TECHNICAL REPORT SERIES
No. 3

# PLANNING OF WATER QUALITY MONITORING SYSTEMS

World Meteorological Organization
Weather • Climate • Water

WMO-No. 1113

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# Foreword

One of the United Nations Millennium Development Goals is to improve access to safe water, which is an engine for socio-economic growth. In this context, the importance of water- resources information systems cannot be overestimated in the socio-economic development process of nations and the world environment.

World Meteorological Organization (WMO) Bulletin 61(1) (2012) states that the timing and spatial distribution of surface water quantity – and the variability in quality of that water – define how we design and build the infrastructure necessary for our energy, agriculture, mining, transportation and industrial sectors. Safe drinking-water sources and entire ecosystems depend on continuous improvements of our understanding of, and efforts to protect, our water resources. One of the main messages from the Fifth Global Environment Outlook (GEO-5, 2012) of the United Nations Environment Programme (UNEP) is that addressing the most challenging water-resources issues facing society can be solved equitably and efficiently with an integrated management approach directed to the sustainable use of water.

In order to achieve this, it is essential that effective water-monitoring programmes, together with sound data and information management, are operational globally. Unfortunately, in many places in the world, such systems are not in place.

This Technical Report: Planning of Water Quality Monitoring Systems, has been developed by WMO jointly with UNEP GEMS/Water in an effort to provide basic know-how and the materials needed to plan, establish and operate water-quality monitoring systems on national levels but also with a view to improving access to water-quality data and information in transboundary basins and globally.

It is largely intended for use by water-agency managers whose dominant technical background is in hydrology, meteorology, engineering or water-resources management, rather than water quality, but who are responsible for the effective monitoring of developments and trends in the state of inland waters. There is an extensive literature on the setting-up and operation of water-monitoring programmes, so this Technical Report should be viewed as a primer or basic tool to be used in conjunction with other more detailed handbooks and academic literature.

It is hoped that national water managers and planners, as well as the international water community, will find this report a useful tool that will lead to improved water-quality networks in conjunction with hydrometric stations that will enhance water-quality monitoring systems and a better assessment of the variability of water resources in terms of both quality and quantity.

## Acknowledgements

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| | | |
|---|---|---|
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# PLANNING OF WATER-QUALITY MONITORING SYSTEMS
## Technical Report No.3

### WMO in collaboration with UNEP GEMS/Water

**Scope and objective**

This publication discusses the monitoring of the quality of inland waters, including rivers and streams of all sizes, from their source to tidal limit (i.e. the influence of saltwater intrusion), canals and interconnecting river systems, lakes of all types and sizes, including marshes and swamps, reservoirs and river impoundments and groundwater. These water bodies comprise inland water resources which may be subject to anthropogenic influences or are intentionally used for municipal or industrial supply, irrigation, recreation, cooling or other purposes.

The target audience for this Technical Report comprises mainly managers of agencies whose primary domain may not be water quality (WQ) but rather hydrology, meteorology, engineering or water-resources management, and who have been tasked with undertaking monitoring to support their main functions.

Many countries have a national WQ authority but also other agencies, whose primary mandate has acquired an environmental dimension. The responsibility for WQ monitoring and assessment is thus fragmented between different government departments, since the information requirements and demands vary.

This Technical Report is intended to guide non-WQ officers through the process of setting up monitoring programmes for the purpose of providing a valid database for water-quality assessments, including general guidance to identify the purpose of the system, its structure, choice of technology, institutional affiliation and expected results. The main emphasis is on the strategies and objectives of the programme and general criteria for the design of the monitoring network. Also described are the kinds of variables needed when WQ is to be monitored for different purposes (such as agriculture/irrigation, drinking-water sources, industrial water demand, livestock needs, etc.). Guidance on the selection of main monitoring methods and techniques for the different variables is then provided. This is followed by the definition of the resources required for the monitoring programme (laboratory facilities, field stations, equipment and instruments, office and field staff and the estimation of costs of the programme). Finally, the essential operational issues of quality assurance and data handling, leading to the reporting and dissemination of results and findings, are also covered.

The main thrust is on the setting-up or strengthening of WQ monitoring programmes for the purposes of human consumption, agriculture/irrigation and industrial uses, etc. Environmental WQ monitoring (e.g. biological systems, wetlands, etc.), although mentioned, goes beyond the scope of this report and is therefore not described in detail.

A wealth of documentation is available on the subject of WQ monitoring and assessment, some of which has been drawn heavily upon in this report, there being two major sources of text: Bartram (1996)[1] and several GEMS/Water publications[2]. Their use in conjunction with the present Technical Report is therefore strongly recommended.

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[1] Bartram, J. and R. Ballance [Eds], 1996: Water Quality Monitoring: A Practical Guide to the Design and Implementation of Fresh Water Quality Studies and Monitoring Programmes. Chapman & Hall, London.

[2] These are available online at http://www.who.int/water_sanitation_health/resourcesquality/waterqualmonitor.pdf and http://www.gemswater.org.

The structure of this treatise is illustrated in Chapter 3, Figure 1. It includes an indication of the chapters where the relevant activities under each of the components of a WQ monitoring programme are described. In addition, Chapter 11 contains a summarized description of international WQ directives and relevant guidance material in related fields that may be consulted as required for the various planning steps.

With a view to complementing the information and as technical support, Annexes 1 and 2 provide a detailed description of, respectively: (a) the main WQ variables; and (b) the various WQ monitoring methods and techniques and monitoring equipment, as well as traditional and special sampling procedures, etc. A summary of WQ guidelines and standards by international organizations or countries is given in Appendix 1 and the key features of each chemical and physicochemical element and each biological element for lakes are given in Appendixes 2 and 3, respectively.

# Chapter 1. Processes affecting water-quality and their effects

Access to clean water for drinking and sanitary purposes is a precondition for human health and well-being. Unpolluted water is also essential for ecosystems. Plants and animals in lakes, rivers and seas react to changes in their environment caused by changes in chemical water quality and physical disturbance of their habitat.

## 1.1 Effects of natural phenomena on water quality[3]

While the degradation of water quality (WQ) is almost invariably the result of human activities, certain natural phenomena can result in WQ falling below the standard required for particular purposes. Natural events such as torrential rainfall and hurricanes lead to excessive erosion, landslides and mudflows, which, in turn, increase the content of suspended material in affected rivers and lakes. Seasonal overturn of the water in some lakes can bring water with little or no dissolved oxygen (DO) to the surface. These events may be frequent or occasional and have increased as a result of climate change. Permanent natural conditions in some areas may make water unfit for drinking or for specific uses, such as irrigation.

Additionally, there are naturally occurring areas of high nutrients, trace metals, salts and other constituents that can limit the use of water. Common examples are the salinization of surface waters through evaporation in arid and semi-arid regions and the high salt content of some aquifers under certain geological conditions. Many aquifers are naturally high in carbonates (alkalinity), thus necessitating their treatment before use for certain industrial applications. They may also contain specific ions (such as fluoride) and toxic elements (such as arsenic IV, V) and selenium) in quantities that are harmful to health, while others contain elements or compounds that cause other types of problems (such as the staining of sanitary fixtures by iron and manganese).

The nature and concentration of chemical elements and compounds in a freshwater system are subject to change by various types of natural processes – physical, chemical, hydrological and biological – caused by climatic, geographical and geological conditions. The major environmental factors are:

- Distance from the ocean: extent of sea spray rich in Na+, Cl-, $Mg^{2+}$, $SO_4^{2-}$ and other ions;

- Climate and vegetation: regulation of erosion and mineral weathering; concentration of dissolved material through evaporation and evapotranspiration; increasing turbidity and high silt load in rivers passing through hills of quaternary or recent origin such as the Himalayan region;

- Rock and sediment composition (lithology) and geological setting: these determine the natural physical and chemical characteristics of the aquifers. The susceptibility of rocks to weathering ranges from 1 for granite to 12 for limestone; it is much greater for more highly soluble rocks (for example, 80 for rock salt);

- Terrestrial vegetation: the production of terrestrial plants and the way in which plant tissue is decomposed in soil affect the amount of organic carbon and nitrogenous compounds found in water;

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3 The content of this section is drawn verbatim from Bartram (1996), 23-25.

- Aquatic vegetation: growth, death and decomposition of aquatic plants and algae will affect the concentration of nitrogenous and phosphorous nutrients, pH, carbonates, DO and other chemicals sensitive to oxidation/reduction conditions. Aquatic vegetation has a profound effect on the chemistry of lake water and a less pronounced, but possibly significant, effect on river water;

Under the influence of these major environmental factors, the concentrations of many chemicals in river water are liable to change from season to season. In small watersheds (<100 $km^2$) the influence of a single factor can cause a variation of several orders of magnitude. WQ is generally more constant in watersheds greater than 100 000 $km^2$, and the variation is usually within one order of magnitude for most of the measured variables, unless regulated. Regarding groundwater, changes in hydrodynamics and redox (reduction-oxidation) conditions can change the interaction between the solid material and the fluid resulting in change in the groundwater quality.

## 1.2 Anthropogenic pressures

Almost all human activities can and do have an adverse impact on water. WQ is influenced by both non-point pollution from farming activities and point-source pollution from sewage treatment and industrial discharge as principal sources. For agriculture, the key pollutants are nutrients, pesticides, sediment and faecal microbes. Oxygen-consuming substances and hazardous chemicals are more associated with point-source discharges.

According to the European Environment Agency (EEA): "the pollution can take many forms and have different effects:

***Faecal contamination*** from sewage makes water unsafe for human consumption and aesthetically unpleasant and unsafe for recreational activities, such as swimming, boating or fishing. Many organic pollutants, including sewage effluent, as well as farm and food-processing wastes, consume oxygen, suffocating fish and other aquatic life. Additionally, this contamination can affect groundwater resources used for drinking-water purposes.

***Nutrients***, such as nitrates and phosphates, from farm fertilizers to household detergents, can "overfertilize" the water, causing the growth of large mats of algae, some of which can be toxic. When the algae die, they sink to the bottom, decompose, consume oxygen and damage ecosystems. Additionally, due to the percolation of nutrients to shallow aquifers, the chemical conditions in those aquifers can change.

***Pesticides and veterinary medicines*** from farmland and some industrial chemicals can threaten wildlife and human health. Some of these damage the hormonal systems of fish, causing "feminization" (endocrine disruption).

***Metals***, such as zinc, lead, chromium, mercury and cadmium, are extremely toxic. Copper complexes are less toxic, and cobalt and ferrous complexes are only weak toxicants. Concentrations of cyanides in waters intended for human use, including complex forms, are strictly limited because of their high toxicity.

***Organic micropollutants***, such as pharmaceuticals, hormones and chemical substances used in products and households, can also threaten health.

***Chlorinated hydrocarbons*** exist in the natural systems and several are highly toxic for humans. These molecules persist in the environment for a longer time and threaten to contaminate aquatic and soil systems.

***Sediment runoff*** from the land can make water muddy, blocking sunlight and, as a result, kill aquatic life. Irrigation, especially when used improperly, can bring flows of salts, nutrients and other pollutants from soils into water. All these pollutants can also make the water unsuitable for drinking purposes."[4]

The physical management of rivers and aquifers and the wider hydrological and hydrogeological environment of a river basin also influence ecological quality and WQ. Changes and disruptions in natural habitats, such as bankside vegetation, can result from the physical disturbance of damming; canalization and dredging of rivers; construction of reservoirs; riverbank management and other changes to the hydrological flow; sand and gravel extraction in coastal waters; bottom trawling by fishing vessels, etc. Pebble riffles where salmon and other fish spawn can also be destroyed. Seasonal flow patterns that are vital to many species can also be changed, as well as the connectivity between habitats – an important factor for the functioning of aquatic ecosystems and the development of the different life stages of aquatic organisms. In urban agglomerations, storm-water carrying contamination from streets and roofs can contribute to water pollution if discharged directly into water bodies.

Plants and aquatic life such as plankton and benthos in lakes, rivers and seas react to changes in their environment caused by changes in chemical WQ and physical disturbance of their habitat. Changes in species composition of organism groups such as phytoplankton, algae, macrophytes, bottom-dwelling animals and fish can be caused by changes in climate. They can also indicate changes in WQ caused by eutrophication, organic pollution, hazardous substances or oil and a changing hydrological regime.

Over time, with the advent of industrialization and increasing populations, the range of requirements for water has increased, together with greater demands for higher-quality water, such as for drinking and personal hygiene, fisheries, agriculture (irrigation and livestock supply), navigation for transport of goods, industrial production, cooling in fossil fuel (and later also in nuclear) power plants, hydropower generation, heat/cold storage in aquifers, recreational activities such as bathing or fishing and nature conservation, e.g. wetlands. Fortunately, the largest demands for water quantity, such as for agricultural irrigation and industrial cooling, require the least in terms of WQ (critical concentrations may be set for only one or two variables, the most critical for the specific use of water, such as salinity or nitrate contents for agricultural usage, etc.). Drinking-water supplies and specialized industrial manufacturers exert the most sophisticated demands on WQ but their quantitative needs are relatively moderate. In parallel with these uses, water has been considered the most suitable medium to clean, disperse, transport and dispose of waste (domestic and industrial waste, mine drainage waters, irrigation returns, etc.). It should be noted that, in a natural water body, it would be better to consider the real pollutant load and not only the pollutant concentration.

Each water use, including abstraction of water and discharge of waste, leads, however, to specific and generally rather predictable impacts on the quality of the aquatic environment. In addition to these intentional water uses, there are several human activities which have indirect, undesirable – and sometimes devastating – effects on the aquatic environment. Examples are uncontrolled land use for urbanization or deforestation and associated soil erosion, accidental (or unauthorized) release of chemical substances and discharge of untreated waste or leaching of noxious liquids from solid-waste deposits. Similarly, the uncontrolled and excessive use of fertilizers and pesticides has long-term effects on ground- and surface-water resources. Restoration of the natural WQ after such events often takes many years, depending on the geographical scale and intensity of the event.

Pollution of groundwater arises commonly from the percolation of polluted water from the surface, but also leaching from contaminated soil, dissolution from oil or dense non-aqueous phase liquids. When polluted water penetrates 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. The rate of

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4 EEA, State of Environment Report (SOE), 2005, 120-121.

travel will depend upon pollutant persistence, hydraulic conductivity, hydraulic gradient and porosity.

The continuing increase in socio-economic activities worldwide has been accompanied by an even faster growth in pollution stress on the aquatic environment. Only after a considerable time lapse, allowing for the public perception of WQ deterioration, have the necessary remedial measures started to be taken.

## 1.3 Point loading and non-point loading

Discharges from wastewater-treatment plants and industry cause pollution by oxygen-consuming substances, nutrients and hazardous substances. The adverse impacts depend very strongly upon the degree to which (if at all) such discharges are treated before reaching waterways or whether such pollutants are degraded by the natural system itself.

By its very nature, the management of diffuse pollution is complex, requiring the careful analysis and understanding of various natural and anthropogenic processes. The estimation of non-point diffuse loading from the different processes to a water body is not easy, because so many different factors affect quantity and spatial variations.

Modern-day agricultural practices often require high levels of fertilizers and manure, leading to high-nutrient (e.g. nitrogen and phosphorus) surpluses that are transferred to water bodies and groundwater through various non-point processes. Excessive nutrient concentrations in water bodies, however, cause adverse effects by promoting eutrophication, with an associated loss of plant and animal species. In high-nutrient waters with sufficient sunlight, algal slimes can cover streambeds, plants can choke channels and algae blooms can turn the water a murky green. Oxygen depletion, the introduction of toxins or other compounds produced by aquatic plants, reduced water clarity and fish kills can also result. Excess nutrient levels can also be detrimental to human health.

Pesticides used in agriculture are transported to both surface water and aquifers. Not only do they threaten wildlife and human health but excessive sediment runoff from agricultural land results in turbid waters and the clogging of spawning areas. This, in turn, leads to loss of aquatic habitats. Microbial pathogens from animal faeces can also pose a significant health risk. High concentrations can restrict the recreational and water-supply uses of water, cause illness and loss of productivity in cattle and limit shellfish aquaculture in estuaries.

In urban areas, where surface runoff is not connected to treatment works, pollutants deposited on impervious surfaces (e.g. roads or pavements) are washed into nearby surface waters or percolate down to the shallow groundwater. Such pollutants include metals, pesticides, hydrocarbons and solvents, as well as those derived from sources such as the atmosphere and the abrasion of roads, tyres and brakes. In some urban areas, surface runoff is discharged into sewers, which then mixes with sewage on its way to treatment. During periods of heavy rainfall, the sewerage system is unable to cope with the volume of water. As a result, the flow is directed away from the treatment works and discharged as combined sewer overflow to surface water. This causes pollution from not only sewer waste but also urban runoff.

Another important phenomenon is the so-called “internal loading” in dimictic lakes. In many cases, it has been observed that, despite having totally stopped wastewater discharge to a certain lake, the improvement of its ecological status has been extremely slow. There are two main causes of internal loading:

- Bottom sediments which, earlier, have deteriorated badly, owing to discharges of insufficiently treated wastewater and which, during the purification process, transfer extra nutrient reserves from the sediment to water, during an unusually long period; and

- Excessively dense fish stocks developed during the increasing eutrophication of lakes, which usually comprise small roach, bream, etc. These are commonly bottom-feeding and return sedimented nutrients, especially phosphorus, back to the epilimnion in mineral form.

The atmosphere is the most pervasive means of transporting pollutants through the global environment. Significant concentrations of certain contaminants (mercury and persistent organic pollutants (POPs)) are even being observed in Arctic and Antarctic snow and ice, with high levels of bioaccumulation magnified through the food chain to mammals and native human populations. Sources of anthropogenic materials to the atmosphere include:

- Combustion of fossil fuels for energy generation;
- Combustion of fossil fuels in automobiles, other forms of transport, heating in cold climates and industrial needs (e.g. steel production);
- Ore smelting, mainly sulphides, but also cadmium, zinc, lead, arsenic and copper;
- Wind-blown soils from arid and agricultural regions; and
- Volatilization from agriculture, waste disposal and previously polluted regions;
- Emission of hydrogen sulphide ($H_2S$) and methane ($CH_4$) from municipal solid-waste disposable sites and sewage drains and open drains in developing countries.

Together, these sources provide an array of inorganic and organic pollutants to the atmosphere, which are then widely dispersed by weather systems and deposited on a global scale. In the vicinity of industrial activity, these atmospheric depositions can infiltrate the subsurface when rainwater recharges the aquifers and cause large-scale, irreversible, groundwater contamination.

## 1.4 Spatial and temporal variations

Spatial variation in WQ is one of the main features of different types of water bodies and is largely determined by the hydrodynamic characteristics of the water body. In surface waters (lakes, streams, wetlands, reservoirs and rivers), WQ may vary in all three dimensions, which are further modified by flow direction, discharge and time. Consequently, WQ cannot usually be measured in only one location within a water body but may require a grid or network of sampling sites. The questions to be answered by water-quality assessment (WQA) would decide whether spatial or temporal variation is the most important determinant needing to be monitored. The water-quality monitoring (WQM) is then structured to cover fixed stations with frequent samples to identify temporal variations or random locations sampled over a short time period to identify spatial variation.

Two important features of groundwater bodies distinguish them from surface waters. First, the relatively slow movement of water through the ground means that residence times in aquifers are generally orders of magnitude longer than in surface waters. Second, there is a considerable degree of physicochemical, chemical and biochemical interdependence between the water and the material of the containing aquifer. There is scope for WQ to be modified by interaction between the two, which is facilitated by the long residence times.

| **Box 1. Characteristics of spatial and temporal variations in WQ** | | |
|---|---|---|
| **Rivers** | **Lakes and reservoirs** | Groundwater |
| Characteristics of spatial variations[1] | | |
| In fully mixed rivers variability only in *x* | No variability at overturn[2] | Usually high variability in *x* and *y* |
| In locations downstream of confluences or effluent discharges, variability in *x* and *y* | High variability in *z* for most systems[3] | In some multi-layer aquifers and in the unsaturated zone, high variability in *x*, *y* and *z* |
| | High variability in *x*, *y* and *z* in some irregularly shaped lakes | |
| Characteristics of time variations | | |
| Depends on river discharge regime | Some predictable variability (hydrodynamic and biological variations) | Low variability[4] |
| | Medium-to-low variability in large systems | |
| Diurnal variation in eutrophicated rivers | Diurnal variation in eutrophicated lakes | |

[1]x - longitudinal dimension; *y* - transverse dimension; *z* - vertical dimension

[2] One sample can describe the whole water body

[3] Two dimensions (*x* and *z*) if there is poor lateral mixing

[4] Except for some alluvial aquifers and for karstic aquifers

Spatial variability differs between surface water and aquifers. It is most pronounced in rivers and the ranges will be greater the nearer the sampling point is to the source or sources of pollution. As the distance from the source increases, longitudinal mixing smoothes out irregularities and fewer samples are needed to meet given confidence limits.

Thus, not only will there be a 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 purposes is located some distance from the area of point of use. Regarding groundwater, the system is three-dimensional, with variability in all three dimensions, depending on the geological setting of the area.

The temporal variation of the chemical quality of water bodies can be described by studying concentrations (also loads in the case of rivers) or by determining rates such as settling rates, biodegradation rates or transport rates. It is particularly important to define temporal variability.

