTHOL METHOD (COLOURIMETRY)
	07556	AMMONIA	2	NH_3	mg/L N	COLOURIMETRY(INDOPHENOL BLUE)
	07557	AMMONIA	2	NH_3	mg/L N	AUTOMATED INDOPHENOL BLUE METHOD
	07564	AMMONIA DISSOLVED	1	AMMONIA DISS	mg/L N	ION CHROMATOGRAPHY
	07601	NITROGEN TOTAL	2	TOTAL NITROGEN	mg/L N	COLOURIMETRY
+	07606	NITROGEN TOTAL	2	TOTAL NITROGEN	mg/L N	ALKALINE PERSULPHATE

						DIGESTION
	07912	NITROGEN ORGANIC - PARTICULATE	3	ORG. NIT. -PART	µg/g	CHN ANALYZER
	08001	PERCENT DO SATURATION	0	PERCENT DO SAT	PERCENT	CALCULATION OR NOMOGRAM
	08005	PERCENT DO SATURATION	0	PERCENT DO SAT	PERCENT	METER (YSI)
	08101	DISSOLVED OXYGEN	1	DISS O_2	mg/L O_2	WINKLER METHOD
	08102	DISSOLVED OXYGEN	1	DISS O_2	mg/L O_2	DISSOLVED OXYGEN METER
	08107	DISSOLVED OXYGEN	1	DISS O_2	mg/L O_2	CALCULATED FROM % SAT., H2O TEMP, AND PRESSURE AT SITE.
	08201	BIOCHEMICAL OXYGEN DEMAND	0	BOD	mg/L O_2	5-DAY DILUTION METHOD
	08202	BIOCHEMICAL OXYGEN DEMAND	0	BOD	mg/L O_2	5 DAY INCUBATION @ 20 DEG. C
	08203	BIOCHEMICAL OXYGEN DEMAND	0	BOD(ATU)	mg/L	5 DAY INCUBATION @ 20°c WITH ALLYL THIOUREA
	08301	CHEMICAL OXYGEN DEMAND	0	COD	mg/L O_2	$K_2Cr_20_7$ METHOD
	08305	TOTAL COD	0	COD	mg/L O_2	$KMnO_4$ METHOD
*	08401	PERMANGANATE VALUE	0	PERM V	mg/L O_2	$KMnO_4$ METHOD
*	08402	PERMANGANATE VALUE	0	PERM V	mg/L O_2	$KMnO_4$ METHOD - 4 HOUR DIGESTION
	09104	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	COLOURIMETRY
	09105	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	SPECIFIC ION ELECTRODE
	09106	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	ELECTRODE POTENTIAL METHOD
	09107	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	POTENTIOMETRIC - SPECIFIC ION
	09110	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	PHOTOMETRIC (LA-ALIZARIN COMPLEX)
	09116	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	ION CHROMATOGRAPHY
	10101	ALKALINITY TOTAL ($CaCO_3$)	2	ALK TOT	mg/L $CaCO_3$	POTENTIOMETRIC TITRATION
	10102	ALKALINITY TOTAL ($CaCO_3$)	2	ALK TOT	mg/L $CaCO_3$	COLOURIMETRIC TITRATION
	10103	ALKALINITY TOTAL ($CaCO_3$)	2	ALK TOT	mg/L $CaCO_3$	TITRATION (BDH 4.5 indicator)
*	10120	ALKALINITY TOTAL	2	ALK TOT	meq/L $CaCO_3$	VISUAL TITRATION
*	10121	ALKALINITY TOTAL	2	ALK TOT	meq/L $CaCO_3$	ELECTROMETRIC TITRATION
	10123	ALKALINITY TOTAL	2	ALK TOT	mg/L $CaCO_3$	ELECTROMETRIC TITRATION
	10151	ALKALINITY PHENOL PHTHALEIN	1	ALKALINITY	mg/L $CaCO_3$	POTENTIOMETRIC TITRATION
	10252	ACIDITY TOTAL	2	TOTAL ACIDITY	mg/L $CaCO_3$	TITROPROCESSOR
	10300	pH	1	pH	pH Units	COLORIMETRIC METHOD
	10301	pH	1	pH	pH Units	pH METER (ELECTROMETRIC)
	10302	pH	1	pH	pH Units	pH METER(ELECTROMETRIC) AT 25 DEG. C
	10401	SUSPENDED SOLIDS 105 DEG	0	SUSP SOL - 105	mg/L	GRAVIMETRIC METHOD
	10408	SUSPENDED SOLIDS 180 DEG	0	SUSP SOL - 180	mg/L	GRAVIMETRIC METHOD
	10452	RESIDUE FILTERABLE	0	RESIDUE - FILT	mg/L	GRAVIMETRIC METHOD
	10473	RESIDUE TOTAL	0	RESIDUE - TOT	mg/L	GRAVIMETRIC MICRO-METHOD
*	10501	FIXED SUSPENDED SOLIDS	0	FIX SUSP SOLIDS	mg/L	GRAVIMETRIC METHOD
*	10511	VOLATILE SUSPENDED SOLIDS	0	VOL SUSP SOLIDS	mg/L	GRAVIMETRIC METHOD
	10521	RESIDUE VOLATILE TOTAL	0	RESIDUE - VOL	mg/L	CALCULATED
*	10531	VOLATILE DISSOLVED SOLIDS	0	VOL DISS SOLIDS	mg/L	GRAVIMETRIC METHOD
	10551	RESIDUE FIXED	0	RESIDUE - FIXED	mg/L	GRAVIMETRIC METHOD
	10571	RESIDUE FIXED TOTAL	0	RESIDUE FIX TOT	mg/L	GRAVIMETRIC
	10603	HARDNESS TOTAL	1	HARDNESS TOTAL	mg/L $CaCO_3$	EDTA TITRATION
*	10702	ANIONIC TENSIDES MBAS	1	TENS AN	mg/L	MBAS

*	11001	SODIUM - TOTAL	0	Na TOTAL	mg/L Na	AAS
*	11002	SODIUM - TOTAL	0	Na TOTAL	mg/L Na	FLAME PHOTOMETRY
	11102	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	AAS
	11103	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	FLAME PHOTOMETRY
	11105	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	AAS - DIRECT ASPIRATION
	11111	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	ICP 1516
	11112	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	ION CHROMATOGRAPHY
	11115	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	ICP 1502
	11116	SODIUM DISSOLVED	2	Na DISS	mg/L Na	AAS - EMISSION
	11201	SODIUM ADSORPTION RATIO	3	SAR	Rel Unit	DIFFERENCE CALCULATION
*	12002	MAGNESIUM - TOTAL	0	Mg TOTAL	mg/L Mg	AAS - DIRECT ASPIRATION
*	12003	MAGNESIUM - TOTAL	0	Mg TOTAL	mg/L Mg	EDTA TITRATION
	12101	MAGNESIUM - DISSOLVED	0	Mg DISS	mg/L Mg	CALCULATED
	12102	MAGNESIUM - DISSOLVED	0	Mg DISS	mg/L Mg	AAS - DIRECT ASPIRATION
	12103	MAGNESIUM - DISSOLVED	0	Mg DISS	mg/L Mg	EDTA TITRATION
	12109	MAGNESIUM - DISSOLVED	0	Mg DISS	mg/L Mg	ION CHROMATOGRAPHY
	12111	MAGNESIUM - DISSOLVED	0	Mg DISS	mg/L Mg	ICP 1516
	12115	MAGNESIUM - DISSOLVED	0	Mg DISS	mg/L Mg	ICP 1502
	13001	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	COLOURIMETRY
	13002	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	AAS - DIRECT ASPIRATION
	13003	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	AAS - SOLVENT EXTRACTION
	13009	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	ICP 1502
	13011	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	ICP 1503
	13090	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	ICP - MS
	13101	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	COLOURIMETRY
	13102	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	AAS - DIRECT ASPIRATION
	13103	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	AAS - SOLVENT EXTRACTION
	13104	ALUMINUM - DISSOLVED	2	Al DISS	mg/L Al	COLOUIMETRY
	13109	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	ICP 1502
	13111	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	ICP 1516
	13190	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	ICP - MS
	13901	ALUMINUM - DISSOLVED	3	AL DISS	mg/L Al	AAS - FLAMELESS
	13911	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	AAS - FLAMELESS
	14019	SILICA - REACTIVE	2	SI REAC	mg/L SiO_2	ICP 1502
	14101	SILICA - REACTIVE	2	SI REAC	mg/L SiO_2	COLOURIMETRY
	14105	SILICA REACTIVE	3	SI REAC	mg/L SiO_2	COLOURIMETRY
	14111	SILICA - DISSOLVED	2	SI DISS	mg/L SiO_2	ICP 1516
*	15103	PHOSPHORUS - DISSOLVED	3	P DISS	mg/L P	COLOURIMETRY
*	15205	ORTHOPHOSPHATE - TOTAL	3	P ORTHO TOTAL	mg/L P	COLOURIMETRY
*	15254	ORTHOPHOSPHATE SOL REACTIVE	3	PO_4-P SOL	mg/L PO_4	COLOURIMETRY
*	15255	ORTHOPHOSPHATE - DISSOLVED	3	P ORTHO DISS	mg/L P	COLOURIMETRY
	15256	ORTHOPHOSPHATE - DISSOLVED	3	P ORTHO DISS	mg/L P	MOLBDENUM BLUE-ASCORBIC ACID REDUCTION
*	15313	PHOSPHATE - TOTAL INORGANIC	3	P INORG AH TOTAL	mg/L P	COLOURIMETRY
*	15403	PHOSPHATE - TOTAL	3	PO_4 TOTAL	mg/L PO_4	COLOURIMETRY

	15405	PHOSPHORUS - TOTAL	3	P TOTAL	mg/L P	COLOURIMETRY
	15406	PHOSPHATE TOTAL	3	P TOTAL	mg/L P	ACID PERSULPHATE DIGESTION
*	15408	PHOSPHATE - TOTAL	3	PO_4 TOTAL	mg/L P	COLOURIMETRY
	15417	PHOSPHORUS TOTAL DISSOLVED	3	P TOTAL DISS.	mg/L P	COLOURIMETRY
*	15901	PHOSPHORUS - PARTICULATE	3	P PART	mg/L P	DIFFERENCE CALCULATION
	15902	PHOSPHORUS TOTAL PARTICULATE	3	P TOTAL PART.	µg/g	DIFFERENCE CALCULATION
	15903	PHOSPHORUS TOTAL PARTICULATE	3	P TOTAL PART.	µg/g	ACID-EXTRACTION COLOURIMETRY
	16301	SULPHATE	0	SULPHATE	mg/L SO_4	GRAVIMETRIC METHOD
	16302	SULPHATE	0	SULPHATE	mg/L SO_4	TURBIDIMETRIC METHOD
	16303	SULPHATE	0	SULPHATE	mg/L SO_4	TITRATION
	16304	SULPHATE	0	SULPHATE	mg/L SO_4	AUTOANALYZER
	16306	SULPHATE	0	SULPHATE	mg/L SO_4	COLOURIMETRY
	16309	SULPHATE	0	SULPHATE	mg/L SO_4	ION CHROMATOGRAPHY
	17201	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	MERCURIC NITRATE TITRATION
	17202	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	SILVER NITRATE POTENTIOMETRIC
	17203	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	COLOURIMETRY
	17204	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	SILVER NITRATE TITRATION
	17205	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	SPECIFIC ION ELECTRODE
	17207	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	ION EXCHANGE
	17209	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	ION CHROMATOGRAPHY
*	17860	ORGANO CL COMPOUNDS TOTAL	3	ORGANO Cl CMPDS	µg/L	GAS CHROMATOGRAPHY
*	18000	P,P-DDT	3	P,P-DDT	µg/L	GAS CHROMATOGRAPHY
	18002	DDT - TOTAL	3	DDT TOTAL	µg/L	GAS CHROMATOGRAPHY
*	18005	O,P-DDT	3	O,P-DDT	µg/L	GAS CHROMATOGRAPHY
*	18010	P,P-DDD	3	P,P-DDD	µg/L	GAS CHROMATOGRAPHY
*	18015	O,P-DDD	3	O,P-DDD	µg/L	GAS CHROMATOGRAPHY
*	18020	P,P-DDE	3	P,P-DDE	µg/L	GAS CHROMATOGRAPHY
*	18025	O,P-DDE	3	O,P-DDE	µg/L	GAS CHROMATOGRAPHY
	18070	LINDANE (GAMMA - BHC)	3	LINDANE	µg/L	GAS-LIQUID CHROMATOGRAPHY (ECD)
*	18075	ALPHA-BHC	3	ALPHA-BHC	µg/L	GAS CHROMATOGRAPHY
*	18125	MIREX	3	MIREX	µg/L	GAS CHROMATOGRAPHY
	18130	ALDRIN	3	ALDRIN	µg/L	GAS CHROMATOGRAPHY
*	18140	ENDRIN	3	ENDRIN	µg/L	GAS CHROMATOGRAPHY
	18150	DIELDRIN	3	DIELDRIN	µg/L	GAS CHROMATOGRAPHY
	18165	PCBS	3	PCBS	µg/L	GAS - LIQUID CHROMATOGRAPHY
	18415	ATRAZINE - TOTAL	1	ATRAZINE	µg/L	GAS - LIQUID CHROMATOGRAPHY
	18444	ALDICARB	2	ALDICARB	µg/L	HIGH PRESSURE LIQUID CHROMATOGRAPHY
	18503	2,4-D	2	2,4-D	µg/L	ELECTRON CAPTURE - GLC
*	18803	P,P-DDD OLEFIN	3	P,P-DDD OLEFIN	µg/L	GAS CHROMATOGRAPHY
*	18814	BHC	3	BHC	µg/L	GAS CHROMATOGRAPHY
*	19001	POTASSIUM - TOTAL	1	K TOTAL	mg/L K	AAS
*	19002	POTASSIUM - TOTAL	1	K TOTAL	mg/L K	FLAME PHOTOMETRY
	19102	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	AAS
	19103	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	FLAME PHOTOMETRY