Five major types, as identified by Bartram (1996)[5] are considered here:

- Minute-to-minute to day-to-day variability, resulting from water mixing, fluctuations in inputs, etc., mostly linked to meteorological conditions and water-body size (e.g. variations during river floods);
- Diurnal variability (24-hour variations), limited to biological cycles, light/dark cycles etc. (e.g. $O_2$, nutrients, pH), and to cycles in pollution inputs (e.g. domestic waste);
- Days-to-months variability, mostly in connection with climatic factors (river regime, lake overturn, etc.) and to pollution sources (e.g. industrial wastewater, runoff from agricultural land);

[5] Bartram, 1996, 30

- Seasonal hydrological and biological cycles (mostly in connection with climatic factors); and

- Year-to-year trends, mostly due to human influence.

## 1.5 Variability of water quality

The quality of water in various water bodies is rarely constant in time. While there may be some relationship between the rates of change of different variables, others alter independently. 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. Variations in WQ are caused by changes (increase or decrease) in 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. Since it is possible for some changes to occur in combination, the reasons behind variations may sometimes be obscured.

Random variations in the quality of water occur as a result of unpredictable events. Sudden storms will lead to increased flows, followed by polluted runoff and leaching 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.

Annual cycles may be the result of regular rainfall patterns, snowmelt and seasonal temperature changes, among others. 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 those caused by photosynthesis and affecting DO 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 and dam management for power generation, navigation or other purposes, tends to be cyclical but can occur randomly. River flows in tropical regions vary widely, especially where large-scale diversions that are permanent in nature adversely affect water quality.

WQ variability in a river depends on the hydrological regime, i.e. water-discharge variability, the number of floods per year and their magnitude, and the occurrence of low flows. During flood periods, WQ usually shows marked variations, owing to the different origins of the water: surface runoff, subsurface runoff (i.e. water circulation within the soil layer) and groundwater discharge. Surface runoff is generally highly turbid and carries large amounts of total suspended solids (TSS), including particulate organic carbon (POC). On the one hand, subsurface runoff leaches dissolved organic carbon and nutrients (nitrogen (N) and phosphorus (P)) from soils, whereas aquifers provide most of the elements resulting from rock weathering. On the other hand, during low flows, a general deterioration of WQ can be observed because of a higher concentration of pollutants.

The salinization of reservoirs in arid and semi-arid areas, where surface water is naturally scarce, is a problem that can be aggravated by the leaching of salts from irrigated soils and their transport in return flows to the reservoirs, as well as by highly seasonal rainfall in these areas increasing the evaporative concentration of the ambient salinities in the water bodies during the dry season. Sudden effects due to the acidification of water can also occur after heavy rain and snowmelt, caused by airborne loading of different acidifying compounds. Finally, thermal pollution of WQ is caused by the use of water as a coolant by power plants and industrial manufacturers, when returned to the natural environment at a higher temperature.

The various causes and origins of the deterioration of WQ that have been described above require tailor-made approaches and solutions for the effective monitoring, management and improvement of the quality of water bodies.

# Chapter 2. The importance of water-quality monitoring

Water-quality monitoring (WQM) provides an understanding of: (*a*) water-quality conditions in national streams, rivers, groundwater and aquatic systems; (*b*) how those conditions vary locally, regionally and nationally; (*c*) whether conditions are changing over time; (*d*) how natural features and human activities affect those conditions; and (*e*) where those effects are most pronounced.

## 2.1 Main purposes of a WQM programme

Traditionally, the principal reason for monitoring WQ has been the need to verify whether observed WQ is suitable for intended uses. Monitoring has evolved over time, however, and the main purposes may be to:

- Enable assessments of the current state of water quantity and quality and its variability in space and time. Often, such assessments are appraisals of the hydrological, morphological, physicochemical, biological and/or microbiological conditions in relation to reference conditions, human-health effects and/or the existing or planned uses of water. Such reference conditions may take into account elevated concentrations of specific parameters due to "natural" geophysical and geochemical processes;

- Classify water in accordance with its individual pattern of physical and chemical characteristics, determined largely by the climatic, geomorphological and geochemical conditions prevailing in the drainage basin and the underlying aquifer;

- Develop composite indexes[6] to assess source WQ across a range of inland water types, globally and over time;

- Support decision-making and operational water management in critical situations. When pollution events occur, reliable data are needed, which may require early warning systems to signal when critical pollution levels are exceeded or toxic effects occur. In these cases, models can often support decision-making. For transboundary waters, information is usually gathered from the national monitoring systems (which are established and operated according to national laws and regulations and international agreements), rather than from monitoring systems specifically established and operated by joint bodies[7];

- Determine trends in the quality of the aquatic environment and how the environment is affected by the release of contaminants, by other human activities, and/or by waste treatment operations, often known as "impact monitoring". More recently, monitoring has been carried out to estimate nutrient or pollutant fluxes discharged by rivers or aquifers to lakes and oceans or across international boundaries. Background quality

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[6] As an example, the composite index developed by GEMS Water has a three-fold approach: (a) selecting guidelines from WHO that are appropriate in assessing global water quality for human health; (b) selecting variables from GEMStat that have an appropriate guideline and reasonable global coverage; and (c) determining, on an annual basis, an overall index rating for each station using the water-quality index equation endorsed by the Canadian Council of Ministers of the Environment. The index allowed measurements of the frequency and extent to which variables exceeded their respective WHO guidelines at each individual monitoring station included within GEMStat, allowing both spatial and temporal assessment of global water quality.

[7] National legislation, as well as obligations under international agreements and other commitments, should be carefully examined in preparation for establishing, upgrading and running these systems (see Section 11.1 for details on international obligations).

monitoring of the aquatic environment is also widely carried out, as it provides a means of comparing and assessing the results of impact monitoring;

- Determine treatment options for polluted or undrinkable water;
- Determine ecological flows;
- Evaluate the effectiveness of water management/remedial measures;
- To identify the low-flow conditions and estimate the compensation water flow. The fundamental role of compensation water flow needs to be mentioned here, which, in a river, is the link between water-quality and water-quantity problems;
- To provide the basis of the formulation of science-based environmental policies and also allow for evaluations of whether or not a policy has resulted in the desired effect and been cost-effective;
- For rational planning of pollution-control strategies and their prioritization;
- To assess the nature and extent of pollution control needed in different water bodies;
- To evaluate effectiveness of pollution-control measures already in existence;
- To evaluate water-quality trend over a period of time;
- To assess assimilative capacity of a water body, thereby reducing costs of pollution control;
- To understand the environmental fate of different pollutants;
- To assess the fitness of water for different uses.

## 2.2 Monitoring for management

When a WQM programme is being planned, water-use managers or similar authorities can reasonably expect that the programme will yield data and information that will be of value for management decision-making.

The analysis of water-management issues and objectives is the basis for specifying the information needs. These are related to:

- Uses (e.g. drinking-water, irrigation, recreation) and functions (maintenance of aquatic life) of the watercourse or groundwater body that put requirements on the quality and availability;
- Issues (e.g. flooding, sedimentation, salinization, pollution) that hinder proper use and functioning of the watercourse or groundwater body; and
- Measures taken to address the issues or improve the use or functioning of the watercourse or groundwater body, including environmental aspects.

Each country or water authority should take into account current or envisaged measures, policies and action plans in water management. In specifying human uses and the ecological functioning of water bodies and in identifying pressure factors, issues and targets, the full range of qualitative and quantitative factors in river-basin management should be considered (Box 2).

**Box 2. Examples of the relationships between uses or functions and issues in a river basin**

| Issues \ Uses/functions | Human health | Ecosystem functioning | Fisheries | Recre–ation | Drinking-water | Irrigation | Industrial use | Hydro-power | Transport medium[1] | Navi-gation |
|---|---|---|---|---|---|---|---|---|---|---|
| Flooding | X | X | | X | | | | | X | X |
| Scarcity | X | X | X | X | X | X | X | X | X | X |
| Erosion/ sedimentation | X | X | | | X | | | X | X | X |
| Biodiversity | | X | X | X | | | | | | |
| River continuity | | X | X | X | | | | X | X | X |
| Salinization | | X | | | X | X | X | | | |
| Acidification[2] | | X | X | | X | | | | | |
| Organic pollution[3] | X | X | X | X | X | | | | | |
| Eutrophication | X | X | X | X | X | X | X | | | |
| Pollution (hazardous substances[4]) | X | X | X | X | X | X | X | | | |

X Major impacts on functions/uses (problematic issues)

1 Transport of water, ice, sediments and wastewater

2 Dry/wet acid deposition

3 Organic matter and bacteriological pollution in wastewater discharges

4 Hazardous substances, including radionuclides, heavy metals, toxic organic compounds and pesticides

The various functions and uses of water bodies – both ecological and human – must be considered. Uses may compete or even conflict, particularly if water is scarce or its quality deteriorating. A multi-functional approach tries to strike a balance between all desired uses, including ecosystem functioning. This allows the introduction of a hierarchy of uses, providing flexibility for the different levels of water-resource management-policy development and for prioritization in scheduling.

Management plans should also consider various land-use issues, including deforestation, erosion and the non-point pollution of water. They should preferably also include an analysis of other information needs, as well as strategies for tailor-made monitoring and assessment, the sharing of information among riparian countries and assessment of the effectiveness of the measures within them.

Finally, monitoring and assessment of water quality and quantity require adequate financial resources. Those responsible for these activities, therefore, need to demonstrate both the benefits of monitoring for integrated water-resources management and the possible costs, in terms of environmental degradation and other impacts, of not monitoring. It is well known that the prevention of an environmental problem is often less costly than its remediation. While solutions for many environmental problems are expensive and technically challenging, what is often not recognized is that the cost of well-designed monitoring programmes is generally much less than either the cost of policy implementation or the monetary benefits associated with the environmental improvement (Lovett et al., 2007). This is particularly crucial for countries in which monitoring activities are still insufficiently funded.

## 2.3 Hydrological monitoring

As an important part of any WQM programme, all basic components of the hydrological cycle should be measured or estimated, taking into account temporal and spatial aspects of hydrological and hydrogeological processes (for more details, see Section 6.3).

In addition, hydrological modelling, both of surface- and groundwater and forecasting are also a necessary component in the WQ assessment process. Operational simulation and forecasting models have proved efficient in drainage-basin management and, in the case of international lakes, they can play an important role. Hydrological monitoring and modelling (of groundwater and surface water) can form supplementary elements for linking with decision-support systems, as well as ecological modelling and assessment.

Water-level and flow forecasts should be provided daily for many functions and uses, including water supply, navigation, ecological functions and river-channelling work, the operation of reservoirs and flood prevention and protection. As the speed of movement of accidental pollution in a river system depends mainly on flow characteristics, provision should be made to use hydrological forecasts when accident or emergency warnings are issued (see also Section 2.5). Forecasting is also important during periods of drought, when river flows are low and the supply of water is inadequate to satisfy different users.

## 2.4 Types of WQM programmes

In principle, there could be as many types of monitoring programmes as there are objectives, water bodies, pollutants and water uses, as well as any combination thereof. In practice, assessments are limited to nine different types of operations: trend monitoring; basic survey; operational surveillance; background monitoring; preliminary surveys; emergency surveys; impact surveys; modelling surveys; and early warning surveillance), as shown in Table 1. It should be noted that, in the past, many countries or water authorities installed multi-purpose or multi-objective monitoring programmes without conducting the necessary preliminary surveys. Critical scrutiny of results after several years of operation has led to a second generation of programmes with more differentiated objectives such as impact assessment, trend analysis or operational management decisions.

For surface water, background monitoring (principally in unpolluted areas) has usually been developed to help the interpretation of trend monitoring (time variations over a long period) and the definition of natural, spatial variations. Models and their related surveys have usually been set up to predict WQ for management purposes prior to pollution treatment, or to test the impact of a new water-pollution source and are thus closely connected to operational surveillance and impact surveys. Early warning surveillance is undertaken for specific uses in the event of any sudden and unpredictable change in WQ, whereas emergency surveys of a catastrophic event should be followed in the medium- and long-term by impact surveys.

As regards groundwater, monitoring normally includes the testing for long-term changes in WQ in major aquifers so as to provide a basis for statistical identification of the possible causes of observed conditions and to provide the statistical basis for the identification of trends.

## 2.5 Early warning systems

The ability to provide early warnings is important for entire river basins which may be affected by pollution events, including lakes and reservoirs. The effects of accidents such as oil and chemical spills in one part of a river basin will inevitably spread downstream and eventually to the sea. It is therefore recommended that early warning systems covering accidents and other emergencies should be set up for whole river basins wherever a use of water (e.g. a water-supply intake), potentially threatened by accidental pollution, can be safeguarded through emergency measures. River-basin early warning systems have four main elements:

- Accident emergency warning systems;
- Hazard identification through databases;
- Models to be used during emergencies; and
- Local screening of river water.

Prior to the establishment of an early warning system[8], potential sources of accidental pollution and all available emission data should be inventoried to find out which accidental pollutants could be threats. Risk analysis should highlight the critical risk factors to the functions and uses of the river.

Such inventories and risk analyses should specify a list of priority pollutants to be the subject of early warning procedures.

The establishment of an accident emergency warning system is recommended as the first step in providing an early warning system for a river basin, which should include:

- A network of alert centres in the river basin, where emergency messages from national or regional authorities can be received and processed without delay on a 24-hour basis;
- Agreements on alerting procedures;
- A reliable international communications system through which emergency messages can be forwarded to alert centres in riparian countries; and
- Finally, early warnings should provide enough time for emergency measures to be taken, both as regards surface- and groundwater pollution.

[8] Section 6.2 provides additional information on this issue.

# Chapter 3. Key elements of a water-quality monitoring programme

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The process of water-quality monitoring and assessment is a sequence of related activities, starting with the definition of objectives and information needs and ending with the dissemination of the information product for use by communities, scientists and decision-makers to effectively allow the protection and sustainable management of national and transboundary water resources.

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The structure of a WQM programme includes the following main elements:

- Objectives;
- Preliminary surveys:
- Monitoring design;
- Field monitoring operations;
- Hydrological monitoring (surface water and groundwater);
- Laboratory activities;
- Quality-assurance procedures;
- Data management and product development.

The linkage of these components is schematically summarized in Figure 1 with an indication of the chapters where the relevant activities under each of the components are described.

These components and their linkages need to be adequately considered during the planning process of a WQM system, so as to ensure that the implementation of the programme will meet with success and generate the required information products. This planning process encompasses three main subsequent phases.

The first phase consists in defining the need for, and establishing the objectives of, monitoring (such as in support of management or research and policy) and what WQ issues are to be addressed. With the objectives defined, it can then be decided what data are needed and how they will be used.

The second phase comprises the design of the monitoring programme, which should consider and include:

- The planning of a monitoring network with the choice of location for the sampling operations, supported by preliminary investigations (inventories and surveys) needed before the programme is started, so that issues, problems and risk factors can be clearly identified and evaluated;
- The selection of physical (e.g. temperature, suspended solids, conductivity), chemical, biological and microbiological variables, i.e. which variables to monitor for different uses – municipal or industrial supply, irrigation, recreation, cooling, drinking-water supply, livestock needs etc. – and in relation to different pollution sources;

- The definition of sampling procedures and operations, such as in situ measurements with different devices, manual or automated measurements, for sampling appropriate media (water, biota, particulate matter), sample pre-treatment and conservation, identification and shipment;
- The planning of field measurements (frequency); and
- The definition of the resources required for the monitoring programme, e.g. the available national laboratory facilities, the inventory of field stations and groundwater-observation wells, equipment and instruments, vehicles and other

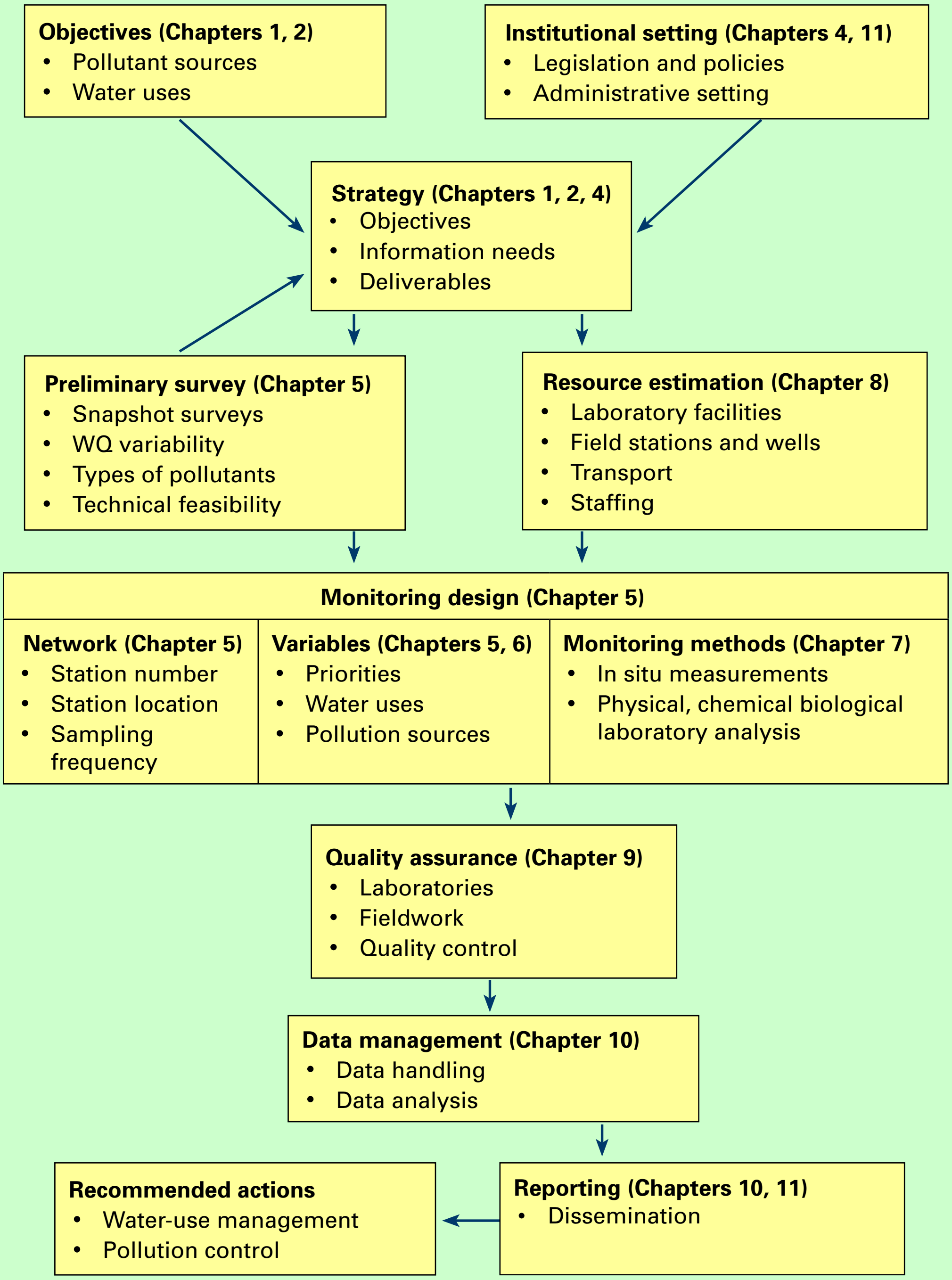


**Figure 1 – Structure of water-quality monitoring operations**

transportation means, office and field staff involved in WQ activities, human-resources development and training required, internal and external communication needs and, finally, the estimated costs of the programme.

The third phase comprises the actual operations (implementation) of the programme, with: (a) the setting up of a quality-assurance system at the strategic/organizational, tactical and operational levels, essential for ensuring the reliability of information obtained by monitoring, covering field and laboratory work, data handling and analysis, as well as the application of WQ standards and indices; and (b) the management of data and development of products, leading to the reporting and dissemination of results and findings.

# Chapter 4. Strategies for meeting information needs of water-quality assessment

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The monitoring of water quality to provide reliable and usable data involves many distinct activities and can be expensive. Thus, the first step in planning the establishment of such a system should be to define the objectives of monitoring (such as in support of management, research or policy) and what WQ issues are to be addressed. With the objectives defined, it can then be decided what data are needed and how they will be used.

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## 4.1. Establishment of objectives of the monitoring programme

In accordance with the goals, answers or information that are sought, WQM and assessment can be looked at from different perspectives in terms of basic variables and present status, time trends and spatial differences, uses, pollution impacts and management needs for information for decisions and action.

All this will result in different approaches to the design and implementation of monitoring programmes, the selection of variables to be measured, the frequency and location of measurements, the additional information needed for interpretation and the way in which information is generated and presented to meet particular information requirements.

When establishing monitoring objectives, the intended uses of the water are particularly important. The environment, aquatic life, drinking-water sources and bathing areas require high-quality requirements, while navigation and water for cooling of industrial processes or cold/heat storage have lower-quality requirements. In the case of livestock watering, irrigation, boiler water and fisheries, each demands a specific level of quality and has its own relative economic importance. To help with the establishment of objectives, the following questions might be addressed:

- Why is monitoring going to be conducted? Is it for basic information, planning and policy information, management and operational information, regulation and compliance, resource assessment, or other purposes?

- What information is required on WQ for various uses? Which variables should be measured, at what frequency and in response to which natural or man-made events?

- What is practical in terms of the human and financial resources available for monitoring? (There is little point in setting unrealistic objectives.)

- Which agency is responsible for the different elements of monitoring?

- Who is going to use the monitoring data and what is the intended use of the information?

- Will monitoring results be used to support management decisions, ensure compliance with standards, identify priorities for action, provide early warning of future problems or detect gaps in current knowledge?