	19105	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	AAS - DIRECT ASPIRATION
	19111	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	ICP 1516
	19112	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	ION CHROMATOGRAPHY
	19115	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	ICP 1502
*	20003	CALCIUM - TOTAL	3	Ca TOTAL	mg/L Ca	AAS
	20101	CALCIUM - DISSOLVED	3	Ca DISS	mg/L Ca	EDTA TITRATION
	20103	CALCIUM - DISSOLVED	3	Ca DISS	mg/L Ca	AAS
	20105	CALCIUM - DISSOLVED	3	Ca DISS	mg/L Ca	FLAME EMISSION
	20106	CALCIUM HARDNESS	1	Ca HARDNESS	mg/L $CaCO_3$	EDTA TITRATION
	20109	CALCIUM - DISSOLVED	3	Ca DISS	mg/L $CaCO_3$	ION CHROMATOGRAPHY
	20111	CALCIUM - DISSOLVED	3	Ca DISS	mg/L Ca	ICP 1516
	20115	CALCIUM - DISSOLVED	3	Ca DISS	mg/L Ca	ICP 1502
	24002	CHROMIUM - TOTAL	3	Cr TOTAL	mg/L Cr	AAS - DIRECT ASPIRATION
	24009	CHROMIUM - TOTAL	3	Cr TOTAL	mg/L Cr	ICP 1502
	24011	CHROMIUM - TOTAL	3	Cr TOTAL	mg/L Cr	ICP 1503
	24052	CHROMIUM - DISSOLVED	3	Cr DISS	mg/L Cr	AAS
	24090	CHROMIUM - TOTAL	3	Cr TOTAL	mg/L Cr	ICP - MS
*	24101	CHROMIUM HEXAVALENT	3	Cr HEX	mg/L Cr	COLOURIMETRY
	24111	CHROMIUM - DISSOLVED	3	Cr DISS	mg/L Cr	ICP 1516
	24190	CHROMIUM - DISSOLVED	3	Cr DISS	mg/L Cr	ICP - MS
	24202	CHROMIUM - SUSPENDED	3	Cr - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
	24901	CHROMIUM - DISSOLVED	3	Cr DISS	mg/L Cr	AAS - FLAMELESS
	24911	CHROMIUM - TOTAL	3	Cr TOTAL	mg/L Cr	AAS - FLAMELESS
	25004	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	AAS - DIRECT ASPIRATION
	25005	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	AAS - SOLVENT EXTRACTION
	25009	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	COLOURIMETRY
	25010	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	ICP 1502
	25011	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	ICP 1503
	25090	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	ICP - MS
	25101	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	COLOURIMETRY
	25104	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	AAS - DIRECT ASPIRATION
	25105	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	AAS - SOLVENT EXTRACTION
	25109	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	ICP 1502
	25111	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	ICP 1516
	25190	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	ICP - MS
	25204	MANGANESE SUSPENDED	3	Mn - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
	25901	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	AAS - FLAMELESS
	25911	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	AAS - FLAMELESS
	26002	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	COLOURIMETRY
	26004	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	AAS - DIRECT ASPIRATION
	26005	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	AAS - SOLVENT EXTRACTION
	26009	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	ICP 1502
	26011	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	ICP 1503
	26090	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	ICP - MS

26102	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	COLOURIMETRY
26104	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	AAS - DIRECT ASPIRATION
26105	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	AAS - SOLVENT EXTRACTION
26109	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	ICP 1502
26111	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	ICP 1516
26190	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	ICP - MS
26204	IRON SUSPENDED	3	Fe - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
26901	IRON - DISSOLVED	2	Fe DISS	mg/L	AAS - FLAMELESS
27009	COLBALT TOTAL	3	Co TOTAL	mg/L Co	ICP 1502
28001	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	AAS - DIRECT ASPIRATION
28002	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	AAS - SOLVENT EXTRACTION
28009	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	ICP 1502
28011	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	ICP 1503
28090	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	ICP - MS
28101	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	AAS - DIRECT ASPIRATION
28102	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	AAS - SOLVENT EXTRACTION
28109	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	ICP 1502
28111	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	ICP 1516
28190	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	ICP - MS
28901	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	AAS - FLAMELESS
28911	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	AAS - FLAMELESS
29001	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	COLOURIMETRY
29005	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	AAS - SOLVENT EXTRACTION
29006	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	AAS - DIRECT ASPIRATION
29009	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	ICP 1502
29011	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	ICP 1503
29090	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	ICP - MS
29101	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	COLOURIMETRY
29105	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	AAS - SOLVENT EXTRACTION
29106	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	AAS - DIRECT ASPIRATION
29109	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	ICP 1502
29111	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	ICP 1516
29190	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	ICP - MS
29206	COPPER SUSPENDED	3	Cu - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
29901	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	AAS - FLAMELESS
29911	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	AAS - FLAMELESS
30001	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	COLOURIMETRY
30004	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	AAS - DIRECT ASPIRATION
30005	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	AAS - SOLVENT EXTRACTION
30009	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	ICP 1502
30011	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	ICP 1503
30090	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	ICP - MS
30101	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	COLOURIMETRY
30104	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	AAS - DIRECT ASPIRATION

	30105	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	AAS - SOLVENT EXTRACTION
	30109	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	ICP 1502
	30111	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	ICP 1516
	30190	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	ICP - MS
	30204	ZINC SUSPENDED	3	Zn - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
	30901	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	AAS - FLAMELESS
	30911	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	AAS - FLAMELESS
	33003	ARSENIC - TOTAL	3	As TOTAL	mg/L As	COLOURIMETRY
	33007	ARSENIC - TOTAL	3	As TOTAL	mg/L As	AAS - FLAMELESS
	33008	ARSENIC - TOTAL	3	As TOTAL	mg/L As	ICP
	33009	ARSENIC - TOTAL	3	As TOTAL	mg/L As	ICP 1502
	33011	ARSENIC - TOTAL	3	As TOTAL	mg/L As	AAS - HYDRIDE
	33090	ARSENIC - TOTAL	3	As TOTAL	mg/L As	ICP - MS
	33103	ARSENIC - DISSOLVED	3	As DISS	mg/L As	COLOURIMETRY
	33104	ARSENIC - DISSOLVED	3	As DISS	mg/L As	AAS - FLAMELESS
	33108	ARSENIC - DISSOLVED	3	As DISS	mg/L As	ICP
	33190	ARSENIC - DISSOLVED	3	As DISS	mg/L As	ICP - MS
	33202	ARSENIC SUSPENDED	3	As - PARTICULATE	µg/g	AAS - FLAMELESS -ACID DIGESTION
	34002	SELENIUM - TOTAL	3	Se TOTAL	mg/L Se	AAS
	34007	SELENIUM - TOTAL	3	Se TOTAL	mg/L Se	AAS - FLAMELESS - HYDRIDE
	34008	SELENIUM - TOTAL	3	Se TOTAL	mg/L Se	ICP
	34090	SELENIUM - TOTAL	3	Se TOTAL	mg/L Se	ICP - MS
	34102	SELENIUM - DISSOLVED	3	Se DISS	mg/L Se	AAS - FLAMELESS
	34108	SELENIUM - DISSOLVED	3	Se DISS	mg/L Se	ICP
	34190	SELENIUM - DISSOLVED	3	Se DISS	mg/L Se	ICP - MS
	36001	COLIFORM - TOTAL	0	COLIFORM TOTAL	No./100 ml MF	MULTIPLE TEST TUBE
	36002	COLIFORM - TOTAL	0	COLIFORM TOTAL	No./100 ml MPN	MEMBRANE FILTRATION
	36011	FAECAL COLIFORM BACTERIA	0	FAEC COL	No./100 ml MF	MULTIPLE TEST TUBE
	36012	FAECAL COLIFORM BACTERIA	0	FAEC COL	No./100 ml MPN	MEMBRANE FILTRATION
*	36101	FAECAL STREPTOCOCCI	0	FAEC STREP	No./100 ml MF	MULTIPLE TEST TUBE
*	36102	FAECAL STREPTOCOCCI	0	FAEC STREP	No./100 ml MPN	MEMBRANE FILTRATION
	36220	SALMONELLA	0	SALMONELLA	No./L	CONCENTRATION BY FILTRATION
*	36301	PHYTOPLANKTON COUNT	0	PHYTO COUNT	No./L	TOTAL NUMBER OBSERVED
*	36302	PHYTOPLANKTON BIOMASS	1	PHYTO BIO	mg/m^3	
*	36304	PHYTOPLANKTON COUNT	0	PHYTO COUNT	No./ml	TOTAL NUMBER OBSERVED
	47101	SILVER DISSOLVED	2	Ag DISS	mg/L	AAS – DIRECT ASPITATION
	48001	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	AAS - DIRECT ASPIRATION
	48002	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	AAS - SOLVENT EXTRACTION
	48009	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	ICP 1502
	48011	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	ICP 1503
	48090	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	ICP - MS
	48101	CADMIUM - DISSOLVED	3	Cd DISS	mg/L Cd	AAS - DIRECT ASPIRATION
	48102	CADMIUM - DISSOLVED	3	Cd DISS	mg/L Cd	AAS - SOLVENT EXTRACTION

	48109	CADMIUM - DISSOLVED	3	Cd DISS	mg/L Cd	ICP 1502
	48111	CADMIUM - DISSOLVED	3	Cd DISS	mg/L Cd	ICP 1516
	48190	CADMIUM - DISSOLVED	3	Cd DISS	mg/L Cd	ICP - MS
	48201	CADMIUM SUSPENDED	3	Cd - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
	48901	CADMIUM - DISSOLVED	3	Cd DISSOLVED	mg/L Cd	AAS - FLAMELESS
	48911	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	AAS - FLAMELESS
	51101	ANTIMONY DISSOLVED	1	Sb DISS	mg/l	AAS – DIRECT ASPIRATION
*	56001	BARIUM - TOTAL	1	Ba TOTAL	mg/L Ba	AAS - DIRECT ASPIRATION
*	56002	BARIUM - TOTAL	1	Ba TOTAL	mg/L Ba	FLAME EMISSION
*	56101	BARIUM - DISSOLVED	1	Ba DISS	mg/L Ba	AAS - DIRECT ASPIRATION
	80011	MERCURY - TOTAL	3	Hg TOTAL	µg/L Hg	AAS - FLAMELESS
	80016	MERCURY - TOTAL	3	Hg TOTAL	µg/L Hg	COLD BR WET OXIDATION P AAS
	80111	MERCURY - DISSOLVED	3	Hg DISS	µg/L Hg	AAS - FLAMELESS
	80201	MERCURY SUSPENDED	3	Hg PARTICULATE	µg/g	AAS - FLAMELESS
	82001	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	AAS - DIRECT ASPIRATION
	82002	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	AAS - SOLVENT EXTRACTION
	82009	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	ICP 1502
	82011	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	ICP 1503
	82090	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	ICP - MS
	82101	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	AAS - DIRECT ASPIRATION
	82102	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	COLOURIMETRY
	82103	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	AAS - SOLVENT EXTRACTION
	82109	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	ICP 1502
	82111	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	ICP 1516
	82190	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	ICP - MS
	82201	LEAD SUSPENDED	3	Pb - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
	82360	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	ICP - AES
	82901	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	AAS - FLAMELESS
	82911	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	AAS - FLAMELESS
	95000	BENZOIC ACID	0	BENZOIC ACID	µg/L	GAS CHROMATOGRAPHY
	95011	PHENOLS	1	PHENOLS	µg/L	GC - MS
	95100	BENZENE	1	BENZENE	µg/L	GC - MS
*	97060	TEMPERATURE - AIR	1	TEMP-AIR	Deg. C	
	97160	INSTANTANEOUS DISCHARGE	1	INST DISCHG	m^3/s	GAUGE HEIGHT
	97184	DISCHARGE MONTHLY MEAN	0	DISCH.MON.MEAN	M3/s	CALCULATED
	97320	CLOUD COVER	0	CLOUD COVER	PERCENT	ESTIMATED PERCENT

ICP 1516 - By inductively coupled argon plasma emission spectroscopy (ICAP). The sample is filtered in the field through a 0.45 U membrane filter and preserved with diluted mineral acid. The sample is aspirated and the emission is measured at the appropriate wave length and compared with that of identically prepared standard solutions. (Codes ending with 111)

ICP 1503 - By inductively coupled argon plasma emission spectroscopy (ICAP). The sample is preserved in the field with dilute mineral acid. A sample aliquot is digested with aqua regia and evaporated to near dryness. The residue is dissolved in conc. HCl and diluted to one-fifth of the aliquot volume. The digested sample is filtered through a 0.45 U membrane filter and aspirated. The emission is measured spectrophotometrically and compared with that of an identically prepared standard solution. (Codes ending with 011)

ICP 1502 - Inductively coupled argon plasma (ICAP) emission spectrometry. Samples preserved with HNO3, digested with conc. HNO3 or aqua regia, concentrated, and aspirated from an autosampler. Emission are compared to Std.
Dissolved: the sample is filtered through 0.45 U membrane filter.
Extractable: samples are concentrated 5 to 10 times, and aspirated.
(Codes ending with 009 for Total and 109 for Dissolved. Codes ending with 115 for Dissolved Sodium, Potassium, Calcium and Magnesium)

*These codes are no longer required by the GEMS/Water Program and are only valid for past data.