A list of monitoring objectives that might be used as the basis for the design of sampling networks, was identified by Bartram (1996)[9], and is shown in Box 3. It is not intended to be exhaustive but merely to provide some examples.

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[9] Bartram, 1996, 38-39.

**Box 3. Typical monitoring objectives**

- Identification of baseline conditions in the watercourse system
- Detection of any signs of deterioration in WQ
- Identification of any water bodies in the watercourse system that do not meet the desired WQ standards
- Identification of any contaminated areas (surface- and/or groundwater)
- Determination of the extent and effects of specific waste discharges
- Estimation of the pollution load carried by a watercourse system and groundwater
- Estimation of the polluting status and its trends in the water body in order to evaluate the effectiveness of a WQM intervention
- Development of WQ guidelines and/or standards for specific water uses
- Development of regulations covering the quantity and quality of waste discharges
- Development of adequate quality assurance/quality control (QA/QC) processes
- Development of a water-pollution control programme

It is particularly important that the objectives are clearly stated and recorded. Written objectives are an effective way of communicating with sponsors and provide assurance that the monitoring programme has been systematically planned. They are also important when the programme is being evaluated to determine whether or not the objectives are being met.

It is rare for a monitoring programme to have a single objective. Programmes and projects may combine multiple objectives and the data used for different purposes. The implementation of the WQ assessment programme objectives may focus on: (a) regular monitoring with good spatial distribution of quality (high number of monitoring stations); (b) trends (high sampling frequency); or (c) pollutants (in-depth inventories). The focus may also be on a snapshot or near-real-time monitoring of selected variables or on an interest in transport of the load or mass of contaminants (fixed-station moderate sampling frequency). Full coverage of all these requirements is virtually impossible and very costly. Consequently, preliminary surveys are necessary to determine the focus of an operational programme (see Section 5.2).

Countries with economies in transition often stress their difficulties in complying with the recommendations of monitoring and assessment guidelines to enable them to collect the type of data which permit useful assessment and coherent environmental management and which can guide investment decisions. To make the best use of available resources and knowledge, a step-by-step approach is often recommended. This entails identifying and agreeing on priorities for monitoring and assessment and progressively proceeding from general appraisal to more precise assessments and from labour-intensive methods to higher-technology ones.

## 4.2. Water-quality monitoring information needs

The specific purpose of the water must be the initial concern when determining the monitoring information required and no programme should be started without critically scrutinizing the real needs for quality information. Since water resources are usually put to several competing uses, monitoring should reflect the data needs of the various water users involved. These can be grouped into three large categories: communities, scientists and decision-makers. The availability of information accessible to the public and decision-makers is a vital pre-condition for the protection and sustainable use of national and transboundary waters and the support of decision-making.

### Definition of information needs

A WQ system should be designed so that it can provide information at all levels, i.e. international, national (federal), regional and local. The requirement for additional information coming from other programmes or agencies will also define the level of assessment to be undertaken. The national (or federal) level can include data taken from other agencies, as well as from regional and local levels. It is necessary to define clearly what information is needed and already available and to identify gaps that need to be filled. Objectives which are too vague, information needs which are inadequately analysed and information gaps which are poorly identified could result in the production of non-useful data.

To specify information needs, information users and producers should interact closely, with the direct involvement of the institutions responsible for protection and sustainable use of the water bodies. The needs should be specified, based on an analysis of the water management of a river basin and the subsequent identification of relevant issues. A distinction should be made between information used for: (a) policy preparation or evaluation; and (b) operational water management. Inventories and preliminary surveys can help significantly in the process of problem identification and specification of information needs (see also Section 5.2).

In summary, the specified information needs should lead to the definition of:

- Appropriate variables to be monitored;
- Criteria for assessment (e.g. indicators, early warning criteria for floods or accidental pollution);
- Specified requirements for reporting and presenting information (e.g. presentation in maps, graphs, geographical information systems (GIS), degree of aggregation);
- Relevant accuracy for each monitoring variable;
- Degree of data reliability;
- Specified response time (the period of time within which the information is needed), such as for flood forecasts or early warning systems (e.g. minutes/hours), for trend detection (e.g. number of weeks after sampling), for survey of groundwater-contamination plume (e.g. months/years), etc.; and
- Priority of the information (e.g. if the same information need arises from a variety of water problems, collecting it once makes it possible to address a variety of issues).

All this will allow the adequate design of a monitoring and assessment programme. The relevant accuracy and the degree of data reliability are decisive factors in the selection of monitoring sites, the determination of monitoring frequencies and the choice of technology and methodologies for data management.

Risk assessment can also be used to determine whether the chosen monitoring strategy will fully meet the information needs. Statistical modelling to help optimize monitoring design (spatial density and sampling frequency) implies an element of risk analysis. For example, it provides information on whether the resulting decreased level of information will still meet all previously specified information needs should either density or frequency be reduced.

### Integrated water-management strategies

While strategies should be developed and become integrated with effective land management and the linkages between water systems and the atmospheric system must be given more attention, WQ cannot be isolated from water quantity (see also Section 2.2). The current direction is that regional/national river WQM networks, groundwater-quality networks and associated databases should be designed and operated in parallel with those for water quantity. Ideally, they should be managed together.

It should also be recognized that continuity is needed in order to produce time-series that make it possible to detect significant and reliable trends. Environmental monitoring programmes should always be seen as requiring long-term commitment. This is especially the case for groundwater as processes (groundwater flow and chemical reactions) in the subsurface take much more time than in surface water.

## 4.3 Legislation and administrative setting

In general, national legislation sets out obligations and responsibilities for relevant agencies, such as hydrometeorological services, environmental and health agencies, geological surveys and operators of water-regulation structures and industrial installations to monitor and assess various components of the environment and report on the results. As river basins usually stretch over different administrative and geographical units and State borders, cooperation between actors is needed. Hydrometeorological services play an essential role in providing water-quantity data and early warning information for extreme hydrological events. Organizations which operate response systems for emergencies involving water-regulation structures and industrial plants are important partners in providing data to mitigate the adverse impacts of failures of such installations. Industrial enterprises that monitor their own water abstractions and wastewater discharges provide data for compliance purposes (in some countries, this part of the national WQM network is substantial). Assessment of watercourses and groundwater bodies also requires socio-economic data, including population and economic statistics, which are collected by statistical offices.

Where WQ legislation is weak or non-existent, the water authority's mandate may be to develop legislation and regulations appropriate to the country's economic development plans. In this case, the monitoring objectives will probably focus, in the first instance, on acquiring background information on WQ. The objectives will change as information on WQ is accumulated, as problems emerge and solutions are developed and as new demands are made on the water resources. As a rule, national assessment systems are designed and operate under the supervision of government agencies responsible for environmental protection and the rational use of water resources, often with the active participation of research institutions belonging to these agencies. In a number of countries, however, there are several government agencies which are responsible for different aspects of WQ protection and management. In this case, the government normally appoints the particular agency responsible for the organization of the national assessment system. Although the legal framework comes from the government, the monitoring and interpretation of results can be outsourced in some cases and carried out by private companies, provided the quality-assurance and public access procedures are in place.

Multilateral environmental agreements (such as the United Nations Economic Commission for Europe (UNECE) conventions and protocols, European Union directives), as well as transboundary-water agreements, contain obligations for countries to monitor and assess watercourses and to report, as appropriate, to a specific body, such as an international commission, secretariat or organization (see Section 11.1). In January 2009, a resolution was adopted by the United Nations on the law of transboundary aquifers, recommending States to make appropriate bilateral or regional arrangements for the proper management of their transboundary aquifers on the basis of the principles enunciated in the articles (resolution A/RES/63/124). Such cooperative arrangements and institutional frameworks greatly influence the efficiency of monitoring and assessment and can help in the planning phase of the national WQM network.

# Chapter 5. Design of a monitoring programme

With the objectives of the WQM programme defined and the decision taken on what data are needed and how they will be used, the sampling locations and frequencies are then chosen with a view to obtaining the required information, while ensuring that the resources are employed to best advantage.

## 5.1 Planning a monitoring network

A monitoring programme commonly covers the watercourse system of a catchment[10] area (i.e. a main river and all its tributaries, streams, brooks, ditches, canals, etc., as well as any lakes or ponds that discharge into the river or tributaries) or it can comprise an administrative unit, e.g. a province. In some cases, groundwater enters the watercourse system from an aquifer or a system of aquifers, all or part of which may lie outside the topographic one. Surface and groundwater catchment areas often do not coincide.

The level of detail that monitoring can provide depends on the density of the network, the frequency of sampling, the size of the basin and the issues under investigation. For example, when a station at the outlet of a river basin reports WQ changes, a more detailed monitoring network is often needed to reveal the source, causal agent and the pathways of pollutants. The interaction between surface and aquifers may also be different in the upper and lower parts of the basin. In these cases, information is needed for smaller sub-basins. The different sources of WQ pollution, such as point source (e.g. sewage, industrial leakage to subsurface) or non-point sources (e.g. agricultural runoff/percolation) also need to be considered.

The monitoring and assessment of groundwater quality is often more complicated because of: (a) the complex structure and composition of aquifers; (b) the recharge and abstraction conditions of the aquifer; and (c) the relatively long timescales of groundwater movement and residence.

Monitoring networks, the frequency of measurements, the selection of parameters, as well as assessment methodologies, should be adapted to all these conditions. To facilitate this, a conceptual model of the river basin might be developed, so that the whole system is well understood, establishing whether interactions between surface- and groundwater exist or not, so that water quantity and quality can be taken into account.

### Monitoring alternatives

At the planning stage, the following alternatives should be considered:

- ***Fixed-site network**,* useful for public information and broad policy issues; should be limited to drinking-water sources that require regular monitoring;
- ***Flexible survey approach,*** more convenient for regulatory purposes, determining management options in cases of pollution and related investment decision-making;
- ***Decentralized monitoring*** alternatives instead of a national network operated by a central agency; and

[10] The catchment area is defined as the area from which all water flows to the watercourse. The land surface that slopes in such a way that precipitation falling on it drains towards the watercourse is called the topographic catchment area.

- ***Monitoring*** of the quality of the aquatic environment should be coupled with the appropriate hydrological monitoring.

When starting a monitoring programme, it is better to have a complete record of reliable data concerning WQ at a few sampling stations rather than many data of questionable quality from many sampling stations. When reported data are not reliable, the programme and its staff will lose credibility and poor or incorrect decisions may be made with potentially serious and costly consequences.

## 5.2 Selection of sampling stations

Processes affecting water quality and their impacts should be taken into account when sampling sites are selected. This requires consideration of: (a) the monitoring objective(s); (b) some knowledge of the geography of the watercourse system; (c) actual and potential water uses; (d) actual and potential sources of pollution; (e) water-control operations; and (f) local geochemical conditions and type(s) of the water body/bodies. In many cases, the precise location of a sampling station can be made only after a field investigation (see Section 5.3).

In the specific case of groundwater-monitoring programmes, the fundamental requirement is to define the distribution of water quality in three dimensions. This requirement is the same, regardless of the specific objectives of the programme. Thus, in all cases, the objective is to obtain representative samples which fully reflect the conditions of the groundwater in situ at a specific point, periodically at known times. Having established the objectives of quality assessment, the next step is to design the sampling network. This is essentially a function of the sampling-point type, density and location, sampling method and frequency and choice of parameters (see also Annex 1, Section 6).

The essential factors to consider for the location of sampling sites, among others, are described in the field operations manual for WQM (WMO, 1988)[11].

As regards the types of sampling sites, the GEMS/Water global monitoring network[12] defines the following three types of monitoring station:

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

- ***Trend stations*** are typically located in major river basins, lakes or aquifers. They are used to follow long-term changes in water quality related to a variety of pollution sources and land uses and provide a basis for the identification of causes or influences on measured conditions or identified trends. Since trend stations are intended to represent human impacts on water quality, the number of trend stations is relatively higher than the other categories of stations, in order to cover the variety of water quality issues facing various basins. Ideally, each country should cover all major human influences on water quality. Most of the stations are located in basins with a range of pollution-inducing activities. Some stations, however, are located in basins with single, dominant activities. Some trend stations may also serve as global river-flux stations;

[11] WMO Manual on Water Quality Monitoring, 1988; WMO Operational Hydrology Report, No. 27, WMO-No. 680, World Meteorological Organization, Geneva, 197 pp.

[12] Verbatim GEMS/Water, 2005, 12

- ***Flux stations*** are located at the mouth of rivers as they exit to the coastal environment. They are used to determine integrated annual fluxes of critical pollutants from river basins to oceans or regional seas, thereby contributing to geochemical cycles. For the calculation of chemical fluxes, it is essential that water-flow measurements be obtained at the location of the global river flux stations. It is for this reason that station co-location is encouraged with those designated stations of WMO's Global Runoff Data Centre (GRDC) (see Section 11.2).

Finally, in large programmes involving several parties, institutional issues are important. Sampling sites may be operated by different entities that might not be cooperating. Such issues should preferably be resolved in the early stages in order to streamline national monitoring and enable the best possible data-sharing.

## 5.3 Preliminary surveys

Preliminary investigations such as inventories and surveys are needed before any monitoring programme is started, so that issues, problems and risk factors can be clearly identified and evaluated with the overall aim of establishing the monitoring systems as effectively as possible. These are short-term, limited activities to determine WQ variability, specific issues in lakes, river basins and groundwater, the type of monitoring media and pollutants to be considered and the technical and financial feasibility of a complete monitoring programme. Inventories and in-depth surveys should provide: (a) relevant background information with respect to the uses of water; (b) the possible presence of pollutants not previously monitored; (c) toxicological factors; (d) the natural background concentrations of components in groundwater; and (e) the spatial and temporal variability of pollutant distributions. Finally, national surveys, together with land-use maps, can provide a rapid overview of possible pressures in the basin. In this context, it is useful to consider homogeneous areas where these preliminary investigations are to be undertaken.

***Inventories*** should bring together all the available data, even when scattered around different agencies or institutions. This can involve the registering of historical data, licenses, etc. in administrative databases, as well as a general screening and interpretation of all the relevant information. For inventories of pollution sources, this will involve examining information at source, such as figures concerning production processes and the use of raw materials, as well as the investigation of suspect incidents through additional questioning.

***WQ surveys*** provide a preliminary insight into the functioning of the aquatic ecosystem, the geochemical characteristics of groundwater and the occurrence of pollution and toxicity in water. The ecological status of a river, lake or estuary can be assessed by investigating the qualitative and quantitative structures of the biotic[13] components of the ecosystems. Chemical screening of surface water, sediment and effluents at hot spots and key locations can be performed with the supporting analyses. Any specific target compounds that inventories suggest might occur can also be analysed and toxic effects in surface water. Sediments and effluents can also be investigated at such locations.

***Preliminary surveys*** also help to refine the logistical aspects of monitoring. For example, access to sampling stations is tested and can indicate whether refinements are necessary to the site selection (a certain site may be found impractical for a variety of reasons, e.g. transport difficulties). Similarly, operational approaches may be tested such as on-site testing techniques or sample preservation and transport methods can be evaluated. Sample volume requirements and preservation methods can then also be refined.

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[13] Phytoplankton, macrophytes, the macroinvertebrate community, fish populations

As a final result of the inventory, a listing of sampling sites should be prepared and sampling stations or wells selected during the design of the monitoring programme (see also Section 8.2).

## 5.4 Documentation

During the design phase of a WQM programme, it is essential that full documentation is compiled. This should initially cover the description of a monitoring area comprising, as a minimum: (a) the definition of the extent of the area where water conditions are to be monitored; (b) a summary of the environmental conditions and processes (including human activities) that may affect WQ; (c) the availability of meteorological and hydrological information; (d) a description of the existing water bodies; and (e) a summary of actual and potential uses of water. Subsequently, the initial steps of the planning process should then be recorded, starting with the monitoring objectives through the choice of sampling locations.

Additional guidelines on documentation requirements are provided in Section 10.3.

# Chapter 6. Selection of water-quality variables

The parameters which characterize WQ comprise physical properties, redox conditions, inorganic and organic chemicals and biological components (both microbiological and macrobiotic), which can indicate the ecological health of the aquatic environment. The parameters selected for evaluation at a station or observation well will be determined largely by the objectives of the monitoring programme.

Water bodies can be fully characterized by the three major components: hydrodynamics, physicochemistry and biology. A complete assessment of WQ therefore needs to be based on appropriate monitoring of these components.

The selection of variables for any WQ assessment programme should be indicative of functions and issues in river basins. The selection must therefore consider known characteristics of the water resource and the polluting sources. The purpose of this chapter is to provide information to assist the selection of variables, i.e. which variables to monitor for different uses (municipal or industrial supply, irrigation, recreation, cooling, agriculture, drinking-water supply, livestock needs, etc.) and in relation to different pollution sources.

## 6.1 Classification of WQ variables

Annex 1 provides a detailed description of the main WQ variables, ranging from: general variables, such as nutrients, organic matter and major ions; other inorganic variables, such as metals and organic contaminants; and biological variables, such as microbiological indicators and sedimentation.

The WQ variables may be listed, grouped and classified in different ways[14]. As an example, a number of broad categories under which parameters may be grouped are shown in Box 4.

River-basin management and water-pollution control have long relied on aggregate parameters, such as biochemical oxygen demand (BOD) and chemical oxygen demand (COD), indicators widely used to assess the amount of organic oxygen-consuming pollution in rivers. For human consumption and public water supply, a set of microbiological indicator organisms (e.g. faecal coliform bacteria) have been identified and are now commonly applied to determine the hygienic suitability of water for drinking.

Typically, drinking-water quality is assessed by comparing water samples to drinking-water quality guidelines or standards. Many countries set such guidelines, based on those of the World Health Organization (WHO) and may modify or tailor them to their domestic context. Appendix 1 provides a summary of international and national WQ guidelines and standards by a number of international organizations (WHO, EU) and selected countries[15] (see also Section 9.6).

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[14] In the GEMS/Water publication Water Quality for Ecosystem and Human Health (2006), the parameters are described following water-quality categories: physical and chemical characteristics of a water body, major ions, nutrients, metals, organic matter, biological components, organic contaminants and hydrological variables. The variables and indices according to the definition of “ecological status” in the EU Water Framework Directive (WFD) are grouped as follows: chemical and physicochemical elements, biological elements, harmful substances, microbiological quality and sediments.

[15] Australia, Canada, New Zealand, Japan and USA

**Box 4. Categories of WQ parameters**

- Basic parameters, e.g. water temperature, pH, conductivity, DO and discharge, used for a general characterization of WQ
- Suspended particulate matter, e.g. suspended solids, turbidity and organic matter (total organic carbon (TOC), BOD and COD
- Indicators of pollution with oxygen-consuming substances e.g. DO, BOD, COD and ammonium
- Indicators of pollution with nutrients and eutrophication effects, e.g. nitrogen and phosphorus, and various biological effect variables, e.g. chlorophyll and Secchi-disc transparency
- Indicators of retention time in a slow-changing water body (lakes, reservoirs, impoundments)
- Indicators of acidification, e.g. pH, alkalinity, conductivity, sulphate, nitrate, aluminium, phytoplankton and diatom sampling
- Indicators for forecasting the future eutrophication state of water bodies
- Specific major ions, e.g. chloride, sulphate, sodium, potassium, calcium and magnesium: these are essential factors in determining the suitability of water for most uses, such as public water supply, livestock watering and crop irrigation
- Specific minor ions, e.g. arsenic and fluoride: above certain concentrations, these ions are toxic to human health
- Metals, e.g. cadmium, mercury, copper and zinc
- Organic micropollutants, such as pesticides and the numerous chemical substances used in industrial processes, products and households
- Indicators of radioactivity, e.g. total alpha and beta activity, 137Cs, 90Sr
- Microbiological indicator organisms e.g. total coliforms, faecal coliforms and faecal streptococci bacteria
- Biological indicators of the ecological quality, e.g. phytoplankton, zooplankton, zoobenthos, fish and macrophytes

A wealth of information (including parameters, pressures in the basin, variability, sampling, instrumentation, usage, standards, advantages, disadvantages and recommendations) on the key features of each chemical and physicochemical, and biological quality element for lakes can be found in Appendices 2 and 3, respectively.

## 6.2 Selection of variables

The variables to be measured as part of any given sampling programme should reflect a consideration of the uses to which the water is put, as well as any known or anticipated impacts on the water quality. In addition, the selection of variables to be included in a WQ assessment should be related to the objectives of the programme. Assessments can be divided broadly into two categories – use- and impact-orientated – as described below. They can, however, also be based on the widely accepted DSPIR[16] (Drivers-Pressures-State-Impact-Responses) framework to guide state and trend assessments of surface- and groundwater ecosystems, shown in Table 3. The following services and uses are covered: human health and drinking-water, agriculture, municipal/industrial, energy, ecosystem stability, structure and health, and tourism and recreation.

For many variables, existing literature on their occurrence in the environment, and particularly in freshwater systems, can provide guidance in prioritization. As an example, the revised list of basic variables used in the GEMS/Water programme (e.g. stations in rivers, lakes/reservoirs, aquifers and global river-flux monitoring stations) are presented in Table 2.

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[16] UNEP GEMS/Water Technical Advisory Paper No. 2, May 2005

There may be a need for those responsible for assessments to decide which monitoring activities have the highest priority. By using risk-assessment techniques (and recording how these were applied), this could be done using the concept of “expected damage”, i.e. determining what goes wrong when there is insufficient information because of lack of monitoring, or what losses are incurred when less-than-optimal decisions are made as a result.

### *Selection of variables in relation to water use*[17]

Use-oriented assessment indicates whether WQ is satisfactory for specific purposes, such as drinking-water supply, industrial use or irrigation. Many water uses have specific requirements with respect to physical and chemical variables or contaminants. In some cases, therefore, the required quality of water has been defined by guidelines, standards or maximum allowable concentrations (see summary in Appendix 1).

These consist of *recommended* (as in the case of guidelines) or *mandatory* (as in the case of standards) concentrations of selected variables which should not be exceeded for the prescribed water use. Existing guidelines and standards define the minimum set of variables for inclusion in assessment programmes. Table 4 presents a selection of variables for assessment of WQ in relation to non-industrial water use, covering background monitoring, aquatic life and fisheries, drinking-water sources, recreation and health, agriculture, irrigation and livestock watering. The suggested variables are appropriate to the specific water uses and can be used where guidelines are not available. The selection should include only those most appropriate to local conditions and it may be necessary to include other variables not indicated under the respective headings.

Other variables can also be monitored, if necessary, according to special conditions related to the intended use. Acceptable WQ is also related to water availability. When water is scarce, a lower level of quality may have to be accepted and the variables measured can be kept to a minimum.

The requirements of industry for WQ are diverse, depending on the nature of the industry and the individual processes using water within it. Table 5 summarizes some of the key variables for some major industrial uses or processes, such as heating, cooling, power generation, iron and steel, pulp and paper, petrol and food processing. Although some proposed guidelines exist, they need to be considered in relation to the specific industrial needs and water availability.

### *Selection of variables in relation to pollutant sources*[18]

WQ assessment often examines the effects of specific activities on WQ. Typically, such an assessment is undertaken in relation to effluent discharges, urban or land runoff or accidental pollution incidents. The selection of variables is governed by knowledge of the pollution sources and the expected impacts on the receiving water body. It is also desirable to know the quality of the water prior to anthropogenic inputs. This can be obtained, for example, by monitoring upstream in a river or prior to the development of a proposed waste-disposal facility. When this cannot be done, background WQ from an adjacent, uncontaminated, water body in the same catchment can be used.

Appropriate variables for assessing WQ in relation to several major sources of pollutants are given in Table 6, which shows a selection of variables for the assessment of WQ in relation to non-industrial pollution sources, comprising sewage and municipal wastewater, urban runoff, agricultural activities, waste disposal to land, solid hazardous municipal chemicals and long-range atmospheric transport. Table 7 provides information on the

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[17] Taken mainly from D. Chapman [Ed.], 1996

[18] Taken mainly from D. Chapman [Ed.], 1996

selection of variables for the assessment of WQ in relation to some common industrial sources of pollution. These cover food processing, mining, oil extraction/refining, chemical/pharmaceutical, pulp and paper, metallurgy, machine production and textiles. There are also accidents related to leakage to groundwater, e.g. at petrol stations.

The suggested variables for different types of assessment given in this section are based on common situations and should be considered as guides only. The final selection depends on the products manufactured or processed, together with any compounds present in local industrial effluents. Any standards or guidelines for specific variables should also be taken into account. The full selection of variables must be made in relation to assessment objectives and specific knowledge of each individual situation.

Most of the variables can be measured by various methods and techniques, depending on the resources available, time constraints (how quickly the results are needed) and the accuracy of the results required. These issues will be discussed in Chapter 7.

### *Selection of variables for early warning systems*[19]

The appropriate indicative variables to be monitored for early warnings will vary and should be selected on the basis of:

- The past history of pollution emergencies (frequently occurring local risk substances);
- Issues specific to the river basin (e.g. DO, pH);
- Any additional need to detect specific micropollutants, such as heavy metals, harmful organic compounds or pesticides, using advanced technologies; and
- Any additional need to detect specific micropollutants which may accumulate in living organisms and generate chronic diseases.

Variables should also be selected for early warning systems according to the availability of equipment for in situ measurements and other cost-benefit considerations, due to the high investment, operating and maintenance costs for automatic measuring devices. Acute toxic effects may also be recognizable with the help of biological systems examining species from different trophic levels and with various functions.

Any potentially hazardous pollutants that frequently occur in a river basin in concentrations that may jeopardize water uses should be targeted by early warning systems. Simple indicative parameters such as DO, pH or oily substances can be routinely measured by automatic in situ sensors. If specific problematic micropollutants such as pesticides need to be detected, more advanced analytical systems can be used, although investment, operating and maintenance costs are high. Toxicological effects in organisms at various trophic levels can be measured with automated biological early warning systems.

Early warnings should provide enough time for emergency measures to be taken. The location of early warning WQM sites, including their observational infrastructure (stations), should therefore be determined with regard to the response time (the interval between the moment of sampling and the issue of an alarm) and the time any contaminant plume in a river will take to flow from the warning station to any site downstream where the water is used, such as a water-supply intake. The diffusion of contaminants may be crucially affected by high river discharges. Sampling points should also be carefully located to ensure that the presence of all the relevant pollutants is observed.

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[19] See also Section 2.5.

The frequency of measurements should be determined by the expected size of contaminant plumes so that no significant pollution is missed. Plumes will inevitably disperse to some extent between their discharge source and the sampling location, according to the characteristics of the river. Furthermore, sampling frequencies should allow sufficient time for action to be taken in the event of an emergency. Additional and intensified sampling is recommended after the first indication of accidental pollution. One example of a river-basin alarm system is that of the River Rhine.

Regarding contamination plumes in groundwater, observations wells should be monitored at specific locations to verify that the plume is not reaching some potential receptors such as deeper aquifers, rivers or the surrounding groundwater system.

## 6.3 Hydrological variables

The main hydrological and hydrometeorological characteristics, such as precipitation, snow cover, water level, river flow, sediment discharges (suspended sediment and bed load), evaporation and evapotranspiration, soil moisture, recharge, groundwater head[20], temperature and data on ice conditions, should also be measured and estimated as an important part of any WQM programme.

In general, a sufficient number of hydrological or river gauging stations should be located along the main river to permit interpolation of water level and discharge between the stations. In addition, water balances require sufficient observation stations at small streams and tributaries. Gauges on lakes and reservoirs are normally located near their outlets, but sufficiently upstream to avoid the influence of drawdown. Continuous river-flow records are necessary in estimating the sediment or chemical loads of streams, including pollutants.

Regarding groundwater, a sufficient number of observation or monitoring wells should be set up through the area at specific locations. As groundwater quantity and quality have to be defined in three dimensions, measurements and sampling should also take place at different depths, which should be chosen according to the characteristics of the aquifer system.

The factors controlling the water balance of a lake should either be measured directly or calculated by means of regional assessment or the water-balance equation. For the latter, the key hydrological variables are typically regional precipitation, lake inflow, lake-water level and evaporation and lake outflow. Measurement of water level is necessary for mass-flow calculations in lakes and aquifers and must be measured at the time and place of water-sampling. Snow cover and groundwater storage are also important factors in many cases. Important physical hydrological phenomena, such as sediment transport, erosion, water temperature and ice phenomena, can also affect chemical and biological processes in lakes.

The morphological characteristics of the lake itself are of key importance. A bathymetric map – preferably in a data system format – can be used for the definition of the morphological features, as well as for various physical, chemical and biological studies.

The velocity (sometimes referred to as the flow rate) of a water body can significantly affect its ability to assimilate and transport pollutants. Thus, measurement of velocity is extremely important in any assessment programme. It enables the prediction of movement of compounds (particularly pollutants) within water bodies, including aquifers.

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[20] Groundwater head is the water pressure expressed in units of length measured in a well. The distribution of hydraulic head determines the direction of groundwater flow.

For example, knowledge of water velocity enables the prediction of the time of arrival downstream of a contaminant accidentally discharged upstream. Regarding groundwater, the flow velocity enables the prediction of the time of arrival of the contamination or a derived one to a production well.

Finally, hydrological modelling and forecasting are a useful component in the WQ assessment process. Modelling the hydrological cycle of a river system is a relatively straightforward process. Operational simulation and forecasting models have proved efficient in drainage-basin management and, in the case of international lakes, can play an important role. Hydrological monitoring and modelling can form supplementary elements for linking with decision-support systems, as well as ecological modelling and assessment. As the speed of movement of accidental pollution in a river system depends mainly on flow characteristics, provision should be made to use hydrological forecasts when accident or emergency warnings are issued.

Flood forecasting is more intensive and requires more frequent observations and data transmission. More observation sites and a wider range of information (e.g. on reservoir operation, dyke failures and emergency measures) are needed. Forecasts can then be issued more frequently and include additional characteristics, such as the timing and magnitude of flood peaks.

Some important water-use data can be calculated by using hydrological observations. Examples include flows at industrial or municipal intakes and outlets, releases from reservoirs and other main diversions to and from lakes. This information can be used for lake regulation or the allocation of water during extreme situations or normal operations.

Low-flow conditions can disrupt the use or consumption of water and the ecological status of a water body. Long-term series of data on hydrological parameters and the corresponding climatic factors are needed for the statistically reliable estimation of drought conditions. During droughts, more frequent exchange of information and data on reservoir operation, diversions and water uses may be necessary, in addition to hydrological and meteorological data. In this regard, it is suggested that suitable methods be developed or adopted in order to calculate or – at least to evaluate –the compensation water flow that is required as minimum flow to maintain a healthy river environment.

# Chapter 7. Selection of water-quality monitoring methods and techniques

There are a variety of monitoring methods and different levels of technology (from low-cost to very expensive instruments) and techniques available and being developed to address the quality of water resources around the globe. There is no single, simple method which can be applied across the board, in every aquatic situation. The challenge for water managers is in the efficient use of a mixture of technologies specifically to address each particular situation.

## 7.1 Methods for field monitoring

Traditionally, water-sampling operations include in situ measurements, sampling of appropriate media (water, biota and particulate matter), sample pre-treatment and conservation, identification and shipment. The various alternative methods that may be chosen are shown in Box 5. Protocols to ensure the comparability of results and to prevent sample contamination should be established for all monitoring methods.

**Box 5. Methods for field monitoring***

- In situ measurements with different devices
- Manual or automated measurements
- Continuous or snapshot monitoring
- Water-sampling, including grab sampling
- Depth-integrated sampling
- Time-proportional composite sampling
- Space-composite sampling
- Water-quality kits
- Vacuum-pumping techniques
- Remote-sensing

* For more details, see Annex 2.

Methods of measuring are determined by a number of factors: the type of material being monitored – surface- or groundwater; bottom or suspended sediment; groundwater-well sampling; the type of sample – grab, composite or integrated; the quality parameter being analysed; the amount of sample; whether the sample is analysed on the spot or sent back to a laboratory.

This chapter[21] summarizes the different monitoring methods and their main advantages and disadvantages. The purpose is to give guidelines so that the manager may be able to choose the most suitable (reliable, cost-effective) methods for the monitoring programme. The process of choosing the variables to be monitored and the methods to be used is iterative, since certain variables may be difficult or expensive to monitor and alternative solutions have to be found.

The methods employed to measure the selected variables depend on access to sampling equipment and reagents, availability of technical staff and their degree of expertise and the level of accuracy required by the objectives of the programme. Detailed descriptions of sampling and analytical methods are available in a number of

[21] A detailed description of the main water-quality monitoring methods and techniques is provided in Annex 2.

guides and reference material published by various authors, international organizations and national agencies.[22]

Traditional water-sampling for laboratory chemical and biological analysis provides accurate results if performed with care and sufficient quality-assurance procedures are used. In many cases, they are also the only acceptable method when high precision is required. Laboratory analyses may, however, be expensive and time-consuming.

Existing groundwater-quality assessment programmes with a range of objectives depend entirely on samples taken from the pump discharge as it comes to ground level. Samples from boreholes and wells are the basis of background and trend-monitoring programmes. Existing boreholes selected for such programmes should be those with the most reliable information, so that a short screen length over the most appropriate depth interval of aquifer and most comprehensive geological log, facilitate subsequent interpretation of the results.

In situ monitoring may be either manual or automated and has to be selected on the basis of specific monitoring objectives, programme resources and suitability of sites. The method selected must be appropriate for programme goals and technically feasible. Automated methods may be more appropriate than manual ones in situations where:

- Highly variable WQ occurs in an hourly/daily time frame;
- Infrequent transient events occur and affect WQ; or
- It is not possible to sample manually or it is difficult to maintain the required sampling frequency.

***WQM equipment***

In situ and portable WQM devices are often used as there is an increasing need to monitor large areas in short time intervals. These devices and methodologies can range from simple, inexpensive devices to capital-intensive, sophisticated equipment. Field measurements reduce the time between sampling and measuring, allowing for real- or near-real-time analyses.

There are instruments for simple field-measured variables such as thermometers or thermistors, portable pH and conductivity meters, DO meters or optodes, optical turbidity meters, fluorometers, etc.

Electrodes are small, low-weight sensors, which can be submerged in the water to be monitored. The advantages are that they provide simple, rapid measurements with high precision in a wide concentration range. Among their disadvantages are their low sensitivity to the single parameter under investigation and malfunctioning arising from clogging, coating, etc. Optical absorption and reflectivity spectrometers are also available for a number of substances. Although these methods are simple, they are limited in their concentration range with only medium sensitivity compared with standard laboratory analysis. The biosensors are fast and efficient for measuring BOD but are rather heavy. UV-absorption devices and fluorometers are often used to measure dissolved organic load. These methods are simple, sensitive and rapid and do not use chemicals. The biofluorometer uses the changes in fluorescence properties of standard solutions, whereas other biosensors are based on the bioluminescence of bacteria when exposed to toxic substances.

[22] Guidebook by Bartram and Ballance, 1996

Partly owing to resource and time constraints to establish well-equipped WQ testing laboratories in sufficient numbers and partly owing to the dynamic nature of WQ, simplified WQ field test kits have been developed in an overall approach to WQM, especially in developing countries. Kits can accomplish the initial screening and periodical monitoring of waters. Such tests are relatively inexpensive and can be conducted at water-user level, thereby improving the potential for involving user communities. Results can be supported by detailed analysis of problem sources in proper laboratories.

There are field kits (discs, test strips, drop test kits, dipslides) that allow qualitative testing for E-coli and bacterial contamination in general, DO, pH, electrical conductivity, temperature difference, turbidity and level of nitrite, nitrate and orthophosphate ions, arsenic, fluoride, iron, residual chlorine, chloride, alkalinity, hardness and aluminium.

The advantages of portable devices for field measurements are readily apparent. They have the potential to reduce operator and analysis error when proper training and operation are performed. The ability of a portable monitoring device to provide an immediate result has application in isolated and developing areas where the safety of drinking-water supplies is of paramount concern.

### *Automatic measurements*

Recent years have seen a significant increase in automated measurements of physical parameters, such as temperature, conductivity/salinity, pressure/depth, with other measurements such as pH, turbidity, transparency and DO and colour-supplemented by water-sampling for offline laboratory analysis. A significant driver for improved sensing of inland waters is reduction of the labour costs involved in water-sampling, sensor maintenance and servicing. Thus, sensors that require less frequent attention are a priority requirement and are becoming more widely used.

In situ sensors play an integral role in the overall data-generation process, which is the first link in the information-management system. They allow for the continuous or intermittent collection of WQ parameter data in real- or near-real-time. High density of measurements over relatively short periods can be critical because water-quality conditions can vary widely, such as before, during and after storms. Sensors can be cost-effective because they minimize costly field visits by scientists and technicians. The monitoring devices may also include flow-through systems that enable rapid measurements, either as continuous stationary measurements or used on a moving platform (boat). In addition, real-time measurements for temperature, conductance and turbidity can be correlated with other important water-quality properties, such as bacteria, that are more costly and difficult to monitor and analyse. These new aspects provide new possibilities for WQM.

It should be stressed, however, that the use of these special, multi-parametric, portable instruments and automatic WQ stations still require regular – and sometimes sophisticated and expensive – maintenance.

Box 6 lists available and reliable variables, suitable for incorporation into an automated WQM programme.

Advances related to monitoring technology are needed to support future water-quality issues successfully. They include, for example, continued development and testing of WQ probes, monitors, data-recorders and telemetry equipment that allow the monitoring of water-quality variables. Sensors can be cost-effective because they minimize costly field visits by scientists and technicians. In addition, real-time measurements for temperature, conductance and turbidity can be correlated with other important properties, such as bacteria, that are more costly and difficult to monitor and analyse. Development, testing and deployment of a new generation of real-time sensors for WQ have the potential greatly to increase the level of information available at a given level of funding.

**Box 6. Selected environmental variables that can be monitored automatically**

| Automatic measurements | Electronic | Optical |
|---|---|---|
| Temperature | x | |
| Conductivity/salinity | x | |
| Chlorophyll a | | x |
| Cyanobacterial | | x |
| pH | x | |
| DO | x | x |
| Turbidity | | x |
| Suspended solids | | x |
| DOC | | x |
| TOC | | x |
| Nitrate | x | x |
| Nitrite | x | x |
| COD | | x |
| Water level | x | |
| Hydrocarbons | | x |
| Water speed/direction | x | |

***Environmental monitoring***

Organisms living in aquatic environments are sensitive to changes, whether these be man-made disruptions or natural environmental fluctuations. The reactions may be subtle, in the form of reduced reproductive capacity and inhibition of specific enzymes necessary for normal metabolism, or the reaction may be extreme, resulting in the death of the organism or complete migration to another habitat. Unlike physical/chemical analyses, which are conducted on water samples, biological indicators yield cumulative information about both past and current situations. This is an ecosystem approach to environmental monitoring, dealing with biological communities and not simply a single, measured, WQ parameter.

***Remote-sensing***

The knowledge of the spatial distribution of different biological, chemical and physical variables is essential in environmental water studies as well as for resource management. Hence, coupled with advanced processing methods and improved sensor capabilities, recent years have seen increasing interest and research in remote-sensing of the quality of inland and coastal waters. Unless a water body is sufficiently instrumented by in situ sensors, remote-sensing is the only satisfactory method to detect the quality of remote and large inland waters. Thermal remote-sensing, for example, can be used to define groundwater-discharge zones.

Remote-sensing technology provides an emerging capability that can significantly augment or replace traditional in situ methods but the field is relatively new, especially in addressing optically complex waters. Satellite-image archives exist, dating back to 1970, enabling change detection of previously unmeasured or unmonitored water bodies. Remote-sensing is a suitable technique for coarse-scale monitoring of inland and coastal WQ. It provides a synoptic view of the spatial distribution of different biological, chemical and physical variables of both the water column and, if visible, the substrate.

**Advantages and shortcomings of the different monitoring methods**

As a conclusion and to serve as guidance, the advantages and shortcomings of biological, chemical and in situ WQM are summarized in Box 7.

| Box 7. Biological, chemical and in situ WQM: advantages and shortcomings | | |
|---|---|---|
| Biological monitoring | Sampling for chemical laboratory analysis | In situ sensors |
| Advantages | | |
| Good spatial and temporal integration | Possibility of very fine temporal variations | Relatively low cost |
| Good response to chronic, minor pollution events | Possibility of precise pollutant determination | Possibilities for continuous surveillance |
| Signal amplification (bioaccumulation, biomagnification) | Determination of pollutant fluxes | Real-time studies |
| Real-time studies (in-line bioassays)<br>Measures the physical degradation of the aquatic habitat | Valid for all water bodies, including aquifers<br>Standardization possible | Valid for all water bodies, including aquifers<br>Possibility of very fine temporal variations and good spatial coverage |
| Shortcomings | | |
| General lack of temporal sensitivity | High detection limits for many routine analyses (micropollutants) | No precise pollutant or trace element determination |
| Many semi-quantitative or quantitative responses possible | No time-integration for water grab samples | General precision lower |
| Standardization difficult | Possible sample contamination for some micropollutants (e.g. metals) | Advanced technology needed |
| Not valid for pollutant flux studies | High costs involved in surveys | |
| Not yet adapted to aquifers | Limited use for continuous surveillance | |

## 7.2 Frequency of sampling

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

The frequency of sampling should be determined by balancing ecological needs with economic possibilities. In the routine monitoring of a lake, the samples will usually be taken several times during one year. The most important monitoring period is summer stratification time. The primary production processes are then at their highest and the decomposition of organic matter is most active. Especially in eutrophied or polluted lakes, several samplings should be performed during the respective summer periods in the northern and southern hemispheres.

Lakes exhibit a wide range of hydrological characteristics, from fast-flushing drainage lakes to seepage lakes with a long residence time. Sampling frequency should be designed to characterize the annual variability of lakes. Monthly samples are recommended for most fast-flushing lakes, whilst more frequent sampling may be required occasionally in lakes that undergo short-lived acidic episodes, algal blooming or nitrate peaks. Also, where flow data are available for calculations of yearly transport values of elements from catchments, increased sampling frequency in flood periods is recommended.

Quarterly or seasonal sampling is likely to be adequate in lakes with long residence times. In remote areas where frequent sampling is impossible for practical and economical reasons, even one sample per year may be useful for long-term monitoring. Such samples must be taken each year at the same time, usually at the end of summer stratification, but in case of monitoring the acidification trend, preferably shortly after autumn overturns.