APPENDIX V – Selection of Method Codes

ANALYTICAL METHOD CODES
(ALPHABETICAL ORDER)

	CODE	ALPHADESCRIPTION	NO. DEC.	ABBREVIATION	UNITS	METHOD
	18503	2,4-D	2	2,4-D	µg/L	ELECTRON CAPTURE - GLC
¤	02003	ABSORBANCE @ 340 nm	1	A340	Abs*1000	SPECTROPHOTOMETRIC ABSORBANCE READING
¤	02004	ABSORBANCE @ 440 nm	1	A440	Abs*1000	SPECTROPHOTOMETRIC ABSORBANCE READING
¤	02005	ABSORBANCE @ 740 nm	1	A740	Abs*1000	SPECTROPHOTOMETRIC ABSORBANCE READING
¤	02006	ABSORBANCE CO-EFFICIENT @ 340 nm	1	G340	M	CALCULATED FROM 440&740 NM ABSORBANCES
¤	02007	ABSORBANCE CO-EFFICIENT @ 440 nm	1	G440	M	CALCULATED FROM 340&740 NM ABSORBANCES
	10252	ACIDITY TOTAL	2	TOTAL ACIDITY	mg/L $CaCO_3$	TITROPROCESSOR
	18444	ALDICARB	2	ALDICARB	µg/L	HIGH PRESSURE LIQUID CHROMATOGRAPHY
	18130	ALDRIN	3	ALDRIN	µg/L	GAS CHROMATOGRAPHY
	10151	ALKALINITY PHENOL PHTHALEIN	1	ALKALINITY	mg/L $CaCO_3$	POTENTIOMETRIC TITRATION
*	10120	ALKALINITY TOTAL	2	ALK TOT	meq/L $CaCO_3$	VISUAL TITRATION
*	10121	ALKALINITY TOTAL	2	ALK TOT	meq/L $CaCO_3$	ELECTROMETRIC TITRATION
	10123	ALKALINITY TOTAL	2	ALK TOT	mg/L $CaCO_3$	ELECTROMETRIC TITRATION
	10101	ALKALINITY TOTAL ($CaCO_3$)	2	ALK TOT	mg/L $CaCO_3$	POTENTIOMETRIC TITRATION
	10102	ALKALINITY TOTAL ($CaCO_3$)	2	ALK TOT	mg/L $CaCO_3$	COLOURIMETRIC TITRATION
	10103	ALKALINTIY TOTAL ($CaCO_3$)	2	ALK TOT	mg/L $CaCO_3$	TITRATION
*	18075	ALPHA-BHC	3	ALPHA-BHC	µg/L	GAS CHROMATOGRAPHY
	13101	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	COLOURIMETRY
	13102	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	AAS - DIRECT ASPIRATION
	13103	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	AAS - SOLVENT EXTRACTION
	13104	ALUMINUM - DISSOLVED	2	Al DISS	mg/L Al	COLOUIMETRY
	13109	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	ICP 1502
	13111	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	ICP 1516
	13190	ALUMINUM - DISSOLVED	3	Al DISS	mg/L Al	ICP - MS
	13901	ALUMINUM - DISSOLVED	3	AL DISS	mg/L Al	AAS - FLAMELESS
	13001	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	COLOURIMETRY
	13002	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	AAS - DIRECT ASPIRATION
	13003	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	AAS - SOLVENT EXTRACTION
	13009	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	ICP 1502
	13011	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	ICP 1503
	13090	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	ICP - MS
	13911	ALUMINUM - TOTAL	3	Al TOTAL	mg/L Al	AAS - FLAMELESS
	13050	ALUMINUM SEDIMENTS	3	Al - PARTICULATE	µg/g	AAS - ACID DIGESTION
	07506	AMMONIA	2	NH_3	mg/L N	ION SELECTIVE ELECTRODE
	07551	AMMONIA	2	NH_3	mg/L N	DIRECT NESSLERIZATION
	07553	AMMONIA	2	NH_3	mg/L N	DISTILLATION AND TITRATION
	07554	AMMONIA	2	NH_3	mg/L N	DISTILLATION + NESSLERIZATION
	07555	AMMONIA	2	NH_3	mg/L N	ALPHA - NAPHTHOL METHOD

						(COLOURIMETRY)
	07556	AMMONIA	2	NH_3	mg/L N	COLOURIMETRY(INDOPHENOL BLUE)
	07557	AMMONIA	2	NH_3	mg/L N	AUTOMATED INDOPHENOL BLUE METHOD
	07564	AMMONIA DISSOLVED	1	AMMONIA DISS	mg/L N	ION CHROMATOGRAPHY
*	10702	ANIONIC TENSIDES MBAS	1	TENS AN	mg/L	MBAS
	51101	ANTIMONY DISSOLVED	1	Sb DISS	mg/l	AAS – DIRECT ASPIRATION
	33103	ARSENIC - DISSOLVED	3	As DISS	mg/L As	COLOURIMETRY
	33104	ARSENIC - DISSOLVED	3	As DISS	mg/L As	AAS - FLAMELESS
	33108	ARSENIC - DISSOLVED	3	As DISS	mg/L As	ICP
	33190	ARSENIC - DISSOLVED	3	As DISS	mg/L As	ICP - MS
	33003	ARSENIC - TOTAL	3	As TOTAL	mg/L As	COLOURIMETRY
	33007	ARSENIC - TOTAL	3	As TOTAL	mg/L As	AAS - FLAMELESS
	33008	ARSENIC - TOTAL	3	As TOTAL	mg/L As	ICP
	33009	ARSENIC - TOTAL	3	As TOTAL	mg/L As	ICP 1502
	33011	ARSENIC - TOTAL	3	As TOTAL	mg/L As	AAS - HYDRIDE
	33090	ARSENIC - TOTAL	3	As TOTAL	mg/L As	ICP - MS
	33202	ARSENIC SUSPENDED	3	As - PARTICULATE	µg/g	AAS - FLAMELESS -ACID DIGESTION
	18415	ATRAZINE - TOTAL	1	ATRAZINE	µg/L	GAS - LIQUID CHROMATOGRAPHY
*	56101	BARIUM - DISSOLVED	1	Ba DISS	mg/L Ba	AAS - DIRECT ASPIRATION
*	56001	BARIUM - TOTAL	1	Ba TOTAL	mg/L Ba	AAS - DIRECT ASPIRATION
*	56002	BARIUM - TOTAL	1	Ba TOTAL	mg/L Ba	FLAME EMISSION
	95100	BENZENE	1	BENZENE	µg/L	GC - MS
	95000	BENZOIC ACID	0	BENZOIC ACID	µg/L	GAS CHROMATOGRAPHY
*	18814	BHC	3	BHC	µg/L	GAS CHROMATOGRAPHY
	06201	BICARBONATE	0	BICARBONATE	mg/L HCO_3	CALCULATED
	08201	BIOCHEMICAL OXYGEN DEMAND	0	BOD	mg/L O_2	5-DAY DILUTION METHOD
	08202	BIOCHEMICAL OXYGEN DEMAND	0	BOD	mg/L O_2	5 DAY INCUBATION @ 20 DEG. C
	08203	BIOCHEMICAL OXYGEN DEMAND	0	BOD(ATU)	Mg/L	5 DAY INCUBATION @ 20°C ALLYL THIOUREA
	05101	BORON - DISSOLVED	1	B DISS	mg/L B	POTENTIOMETRIC - Mannitol
	05102	BORON - DISSOLVED	1	B DISS	mg/L B	CURCUMIN METHOD
	05105	BORON - DISSOLVED	1	B DISS	mg/L B	COLOURIMETRY
	05107	BORON - DISSOLVED	1	B DISS	mg/L B	ICP 1516
	05109	BORON - DISSOLVED	1	B DISS	mg/L B	ICP 1502
	05111	BORON - DISSOLVED	1	B DISS	µg/L B	ICP 1516
	05190	BORON - DISSOLVED	1	B DISS	mg/L B	ICP - MS
	05001	BORON - TOTAL	1	B TOTAL	mg/L B	AAS
	05002	BORON - TOTAL	1	B TOTAL	mg/L B	COLOURIMETRY
	05009	BORON - TOTAL	1	B TOTAL	mg/L B	ICP 1502
	05011	BORON - TOTAL	1	B TOTAL	mg/L B	ICP 1503
	05090	BORON - TOTAL	1	B TOTAL	mg/L B	ICP - MS
	48101	CADMIUM - DISSOLVED	3	Cd DISS	mg/L Cd	AAS - DIRECT ASPIRATION
	48102	CADMIUM - DISSOLVED	3	Cd DISS	mg/L Cd	AAS - SOLVENT EXTRACTION
	48109	CADMIUM - DISSOLVED	3	Cd DISS	mg/L Cd	ICP 1502

	48111	CADMIUM - DISSOLVED	3	Cd DISS	mg/L Cd	ICP 1516
	48190	CADMIUM - DISSOLVED	3	Cd DISS	mg/L Cd	ICP - MS
	48901	CADMIUM - DISSOLVED	3	Cd DISSOLVED	mg/L Cd	AAS - FLAMELESS
	48001	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	AAS - DIRECT ASPIRATION
	48002	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	AAS - SOLVENT EXTRACTION
	48009	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	ICP 1502
	48011	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	ICP 1503
	48090	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	ICP - MS
	48911	CADMIUM - TOTAL	3	Cd TOTAL	mg/L Cd	AAS - FLAMELESS
	48201	CADMIUM SUSPENDED	3	Cd - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
	20101	CALCIUM - DISSOLVED	3	Ca DISS	mg/L Ca	EDTA TITRATION
	20103	CALCIUM - DISSOLVED	3	Ca DISS	mg/L Ca	AAS
	20105	CALCIUM - DISSOLVED	3	Ca DISS	mg/L Ca	FLAME EMISSION
	20109	CALCIUM - DISSOLVED	3	Ca DISS	mg/L $CaCO_3$	ION CHROMATOGRAPHY
	20111	CALCIUM - DISSOLVED	3	Ca DISS	mg/L Ca	ICP 1516
	20115	CALCIUM - DISSOLVED	3	Ca DISS	mg/L Ca	ICP 1502
*	20003	CALCIUM - TOTAL	3	Ca TOTAL	mg/L Ca	AAS
	20106	CALCIUM HARDNESS	1	Ca HARDNESS	mg/L $CaCO_3$	EDTA TITRATION
*	06001	CARBON - TOTAL ORGANIC	0	TOC	mg/L C	INFRARED ANALYSIS - DUAL CHANNEL
	06101	CARBON ORGANIC - DISSOLVED	1	ORG. CARBON-DISS	mg/L	INFRARED ANALYSIS
	06076	CARBON ORGANIC - PARTICULATE	3	ORG. CARBON-PART	µg/g	CHN ANALYZER
	06077	CARBON ORGANIC - PARTICULATE	3	ORG. CARBON-PART	µg/g	FLAME IONIZATION
	06301	CARBONATE	0	CARBONATE	mg/L CO_3	CALCULATED
	08301	CHEMICAL OXYGEN DEMAND	0	COD	mg/L O_2	$K_2Cr_20_7$ METHOD
	17201	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	MERCURIC NITRATE TITRATION
	17202	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	SILVER NITRATE POTENTIOMETRIC
	17203	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	COLOURIMETRY
	17204	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	SILVER NITRATE TITRATION
	17205	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	SPECIFIC ION ELECTRODE
	17207	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	ION EXCHANGE
	17209	CHLORIDE - DISSOLVED	0	Cl DISS	mg/L Cl	ION CHROMATOGRAPHY
	06711	CHLOROPHYLL A	4	CHLORO A	mg/L	SCOR - UNESCO (COLOURIMETRY)
	24052	CHROMIUM - DISSOLVED	3	Cr DISS	mg/L Cr	AAS
	24111	CHROMIUM - DISSOLVED	3	Cr DISS	mg/L Cr	ICP 1516
	24190	CHROMIUM - DISSOLVED	3	Cr DISS	mg/L Cr	ICP - MS
	24901	CHROMIUM - DISSOLVED	3	Cr DISS	mg/L Cr	AAS - FLAMELESS
	24202	CHROMIUM - SUSPENDED	3	Cr - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
	24002	CHROMIUM - TOTAL	3	Cr TOTAL	mg/L Cr	AAS - DIRECT ASPIRATION
	24009	CHROMIUM - TOTAL	3	Cr TOTAL	mg/L Cr	ICP 1502
	24011	CHROMIUM - TOTAL	3	Cr TOTAL	mg/L Cr	ICP 1503
	24090	CHROMIUM - TOTAL	3	Cr TOTAL	mg/L Cr	ICP - MS
	24911	CHROMIUM - TOTAL	3	Cr TOTAL	mg/L Cr	AAS - FLAMELESS
*	24101	CHROMIUM HEXAVALENT	3	Cr HEX	mg/L Cr	COLOURIMETRY
	02070	CLARITY	1	CLARITY	m	HORIZONTAL BLACK DISC