Riverine fluxes of material are highly variable in time at a given sampling station. Generally, TSS fluxes vary more than water discharge, while most major ion fluxes vary less (owing to decreasing concentrations with increasing discharge). Consequently, the optimum frequency for discrete sampling for flux determination is influenced by these relationships. The optimum sampling frequency is the one above which there is no significant gain in the accuracy of the flux determination with respect to other errors involved (e.g. analytical error and errors arising from the non-uniformity of the river section). For any given basin, the range of optimum sampling frequency is affected by the basin relief and climatic influences; steep, heterogeneous and dry basins need greater sampling frequencies than lowland, homogeneous and humid basins of the same size. In small basins, more than four samples a day may be necessary, whereas for large rivers such as the Amazon, Mekong, Nile, Plata and Zaire, a single sample a month may be sufficient.

For groundwater, the sampling frequency is usually much lower – one to four times a year – depending on the purpose of the monitoring. In specific cases, in aquifers with high-flowing rates or in specific areas that are polluted or vulnerable to pollution, the sampling frequency can become much higher.

The recommended annual sampling frequencies for stations in the GEMS/Water global network are given in Table 8.

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. Aquifers may exhibit regular patterns of quality but rates of change are relatively slow, except for highly permeable aquifers (see also Section 1.6).

## 7.3 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, the successive results will be directly comparable for the purposes of assessing changes in WQ. 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 + 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 + 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.

# Chapter 8. Resources for a monitoring programme

The available national laboratory facilities, the inventory of field stations, equipment and instruments, vehicles and transportation means and the office and field staff involved in WQ activities, together with the financial means, constitute the main resources required for a monitoring programme.

## 8.1 Laboratory facilities

Laboratory activities for WQ include concentration measurements and biological determinations, which could also comprise the preparation of sample-collection devices and sample containers, calibration of in situ meters prior to use in the field, quality-control checks, collating data, etc.

Laboratories should be selected or set up to meet the objectives of each programme, with attention being paid mainly to the choice of analytical methods. The range of concentrations measured by the chosen methods must correspond to the concentrations of the variable in a water body and to the concentrations set by any applicable WQ standards.

During the initial stages of development of a national monitoring system, the focus should be on the basic quality variables which, as a rule, do not require expensive, sophisticated equipment. Gradually, the number of variables measured can be increased in relation to the financial resources of the monitoring agency. The elaborate equipment and technical skills necessary for the measurement of complex variables are not needed in every laboratory.

In Bartram (1996)[23] a number of options are highlighted that may be available for conducting analyses of water samples. The agency responsible for the monitoring programme may have its own laboratory or laboratories, the facilities of another agency or of a government ministry may be available or some or all of the analytical work may be done under contract by a private laboratory. Some analytical work will inevitably be done in the field, using either field kits or a mobile laboratory. Regardless of the options chosen, the analytical services must be adequate for the volume of work expected and for the quality of data required by the project's data-quality objectives. Some of the relevant considerations in this context are given below.

***Variables to be analysed***

If only a few simple tests are required, analyses can be undertaken in the field using field kits. More complex testing programmes may require the services of specialized laboratories.

***Sampling frequency and number of sampling stations***

The frequency with which samples must be taken and the number of sampling stations involved will obviously influence the volume of work necessary and the staff and facilities required.

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[23] The rest of this section is taken verbatim from Bartram (1996).

### *Existing laboratory facilities*

Laboratory facilities may be under the direct control of the monitoring agency or be associated with another agency (e.g. the health ministry, a regional hospital or a college or university). The major concern is that the laboratory is sufficiently close to the sampling stations to permit samples to be delivered without undue delay.

### *On-site testing*

Some analyses must be performed in the field. On-site monitoring instruments and field-test kits are available that permit analyses of a wide range of variables. This makes it possible to run a monitoring programme without the need for a fixed laboratory but raises certain problems of analytical quality-control.

### *Temporary laboratories*

If a monitoring programme is expected to be of short duration, it may be expedient to set up a temporary laboratory. Sufficient space, water and electricity supplies are essential but equipment and supplies can be brought in and then removed after the monitoring programme is completed.

### *Mobile laboratories*

It is possible to set up a laboratory in a suitable motor vehicle: truck, van, boat or even an airplane. In effect, this is a variant of on-site testing, but may provide better facilities than field kits.

In practice, the usual arrangement is for the agency responsible for WQM to establish its own central laboratory, which can be organized to also provide training and supervision of staff, equipment repair and various other services. If the monitoring area is large or transportation is difficult, however, regional laboratories may be set up or field kits used for certain analyses. Analyses that require expensive and sophisticated equipment or that can be undertaken only by highly trained personnel are performed solely at the central laboratory (e.g. analysis for heavy metals, using atomic absorption spectrophotometry (AAS) and analysis for pesticides and herbicides, using gas chromatography).

Whatever arrangements are finally chosen, it is essential that procedures are established for quality-control of analytical work (described in Section 9.4). This is important in all aspects of fieldwork, including sampling, sample handling and transport, as well as on-site testing. Comparability of WQ data from different laboratories can only be ensured if identical or, at least, similar methods are used or through interlaboratory performance evaluation studies or proficiency testing in accreditation schemes[24].

There are many comprehensive standard manuals and guidebooks describing laboratory methods in detail, such as Analytical Methods for Environmental Quality (UNEP GEMS/Water, 2004). Their use helps to ensure the compatibility of data supplied to national and global monitoring systems.

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[24] Bartram, 1996, 60-61

## 8.2 Inventory of field stations, monitoring wells, equipment and instruments

A list of sampling sites (surface- and groundwater) will have been made and sampling stations will have been chosen during the design of the monitoring programme. As indicated in Section 5.2, an inventory of the sampling stations should be prepared that includes:

- A map of the general area showing the location of the site and directions for getting there;
- A description of the sampling station or observation well and means of access, times of day when samples are to be obtained, special equipment (e.g. ropes, lifebelts) and clothing (e.g. waders) that are required when sampling at this station, tests that are to be made on-site, travel time from the site to the nearest laboratory, etc.

There are numerous modern field instruments in many different price classes, which can be used on-site for snapshot or continuous monitoring of several parameters (see also Section 7.1 and Annex 2). The type of instrument relevant for the chosen programme must be investigated.

Steps should be taken to ensure sufficient and stable financing, as well as the supply of the stations with required spare parts or their replacement, the provision of up-to-date equipment for laboratory devices, adequate means for sampling and sample transport from remote stations. Adequate funding would also prevent departure of qualified staff.

Plans to upgrade existing networks or to re-activate previously existing ones should be based on a thorough analysis of the prevailing WQ situation and information needs, so that informed decisions can be taken. There is also a need to set priorities which have been agreed jointly with the major actors, both nationally and in the transboundary context.

Regarding the sampling of groundwater, drilling holes to set up monitoring wells is expensive. It is important to investigate the area and the presence of existing wells and prepare a sound monitoring location plan so that future adjustments to the network are avoided. If groundwater quality is measured at a spring, this should be effectively protected, as the location cannot be changed.

## 8.3 Transport

The types of vehicle needed for field-sampling operations depend, to a large extent, on the ease of access to the various sampling stations. If access is difficult, a four-wheel drive vehicle may be necessary and, in some remote or rural areas, a light motorcycle can be useful for transporting one person (with a minimum of equipment, e.g. portable kit), although it is important to consider the safety aspects of the latter arrangement.

When measuring and sampling are carried out by a specialized team, it is desirable that the means of transportation can also be used as a mobile "laboratory" for filtration, field measurements and sample storage. When working in lakes and reservoirs, different types of vessels, including small boats, may be used. Special ships with on-board laboratories are only justified for large water bodies for which the travel time exceeds 48 hours and/or if systematic investigations of high intensity are required.

In countries or regions where reliable public transport is available, it may be possible to arrange for samples to be transported to the laboratory by bus or train. Local agents, appropriately trained and supplied with the necessary equipment, can take samples at prescribed times and send them to the laboratory. This system requires careful supervision and particular attention to sample quality-control.

## 8.4 Staffing

Staff on a monitoring programme fall into four broad categories: programme management, field staff, laboratory staff and data processors. The numbers required in each category will depend on the size and scope of the programme and one person may take part in several types of activity. In resource planning, it should be taken into account that the need for qualified and experienced staff will place further demands on the budget.

### *Programme manager*

The manager will probably require the assistance of several technical and administrative staff members during the design and planning phases of the programme. Once the implementation stage has been reached, some of these can be transferred to operations, possibly as supervisors of field and laboratory work. Others, together with the programme manager, will assume responsibility for data manipulation, preparation of reports, staff training and programme coordination (if other agencies are involved in the programme).

The coordination tasks may become quite complex if programme implementation depends on other agencies, part-time staff, temporary or rented facilities and public transport. A possible description of the responsibilities of a programme manager is presented In Table 9 as an example of what may be expected, although it may not be complete for any specific situation.

### *Field staff*

The personnel in charge of field measurements, sample collection and field handling may not have had previous experience in WQM and must be specially trained for these activities. The choice depends on a number of factors, which include the geographical features of the region and the system of transportation. In large countries which have a poor transportation system, relatively more personnel are required and more automated systems are preferable. In this situation, specialists from hydrometeorological and hydrological stations, for example, may be used, although these personnel often do not possess the necessary training in water-sampling for WQM.

For staff recruited for fieldwork and sampling, new observation and sampling methods or procedures might need to be introduced from time to time. A short period of training is, therefore, appropriate. Assuming that candidates have a good general education, a well-organized training session that includes practical fieldwork will require one to two weeks. If field testing is also to be carried out, the training period will have to be somewhat longer. Staff should be evaluated after training and, if satisfactory, should work under fairly close supervision until they are sufficiently experienced to require this only on occasion. Periodic short-term training sessions should be arranged for reviewing, reinforcing or extending knowledge. The responsibilities of field staff are also shown in Table 9.

### *Laboratory staff*

Two, or possibly three, categories of laboratory staff may be required to undertake the required chemical, microbiological and biological analyses of the programme:

- ***Laboratory chiefs***: in liaison with the programme manager, the chiefs of each type of laboratory would typically be responsible for laboratory management, with tasks as given in Table 9;

- ***Laboratory technician (analyst)***: laboratory technicians will usually have had formal training and possibly practical experience in analytical work. Working under the direction of the laboratory chief, a technician will be responsible for preparing and carrying out analytical work in the laboratory. The technicians will teach the assistants how to use laboratory equipment and carry out analyses; and

- ***Laboratory assistants***: this category of staff might have had some formal training but are usually untrained and often learn on the job. Their duties (see Table 9) are performed under the direct supervision of the laboratory technician(s). In time, and with appropriate training and experience, an assistant can be promoted to a higher level of laboratory work. The assistants will use various items of laboratory equipment, prepare reagent solutions and carry out certain analyses.

***Quality assurance officer***

It is considered good practice to designate a staff member as quality assurance officer (QAO). Where financial/organizational constraints do not allow the appointment of a specific QAO, the responsibility for QA may be delegated to a member of staff, in addition to existing duties. QA is dealt with in more detail in Chapter 9.

## 8.5 Human-resources development and training

The quality of data produced by a programme depends on the quality of the work done by field and laboratory staff. It is therefore important that staff are adequately trained for the work to be done. As a result, monitoring agencies often develop training programmes that are specific to their needs. Their content and extent depend on the previous training and experience of staff, the range of activities involved in the monitoring programme and whether analytical work will be done at a central laboratory or regional laboratories and the extent to which analyses will be performed in the field. These types of activity may also include capacity-building.

For large, permanent monitoring programmes, a comprehensive strategy for personnel development is advisable. It should include:

- Clear lines of responsibility and accountability;

- Job descriptions;

- Recruitment guidelines (qualifications, experience, skill requirements, etc.);

- Career structures;

- Mechanisms for enhancing the motivation of staff at all levels;

- Systems for staff appraisal and feedback; and

- Use of standardized training packages, procedure manuals and training manuals as appropriate to the work of all staff (e.g. field and laboratory staff, regional and national managers).

Training should be a continuing process: ideally, there should be a basic framework of courses for staff at all levels, followed by short courses, seminars and workshops. Supervision of work, in both the laboratory and the field, is essential and contributes to in-service training. It is particularly valuable because it permits staff to gain “hands-on” experience, thus reinforcing what was learned in formal training sessions.

Training should be flexible, responding to experience and feedback and taking account of the specific needs of individual staff members. In-house training can be readily tailored to local requirements but needs staff familiar with the necessary training techniques (usually senior laboratory and field staff – which also makes heavy demands on them). Training may also generate significant demands on financial resources and requires access to classrooms, fieldwork sites and training laboratories with appropriate equipment. Many agencies will therefore make use of courses already available at local education centres, supplementing these as needed with short courses, workshops and refresher-training in specific topics.

In its broadest sense, training should also be understood to include encouraging staff to join appropriate professional organizations, attend conferences and symposia and communicate with peers in technical schools, colleges, universities and similar establishments.

## 8.6 Communication

Good communication is important, not only for achieving programme outputs, but also to ensure that wider aims (such as increasing awareness of environmental issues and ensuring that staff of all types see their role positively) are met. It is also indirectly important as a means of ensuring continued outside interest in, and support for, the work being undertaken.

It is good practice to ensure that responsibilities for communication are identified in staff job descriptions. Communication may be general, aimed at a wide audience, such as writing reports or speaking at a seminar, or more specific, such as communicating results from analyst to laboratory chief or the discussion of fieldwork plans between coordinator and field staff.

Communication with external agencies is especially important if these play a role in national or international assessments and if they provide other types of support (such as training or equipment). For consistency, any liaison with such agencies should be the specific responsibility of an identified member of staff. Internal communication in the form of short discussions, such as lunch-time seminars or workshops, are a good means of ensuring that staff are kept informed about issues and are aware of programme progress and findings.

Representatives of monitoring programmes may attend committees at both local and national levels. This representation is important as a means of communication, and maintaining the profile of the programme should also be the specific responsibility of an identified member of staff. Communication functions, such as those noted above, may demand a significant proportion of time and this should be borne in mind when preparing job descriptions.

## 8.7 Estimation of costs of the programme

The costs of monitoring should be estimated before programmes begin or when major revisions are planned. If the information needs are well defined, the estimate can be rather detailed. Monitoring costs can be divided into a number of components, as shown in Box 8.

The costs associated with administration, as well as assessment and reporting, are largely fixed and almost independent of the extent of the network. In contrast, the costs of other activities are strongly influenced by the number and types of sampling points, the frequency of sampling and the range of parameters to be analysed. The

**Box 8. Main water-quality programme cost components**

- Network administration, including design and revision
- Capital costs of monitoring and sampling equipment, automatic measuring stations and data-transmission systems, construction of observation wells or surface-water-sampling sites and gauging stations, transport equipment, data-processing hardware and software
- Labour and associated operating costs of:
  - Sampling, field analysis of WQ variables and field measurements of water levels and discharge characteristics
  - Laboratory analyses
  - Data storage and processing
- Operating costs of online data transmission systems (e.g. water levels, accidental water pollution)
- Laboratory performance evaluations and proficiency testing
- Assessment and reporting: production of outputs, including GIS or presentation software and report-printing costs

number of sampling points can be multiplied with frequency and parameters to obtain rough cost estimates.

The most resource- and labour-intensive phase in monitoring is the one that includes sampling, in situ physicochemical analysis and water-quantity-related measurements, and laboratory analysis. This phase also entails high risks in producing reliable and accurate data. It is therefore important to employ qualified and experienced personnel and comply with guidelines and standards. It is also important to ensure that the supporting infrastructure, such as reliable power and water supply, is in place.

It is important not to underestimate the labour and operating costs of sample collection and field analysis, laboratory analysis and data processing, interpretation, reporting and output production. A lack of knowledge or inadequate assessments of these costs may lead to a cessation of activities, should sufficient funds be lacking.

The projected cost of what is considered to be the best proposal may often be too high for the agency planning to carry out the monitoring. When faced with such a situation, some of the possible solutions are a re-examination of:

- Objectives of the programme, deleting some of the less important and/or relaxing some of the conditions, e.g. changes to be detected;
- Proposed sampling locations, eliminating some of the less important sites (e.g. those at which WQ can be inferred from data already existing or from data collected at other points in the system);
- A proposed list of parameters to be analysed, deleting, for instance, those that can be predicted from other measurements or that have a small or no environmental significance at a given site; and
- Frequency of sampling, especially when objectives of the monitoring have been changed.

***Programme funding***

Because of the continuous character of monitoring, a long-term commitment to funding is crucial to ensure the sustainability of monitoring and assessment activities. This means that funding should come mainly from the national budget.

Water users, such as municipalities, water and waste utilities, industries, farmers and irrigation systems, should contribute to funding the programmes. Funds may also be raised by using income from water-abstraction fees or by invoking the polluter-pays principle.

Additional sources of funding might also be explored, a possibility being through international assistance projects. These should be embedded in the national plans and with system requirements adapted to countries' needs, so that operations can continue after a project is completed. Donor-funded projects concerning transboundary watercourses and aquifers should be coordinated with national authorities to ensure the continuity of monitoring activities that have been established in the project.

# Chapter 9. Quality-assurance procedures

Quality assurance (QA) is a management method defined as "all those planned and systematic actions needed to provide adequate confidence that a product, service or result will satisfy given requirements for quality and be fit for use". It is also defined as "the sum total of the activities aimed at achieving that required standard" (International Organization for Standardization (ISO), 1994).

Any monitoring programme or assessment must aim to produce information that is accurate, reliable, comparable and adequate for the intended purpose. This means that a clear idea of the type and specifications of the information sought must be known before the project starts, i.e. there must be a data-quality objective. These objectives are qualitative and quantitative specifications that are used to design the system that will limit uncertainty to an acceptable level within the constraints allowed. They are often set by the end-users of the data (usually those funding the project) in conjunction with the technical experts concerned.

QA for a water-monitoring programme will, apart from helping to ensure that the results obtained are correct, increase the confidence of funding bodies and the public. It extends to all aspects of data collection from surveys to laboratory procedures. Unless the data can be checked, they should not be included in any assessment; unconfirmed observations have little value and can result in misclassification.

The purpose of this chapter is, therefore, to provide general guidance on the setting-up of a quality system essential for ensuring the reliability of information obtained by monitoring. It should be organized around all elements of the monitoring and assessment cycle, starting with documenting procedures for the specification of information needs and developing an information strategy. To assist this process, there are standards, established under the auspices of ISO, the European Committee for Standardization (CEN) and other organizations for sample collection, transport and storage and laboratory analysis, as the basis for the quality system. Protocols for data validation and storage and exchange, as well as data analysis and reporting, should be established and documented.

It is essential to stress that the trend is to strengthen laboratory QA in a step-by-step approach: from simple internal quality-control measures to laboratory accreditation and, finally, to the application of international standards, such as ISO/IEC 17025, covering general requirements for the competence of calibration and testing laboratories.

## 9.1 Components of quality assurance

These are often grouped under three levels:

- Strategic or organizational level (dealing with quality policy, objectives and management and usually produced as a quality manual);
- Tactical or functional level (dealing with general practices such as training, facilities, operation of QA); and
- Operational level (dealing with the standard operating procedures (SOPs), worksheets and other aspects of day-to-day operations).

The quality manual is composed of a number of management documents needed to implement the QA programme (ISO/IEC 17025, 2005), covering a whole range of areas from quality policy statement to final procedures for audit and review. The list of documents is provided in Table 10.

SOPs are the documents detailing all specific operations and methods, including sampling, transportation, analysis, use and calibration of equipment, production of reports and interpretation of data. They are the internal reference manual for the particular procedure and should detail every relevant step. Anybody with the appropriate training level should be able to follow the SOP.

Laboratories should use test methods which meet the needs of the customer and are appropriate for the tests they undertake[25]. Method SOPs may have originated from a number of organizations[26] or from the instructions that come with the test kit when a commercially produced method is used. Such SOPs have the advantage of not requiring verification and save time in writing "in-house" SOPs. If they are applied, however, they must be used without modification. Sometimes, in-house methods are preferred and it is vital that they are appropriate for the intended use and fully validated. In order to maintain the QA system, it is necessary to check periodically each area of the system for compliance.

## 9.2 Laboratory facilities

It is essential that any laboratory facilities are adequately equipped to deal with the analyses required and convenient for the delivery of samples. Small-scale organizations responsible for monitoring may find it more convenient to use outside facilities for analysis and sometimes for sampling. In these cases, the use of a laboratory belonging to an accreditation scheme is advisable and, moreover, the laboratory should be inspected for compliance by an experienced member of the monitoring programme. An inspection should take into account the following features: (a) the lines of communication between staff and management; (b) staff training and qualifications; (c) resources; (d) equipment maintenance and calibration; (e) SOPs; (f) traceability of results; and (g) sample handling and storage.

Where in-house facilities are used, it is essential that the monitoring work does not overload the laboratory. Resources (staff, space, equipment and supplies) must be sufficient for the planned workload. The laboratory must be well managed and conform to all relevant health-and-safety guidelines. All analyses performed must be within the remit and expertise of the facility and SOPs must be in operation for all analyses.

## 9.3 Equipment maintenance, calibration and quality-control of fieldwork

All equipment, whether field, office or laboratory, must be maintained on a regular basis as documented in the relevant SOPs, codes of practice and manufacturers' guidelines. Laboratories must apply standards within the limits established for the care of a particular piece of equipment: this applies to general equipment, as well as to sophisticated analytical instruments and vehicles, and especially to field equipment. Equipment should be checked for contamination, using blanks to ensure that it does not contribute to the sample concentration or could be the source of cross-contamination between sampling locations.

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[25] ISO/IEC 17025:2005, clause 5.4.2

[26] For example: ISO, British Standards Institute, American Standard Technical Method

The care and cleaning of equipment are important to ensure analytical quality. Regular internal and external calibration checks must be performed on equipment such as balances, pipettes and all in situ sensors. The frequency of these checks depends on the stability of the equipment in question but should be based on established practice and their form and frequency should be documented in the relevant SOPs. Calibration and maintenance records should be kept for all equipment, thus allowing the repair status to be monitored.

All automated sampling equipment must be calibrated and bench-tested prior to field deployment. Calibration ensures that readings from instruments will be representative of environmental conditions. Bench-testing provides the assurance that all components of the system are functional. Each instrument will have a duty cycle that defines the period between calibrations for which there should be confidence in the data. This cycle, which is dependent on instrument type and deployment environment, must be determined for each monitoring programme. For each instrument, a log of the calibration date and the next calibration should be maintained and entered into the water-quality data-management system. Each installation will also have a specific service cycle or the period between required maintenance to be adhered to in order to maintain the functionality of the instrumentation.

QA is critical in all fieldwork. If a good, practical, field QA programme is put into operation, confidence in the data collected should be ensured (WHO/UNEP/VKI, 1997). Conditions in the working area should not expose the operator to any undue risk. Standardized and approved methodologies must be used at all times. If a method proves unworkable on-site, then an alternative must be found and agreed by all involved. Operators must not change procedures without referral to the management procedure. Where unavoidable changes are made (e.g. in adverse weather conditions), they must be fully documented. Nevertheless, a sampling plan should make provisions for such situations.

The quality of data generated in a laboratory depends primarily on the integrity and representativeness of the samples that arrive at the laboratory. Consequently, the field staff must take the necessary precautions to protect samples from contamination and deterioration. In addition to standardized field procedures, field-quality control requires the submission of blank and duplicate samples to: (a) test the purity of chemical preservatives; (b) check for the contamination of sample containers, filter papers, filtering equipment or any other equipment that is used in sample collection or handling; and (c) detect other systematic and random errors occurring from the time of sampling to the time of analysis. Replicate samples must also be collected to check the reproducibility of the sampling. The timing and frequency of blank, duplicate and replicate samples are established in the project design.

## 9.4 Analytical quality-control

This consists of two elements: internal quality control (IQC) and external quality control (EQC). IQC consists of the operational techniques used by the laboratory staff for continuous assessment of the quality of the results of individual analytical procedures. EQC – or interlaboratory control – is carried out periodically and checked by the laboratory responsible for the monitoring system. Whereas QA strives to achieve quality by regulating procedures using management techniques, IQC focuses on the individual method and tests its performance against mathematically derived quality criteria.

A summary of the IQC programme recommended by the GEMS/Water programme is described in more detail in the GEMS/Water Operational Guide (WHO, 1992).

EQC is a way of establishing the accuracy of methods and procedures by comparing the results of analyses made in one laboratory with the results obtained by others conducting the same analyses on the same material. This is usually accomplished by one laboratory sending out sets of samples, with known and unknown concentrations of variables, to all the specified laboratories. These analyse the samples for the specified variables and report the results to the reference laboratory. The results from all participating laboratories are collated by the organizers of the EQC programme and then subjected to detailed statistical analysis. A report to each laboratory is generated, giving a target value for the reference sample or samples (usually consensus mean or median), a histogram illustrating distribution of results for each material and an individual performance score relating the individual laboratory results to the target value. The calculations of performance indicators are often quite complex because multiple specimens have to be considered and the method varies with the concentration of the variable and its chemical status (i.e. Fe(III) or Fe(IV)). Nevertheless, the general principle of providing a method of performance comparison remains the same in all EQC exercises.

## 9.5 Quality assurance of data

Data QA is an important element of data analysis and use. While effective quality-control procedures during sampling and analyses help to eliminate sources of error, a second series of data checks and precautions should be carried out to identify any problems that might lead to incorrect conclusions and costly mistakes in management or decision-making. The procedures involved commonly rely on the identification of outlying values (values that fall outside the usual distribution) and procedures such as ensuring that data fall within the limits of detection of a particular method of measurement.

QA should be applied at all stages of data gathering and subsequent handling. For the collection of field data, design of field records must be such that sufficient necessary information is recorded with as little effort as possible. Pre-printed record sheets requiring minimal and simple entries are essential. Analytical results must be verified by the analysts themselves checking, where appropriate, the calculations, data transfers and certain ratios or ionic balances. Laboratory managers must further check the data before they allow them to leave the laboratory. Checks at this level should include a visual screening and, if possible, a comparison with historical values of the same sampling site. The detection of abnormal values should lead to a further check of the analysis, related computations and data transcriptions.

The QA of data-storage procedures ensures that the transfer of field and laboratory data and information to the storage system is done without introducing any errors. It also ensures that all the information needed to identify the sample has been stored, together with the relevant information about sample site, methods used, etc.

Data analysis and interpretation should be undertaken in the light of the results of any QA checks. A data-storage and retrieval system must, therefore, provide access to the results of these checks. This can be done in various ways, such as:

- Accepting data into the system only if they conform to certain pre-established quality standards;
- Storing the QA results in an associated system; and
- Storing the quality-control data together with the actual WQ data.

The choice of one of these methods depends on the extent of the QA programme and on the objectives and magnitude of the data-collection programme itself.

## 9.6 WQ standards and indices

Monitoring and assessment of WQ is performed against existing standards and guidelines that serve as reference and may predetermine which measures have to be undertaken to improve WQ. In addition to many national standards are those of an internationally recognized nature such as the WHO standard on drinking-water. Indices, such as measured by aggregate parameters (BOD, COD, DOC and others) serve to characterize the overall status of WQ that can then be documented in maps.

Typically, drinking-water quality is assessed by comparisons of samples to drinking-water quality *guidelines* or *standards*. There is a distinction between these two terms. The WHO Drinking-water Quality Guidelines provide international norms on WQ and human health that are used as the basis for regulation and standard-setting in developing and developed countries worldwide. They are adopted by countries as national guidelines to follow, even if they are not necessarily enforceable by law. In contrast, drinking-water quality *standards* are primarily set by nations and can be enforceable by law. For example, the US Environmental Protection Agency has two sets of standards: *primary standards*, that directly link human safety to drinking-water and are enforceable by law; and *secondary standards*, that relate to aesthetic effects and are not legally required.

Another example of binding standards is the EU Water Framework Directive (WFD), under which drinking-water parameters are provided that include an obligation for EU countries to inform the consumer on drinking-water quality and measures to be taken to comply with the requirements of this Directive (see also Section 11.1). EU members have agreed to comply with these parameters.

In addition, ISO publishes a series of approved *International Standards*, which includes methods for determining WQ.

Appendix 1 provides a summary of international and national drinking-water quality guidelines and standards by a number of international organizations (WHO, EU) and selected countries[27] (see also Section 6.2).

Many countries set drinking-water-quality guidelines based on the WHO guidelines but may modify them, taking into account what is achievable in-country. For example, the financial requirements and infrastructure needed to monitor and assess drinking-water quality can be a constraint in some developing countries. For these and other reasons, the guidelines may also vary between rural areas and urban centres within a country.

Composite indexes have also been developed to assess source WQ across a range of inland water types, globally and over time. An example is the composite index developed by GEMS/Water, with a three-fold approach: (a) selecting guidelines from WHO that are appropriate in assessing global water quality for human health; (b) selecting variables from GEMStat that have an appropriate guideline and reasonable global coverage; and (c) determining, on an annual basis, an overall index rating for each station, using the WQ index equation endorsed by the Canadian Council of Ministers of the Environment. The index allows measurements of the frequency and extent to which variables exceed their respective WHO guidelines at each individual monitoring station included within GEMStat, allowing both spatial and temporal assessment of global water quality.

Important criteria for selecting indicators include:

- Communication: indicators should be suitable for all users;
- Simplification: indicators should provide insight, without giving too much unnecessary detail; and
- Availability of data: enough data must be available to formulate reliable indicators.

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[27] Australia, Canada, Japan, New Zealand and USA

The Indicators for Sustainable Development devised by the United Nations (UN, 2001) and the list of indicators in the EEA's Environmental Signals 2001 (EEA, 2001) report are of great assistance in selecting suitable indicators.

Finally, efforts are now being made to develop and apply indicators of WQ stress and long-term change. Indicators can be used to relate WQ to environmental stressors (e.g. expanding population, climate change, industrialization and sanitation).

# Chapter 10. Data management and product development

Data produced by monitoring programmes should be validated, archived and made accessible. The goal of data management is to convert data into information that will meet needs and the associated monitoring objectives. The combined use of data from multiple sources places high demands on data exchange and data-management systems.

To safeguard the productive future use of the data collected, four data-management steps are required before the information can be properly used:

- Data should be analysed, interpreted and converted into defined forms of information, using the appropriate data-analysis techniques;
- Data should be validated or approved before they are made accessible to users or archived;
- Information should be reported to users for decision-making, management evaluation or in-depth investigation. Information should also be made accessible to the public and presented in tailor-made formats for different target groups;
- Data needed for future use should be stored and the exchange of data should be facilitated at all other appropriate levels (international, regional, river basin, etc.), as well as within the monitoring body itself.

It is of utmost importance that policymakers and planners are fully aware of the various steps in data management. This will facilitate data exchange among the institutions undertaking the monitoring and assessment, including joint bodies. The purpose of this chapter is therefore to provide general guidance on each of the above four data-management steps to allow a proper use of the information obtained by monitoring.

## 10.1 Data handling and management

The first archiving of monitoring data generally takes place at the monitoring agency. To facilitate the comparability of data, clear and precise agreements should be made on the coding of data and meta-information. Standardized software packages for data management should be applied where data are to be stored, with storage formats used to allow for data exchange. Framework agreements regarding the availability and distribution of data can further facilitate their exchange. The relevant data terminology should be jointly compiled and agreed, including definitions of terms used during the exchange of information or data.

Furthermore, a sufficient amount of the secondary data – metadata – needed to interpret the data should also be stored. Details of the times and places of sampling, the type of sample and any preconditioning and analytical techniques used are commonly stored for these purposes. If monitoring is performed in any media other than water (e.g. in suspended solids or biota), relevant metadata such as the total amounts of substances in different media and particle size distributions should be recorded.

GIS are important tools for the integrated interpretation of data, together with any other information (e.g. maps, satellite images, land-use data, etc.) that may be needed to assess water quality and quantity or, in the event of accidental pollution, flooding, etc.

This allows models to be used with controlled access to the system given to a range of information users and reports adapted to suit the recipients.

Over the past few years, GIS technology has also been increasingly used for groundwater-quality data collection.

The data needed for purposes such as the assessment of the ecological state of a water body or for load calculations are often produced by separate monitoring programmes run by various laboratories or agencies. Data from other sources are often indispensable for assessment purposes, in addition to the monitoring data. Special attention should be paid to the validation and quality-control of the process of data collection from these multiple sources. Steps should also be taken to ensure interoperability of the WQ data from different observation platforms and networks.

Databases should be suitably harmonized. Standardized interfaces should be used to interconnect databases and provide for integration with a GIS. Relational databases should preferably be used to facilitate integration with GIS and models. Data processing based on jointly accepted, compatible standards will make assessment and reporting comparable, even when the software used in the various countries differs.

The scope and nature of computerized data-handling processes will be dictated by the objectives of the WQM programme. However, a database offers the best means of handling large quantities of data and should be capable of exporting data in formats that are accepted by all good statistical, spreadsheet and GIS packages.

Designing a WQ data-storage system needs careful consideration to ensure that all the relevant information is stored such that it maintains data accuracy and allows easy access, retrieval and manipulation of data. While it is difficult to recommend one single system to serve all agencies carrying out WQ studies, some general principles may serve as a framework for designing and implementing effective WQ data-storage and retrieval systems which will serve the particular needs of each agency or country.

For international data-storage purposes, a central system may be considered. This task could be given to joint bodies, including representatives of the national authorities of the riparian countries concerned. Guidelines and tools developed within the framework of, for example, the common Water Information System for Europe (WISE)[28], supports such activities.

## 10.2 Data analysis and dissemination

In monitoring programmes where large amounts of different data are collected continuously over several years, statistical methods are needed to summarize effectively the results of monitoring. In particular, different types of trend calculations are being used to assess monitoring data. In interpreting trends, particular attention should be paid to water-quantity data, since hydrology strongly affects WQ. It is also necessary to be able to give some indication of the “confidence” the user may have in the statistical outputs.

Data analysis should be embedded in a data analysis protocol (DAP) that clearly defines an analysis strategy, taking into account the specific characteristics of the data concerned, such as missing data, detection limits, censored data and outliers, non-normality and serial correlation. The adoption of a DAP gives the data-gathering agency a certain flexibility in its data analysis but requires that the procedures be documented.

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[28] http://water.europa.eu

Production and display of graphical material can be made in several ways, depending on the analysis underway. Typically, XY, scatter time-series and regression plots are desirable for displaying data to identify preliminary WQ conditions. Graphs can reveal patterns in sets of data and are often more illustrative than statistical computations. By using the tailor-made software, graphical output can be included in map format. This type of presentation is useful for producing reports on environmental conditions. 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. 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 WQ, time-series analyses of instantaneous discharge records in combination with one or more specific parameters can easily depict dependent and/or independent relationships. Data summaries in the form of statistical tables can provide the necessary information for many components of environmental assessments.

The use of water-classification systems to assess watercourses is common. Some of these are based on physical-chemical variables, but biological approaches (such as ecological classification under the WFD) are also used. For transboundary water assessments, whether based on classification systems or on other assessment methods, it is important to strive for comparability of results rather than unification of methods.

WQ issues are basically site-specific, but local actions and regional activities can greatly benefit from linkages at the global level, such as: (a) sharing experiences between sites and regions; (b) exchanging data and information on global scientific and Internet developments; and (c) situating WQ data within a broader geo-spatial context for analysis and assessment. Data exchange is important in WQ studies. Data-exchange protocols exist for national and international purposes, one useful example being the WMO policy on the exchange of hydrological data and products (Resolution 25 (Cg-XIII) – Exchange of hydrological data and products).

Many policy- and decision-makers at local, national and regional levels are concerned about investing adequately in data-collection systems. Many governments around the world are becoming increasingly interested in developing national data and information systems, as well as in ensuring their interoperability. This refers to the ability of a database or system to exchange information and to use the information that has been exchanged. This is often achieved using open Web services.

Unfortunately, long-term monitoring records are rare because of the lack of resources available to sustain them, but they are extremely valuable when available. The GEMS/Water Programme collects WQ data on a global scale and maintains an online database (GEMStat) with almost four million entries covering the period 1965-2009 (www.gemstat.org, see also Section 11.2). GEMStat provides environmental WQ data and information with high integrity, accessibility and interoperability. These data serve to strengthen the scientific basis for global and regional water assessments, indicators and early warnings. The success of the database depends on the important role that participating countries play in regional and global water-information systems, to ensure the widest coverage possible and, consequently, the ability to share data and information. The International Groundwater Resources Assessment Centre (IGRAC, www.igrac.net) currently provides information on groundwater quality on a global scale on fluoride, arsenic and salinity. Additionally, a database on guidelines and protocols for groundwater data acquisition with about 400 documents is available via the Internet[29].

[29] http://www.igrac.net/publications/128

## 10.3 Reporting

This is the final step in the processing of information and links the process to the information users. The main issue is to present the interpreted data in an accessible way. How this information is to be presented depends greatly on the audience to be addressed.

The several different types of reports that are possible have certain elements in common, including the statement of objectives and the description of the study area. To avoid any misunderstandings, it is important that all elements of the monitoring programme are precisely and clearly described. There are four principal types of reports:

- The ***study plan report*** defines the objectives of the monitoring programme, including the questions to be addressed and the present understanding of the environment to be studied. It also defines the sampling and data review strategy that will be followed to meet the objectives;

- The ***protocol and methods*** *report*, also defined as the SOP, describes methods and equipment in sufficient detail for other scientists to be able to assess the scientific validity of the results reported;

- The ***data report***, whose primary purpose is to transmit information assembled in a well-organized format so that the reader can easily review it; and

- The ***interpretative report***, which provides a synthesis of the data and recommends future actions. Interpretative reports should be produced regularly to ensure that programme objectives are being met and are currently valid.

In general, reports should be prepared on a regular basis. They need not necessarily be printed but can take other forms, such as oral reports or digital presentations. Their content, which may involve transferring data analyses or merely give a brief overview of conclusions and frequency and level of detail, will depend on how the information is to be used. Technical staff will need reports more frequently than policymakers, for instance.

Reporting has to be tailored to meet the needs of those who request the information. Public authorities, including joint bodies, usually request information in a formalized manner. In such cases, the content and frequency of reports are defined in reporting protocols. Such reports are usually presented in writing to ensure that results are clearly understood.

National authorities may also receive ad hoc requests (e.g. from individuals, environmental groups or organizations) for information which is not routinely included in reporting protocols, but which may be related to specific, current water-management issues. Raising the awareness of progress in water management will increase governmental and public support for governmental interventions.

***Quality status reports*** or ***environmental indicator reports*** should provide concise information to support decision-making in water management. These reports typically provide information on the functions of water bodies, describe problems and the pressures to which they lead and give insight into the intended impacts of corrective measures. They are much more useful for decision-making purposes where simplifying indicators and visuals are used.

Standardization of reports is encouraged within river basins and at the international level. Joint river-basin quality status reports should preferably be produced. National and international reporting obligations should be inventoried to ensure all reporting requirements laid down in water-management legislation are fulfilled. For example, the EEA’s Reporting Obligations Database includes an overview of many international reporting obligations. This database may be complemented with reporting obligations under national, bilateral or multilateral legislation.

# Chapter 11. International water-quality directives and guidance material

Multilateral environmental agreements, international conventions and transboundary water agreements contain obligations for countries to monitor, assess and report on the water-quality status of their watercourses and groundwater. Coupled with international guidance material on the subject, these should assist in steering and guiding related national activities.

## 11.1 International frameworks

Multinational environmental agreements, conventions and protocols, directives and bilateral and multilateral transboundary water agreements contain obligations for countries to monitor and assess watercourses and groundwater and to report, as appropriate, to a specific body, such as an international commission, secretariat or organization. Such cooperative arrangements and institutional frameworks greatly influence the efficiency of monitoring and assessment and help in the planning phase of the monitoring network. Ideally, these obligations should become part of the national legislation to steer the activities of competent national bodies. Regional, national and international legislation and policies can determine the main objectives for WQ assessments. In some countries, WQ standards or guidelines may be laid down by national legislation. It is, however, not realistic to expect all countries to amend their national legislation in the short term. A few examples are described below.

The EU WFD legislation and Infrastructure for Spatial Information in the European Community (INSPIRE, http://inspire.jrc.ec.europa.eu/) provide a major tool for defining how European waters should be used, protected and restored. EU Member States are solely responsible for the implementation of the requirements set in water-related directives. The most important where monitoring is concerned is the WFD. Its main aims are to prevent further deterioration in aquatic ecosystems, while protecting and enhancing their status, to promote sustainable water use and to mitigate the effects of floods and droughts. The environmental objective of the WFD is to ensure that the ecological and chemical status of all waters within the EU is at least good by 2015 at the latest. The programme is based both on the use of hydrobiological characteristics, supported with some key physicochemical variables, and on surveillance of certain harmful substances, including priority substances. The WFD also takes into account hydrological variations during the monitoring period.

The Groundwater Daughter Directive (GWD)30 to WFD establishes specific measures as provided for in Article 17(1) and (2) of Directive 2000/60/EC in order to prevent and control groundwater pollution. These measures include, in particular: (a) criteria for the assessment of good groundwater chemical status; and (b) criteria for the identification and reversal of significant and sustained upward trends and for the definition of starting points for trend reversals. The GWD also complements the provisions preventing or limiting inputs of pollutants into groundwater, already contained in Directive 2000/60/EC, and aims to prevent the deterioration of the status of all bodies of groundwater. For some groundwater-quality assessments, specific threshold values or standards exist for the different objectives (Blum et al., 2009). A description of different methodological aspects of trend analysis in relation to the GWD can be found in Broers at al., 2009.

[30] http://rod.eionet.europa.eu/instruments/625

Finally, the Nitrates Directive[31] (91/676/EEC) has the objective of reducing water pollution caused or induced by nitrates from agricultural sources.

The INSPIRE Directive (May 2007) establishes an infrastructure for spatial information in the European Community to support environmental policies and policies or activities which may have an impact on the environment. It addresses 34 spatial data themes needed for environmental applications, with key components specified through technical implementing rules.

As regards transboundary waters and international lakes, one essential basis for the required monitoring and assessment activities is the 1992 UNECE Convention on the Protection and Use of Transboundary Watercourses and International Lakes (Water Convention). The Convention aims to establish effective systems for monitoring and assessing situations likely to result in outbreaks or incidents of water-related disease, along with suitable response-and-prevention procedures. This will include inventories of pollution sources, high-risk area surveys regarding microbiological contamination and toxic substances, and reporting on water-related diseases. Parties to the Protocol on Water and Health will also develop integrated information systems covering long-term trends in water and health, focusing on both current concerns and past problems and their successful solutions, whilst ensuring that such information is provided to the relevant authorities. Moreover, comprehensive national and local early warning systems are to be established, improved or maintained. In January 2009, a resolution was adopted by the United Nations on the law of transboundary aquifers[32], recommending States to make appropriate bilateral or regional arrangements for the proper management of their transboundary aquifers on the basis of the principles enunciated in the articles (Resolution A/RES/63/124).