	97320	CLOUD COVER	0	CLOUD COVER	PERCENT	ESTIMATED PERCENT
*	06402	CO_2 - DISSOLVED	0	CO_2 DISS	mg/L	
	27009	COLBALT TOTAL	3	Co TOTAL	mg/L Co	ICP 1502
	36001	COLIFORM - TOTAL	0	COLIFORM TOTAL	No./100 ml MF	MULTIPLE TEST TUBE
	36002	COLIFORM - TOTAL	0	COLIFORM TOTAL	No./100 ml MPN	MEMBRANE FILTRATION
	02011	COLOUR APPARENT	1	COLOUR APPARENT	Rel. Units	VISUAL COMPARISON
	29101	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	COLOURIMETRY
	29105	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	AAS - SOLVENT EXTRACTION
	29106	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	AAS - DIRECT ASPIRATION
	29109	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	ICP 1502
	29111	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	ICP 1516
	29190	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	ICP - MS
	29901	COPPER - DISSOLVED	3	Cu DISS	mg/L Cu	AAS - FLAMELESS
	29001	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	COLOURIMETRY
	29005	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	AAS - SOLVENT EXTRACTION
	29006	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	AAS - DIRECT ASPIRATION
	29009	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	ICP 1502
	29011	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	ICP 1503
	29090	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	ICP - MS
	29911	COPPER - TOTAL	3	Cu TOTAL	mg/L Cu	AAS - FLAMELESS
	29206	COPPER SUSPENDED	3	Cu - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
*	06606	CYANIDE	3	CN	mg/L CN	COLOURIMETRY
	18002	DDT - TOTAL	3	DDT TOTAL	µg/L	GAS CHROMATOGRAPHY
	18150	DIELDRIN	3	DIELDRIN	µg/L	GAS CHROMATOGRAPHY
	97184	DISCHARGE MONTHLY MEAN	0	DISCH.MON.MEAN	M3/s	CALCULATED
	08101	DISSOLVED OXYGEN	1	DISS O_2	mg/L O_2	WINKLER METHOD
	08102	DISSOLVED OXYGEN	1	DISS O_2	mg/L O_2	DISSOLVED OXYGEN METER
	08107	DISSOLVED OXYGEN	1	DISS O_2	mg/L O_2	CALCULATED FROM % SAT., H2O TEMP, AND PRESSURE AT SITE.
	02040	ELECTRICAL CONDUCTANCE	0	ELEC. COND.	µs/cm	ELECTROMETER
	02049	ELECTRICAL CONDUCTANCE	0	ELEC COND	µs/cm	RADIOMETER CDM 83
	02041	ELECTRICAL CONDUCTIVITY	0	ELEC COND	µs/cm	CONDUCTIVITY METER
*	18140	ENDRIN	3	ENDRIN	µg/L	GAS CHROMATOGRAPHY
	36011	FAECAL COLIFORM BACTERIA	0	FAEC COL	No./100 ml MF	MULTIPLE TEST TUBE
	36012	FAECAL COLIFORM BACTERIA	0	FAEC COL	No./100 ml MPN	MEMBRANE FILTRATION
*	36101	FAECAL STREPTOCOCCI	0	FAEC STREP	No./100 ml MF	MULTIPLE TEST TUBE
*	36102	FAECAL STREPTOCOCCI	0	FAEC STREP	No./100 ml MPN	MEMBRANE FILTRATION
*	10501	FIXED SUSPENDED SOLIDS	0	FIX SUSP SOLIDS	mg/L	GRAVIMETRIC METHOD
	09104	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	COLOURIMETRY
	09105	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	SPECIFIC ION ELECTRODE
	09106	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	ELECTRODE POTENTIAL METHOD
	09107	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	POTENTIOMETRIC - SPECIFIC ION
	09110	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	PHOTOMETRIC (LA-ALIZARIN COMPLEX)
	09116	FLUORIDE - DISSOLVED	1	F DISS	mg/L F	ION CHROMATOGRAPHY

	10603	HARDNESS TOTAL	1	HARDNESS TOTAL	mg/L $CaCO_3$	EDTA TITRATION
	06570	HYDROCARBONS - TOTAL	1	HYDROCAR.-TOTAL	µg/L	IR INTENSITY SPECTROSCOPY
*	01000	HYDROGEN SULPHIDE	2	H_2S	mg/L	
	97160	INSTANTANEOUS DISCHARGE	1	INST DISCHG	m^3/s	GAUGE HEIGHT
	00190	INTEGRATED SAMPLE Code is for internal use only	0	INTEG SAMPLE	N/A	VERTICAL(V),HORIZONTAL(H), TIME(T)
	26102	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	COLOURIMETRY
	26104	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	AAS - DIRECT ASPIRATION
	26105	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	AAS - SOLVENT EXTRACTION
	26109	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	ICP 1502
	26111	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	ICP 1516
	26190	IRON - DISSOLVED	2	Fe DISS	mg/L Fe	ICP - MS
	26901	IRON - DISSOLVED	2	Fe DISS	mg/L	AAS - FLAMELESS
	26002	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	COLOURIMETRY
	26004	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	AAS - DIRECT ASPIRATION
	26005	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	AAS - SOLVENT EXTRACTION
	26009	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	ICP 1502
	26011	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	ICP 1503
	26090	IRON - TOTAL	2	Fe TOTAL	mg/L Fe	ICP - MS
	26204	IRON SUSPENDED	3	Fe - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
	82101	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	AAS - DIRECT ASPIRATION
	82102	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	COLOURIMETRY
	82103	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	AAS - SOLVENT EXTRACTION
	82109	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	ICP 1502
	82111	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	ICP 1516
	82190	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	ICP - MS
	82901	LEAD - DISSOLVED	3	Pb DISS	mg/L Pb	AAS - FLAMELESS
	82001	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	AAS - DIRECT ASPIRATION
	82002	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	AAS - SOLVENT EXTRACTION
	82009	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	ICP 1502
	82011	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	ICP 1503
	82090	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	ICP - MS
	82360	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	ICP - AES
	82911	LEAD - TOTAL	3	Pb TOTAL	mg/L Pb	AAS - FLAMELESS
	82201	LEAD SUSPENDED	3	Pb - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
X	18070	LINDANE (GAMMA - BHC)	3	LINDANE	µg/L	GAS-LIQUID CHROMATOGRAPHY (ECD)
*	03101	LITHIUM - DISSOLVED	1	Li DISS	mg/L Li	AAS - DIRECT ASPIRATION
*	03001	LITHIUM - TOTAL	1	Li TOTAL	mg/L Li	AAS - DIRECT ASPIRATION
	12102	MAGNESIUM - DISSOLVED	0	Mg DISS	mg/L Mg	AAS - DIRECT ASPIRATION
	12103	MAGNESIUM - DISSOLVED	0	Mg DISS	mg/L Mg	EDTA TITRATION
	12109	MAGNESIUM - DISSOLVED	0	Mg DISS	mg/L Mg	ION CHROMATOGRAPHY
	12111	MAGNESIUM - DISSOLVED	0	Mg DISS	mg/L Mg	ICP 1516
	12115	MAGNESIUM - DISSOLVED	0	Mg DISS	mg/L Mg	ICP 1502
*	12001	MAGNESIUM - TOTAL	0	Mg TOTAL	mg/L Mg	COLOURIMETRY
*	12002	MAGNESIUM - TOTAL	0	Mg TOTAL	mg/L Mg	AAS - DIRECT ASPIRATION

*	12003	MAGNESIUM - TOTAL	0	Mg TOTAL	mg/L Mg	EDTA TITRATION
	25101	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	COLOURIMETRY
	25104	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	AAS - DIRECT ASPIRATION
	25105	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	AAS - SOLVENT EXTRACTION
	25109	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	ICP 1502
	25111	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	ICP 1516
	25190	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	ICP - MS
	25901	MANGANESE - DISSOLVED	2	Mn DISS	mg/L Mn	AAS - FLAMELESS
	25004	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	AAS - DIRECT ASPIRATION
	25005	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	AAS - SOLVENT EXTRACTION
	25009	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	COLOURIMETRY
	25010	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	ICP 1502
	25011	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	ICP 1503
	25090	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	ICP - MS
	25911	MANGANESE - TOTAL	2	Mn TOTAL	mg/L Mn	AAS - FLAMELESS
	25204	MANGANESE SUSPENDED	3	Mn - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION
	80111	MERCURY - DISSOLVED	3	Hg DISS	µg/L Hg	AAS - FLAMELESS
	80011	MERCURY - TOTAL	3	Hg TOTAL	µg/L Hg	AAS - FLAMELESS
	80016	MERCURY - TOTAL	3	Hg TOTAL	µg/L Hg	COLD BR WET OXIDATION P AAS
	80201	MERCURY SUSPENDED	3	Hg PARTICULATE	µg/g	AAS - FLAMELESS
*	18125	MIREX	3	MIREX	µg/L	GAS CHROMATOGRAPHY
	28101	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	AAS - DIRECT ASPIRATION
	28102	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	AAS - SOLVENT EXTRACTION
	28109	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	ICP 1502
	28111	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	ICP 1516
	28190	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	ICP - MS
	28901	NICKEL - DISSOLVED	3	Ni DISS	mg/L Ni	AAS - FLAMELESS
	28001	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	AAS - DIRECT ASPIRATION
	28002	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	AAS - SOLVENT EXTRACTION
	28009	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	ICP 1502
	28011	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	ICP 1503
	28090	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	ICP - MS
	28911	NICKEL - TOTAL	3	Ni TOTAL	mg/L Ni	AAS - FLAMELESS
	07300	NITRATE	3	NO_3-N	mg/L N	AUTOMATED HYDRAZINE REDUCTION
*	07306	NITRATE	2	NO_3-N	mg/L N	BRUCINE METHOD
*	07309	NITRATE	2	NO_3-N	mg/L N	CHROMOTROPIC ACID
*	07313	NITRATE	2	NO_3-N	mg/L N	CADMIUM REDUCTION
*	07314	NITRATE	2	NO_3-N	mg/L N	DEVARDA'S ALLOY METHOD
	07320	NITRATE	1	NO_3-N	mg/L N	ION SPECIFIC ELECTRODE
	07321	NITRATE	2	NO_3-N	mg/L N	ION CHROMATOGRAPHY
	07316	NITRATE + NITRITE	2	NO_3NO_2	mg/L N	ION CHROMATOGRAPHY
*	07207	NITRITE	2	NO_2-N	mg/L N	COLOURIMETRY (SULFANILAMIDE)
	07210	NITRITE	3	NO_2-N	mg/L N	COLOURIMETRIC (CLEVE'S ACID)
	07302	NITROGEN (NO_3-N + NO_2-N)	2	NO_3NO_2	mg/L N	CALCULATED (CODES 07321 + 07210)