Outside Europe, a large number of new bilateral and multilateral water agreements[33], governing basins in Asia, Africa, the Middle East and North and South America were concluded during the 1990s. Provisions concerning information exchange, monitoring and evaluation are included in many treaties and a growing percentage of agreements address some aspect of WQ management in international rivers. Some significant examples are the Mekong River Initiative, the Nile Basin Initiative and the Zambezi Water Agreement. The International Joint Commission has been implementing the Boundary Waters Treaty in North America since 1909.

## 11.2 Global databases

Monitoring and assessment activities under the auspices of UN organizations and programmes produce valuable information which can be used for carrying out assessments of national and transboundary watercourses and groundwater. The UNEP GEMS/Water Programme is a primary source of global WQ data and provides information on the state and trends of regional and global water quality. GEMS/Water receives WQ data derived from national focal points in participating countries from their ongoing national monitoring programmes and from collaborating focal points at universities, international partner agencies and organizations such as transboundary water-basin authorities. These data are housed in GEMStat, a global database with almost four million WQ data from lakes, rivers and groundwater in more than 100 countries. Information on aquifers can be obtained from the International Shared Aquifer Resources Management programme, which aims to develop methods and techniques for improving understanding of the management of shared groundwater systems, taking into consideration both

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[31] http://ec.europa.eu/environment/water/water-nitrates/directiv.html?lang=_e

[32] In the Netherlands, there is at least one case of sampling at the border to prevent inflow of contaminated groundwater.

[33] http://www.waterencyclopedia.com/St-Ts/Transboundary-Water-Treaties.html#ixzz0VueDqySO

technical and institutional aspects. IGRAC, which facilitates and promotes the worldwide exchange of groundwater knowledge to improve assessment, development and management of groundwater resources, is another important source of information. Regarding groundwater quality, IGRAC's focus relates to fluoride, arsenic in groundwater and saline groundwater. The Global Groundwater Monitoring Network (GGMN) aims to collect aggregated groundwater-quantity and quality data to assess the status of groundwater worldwide.

The Statistical Office of the European Commission (Eurostat) collects statistics on water resources, water abstraction and use and wastewater treatment and discharges through the Eurostat/OECD joint questionnaire. One important source of information on the status of rivers, lakes and groundwater bodies is WISE, created by the EEA. It is being further developed to comply with the recommendations on the strengthening of national and transboundary environmental monitoring and information systems in countries of eastern Europe, the Caucasus and Central Asia.

The National Meteorological and Hydrological Services of Members of WMO operate more than 475 000 hydrological stations worldwide. National databases are good sources of water-quantity data and related information. WMO's GRDC is a worldwide, digital depository of discharge data and associated metadata and serves as a facilitator between data providers and data users.

Data on water-related disease can be accessed through the Health for All Database of WHO. This database includes data on diarrhoeal diseases, viral hepatitis A and malaria incidence, as well as the number of people being connected to water-supply systems and having access to sewerage systems, septic tanks or other hygienic sewage-disposal systems. Supporting data are available from the Joint Monitoring Programme (JMP), carried out under the auspices of WHO and the United Nation's International Children's Fund (UNICEF). The goal of JMP is to report on the status of water supply and sanitation in the context of meeting the UN Millennium Development Goals.

## 11.3 Related guidance material

A wealth of experience has been accumulated and is available through a number of other guidebooks and reports on the basic methods, procedures, techniques, field equipment and analytical instruments, etc. required to monitor water quality and quantity. Their use in conjunction with the present Technical Report is therefore strongly recommended. A summarized description of relevant guidance material[34] in various related fields that may be consulted as required for the various planning steps follows.

UNEP GEMS/Water aims to improve the understanding of emerging WQ issues around the world, its main goals being monitoring, assessment and capacity-building. The implementation of GEMS/Water involves several UN agencies active in the water sector, as well as various authorities, institutions and organizations. GEMS/Water has based its monitoring operations on a practical guidebook, the GEMS/Water Operational Guide (GEMS/Water, 1992/2004) which provides detailed information on site selection, sampling, analysis, quality control and data processing.

There are many comprehensive standard manuals and guidebooks describing laboratory methods in detail, such as the GEMS/Water Analytical Methods for Environmental Quality (UNEP GEMS/Water, 2004). Their use helps to ensure the compatibility of data supplied to national and global monitoring systems.

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[34] As appropriate, reference has been made to this material throughout the text of this Technical Report.

Although analytical reference methods are given in several general publications, it is also convenient to consult the ISO Standard Methods series of publications and the WHO Water Quality Guidelines and to refer to recognized national publications, such as the standard methods produced by the American Public Health Association (APHA, 1989), the German Institute for Standardization[35] (DIN) and those of the former USSR State Committee for Hydrometeorology and Environmental Control (1987, 1989) which are now used in the Russian Federation and other countries of the Commonwealth of Independent States.

It should be noted, however, that, while most chemical analyses required for WQM are adequately covered in the above reference guidance material, non-standardized methods for biological monitoring have to be developed for local or regional situations.

Hydrological measurements are an indispensable accompaniment to any surface WQM operation. Groundwater-quality data also require adequate hydrological information for any meaningful interpretation. WMO has developed practical guidelines for hydrological practices (WMO, 1994) and the United Nations Educational, Scientific and Cultural Organization (UNESCO) has also issued groundwater hydrology guidebooks. These publications contain methodology for WQ data collection, interpretation and presentation. With respect to the field operations for WQM, a practical manual was produced by WMO (WMO, 1988), of which several main items are still valid. It describes essential factors to consider in monitoring, for example: the location of sampling sites, the collection of surface-water samples, field measurements, sampling for biological analysis, shipment of samples, field safety and training programmes related to all of the above.

IGRAC has developed a database on guidelines and protocols for groundwater data acquisition with about 400 documents.

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[35] DIN 38414-11, August 1987: German standard methods for the examination of water, wastewater and sludge; sludge and sediments (group S); sampling of sediments (S 11).

## Chapter 12. Summary and future needs in water-quality monitoring

Despite some progress over the last 15 years, inadequate freshwater supplies and the lack of sanitary wastewater systems continue to plague vast regions and populations of the planet. Approximately 1.1 billion people lack access to clean drinking-water, while 2.6 billion people suffer from inadequate sanitation. As a result, diarrhoeal diseases associated with tainted water and inadequate sanitation kill 1.8 million people annually – mostly children.

Building the capacity of communities, local, regional and national governments, NGOs and enterprises to manage and deliver water and sanitation services are key challenges in meeting the UN Millennium Development Goals for water.

While capacity-building encompasses financial, educational and social goals, there is also a technological element, in which WQM and analysis equipment must be deployed on an increasingly wide scale in developing countries where water supply and wastewater treatment are inadequate.

In addition to many of the ongoing problems associated with WQ that have as yet not been solved, the world is also facing new environmental problems that threaten aquatic and terrestrial ecosystems. Climate variability, biotic invasions and the introduction of new chemicals and microbes to water bodies continuously pose new threats to aquatic ecosystem health that must be addressed by regulatory authorities on local, national and global scales (Water Quality Outlook, GEMS/Water, 2007).

Changes in average temperature, precipitation levels and rising sea level are expected to occur over the coming decades, partially in response to changes in atmospheric circulation indices such as the El Niño Southern Oscillation and North Atlantic Oscillation. These are likely to influence both the quantity and quality of inland waters (rivers, lakes, reservoirs and groundwater). Long-term monitoring records for lakes and reservoirs worldwide show increases in temperature over the last three decades. The success of local, regional and global efforts to curb rates of WQ degradation can only be measured if sufficient data are available to track trends over time and space. New approaches and techniques need to be developed and applied to address emerging issues and to provide decision-makers with relevant and accurate assessment data and information.[36]

WQ issues in developed countries have increased in complexity as a result of the move from point-source controls, focusing on "end-of-pipe" site-specific data, to investments in WQ protection and enhancement, focusing on non-point-source pollution and a whole-watershed approach. Eight priorities have been identified to meet future needs for WQM and assessment (see Box 9). A commitment to these priorities will provide the critical scientific basis for the multitude of decisions involving the increasing number of competing demands for safe drinking-water, irrigation, industry, aquatic ecosystem health, wetland protection, the preservation of native and endangered species, and recreation.

In addition to the importance of being able to access existing WQ data sources, new technologies for WQM that are rapid, quantitative, field-deployable, comprehensive, simple to use and cost-effective are needed to increase the availability of worldwide WQ data. Currently, data gaps exist in many regions without national WQM programmes, while existing surveys do not necessarily provide essential quantitative information on source or end-user WQ. Furthermore, the need for new WQ assessment tools is not limited to developing countries.

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[36] GEMS/Water 2007.

**Box 9. Priorities to meet future needs for WQM and assessment[37]**

- Understanding the relations between WQ conditions and the natural landscape, hydrological processes, the subsurface and the human activities that take place on the landscape within watersheds
- Assessing WQ in a "total resource" context
- Evaluating WQ in concert with water quantity
- Evaluating WQ in concert with biological systems
- Monitoring over long timescales, taking care to place measurements in a historical, hydrological context
- Early warning of accidental pollution
- Moving from monitoring to prediction and applying the understanding of the hydrological system and water-quality conditions to non-monitored, yet comparable areas
- Investing resources to gather ancillary information on landscape and human factors controlling WQ
- Advancing monitoring technology, such as that for measuring WQ in real-time

Current WQM information and assessment are based mainly on in situ data. One exciting future prospect is that such assessments can benefit from other sources of data, particularly space-based observations, in a reliable and operational manner. Linking the two sources of data would be a valuable scientific resource because of potentially extending the scope, scale and replicability of data gathering for assessment purposes, as well as of developing new models and methodologies.

In conclusion, the important results to be expected of successful WQM programmes may be summarized as follows:

- Identification of management and policy information needs;
- Linkage to institutional arrangements with regulatory ability (i.e. to establish standards);
- Improved coordination among the organizations involved in water, sanitation and ecosystems and human health;
- Definition of data and information needs and the subsequent design of the monitoring network to meet them;
- Reliable and timely data collection and reporting;
- Co-location of WQ and quantity stations for the calculation of fluxes;
- An adequate number of monitoring stations strategically located to have accurate and reliable country/basin coverage, i.e. stations at headwaters and where a river enters the marine environment or a large inland groundwater body or crosses an international border;
- Response to unexpected problems and emerging issues;
- Addressing country needs by building capacity and empowerment;

[37] 3Source: Hirsch et.al., 2006

- Strengthening existing network infrastructure and institutions rather than creating new ones;
- Promotion of free access to information through the interoperability and comparability of methods; and
- Systems kept up to date (IT, analytical etc.).[38]

All this should lead to providing the needed basis for decision-makers effectively to allow the management and protection of water resources across nations and in specific geographical areas, now and in the future.

[38] GEMS/Water 2005.

## Tables

### Table 1. Categories and principal characteristics of water-quality monitoring operations

| Type of operation | Station density and location | Sampling or observation frequencies | Number of variables considered | Duration | Interpretation lag |
|---|---|---|---|---|---|
| **Multi-purpose monitoring** | Medium | Medium (12 per year) | Medium | Medium (> 5 years) | Medium (1 year) |
| **Other common water-quality operations** | | | | | |
| **Trend monitoring** | Low: major uses and international stations | ***Very high*** | Low for single objective; high for multiple objective | **> 10 years** | > 1 year |
| **Basic survey** | **High** | Depending on media considered | Medium to high | Once per year to once every 4 years | 1 year |
| **Operational surveillance** | Low: at specific uses | Medium | **Specific** | Variable | Short (month/week) |
| **Specific water-quality operations** | | | | | |
| **Background monitoring** | **Low** | Low | Low to high | Variable | Medium |
| **Preliminary surveys** | High | Usually low | Low to medium (depending on objectives) | **Short < 1 year** | Short (months) |
| **Emergency surveys** | Medium to high | High | **Pollutant inventory** | Very short (days-weeks) | **Very short** (days) |
| **Impact surveys** | Limited downstream pollution sources | Medium | **Specific** | Variable | Short to medium |
| **Modelling surveys** | **Specific** (e.g. profiles) | **Specific** (e.g. diel cycles) | **Specific** (e.g. DO, BOD) | Short to medium, two periods: calibration and validation | Short |
| **Early warning surveillance** | Very limited | **Continuous** | Very limited | Unlimited | Instantaneous |

Source: D. Chapman (Ed.), 1996

The levels (high, medium, low) of all operation characteristics (frequency, density, number of variables, duration and interpretation lag) are given in relation to multi-purpose monitoring, which has been taken as a reference. Important monitoring characteristics are emphasized in bold.

**Table 2. GEMS/Water variables**

**General water quality**

Water discharge/level
Total suspended solids (R)
Temperature
pH
Electrical conductivity
DO
Transparency (L)

**Dissolved salts**

Calcium
Magnesium
Sodium
Potassium
Chloride
Fluoride (GW)
Sulphate
Alkalinity

**Ionic balance**

Sum of cations
Sum of anions
Sodium adsorption ratio

**Nutrients**

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

**Organic matter**

Organic carbon, dissolved
Organic carbon, particulate
BOD
COD
Chlorophyll a (R,L)

**Microbial pollution**

Faecal coliforms
Total coliforms

**Inorganic contaminants**

Aluminium, dissolved
Aluminium, total
Arsenic, dissolved
Arsenic, total
Boron, dissolved
Boron, total
Cadmium, dissolved
Cadmium, total
Chromium, dissolved
Chromium, total
Copper, dissolved
Copper, total
Iron, dissolved
Iron, total
Lead, dissolved
Lead, total
Manganese, dissolved
Manganese, total
Mercury, dissolved
Mercury, total
Nickel, dissolved
Nickel, total
Selenium, dissolved
Selenium, total
Zinc, dissolved
Zinc, total

**Particulate matter**

Aluminium, particulate (GRF)
Arsenic, particulate (GRF)
Cadmium, particulate (GRF)
Chromium, particulate (GRF)
Copper, particulate (GRF)
Iron, particulate (GRF)
Lead, particulate (GRF)
Manganese, particulate (GRF)
Mercury, particulate (GRF)
Selenium, particulate (GRF)
Zinc, particulate (GRF)

**Organic contaminants**

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

Basic variables to be monitored at all GEMS/Water stations:
R - Basic variables for river stations only
L - Basic variables for lake/reservoir stations only
GW - Basic variables for groundwater stations only
R,L - Basic variables for river, lake/reservoir stations only
GRF - Essential for Global River Flux monitoring stations

**Table 3. DPSIR[39] framework for water quality of surface- and groundwater ecosystems**

| **Service and use (drivers)** | **Human health, drinking-water** | **Agriculture** | **Municipal/ industrial, energy** | **Ecosystem stability, structure and health** | **Tourism and recreation** |
|---|---|---|---|---|---|
| Pressures | Pollution | Runoff, pollution from fertilizer and pesticide use | Pollution from effluents, construction and other supporting infrastructural impacts | Human activities; climate change and variability | Pollution |
| | | | | | |
| *Parameter* | Total coliform | Salinity | Nutrients | Temperature | Parasites |
| *State* | Faecal coliform | Nutrients | Temperature | pH | Pathogens |
| | Pathogens | Chlorophyll a | DO | Conductivity | Chlorophyll a |
| | POPs | Pathogens | Pathogens | Major ions | Nutrients |
| | DOC | Pesticides | Organic contaminants | DO | |
| | Chlorophyll a | Suspended solids | Other contaminants such as metals | Nitrogen | |
| | Turbidity | Trace metals | BOD and COD | Phosphorus | |
| | | | Heavy metals (particularly in sediment), radioactivity, acid mine drainage | Suspended solids | |
| | | | | | |
| *Impact* | Gastrointestinal outbreaks; potential death especially of vulnerable persons | Eutrophication, pesticide and faecal contamination of receiving waters | Thermal and contaminant pollution of receiving waters affect food chains, biological productivity and species composition | Loss of species, altered food webs | Closed beaches, leisure boating restrictions and effects on other water uses |
| | Lost productivity and economic losses | | | Increased/ decreased biological productivity | |
| | | | | | |
| *Response* | Water guidelines and standards | Green belts and riparian buffer strips | Guidelines and standards | Appropriate treatment facilities for point sources but limited responses for climate change and variability | Guidelines and standards |
| | Treatment plants | Prevention of direct inputs contaminants | Treatment facilities | | Water-use advisories |
| | | Appropriate practices to minimize impacts | Polluter pays principle | | |

Source: UNEP GEMS/Water Technical Advisory Paper No. 2, May 2005

[39] Drivers-Pressures-State-Impact-Responses

**Table 4. Selection of variables for assessment of water quality in relation to non-industrial water use**

| | Background monitoring | Aquatic life and fisheries | Drinking-water sources | Recreation and health | Agriculture/ irrigation | Livestock watering |
|---|---|---|---|---|---|---|
| **General variables** | | | | | | |
| Temperature | xxx | xxx | | x | | |
| Colour | xx | | xx | xx | | |
| Odour | | | xx | xx | | |
| Suspended solids | xxx | xxx | xxx | xxx | | |
| Turbidity/ transparency | x | xx | xx | xx | | |
| Conductivity | xx | x | x | | x | |
| Total dissolved solids | | x | x | | xxx | x |
| pH | xxx | xx | x | x | xx | |
| DO | xxx | xxx | x | | x | |
| Hardness | | x | xx | | | |
| Chlorophyll a | x | xx | xx | xx | | |
| **Nutrients** | | | | | | |
| Ammonia | x | xxx | x | | | |
| Nitrate/nitrite | xx | x | xxx | | | xx |
| Phosphorus or phosphate | xx | | | | | |
| **Organic matter** | | | | | | |
| TOC | xx | | x | x | | |
| COD | xx | xx | | | | |
| BOD | xxx | xxx | xx | | | |
| Major ions | | | | | | |
| Sodium | x | | x | | xxx | |
| Potassium | x | | | | | |
| Calcium | x | | | | x | x |
| Magnesium | xx | | x | | | |
| Chloride | xx | | x | | xxx | |
| Sulphate | x | | x | | | x |
| **Other inorganic variables** | | | | | | |
| Fluoride | | | xx | | x | x |
| Boron | | | | | xx | x |
| Cyanide | | x | x | | | |

Table 4 continued

| | Background monitoring | Aquatic life and fisheries | Drinking-water sources | Recreation and health | Agriculture/ irrigation | Livestock watering |
|---|---|---|---|---|---|---|
| **Trace elements** | | | | | | |
| Heavy metals | | xx | xxx | | x | x |
| Arsenic and selenium | | xx | xx | | x | x |
| ***Organic contaminants*** | | | | | | |
| Oil and hydrocarbons | | x | xx | xx | x | x |
| Organic solvents | | x | xxx | | | x |
| Phenols | | x | xx | | | x |
| Pesticides | | xx | xx | | | x |
| Surfactants | | x | x | x | | x |
| **Microbiological indicators** | | | | | | |
| Faecal coliforms | | | xxx | xxx | xxx | |
| Total coliforms | | | xxx | xxx | x | |
| Pathogens | | | xxx | xxx | x | xx |

X – XXX - Low to high likelihood that the concentration of the variable will be affected and the more important it is to include the variable in a monitoring programme. Variables stipulated in local guidelines or standards for a specific water use should be included when monitoring for that specific use.

Source: D. Chapman [Ed.], 1996

**Table 5. Selection of variables for the assessment of water quality in relation to some key industrial uses**

| | Heating | Cooling | Power generation | Iron and steel | Pulp and paper | Petrol | Food processing |
|---|---|---|---|---|---|---|---|
| **General variables** | | | | | | | |
| Temperature | xxx | xxx | | xxx | x | | |
| Colour | x | | | | x | | xx |
| Odour | | | | | | | xxx |
| Suspended soils | xxx | xxx | xx | xx | x | xxx | xx |
| Turbidity | xx | | | | xx | | xx |
| Conductivity | x | x | | | | | |
| Dissolved solids | xx | xx | xxx | xx | xxx | x | xxx |
| pH | x | xxx | xxx | xx | xx | xxx | xxx |
| DO | xxx | | x | xxx | x | | |
| Hardness | xxx | xx | xxx | xx | xxx | xxx | xxx |
| **Nutrients** | | | | | | | |
| Ammonia | xxx | | x | | | | x |
| Nitrate | | | | | | x | xx |
| Phosphate | | | | | x | | |
| **Organic matter** | | | | | | | |
| COD | | x | xx | | | | |
| ***Major ions*** | | | | | | | |
| Calcium | | xxx | xxx | | x | xxx | x |
| Magnesium | | | x | | x | xxx | x |
| Carbonate components | xx | | xxx | | xxx | x | x |
| Chloride | x | x | xx | xx | x | xxx | xxx |
| Sulphate | | x | xx | xx | xx | x | xxx |
| **Other inorganic variables** | | | | | | | |
| Hydrogen sulphide | xxx | x | | | | | xx |
| Silica | xx | xx | x | | x | x | x |
| Fluoride | | | | | | x | xx |
| **Trace elements** | | | | | | | |
| Aluminium | | x | x | | | | |
| Copper | | x | x | | | | |
| Iron | xx | x | x | | x | x | xx |
| Manganese | xx | x | x | | x | | xx |
| Zinc | | | x | | | | |

Table 5 continued

| | Heating | Cooling | Power generation | Iron and steel | Pulp and paper | Petrol | Food processing |
|---|---|---|---|---|---|---|---|
| **Organic contaminants** | | | | | | | |
| Oil and hydrocarbons | x | x | x | x | | x | x |
| Organic solvents | | | | | | | x |
| Phenols | | | | | | | x |
| Pesticides | | | | | | | x |
| Surfactants | x | x | x | | | | x |
| **Microbiological indicators** | | | | | | | |
| Pathogens | | | | | | | xxx |

X – XXX - Low to high likelihood that the concentration of the variable will be affected and the more important it is to include the variable in a monitoring programme. The precise selection of variables depends on the required quality of the water in the individual industrial processes and any standards or guidelines that are applied.