	07303	NITROGEN (NO_3-N + NO_2-N)	1	NO_3NO_2	mg/L N	CALCULATED (CODES 07320 + 07210)
*	07001	NITROGEN KJELDAHL ORGANIC	1	N KJEL	mg/L N	KJELDAHL METHOD
*	07004	NITROGEN KJELDAHL ORGANIC	1	N KJEL	mg/L N	COLOURIMETRY
	07912	NITROGEN ORGANIC - PARTICULATE	3	ORG. NIT. -PART	µg/g	CHN ANALYZER
	07401	NITROGEN ORGANIC DISSOLVED	1	ORG. NIT.-DISS	mg/L	KJELDAHL WITH REMOVAL OF NH_3
	07403	NITROGEN ORGANIC DISSOLVED	1	ORG. NIT.-DISS	mg/L	DIFFERENCE CALCULATION
	07601	NITROGEN TOTAL	2	TOTAL NITROGEN	mg/L N	COLOURIMETRY
+	07606	NITROGEN TOTAL	2	TOTAL NITROGEN	mg/L N	ALKALINE PERSULPHATE DIGESTION
	07507	NITROGEN TOTAL AMMONIA	2	NH_4-N	mg/L N	COLOURIMETRIC (SALICYLATE METHOD)
	07550	NITROGEN TOTAL AMMONIA	2	NH_4-N	mg/L N	NESSLERIZATION & DISTILLATION
	07105	NITROGEN,NITRATE + NITRITE	2	NO_3NO_2	mg/L N	COLOURIMETRY
*	18015	O,P-DDD	3	O,P-DDD	µg/L	GAS CHROMATOGRAPHY
*	18025	O,P-DDE	3	O,P-DDE	µg/L	GAS CHROMATOGRAPHY
*	18005	O,P-DDT	3	O,P-DDT	µg/L	GAS CHROMATOGRAPHY
	06521	OIL AND GREASE	0	OIL AND GREASE	mg/L	PETROLEUM ETHER EXTRACTION
*	17860	ORGANO CL COMPOUNDS TOTAL	3 2	ORGANO Cl CMPDS	µg/L	GAS CHROMATOGRAPHY
*	15255	ORTHOPHOSPHATE - DISSOLVED	3	P ORTHO DISS	mg/L P	COLOURIMETRY
	15256	ORTHOPHOSPHATE - DISSOLVED	3	P ORTHO DISS	mg/L P	MOLBDENUM BLUE-ASCORBIC ACID REDUCTION
*	15205	ORTHOPHOSPHATE - TOTAL	3	P ORTHO TOTAL	mg/L P	COLOURIMETRY
*	15254	ORTHOPHOSPHATE SOL REACTIVE	3	PO_4-P SOL	mg/L PO_4	COLOURIMETRY
*	18010	P,P-DDD	3	P,P-DDD	µg/L	GAS CHROMATOGRAPHY
*	18803	P,P-DDD OLEFIN	3	P,P-DDD OLEFIN	µg/L	GAS CHROMATOGRAPHY
*	18020	P,P-DDE	3	P,P-DDE	µg/L	GAS CHROMATOGRAPHY
*	18000	P,P-DDT	3	P,P-DDT	µg/L	GAS CHROMATOGRAPHY
	18165	PCBS	3	PCBS	µg/L	GAS - LIQUID CHROMATOGRAPHY
	08001	PERCENT DO SATURATION	0	PERCENT DO SAT	PERCENT	CALCULATION OR NOMOGRAM
	08005	PERCENT DO SATURATION	0	PERCENT DO SAT	PERCENT	METER (YSI)
*	08401	PERMANGANATE VALUE	0	PERM V	mg/L O_2	$KMnO_4$ METHOD
*	08402	PERMANGANATE VALUE	0	PERM V	mg/L O_2	$KMnO_4$ METHOD - 4 HOUR DIGESTION
	10300	pH	1	pH	pH Units	COLORIMETRIC METHOD
	10301	pH	1	pH	pH Units	pH METER (ELECTROMETRIC)
	10302	pH	1	pH	pH Units	pH METER(ELECTROMETRIC) AT 25 DEG. C
*	06532	PHENOLS	3	PHENOLS	mg/L	COLOURIMETRY
	95011	PHENOLS	1	PHENOLS	µg/L	GC - MS
*	15403	PHOSPHATE - TOTAL	3	PO_4 TOTAL	mg/L PO_4	COLOURIMETRY
*	15408	PHOSPHATE - TOTAL	3	PO_4 TOTAL	mg/L P	COLOURIMETRY
*	15313	PHOSPHATE - TOTAL INORGANIC	3	P INORG AH TOTAL	mg/L P	COLOURIMETRY
	15406	PHOSPHATE TOTAL	3	P TOTAL	mg/L P	ACID PERSULPHATE DIGESTION
*	15103	PHOSPHORUS - DISSOLVED	3	P DISS	mg/L P	COLOURIMETRY
*	15901	PHOSPHORUS - PARTICULATE	3	P PART	mg/L P	DIFFERENCE CALCULATION
	15405	PHOSPHORUS - TOTAL	3	P TOTAL	mg/L P	COLOURIMETRY
	15417	PHOSPHORUS TOTAL DISSOLVED	3	P TOTAL DISS.	mg/L P	COLOURIMETRY
	15902	PHOSPHORUS TOTAL PARTICULATE	3	P TOTAL PART.	µg/g	DIFFERENCE CALCULATION

	15903	PHOSPHORUS TOTAL PARTICULATE	3	P TOTAL PART.	µg/g	ACID-EXTRACTION COLOURIMETRY
*	36302	PHYTOPLANKTON BIOMASS	1	PHYTO BIO	mg/m^3	
*	36301	PHYTOPLANKTON COUNT	0	PHYTO COUNT	No./L	TOTAL NUMBER OBSERVED
*	36304	PHYTOPLANKTON COUNT	0	PHYTO COUNT	No./ml	TOTAL NUMBER OBSERVED
*	06510	POLY AROMATIC HYDROCARBONS	3	PAH	µg/L	FLUORESCENCE SPECTROPHOTOMETRY
	06505	POLYAROMATIC HYDROCARBONS	2	PAH	µg/L	GC - MS
	19102	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	AAS
	19103	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	FLAME PHOTOMETRY
	19105	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	AAS - DIRECT ASPIRATION
	19111	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	ICP 1516
	19112	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	ION CHROMATOGRAPHY
	19115	POTASSIUM - DISSOLVED	1	K DISS	mg/L K	ICP 1502
*	19001	POTASSIUM - TOTAL	1	K TOTAL	mg/L K	AAS
*	19002	POTASSIUM - TOTAL	1	K TOTAL	mg/L K	FLAME PHOTOMETRY
	10452	RESIDUE FILTERABLE	0	RESIDUE - FILT	mg/L	GRAVIMETRIC METHOD
	10551	RESIDUE FIXED	0	RESIDUE - FIXED	mg/L	GRAVIMETRIC METHOD
	10571	RESIDUE FIXED TOTAL	0	RESIDUE FIX TOT	mg/L	GRAVIMETRIC
	10473	RESIDUE TOTAL	0	RESIDUE - TOT	mg/L	GRAVIMETRIC MICRO-METHOD
	10521	RESIDUE VOLATILE TOTAL	0	RESIDUE - VOL	mg/L	CALCULATED
	02055	SALINITY	0	SALINITY	ppt	TDS-SALINITY-CONDUCTIVITY METER @ 25°C
	36220	SALMONELLA	0	SALMONELLA	No./L	CONCENTRATION BY FILTRATION
	34102	SELENIUM - DISSOLVED	3	Se DISS	mg/L Se	AAS - FLAMELESS
	34108	SELENIUM - DISSOLVED	3	Se DISS	mg/L Se	ICP
	34190	SELENIUM - DISSOLVED	3	Se DISS	mg/L Se	ICP - MS
	34002	SELENIUM - TOTAL	3	Se TOTAL	mg/L Se	AAS
	34007	SELENIUM - TOTAL	3	Se TOTAL	mg/L Se	AAS - FLAMELESS - HYDRIDE
	34008	SELENIUM - TOTAL	3	Se TOTAL	mg/L Se	ICP
	34090	SELENIUM - TOTAL	3	Se TOTAL	mg/L Se	ICP - MS
	14111	SILICA - DISSOLVED	2	SI DISS	mg/L SiO_2	ICP 1516
	14019	SILICA - REACTIVE	2	SI REAC	mg/L SiO_2	ICP 1502
	14101	SILICA - REACTIVE	2	SI REAC	mg/L SiO_2	COLOURIMETRY
	14105	SILICA REACTIVE	3	SI REAC	mg/L SiO_2	COLOURIMETRY
	47101	SILVER DISSOLVED	2	Ag DISS	mg/L	AAS – DIRECT ASPITATION
	11102	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	AAS
	11103	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	FLAME PHOTOMETRY
	11105	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	AAS - DIRECT ASPIRATION
	11111	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	ICP 1516
	11112	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	ION CHROMATOGRAPHY
	11115	SODIUM - DISSOLVED	0	Na DISS	mg/L Na	ICP 1502
*	11001	SODIUM - TOTAL	0	Na TOTAL	mg/L Na	AAS
*	11002	SODIUM - TOTAL	0	Na TOTAL	mg/L Na	FLAME PHOTOMETRY
	11201	SODIUM ADSORPTION RATIO	3	SAR	Rel Unit	DIFFERENCE CALCULATION
	11116	SODIUM DISSOLVED	2	Na DISS	mg/L Na	AAS - EMISSION
	16301	SULPHATE	0	SULPHATE	mg/L SO_4	GRAVIMETRIC METHOD

	16302	SULPHATE	0	SULPHATE	mg/L SO_4	TURBIDIMETRIC METHOD
	16303	SULPHATE	0	SULPHATE	mg/L SO_4	TITRATION
	16304	SULPHATE	0	SULPHATE	mg/L SO_4	AUTOANALYZER
	16306	SULPHATE	0	SULPHATE	mg/L SO_4	COLOURIMETRY
	16309	SULPHATE	0	SULPHATE	mg/L SO_4	ION CHROMATOGRAPHY
	00125	SUM OF ANIONS	3	SUM OF ANIONS	meq/L	CALCULATED
	00120	SUM OF CATIONS	3	SUM OF CATIONS	meq/L	CALCULATED
	00130	SUM OF CATIONS + ANIONS	3	SUM OF CATIONS + ANIONS	meq/L	CALCULATED
	10401	SUSPENDED SOLIDS 105 DEG	0	SUSP SOL - 105	mg/L	GRAVIMETRIC METHOD
	10408	SUSPENDED SOLIDS 180 DEG	0	SUSP SOL - 180	mg/L	GRAVIMETRIC METHOD
	02061	TEMPERATURE	1	TEMP	Deg. C	MERCURY THERMOMETER
	02062	TEMPERATURE	1	TEMP	Deg. C	BATTERY THERMOMETER
*	97060	TEMPERATURE - AIR	1	TEMP-AIR	Deg. C	
	08305	TOTAL COD	0	COD	mg/L O_2	$KMnO_4$ METHOD
	02050	TOTAL DISSOLVED SOLIDS	0	TDS	mg/L	CALIBRATED CONDUCTIVITY @25°C
	02076	TRANSPARENCY	1	TRANS	Metre	30 CM SECCHI DISC
	02071	TURBIDITY	1	TURBIDITY	JTU	VISUAL
	02073	TURBIDITY	1	TURBIDITY	JTU	PHOTOMETRY
	02074	TURBIDITY	1	TURBIDITY	NTU	NEPHELOMETRIC - HACH
	02075	TURDIBITY LIGHT PENETRATION (transparency)	1	TRANSPARENCY	Metre	SECCHI DEPTH
*	10531	VOLATILE DISSOLVED SOLIDS	0	VOL DISS SOLIDS	mg/L	GRAVIMETRIC METHOD
*	10511	VOLATILE SUSPENDED SOLIDS	0	VOL SUSP SOLIDS	mg/L	GRAVIMETRIC METHOD
	30101	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	COLOURIMETRY
	30104	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	AAS - DIRECT ASPIRATION
	30105	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	AAS - SOLVENT EXTRACTION
	30109	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	ICP 1502
	30111	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	ICP 1516
	30190	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	ICP - MS
	30901	ZINC - DISSOLVED	3	Zn DISS	mg/L Zn	AAS - FLAMELESS
	30001	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	COLOURIMETRY
	30004	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	AAS - DIRECT ASPIRATION
	30005	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	AAS - SOLVENT EXTRACTION
	30009	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	ICP 1502
	30011	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	ICP 1503
	30090	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	ICP - MS
	30911	ZINC - TOTAL	3	Zn TOTAL	mg/L Zn	AAS - FLAMELESS
	30204	ZINC SUSPENDED	3	Zn - PARTICULATE	µg/g	AAS - DIRECT ASPIRATION

ICP 1516 - By inductively coupled argon plasma emission spectroscopy (ICAP). The sample is filtered in the field through a 0.45 U membrane filter and preserved with diluted mineral acid. The sample is aspirated and the emission is measured at the appropriate wave length and compared with that of identically prepared standard solutions. (Codes ending with 111)

ICP 1503 - By inductively coupled argon plasma emission spectroscopy (ICAP). The sample is preserved in the field with dilute mineral acid. A sample aliquot is digested with aqua regia and evaporated to near dryness. The residue is dissolved in conc. HCl and diluted to one-fifth of the aliquot volume. The digested sample is filtered through a 0.45 U membrane filter and aspirated. The emission is measured spectrophotometrically and compared with that of an identically prepared standard solution. (Codes ending with 011)

ICP 1502 - Inductively coupled argon plasma (ICAP) emission spectrometry. Samples preserved with HNO3, digested with conc. HNO3 or aqua regia, concentrated, and aspirated from an autosampler. Emission are compared to Std.
Dissolved: the sample is filtered through 0.45 U membrane filter.
Extractable: samples are concentrated 5 to 10 times, and aspirated.
(Codes ending with 009 for Total and 109 for Dissolved. Codes ending with 115 for Dissolved Sodium, Potassium, Calcium and Magnesium)

*These codes are no longer required by the GEMS/Water Program and are only valid for past data.

CHAPTER X: DATA ANALYSIS AND PRESENTATION

CONTENTS

1. INTRODUCTION

Regional and global environmental assessments and reports on water quality, rely on standardized statistical summaries of monitoring results from all stations, by country during the reference year. After routine screening of submitted data, monitoring results are examined for significant changes or unusual values in comparison with previous data.

These types of assessments often contain maps, graphs and tables allowing comparison of the results with use - related water quality criteria. For example, pollution load can be given for the global river flux stations. Some of the material can be produced using the RAISON software system described earlier.

This chapter outlines the capabilities of RAISON™, the application software used for the quantitative numerical and statistical evaluation of the GEMS/Water database and presents examples of typical outputs that will be used in assessments.

2. A SOFTWARE SYSTEM FOR THE ANALYSIS OF GEMS/Water DATA

2.1 Description of RAISON

The acronym RAISON stands for **R**egional **A**nalysis by **I**ntelligent **S**ystems **ON** a micro computer. RAISON is a quantitative numerical analysis system with GIS (Geographical Information System) graphics and expert systems capabilities. RAISON also provides a platform for the development and application of environmental simulation and predictive models. RAISON is configured to run in a micro computer environment. The system operates on any PC compatible system with sufficient speed and storage (a minimum of 40 Mb is recommended). The system was developed specifically to address the requirements for assessments and research into large scale environmental issues. The system consists of database, spreadsheet, analysis and graphics components. Each of these elements is fully integrated to the overall system allowing transparent movement and transfer of information between all of the components.

The database is a schema based system that allows the user to design the database interface according to individual requirements. The user defined layouts can contain both numeric and character information and therefore, databases are very versatile in allowing the combination of variable data types in one structure. Import and export capabilities support common commercial database packages. Data can be reviewed and edited directly in the database files. Retrievals of data are available directly from the spreadsheet and the mapping system as well as the database system itself.

Spreadsheets have become widely used for data evaluation in many fields. RAISON provides a fully functional spreadsheet integrated to the system such that functions and relationships determined in spreadsheet form can be easily passed to the GIS (Geographical Information System) for manipulation and presentation. The main menu contains commands that access the graphics and database systems directly. For data treatment, a scientific graphing system with full editing capability is available to the user. The spreadsheet also supports a suite of library functions for data manipulation. User constructed functions can be applied to spreadsheet cells allowing numerical analysis to be done quickly and efficiently.

In addition to the user defined functions, RAISON has standard statistical functions available. Frequency distribution analysis, percentile box plots, regression and correlation analysis and standard descriptive statistics are callable from the main menu. All analyses conducted within the integrated environment can be transferred through the graphics system for display. The user may construct multiple component screens combining numeric, graphical and map based imagery.

RAISON also contains a full featured graphics editor and toolkit for manipulation and control of imagery. Features include, cut and paste, pixel based colour control, text manipulation for titles and annotation and assorted drawing tools. The graphics editor enables a wide variety of graphics formats to be handled including scanner imagery.

The RAISON mapping and GIS component enables map based retrievals where parameters can be selected from multiple databases of differing characteristics. Individual or regional grouped stations are accessible. Once analyzed, numerical results or calculated map attribute information can be transferred directly to the mapping system. Logical constructs of attribute information can also be made and presented within the system. Map resolution is dependent only upon the map scaling used for input. The system allows rapid zooming between various maps with full access to data sets at whichever map scale is selected. Icons are used to select maps and stations for assessment. Data may be retrieved via the map system either by individual monitoring station or by selecting a group of stations by encircling them with a polygon. All stations within the group will be accessed together into a single working file.

The macro language RPL (RAISON Programming Language) which is designed to access all RAISON functionality in a batch mode, enables the user to construct procedures to implement on multiple files. By using this feature, for example, a particular procedure could be run on a station by station basis with results compiled by country including the mapping and graphics required for the interpretation and reporting function.

The overall nature of the RAISON system provides a flexible platform on which to undertake a wide variety of environmental assessment and research topics. The integrated features of RAISON enhance the users ability to quickly and efficiently analyze and evaluate monitoring data and produce presentation quality output to aid in interpretation.

2.2 RAISON/GEMS Application

RAISON/GEMS is the current application system used for quantitative numerical and statistical evaluations of the GEMS/Water database. The system is geographically based allowing for interactive assessment and display of all parameters currently on file in the GEMS/Water archives, using a geographical framework. The RAISON/GEMS application was developed to facilitate interpretation of GEMS/Water data. By integrating the analytical functions of database, spreadsheet, graphics and geographical information system with numerical and statistical methods, the RAISON/GEMS system is a powerful tool for interpreting and determining aquatic effects issues on local, regional and global scales. The database structure allows variable data formats to be used. This flexibility simplifies operations of multi-disciplinary integrated studies.

Although the RAISON system includes expert systems capabilities, the RAISON/GEMS application does not support this component. The segmenting of RAISON capability is designed to enable a graduated development in RAISON usage. The GEMS/Water application is fully functional for the current requirements of database manipulation, analysis and display. As the interpretive requirements of GEMS/Water increase this type of capability may be included.

Whereas it is recognized that there are many and varied approaches to analyzing, presenting and interpreting water data for both quantity and quality, this chapter attempts to provide some basic procedures that should simplify and make more consistent the approach to GEMS/Water data. Effective and clear data presentation can significantly increase the ease with which interpretation can be made. By using a suite of standardized data analysis procedures the presentation of statistically treated results can effectively assist in the identification of issues of concern and the existence of trends in water quality and quantity variables. Recognizing the emergence of regional and global trends in the water sector may assist in the early identification of long and short term changes effecting large sectors of the global population.

3. DATA ANALYSIS AND PRESENTATION

3.1 Display of Sampling Locations

Monitoring activities under GEMS/Water are station based. It is desirable however, to review information at the regional and global scales in addition to that which can be achieved by examining individual monitoring stations. Figure 1 displays the locations of all existing monitoring stations for which data is available in the GEMS/Water archives monitored during Phase One. Maps of this type are useful for global evaluations and the identification of global parameter distributions.

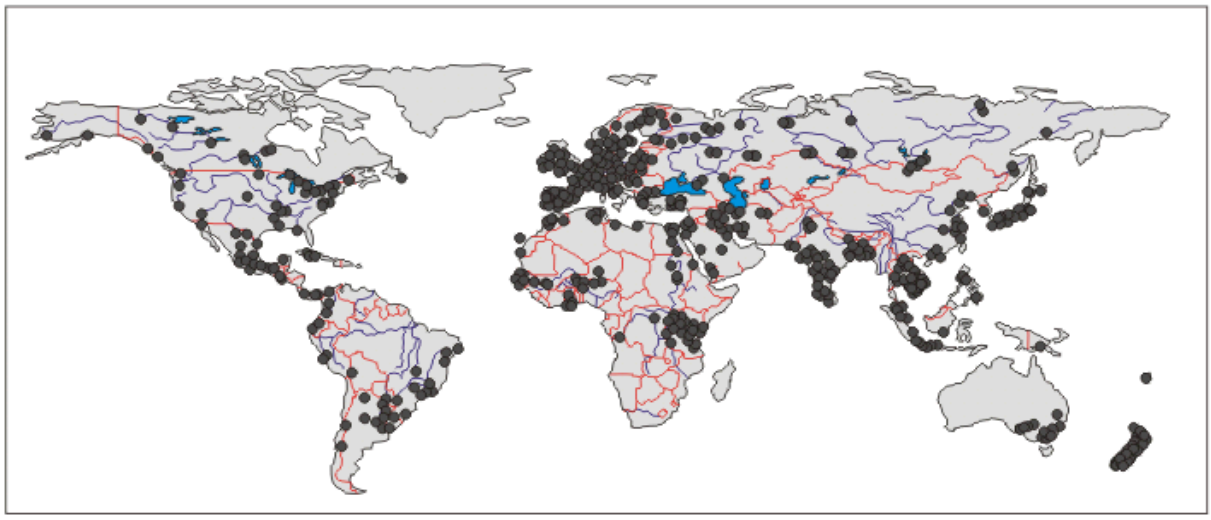


Figure 1: Distribution of GEMS/Water Monitoring Stations

3.2 Standard Data Evaluation on Global and Regional Scales

Investigations that are carried out at the national level can be depicted with increased resolution and clarity. Figure 2 shows a close up look at the GEMS/Water monitoring stations sampled in India. Such maps can also be used by the RAISON/GEMS application for direct access to databases with selective retrieval criteria. Numerical and statistical analyses can proceed at this point with results produced for map based output.

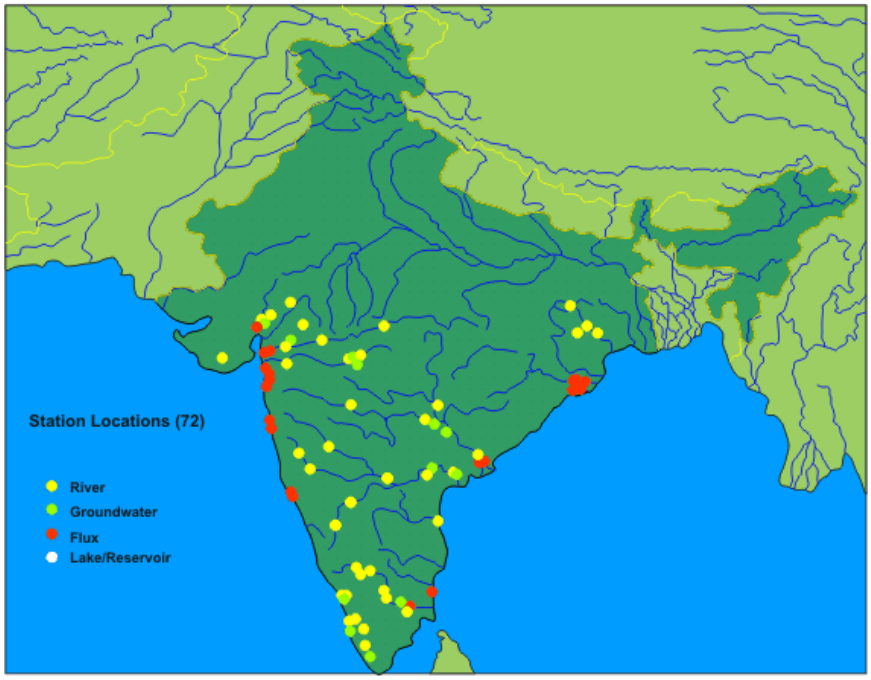


Figure 2: Monitoring Sites for GEMS/Water in India.

To begin a standard data evaluation, percentile box plots can be constructed for individual stations or accumulated at various levels of amalgamation (eg. including station types at national, regional and global levels). Figure 3 is an example of a percentile boxplot summarizing alkalinity (mg/L) measured at all GEMS/Water stations and presented according to the six GEMS/Water global regions. The box statistics used are

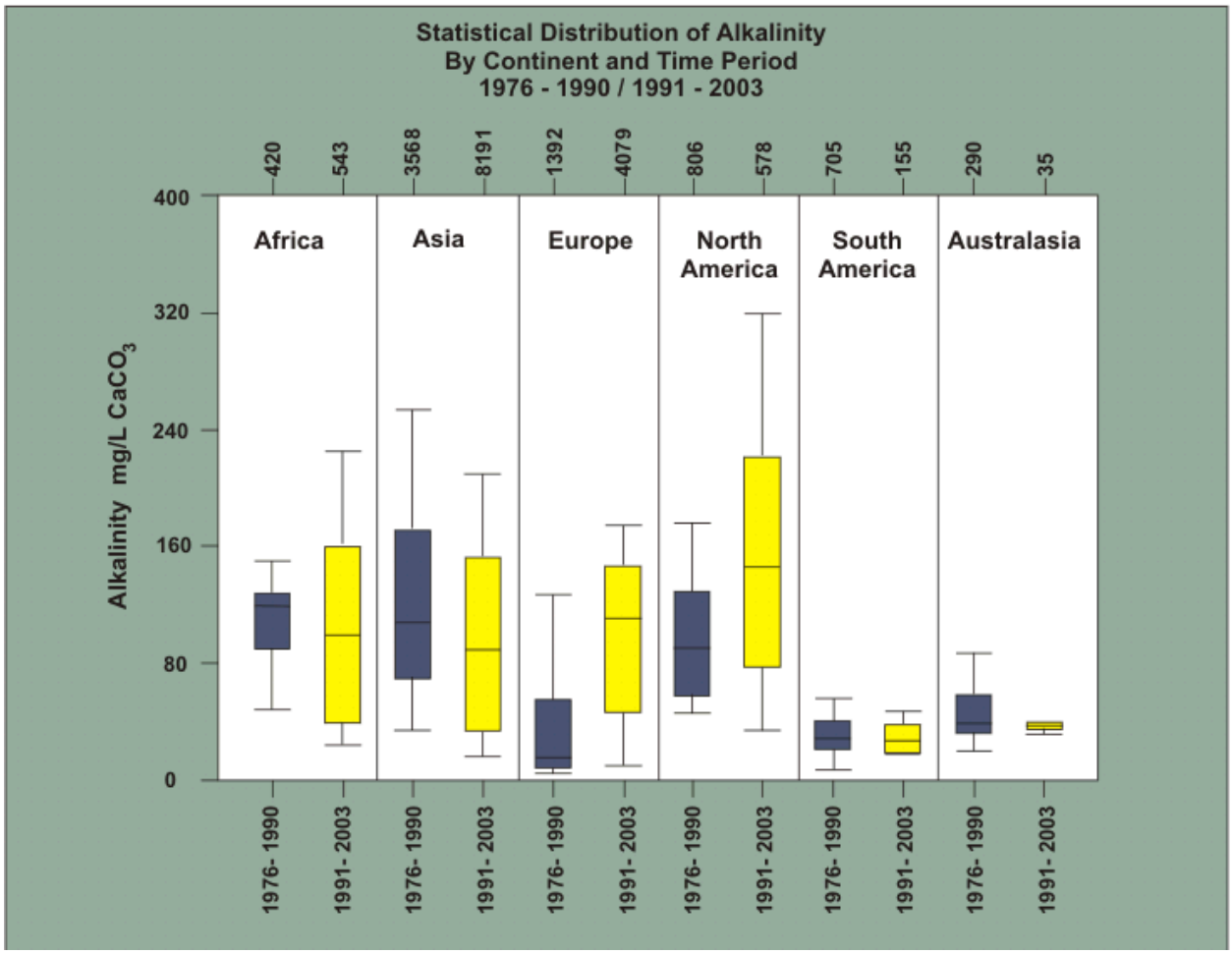


Figure 3: Alkalinity (mg/L) Expressed as Percentiles
(see text for detailed explanation).

the 10th percentile at the extended base of the box; the 25th percentile, which is the base of the box; the 50th percentile, which is shown as the horizontal line within the box; the 75th percentile, which is the upper edge of the box; the 90th percentile is shown as the extended upper edge of the box. Included in the upper portion of Figure 3 is the number of samples used in each computation. Data are presented for the six GEMS/Water Regions, ie. Africa, Asia, Europe, North America, South America and Australasia.

Statistical procedures including frequency distribution analysis are used to identify the characteristics of data prior to interpretive analysis. Figure 4 is an example for the variable biochemical oxygen demand (BOD) for a station on the Sabarmati River, India.

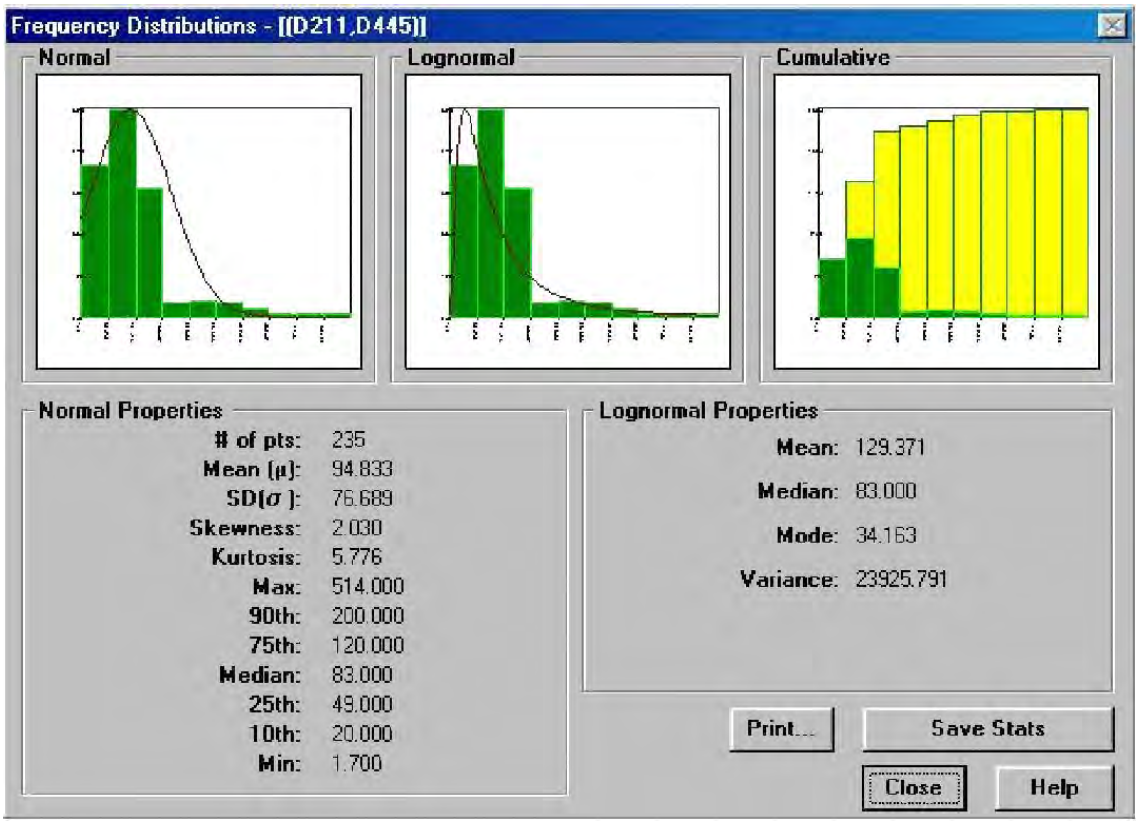


Figure 4: Frequency Distribution of BOD for a station on the Sabarmati River, India

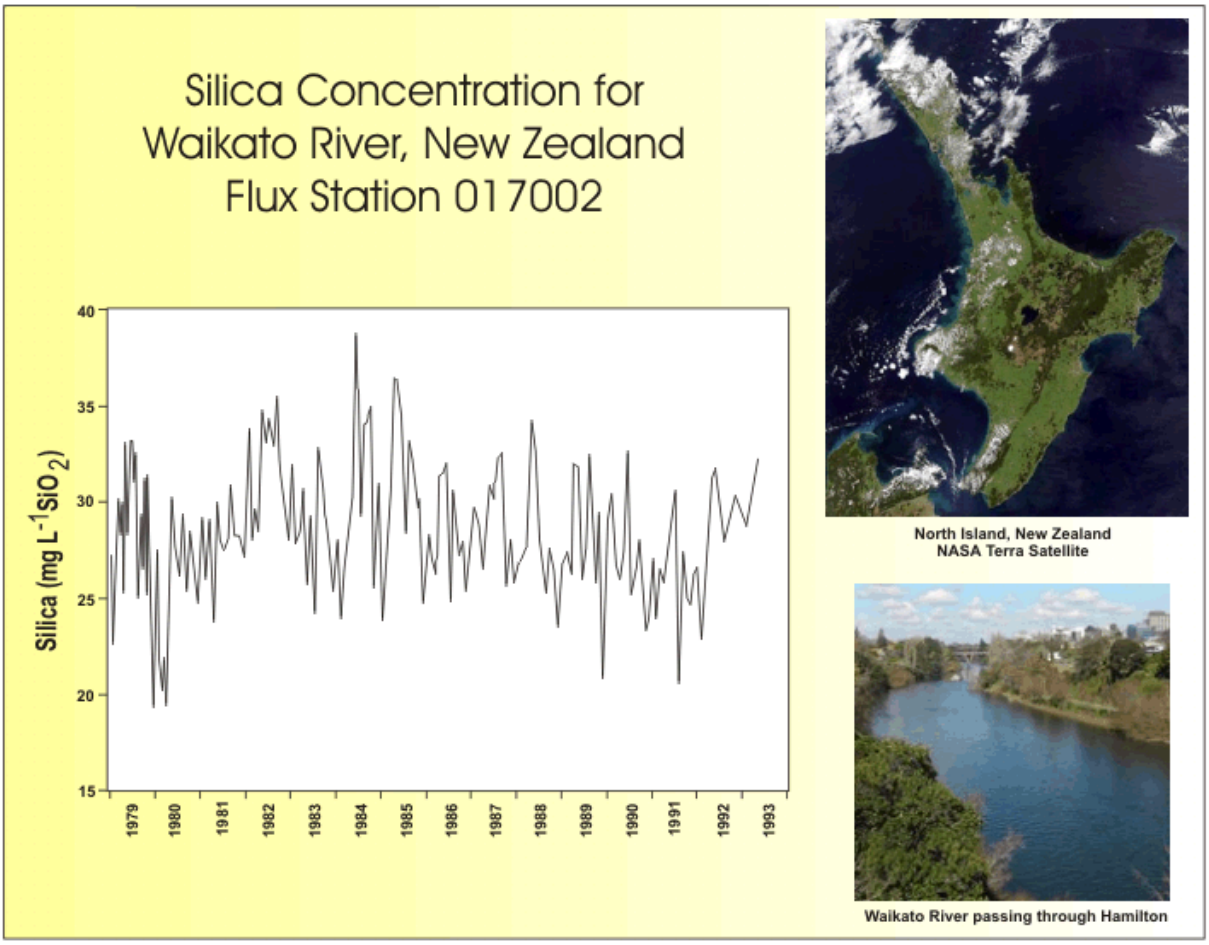


Figure 5: Time series for Silica on the Waikato River, New Zealand

3.3 Data Interpretation and Presentation at the Local Scale

Production and display of graphical material can be made in several ways dependant upon the analysis underway. Typically, XY, scatter, time-series and regression plots are desirable for displaying data to identify preliminary water quality conditions.

By using the RAISON system, graphical output can be included in map format as shown in Figure 5. This type of presentation is very useful for producing reports on environmental conditions. Figure 5 gives an example for the Waikato River in New Zealand presenting data for silica at an individual station. Groupings of stations within a watershed, nation or region can be accomplished by retrieving and aggregating data.

Statistical tests including regression analysis can be used for both data quality scans and trend identification. Figure 6 is an example of a regression analysis assessing the relationship between BOD and COD at a station on the Liaozhong-Liache River in China.

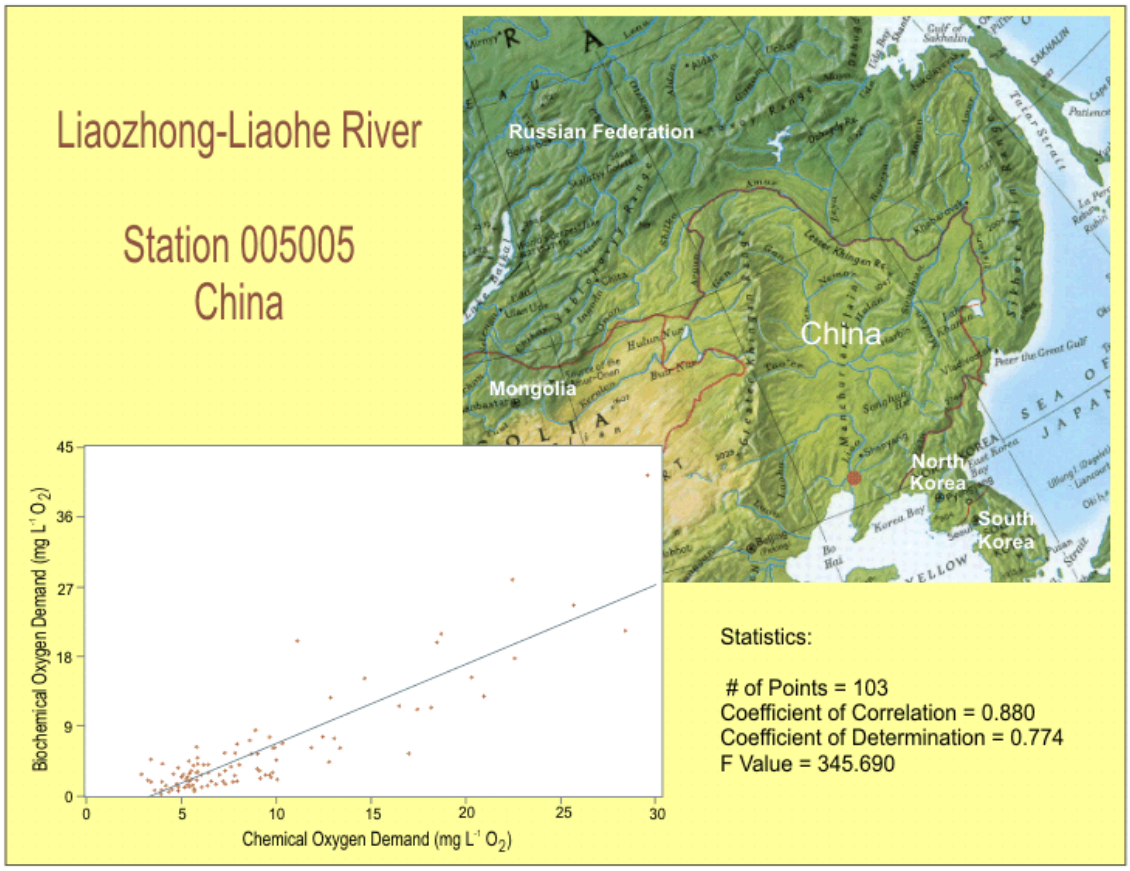


Figure 6: Regression Analysis for BOD/COD for Liaozhong-Liaohe River, China

Time Series

Standards and water quality criteria that are set for potable water supplies, irrigation water and industrial usage of water supplies can be displayed for station data sets individually or collectively on a watershed basis. The Krishna River, India provides an example for this type of analysis (Figure 7).

Long term changes relative to specific criteria can provide indications of emerging environmental issues that could be addressed prior to larger scale difficulties in water usage presenting themselves. In investigating long term changes in river water quality, time series analysis of instantaneous discharge records in combination with one or more specific parameters can easily depict dependent and/or independent relationships.

An example is provided in Figure 8, where Biological Oxygen Demand (BOD) concentrations and instantaneous discharge are presented in series, simultaneously for the river Huang He in China. The figure shows a relationship between BOD concentration and discharge. When identified, relationships such as this can form the basis of deterministic or stochastic process models which can lead to improved management policies for remediation when necessary.

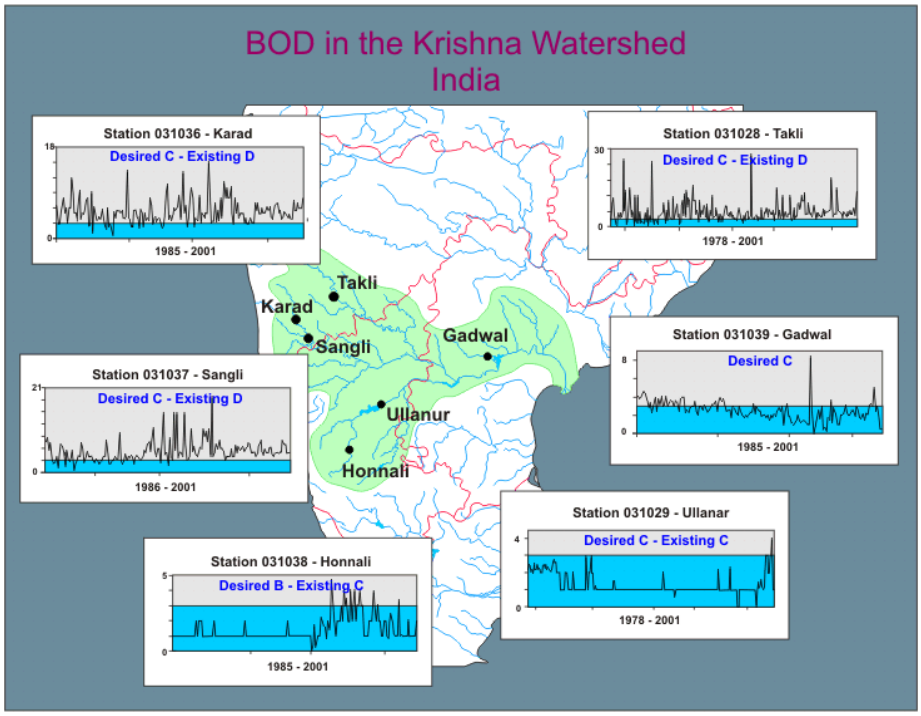


Figure 7: Time series excursion plots for the Krishna River, India

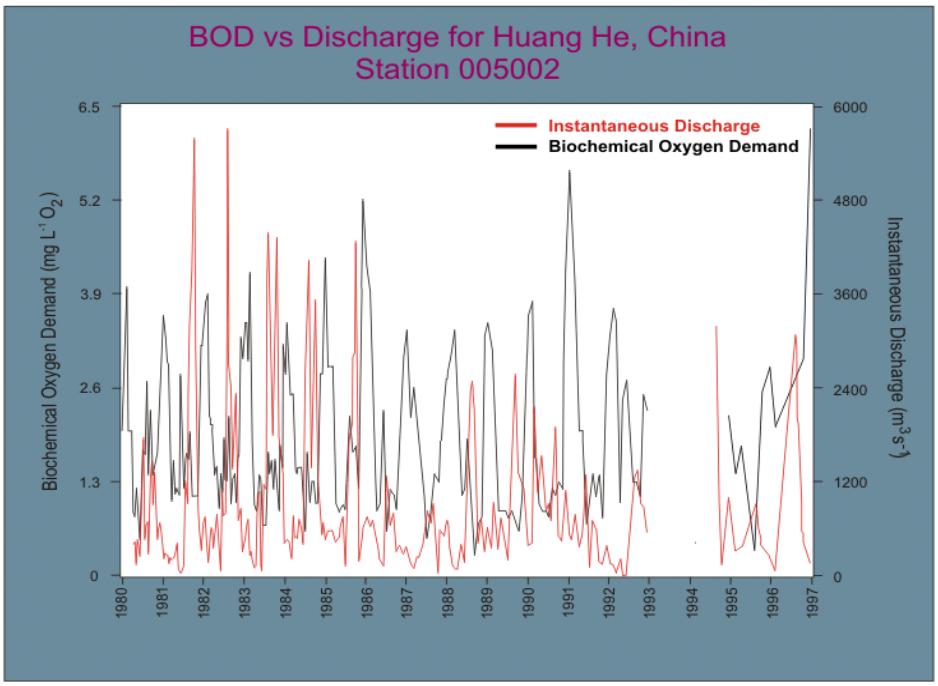


Figure 8: Time Series Plot for BOD and Discharge in the Huang He River, China.

3.4 Data Summary Tables

Data summaries in the form of statistical tables can provide the necessary information for many components of environmental assessments.

Figure 9 shows a table of medians for a selection of parameters depicting the overall record and trend for a station on the Narmada River, India. This type of output can be constructed in many forms. One of the most useful statistics to produce in tabular form is the median as this statistic is a robust indicator of the data distribution. To help in identifying year to year changes in parameter values, annual medians can be presented on a station by station basis through time. Parameters should be grouped into a functional domain for ease of comparison in evaluating particular concerns. Changes in values can be readily seen and further investigated where necessary.

Station 031007 - Narmada River, India

Annual Median Values for Selected Parameters

Year	Electrical Conductivity (µsie/cm)	Temperature (°C)	Nitrogen, Nitrate+Nitrite (mg/L N)	Biochemical Oxygen Demand (mg/L O_2)	Alkalinity (mg/L $CaCO_3$)	pH (pH units)	Phosphate Total (mg/L P)	Calcium Dissolved (mg/L Ca)	Total Coliform (No./100 ml)	Faecal Coliform (No./100 ml)	Instantaneous Discharge (m^3/sec)
	33	30.0	0.50	4	136.00	8.4		68.000	242000	12750	
1981	35	24.6	0.37	1	185.00	7.4		85.000	3550	2150	
1982	29	28.5	0.20	2	192.00	7.5		66.000	1660	82	
1983	27	26.5	0.17	2	165.00	8.4		50.000	4600	11000	
1984	28	25.5	0.30	1	190.00	8.4		62.000	24000	24000	
1985	27	27.7	0.24	2	182.00	8.5		24.400	17500	17500	592.7
1986	30	26.0	0.18	2	169.00	8.4		26.800	14	2	123.6
1987	38	26.0	0.22	4	170.00	8.4		52.000	110000	110000	170.0
1988	37	26.0	0.36	2	175.00	8.4		70.000	1370	1370	158.9
1989	37	25.5	0.27	2	168.00	8.4	0.015	72.500	26000	24000	131.1
1990	45	27.0	9.58	1	148.00	8.4	0.030	75.000	17500	2400	5.0
1991	27	27.0	0.28	2	139.50	8.4	0.030	68.000	24000	930	295.8
1992	29	27.5	0.13	2	156.00	8.2	0.050	26.500	2400	235	152.5
1993	25	29.0	0.38	1	124.00	8.2	0.065	35.500	1200	70	303.0
1995	50	26.0	0.14	1	168.00	8.4	0.037	33.500	2400	34	308.1
1996	27	24.5	0.12	2	160.00	8.1	0.150	27.000	1320	26	341.7
1997	29	26.5	0.17	2	176.00	8.2	0.082	34.000	180	10	192.0
1998	255	26.5	0.00	2	140.00	8.0	0.000	84.000	7	3	356.0
1999	338	27.0	0.18	1	140.00	7.8	0.047	85.000	15	7	264.6
2000	315	25.0	0.18	1	170.00	8.0	0.080	87.000	9	4	377.0
2001	235	26.0	0.30	0	105.00	7.4	0.030	27.000	260	21	779.0

Figure 9: Annual Median Values for Selected Parameters (1981-2001) for the Narmada River, India

In any assessment of riverine quality, variations both within a year and in the overall period of record should be examined. The use of the percentile distribution of annual parameter data in comparison to the long term frequency distribution can assist in identifying perturbations on the overall system. When encountered such changes should prompt investigations into the causes (eg. water diversions, changes in pollutant loads, and urban, industrial and agricultural activity). Figure 9 provides an example of this type of tabular treatment for selected parameters for a station on the Narmada River, India.

3.5 Water Quality Indicators

In recent years efforts have been made to develop and apply indicators of water quality stress and long term change. Indicators can be used to relate water quality to environmental stressors including expanding population, climate change, industrialization, and sanitation. Figure 10 is an example of impacts for urban sanitation, which relates urban population to faecal coliform concentrations.

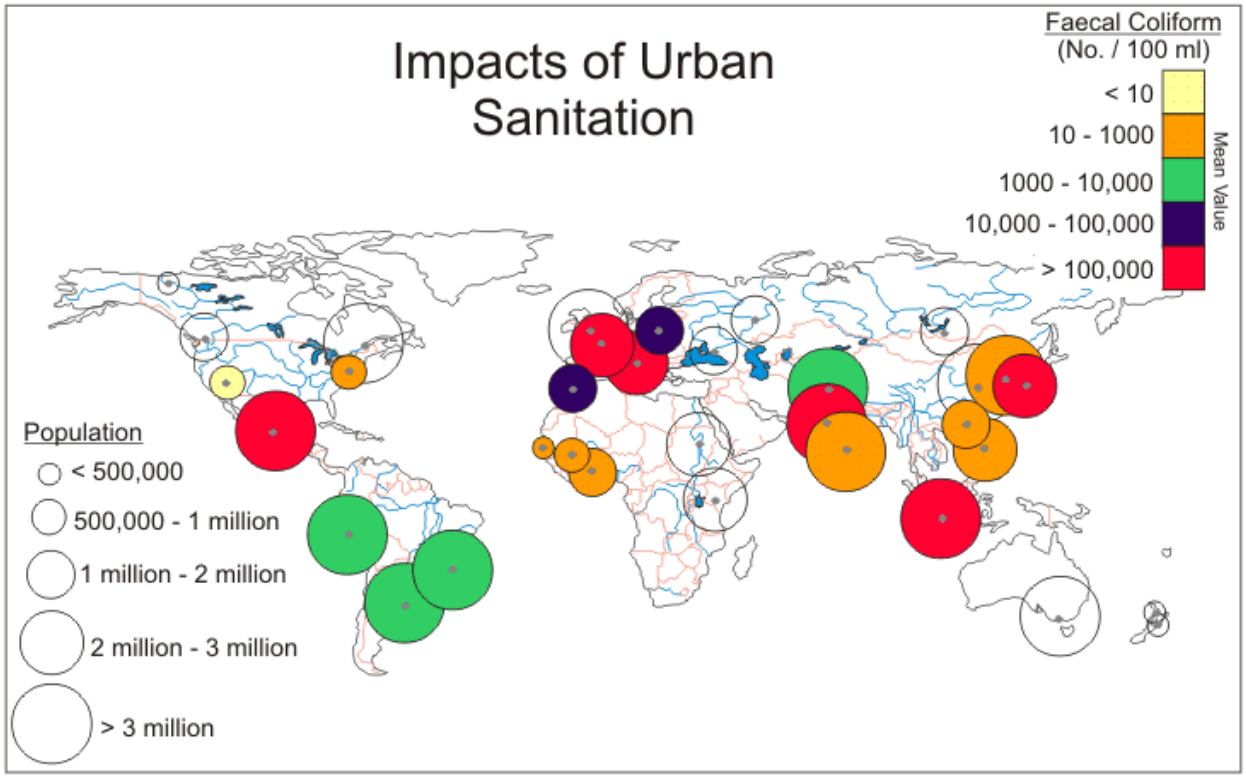


Figure 10: Urban population and sanitation

In combination with descriptive information identifying GEMS/Water station number and location (latitude/longitude), country, watershed, designation and drainage area, the preceding examples of descriptive station statistics, regional scale assessments and global data reviews can be processed and placed in report files for presentation.

The preceding examples have depicted the basic types of data handling and display that will be used in preliminary analysis of GEMS/Water data. Specific issues and requirements will dictate the types of data manipulation, analyses and presentation that will be used to assist in interpretation. Additional types of analysis not described here may also be incorporated, particularly where additional detailed analysis is required to highlight issues of major concern or broad environmental scope.