Source: D. Chapman (Ed.), 1996

**Table 6. Selection of variables for the assessment of water quality in relation to non-industrial pollution sources**

| | Sewage and municipal wastewater | Urban runoff | Agricultural activities | Waste disposal to land | Solid hazardous municipal chemicals | Long-range atmospheric transport |
|---|---|---|---|---|---|---|
| **General variables** | | | | | | |
| Temperature | x | x | x | | | |
| Colour | x | x | x | x | | |
| Odour | x | x | x | | | |
| Residues | x | x | xxx | xxx | xx | |
| Suspended solids | xxx | xx | xxx | xx | xx | |
| Conductivity | xx | xx | xx | xxx | xxx | xxx |
| Alkalinity | | | | xx | | xxx |
| pH | x | x | x | xx | xxx | xxx |
| Redox potential (Eh) | x | x | x | | | |
| DO | xxx | xxx | xxx | xxx | xxx | |
| Hardness | x | x | x | | x | x |
| **Nutrients** | | | | | | |
| Ammonia | xxx | xx | xxx | xx | | |
| Nitrate/nitrite | xxx | xx | xxx | xx | | xxx |
| Organic nitrogen | xxx | xx | xxx | xx | | |
| Phosphorus compounds | xxx | xx | xxx | x | | x |
| **Organic matter** | | | | | | |
| TOC | x | x | x | | | |
| COD | xx | xx | x | xxx | xxx | |
| BOD | xxx | xx | xxx | xxx | xx | |
| ***Major ions*** | | | | | | |
| Sodium | xx | xx | xx | | | |
| Potassium | x | x | x | | | |
| Calcium | x | x | x | | | |
| Magnesium | x | x | x | | | |
| **Carbonate components** | | | | | | |
| Chloride | xxx | xx | xxx | xx | xx | |
| Sulphate | x | x | x | | | xxx |
| **Other inorganic variables** | | | | | | |
| Sulphide | xx | xx | x | | x | |
| Silica | | x | | | | |
| Fluoride | | x | | | | |
| Boron | | | x | | | |

Table 6 continued

| | Sewage and municipal wastewater | Urban runoff | Agricultural activities | Waste disposal to land | Solid hazardous municipal chemicals | Long-range atmospheric transport |
|---|---|---|---|---|---|---|
| **Trace elements** | | | | | | |
| Aluminium | | | | | | xx |
| Cadmium | | x | | xxx | xxx | x |
| Chromium | | x | | xxx | xx | x |
| Copper | x | x | xx | xxx | xx | x |
| Iron | xx | xx | | xxx | xx | x |
| Lead | xx | xxx | | xxx | xx | xx |
| Mercury | x | xx | xxx | xxx | xxx | |
| Zinc | | | xx | xxx | xx | x |
| Arsenic | | x | xxx | xx | xxx | x |
| Selenium | | x | xxx | x | x | |
| **Organic contaminants** | | | | | | |
| Fats | x | x | | | | |
| Oil and hydrocarbons | xx | xxx | | xx | x | |
| Organic solvents | x | x | | xxx | xxx | |
| Methane | | | | xxx | | |
| Phenols | x | | | xx | xx | |
| Pesticides | | x | xxx | xx | xxx | xxx |
| Surfactants | xx | | x | | x | |
| Microbiological indicators | | | | | | |
| Faecal coliforms | xxx | xx | xx | xxx | | |
| Other pathogens | xxx | | xx | xxx | | |

X – XXX - Low to high likelihood that the concentration of the variable will be affected and the more important it is to include the variable in a monitoring programme.

The final selection of variables is also dependent on the nature of the water body.

**Table 7. Selection of variables for the assessment of water quality in relation to some common industrial sources of pollution**

| | Food processing | Mining | Oil extraction/ refining | Chemical/ pharma-ceutical | Pulp and paper | Metal-lurgy | Machine production | Textiles |
|---|---|---|---|---|---|---|---|---|
| **General variables** | | | | | | | | |
| Temperature | x | x | x | x | x | x | x | x |
| Colour | x | x | x | x | x | x | x | x |
| Odour | x | x | x | x | x | x | x | x |
| Residues | x | x | x | x | x | x | x | x |
| Suspended solids | x | xxx | xxx | x | xxx | xxx | xxx | xxx |
| Conductivity | xxx | xxx | xxx | x | xxx | xxx | xxx | xxx |
| pH | xxx | xxx | x | xxx | x | xxx | x | x |
| Redox potential (Eh) | x | x | x | x | x | x | x | x |
| DO | xxx | xxx | xxx | xxx | xxx | x | x | xxx |
| Hardness | x | x | x | x | x | xx | x | x |
| **Nutrients** | | | | | | | | |
| Ammonia | xxx | | xx | xx | x | x | x | x |
| Nitrate/nitrite | xx | x | | xx | x | x | | x |
| Organic nitrogen | xx | | | x | x | | | x |
| Phosphorus compounds | xx | | | xx | | | x | x |
| **Organic matter** | | | | | | | | |
| TOC | x | x | x | xx | xxx | x | x | x |
| COD | x | x | x | xxx | xxx | x | x | x |
| BOD | xxx | x | xxx | xx | xxx | x | x | xxx |
| ***Major ions*** | | | | | | | | |
| Sodium | x | x | x | x | | | | x |
| Potassium | x | x | x | x | | | | x |
| Calcium | x | x | x | x | x | xx | x | x |
| Magnesium | x | x | x | x | x | x | | x |
| Carbonate components | x | x | x | x | | | | |
| Chloride | xx | xxx | xx | xx | x | x | x | xxx |
| Sulphate | x | x | xx | xx | xxx | x | x | x |
| **Other inorganic variables** | | | | | | | | |
| Sulphide | | x | xxx | xxx | xxx | xxx | | x |
| Silica | | x | x | x | | | x | x |
| Fluoride | | | | xx | | x | | x |
| Boron | | x | x | x | x | x | x | x |
| Cyanide | | x | | x | | x | x | x |
| **Trace elements** | | | | | | | | |
| Heavy metals | | xxx | xx | xx | x | xxx | xxx | xx |
| Arsenic | | x | | x | | x | | x |
| Selenium | | x | | x | | x | x | x |

Table 7 continued

| | Food processing | Mining | Oil extraction/ refining | Chemical/ pharma-ceutical | Pulp and paper | Metal lurgy | Machine production | Textiles |
|---|---|---|---|---|---|---|---|---|
| **Organic contaminants** | | | | | | | | |
| Fats | xx | | | | | | xx | |
| Oil and hydrocarbons | | | xxx | xx | | xx | xxx | x |
| Organic solvents | | | | xxx | xxx | | x | x |
| Phenols | x | | xx | xxx | xxx | x | | x |
| Pesticides | x | | | xxx | | | | |
| Other organics | | | | xxx | xxx | x | | |
| Surfactants | xx | | xx | xxx | x | x | x | xx |

X – XXX - Low to high likelihood that the concentration of the variable will be affected and the more important it is to include the variable in a monitoring programme. The final selection of variables to be monitored depends on the products manufactured or processed together with any compounds present in local industrial effluents. Any standards or guidelines for specific variables should also be taken into consideration.

**Table 8. Recommended annual sampling frequencies for GEMS/Water stations**

| Station types | Type of water | | |
|---|---|---|---|
| | Rivers/streams | Lakes/reservoirs | Aquifers |
| Baseline | **Minimum** – 4, including high- and low-water stages | Minimum – 1 at turnover (sampling at lake outlet) | |
| | | | |
| | **Optimum** – 24, i.e. fortnightly sampling, and weekly for total suspended solids | Optimum – 1 at turnover and 1 vertical profile at end of stratification period | |
| Trend | **Minimum** – 12 for large drainage area (c. 100 000 $km^2$) | **Eutrophication issue** – 12, including twice monthly during summer | **Minimum** – 1 for large, stable aquifers |
| | | | |
| | Maximum – 24 for small drainage area (c. 10 000 $km^2$) | **Other issues**<br>Minimal – 1 at turnover<br>**Maximal** – 2: 1 at turnover and 1 at maximum thermal stratification | **Maximum** – 4 for small, alluvial aquifers<br><br>**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 TSS are recommended.
(2) For particulate arsenic, cadmium, chromium, copper, lead, mercury, selenium, zinc
(3) For temperature, pH, electrical conductivity, DO, calcium, magnesium, sodium, potassium, chloride, sulphate, alkalinity, nitrate plus nitrite, total phosphorus filtered and unfiltered, silica, chlorophyll a, dissolved and particulate organic carbon, dissolved and particulate organic nitrogen
(4) For dissolved and particulate fractions of aluminium, iron and manganese; and for dissolved arsenic, cadmium, chromium, copper, lead, mercury, selenium and zinc

Source: GEMS/Water Operational Guide v.3.1

**Table 9. Examples of responsibilitie[40] of staff on a water-quality monitoring programme**

***Responsibilities of the programme manager***

- Planning of water-quality monitoring activities
- Coordination with regional centres, collaborating agencies, participating laboratories and others not under his/her direct control
- Procurement of necessary equipment and consumable supplies
- Arranging suitable transport
- Recruitment of staff
- Training of staff
- Preparation of training manuals
- Safety in the field and in the laboratory
- Preparation of SOPs
- Organizing and managing central office facilities for the storage, handling, interpretation and distribution of data
- Supervising and evaluating the performance of all staff
- Reviewing and evaluating procedures
- Preparation of reports and dissemination of the findings of the monitoring programme

***Responsibilities of field staff***

- Undertaking sampling expeditions in accordance with a planned programme
- Obtaining samples according to SOPs
- Sample handling: labelling sample bottles, preparing samples, etc.
- Performing on-site measurements with proper devices
- Maintenance of equipment used in the field
- Performing field tests for selected variables

***Responsibilities of laboratory staff***

**Laboratory chief**
- Responsible for laboratory management
- Determining and procuring the equipment and supplies needed
- Ensuring that SOPs are being followed
- Quality-control of analytical procedures
- Enforcing safety precautions and procedures

**Laboratory technician (analyst)**
- Preparation and carrying-out of analytical work in the laboratory
- Teaching the assistants how to use various items of laboratory equipment and carry out certain analyses

**Laboratory assistant**
- Use of various items of laboratory equipment
- Preparation of reagent solutions
- Carrying out of certain analyses

[40] Examples of what may be expected of the different types of staff, although it may not be complete for any specific situation.

**Table 10. Management documents needed (ISO/IEC 17025, 2005) to implement the quality-assurance programme (quality manual)**

- A quality policy statement, including objectives and commitments
- The organization and management structure of the project, its place in any parent organization and relevant organizational charts
- The relationship between management, technical operations, support services and the quality system
- Procedures for control and maintenance of documentation
- Job descriptions for key staff and reference to the job descriptions of other staff
- Identification of approved signatories
- Procedures for ensuring traceability of all paperwork, data and reports
- The laboratory's scope for calibrations and tests
- Arrangements for reviewing all new projects to ensure that there are adequate resources to manage them properly
- Reference to the calibration, verification and testing procedures used
- Procedures for handling calibration and test items
- Reference to the major equipment and reference measurement standards used
- Reference to procedures for calibration, verification and maintenance of equipment
- Reference to verification practices, including interlaboratory comparisons, proficiency testing programmes, use of reference materials and internal quality-control schemes
- Procedures to be followed for feedback and corrective actions whenever testing discrepancies or departures from documented procedures are detected
- Complaints procedure
- Procedures for protecting confidentiality and property rights
- Procedures for audit and review

## Annex 1. Description of the main water-quality variables

### 1. General variables

***Temperature***

The temperature of surface waters is influenced by latitude, altitude, season, time of day, air circulation, cloud cover and the flow and depth of the water body. In turn, temperature affects physical, chemical and biological processes in water bodies and, therefore, the concentration of many variables. As water temperature increases, the rate of chemical reactions generally increases, together with the evaporation and volatilization of substances from the water. Increased temperature also decreases the solubility of gases in water, such as oxygen ($O_2$), carbon dioxide ($CO_2$), nitrogen ($N_2$), methane ($CH_4$) and others. The metabolic rate of aquatic organisms is also related to temperature and, in warm waters, respiration rates increase, leading to increased oxygen consumption and increased decomposition of organic matter. Growth rates also increase (this is most noticeable for bacteria and phytoplankton, which double their populations in very short time periods), leading to increased water turbidity, macrophyte growth and algal blooms, when nutrient conditions are suitable.

Measurements of temperature are required in studies of the self-purification of rivers and reservoirs and for the control of waste-treatment plants. They are important in relation to fishlife and other biological activity and are also necessary for cooling purposes, for process use in industry and heat/cold storage for thermal energy. 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.

***Colour***

The colour and turbidity of water indicate the depth to which light is transmitted. This, in turn, controls the amount of primary productivity that is possible by controlling the rate of photosynthesis of the algae present. The visible colour of water is the result of the different wavelengths not absorbed by the water itself or the result of dissolved and particulate substances present. It is possible to measure both true and apparent colour in water. Minerals such as ferric hydroxide and organic substances such as humic acids give true colour to water. True colour can be measured in a sample only after filtration or centrifugation. Apparent colour is caused by coloured particulates and the refraction and reflection of light on suspended particulates. Polluted water may, therefore, have quite a strong apparent colour.

Different species of phyto- and zooplankton can also give water an apparent colour. A dark or blue-green colour can be caused by blue-green algae, a yellow-brown colour by diatoms or dinoflagellates and reds and purples by the presence of zooplankton such as *Daphnia sp.* or copepods.

***Taste and odours***

Water odour is usually the result of labile, volatile organic compounds and may be produced by phytoplankton and aquatic plants or decaying organic matter. Industrial and human waste can also create odours, either directly or as a result of stimulating biological activity. Organic compounds, inorganic chemicals, oil and gas can all impart odour to water, although an odour does not automatically indicate the presence of harmful substances. Regarding groundwater, hydrogen sulphide ($H_2S$), has a strong odour, which is easily recognized by the human sense of smell.

### *Residue and total suspended solids*

The term "residue" applies to the substances remaining after evaporation of a water sample and its subsequent drying in an oven at a given temperature. It is approximately equivalent to the total content of dissolved and suspended matter in the water since half the bicarbonate (the dominant anion in most waters) is transformed into $CO_2$ during this process. The term "solids" is widely used for the majority of compounds which are present in natural waters and remain in a solid state after evaporation (some organic compounds will remain in a liquid state after the water has evaporated). TSS and TDS correspond to non-filterable and filterable residue, respectively.

### *Suspended matter, turbidity and transparency*

The type and concentration of suspended matter control the turbidity and transparency of the water. Suspended matter consists of silt, clay, fine particles of organic and inorganic matter, soluble organic compounds, plankton and other microscopic organisms.

Such particles vary in size from approximately 10 nm in diameter to 0.1 mm in diameter, although it is usually accepted that suspended matter is the fraction that will not pass through a 0.45 µm pore diameter filter. Turbidity results from the scattering and absorption of incident light by the particles and the transparency is the limit of visibility in the water. Both can vary seasonally, according to biological activity in the water column and surface runoff carrying soil particles. Heavy rainfall can also result in hourly variations in turbidity. At a given river station, turbidity can often be related to TSS, especially where there are large fluctuations in suspended matter. Therefore, following an appropriate calibration, turbidity is sometimes used as a continuous, indirect measurement for TSS.

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. A lower depth of light penetration may impact sight-feeding fish, zooplankton migrations and benthic invertebrate reproduction. Transparency can be measured easily in the field and is, therefore, included in many regular sampling programmes, particularly in lakes and reservoirs, to indicate the level of biological activity. It is determined by a Secchi disc. Turbidity should be measured in the field but, if necessary, samples can be stored in the dark for not more than 24 hours.

### *Conductivity*

Conductivity, or specific conductance, is a measure of the ability of water to conduct an electric current. It is sensitive to variations in dissolved solids and major ions, mostly mineral salts. In addition to being a rough indicator of mineral content when other methods cannot easily be used, conductivity can be measured to establish a pollution zone, e.g. around an effluent discharge, or the extent of influence of runoff waters. It is usually measured in situ with a conductivity meter, and may be continuously measured and recorded. Such continuous measurements are particularly useful in rivers and groundwater for the management of temporal variations in total dissolved solids and major ions.

### *pH, acidity and alkalinity*

The acidification of lakes is a real risk, especially in countries where the natural salt concentration is low, as is the case in the Nordic countries and North America, e.g. the

Canadian Shield. Alkalinity[41] is a measure of the buffering capacity of water or the capacity of bases to neutralize acids. Measuring alkalinity is important in determining a stream's ability to neutralize acidic pollution from rainfall or wastewater. Alkalinity does not refer to pH, but rather the ability of water to resist change in pH. The presence of buffering materials helps neutralize acids as they are added to the water. These buffering materials are primarily the bases bicarbonate ($HCO_3^-$) and carbonate ($CO_3^{2-}$), and occasionally hydroxide ($OH^-$), borates, silicates, phosphates, ammonium, sulphides and organic ligands. Where limestone and sedimentary rocks and carbonate-rich soils are predominant, groundwater will often have high alkalinity.

Original alkalinity values are very small (and may differ for groundwater or saline surface water) and the buffering capacity therefore is extremely low. Because of relatively high concentrations of natural humic substances, the original pH is usually distinctly below 7.0. Airborne loading of different acidifying compounds such as sulphates and nitrates can lower pH values significantly so that harmful biological consequences occur. Some fish species are especially sensitive to acidification.

The pH is an important variable in WQ assessment as it influences many biological and chemical processes within a water body and all processes associated with water supply and treatment. When measuring the effects of an effluent discharge, it can be used to help determine the extent of the effluent plume in the water body.

The pH is a measure of the acid balance of a solution. The pH scale runs from 0 to 14 (i.e. very acidic to very alkaline), with pH 7 representing a neutral condition. At a given temperature, pH (or the hydrogen ion activity) indicates the intensity of the acidic or basic character of a solution and is controlled by the dissolved chemical compounds and biochemical processes in the solution. In unpolluted waters, pH is principally controlled by the balance between the carbon dioxide, carbonate and bicarbonate ions, as well as other natural compounds such as humic and fulvic acids.

### *Oxygenation conditions*

Oxygen is without doubt the most important gas that dissolves in water from the atmosphere, owing to the fact that it is the dominant biotope factor regulating life in waters. The oxygen content of natural waters varies with temperature, salinity, turbulence, the photosynthetic activity of algae and plants, and atmospheric pressure. The solubility of oxygen decreases as temperature and salinity increase. DO can also be expressed in terms of percentage saturation, and levels less than 80 per cent saturation in drinking-water can usually be detected by consumers as a result of poor odour and taste.

Variations in DO can occur seasonally – or even over 24 hour periods – in relation to temperature and biological activity (i.e. photosynthesis and respiration). Biological respiration, including that related to decomposition processes, reduces DO concentrations. In still waters, pockets of high and low concentrations of DO can occur, depending on the rates of biological processes. Waste discharges high in organic matter and nutrients can lead to decreases in DO concentrations as a result of increased microbial activity (respiration) occurring during the degradation of the organic matter. In severe cases of reduced oxygen concentrations (whether natural or man-made), anaerobic conditions can occur, particularly close to the sediment-water interface as a result of decaying, sedimenting material.

### *Carbon dioxide*

The other gas measured in WQM is $CO_2$. There is a certain balance between $O_2$ and $CO_2$ concentrations, because the changes of these gases in lakes are significantly connected to biological reactions. $CO_2$ is highly soluble in water and atmospheric $CO_2$ is absorbed at the

[41] From http://bcn.boulder.co.us/basin/data/BACT/info/Alk.html

air-water interface. In addition, $CO_2$ is produced within water bodies by the respiration of aquatic biota during aerobic and anaerobic heterotrophic decomposition of suspended and sedimented organic matter. $CO_2$ dissolved in natural water is part of an equilibrium involving bicarbonate and carbonate ions. The concentrations of these forms are dependent to some extent on the pH.

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Free $CO_2$ is that component in gaseous equilibrium with the atmosphere, whereas total $CO_2$ is the sum of all inorganic forms of carbon dioxide, i.e. $CO_2$, carbonic acid ($H_2CO_3$), $HCO_3^-$ and $CO_3^{2-}$.

### *Chlorophyll*

The green pigment chlorophyll (which exists in three forms: chlorophyll a, b and c) is present in most photosynthetic organisms and provides an indirect measure of algal biomass and an indication of the trophic status of a water body. It is usually included in assessment programmes for lakes and reservoirs and is important for the management of water abstracted for drinking-water supply, since excessive algal growth makes water unpalatable or more difficult to treat.

In waters with little sediment input from the catchment or with little re-suspension, chlorophyll can give an approximate indication of the quantity of material suspended in the water column. The growth of planktonic algae in a water body is related to the presence of nutrients (principally nitrates and phosphates), temperature and light. The correlation between different nutrients and chlorophyll a can provide a good basis for discussions of the relevant minimum factors of primary production.

### *Salinity*

Salinity is a general term[42, 43] used to describe the levels of different salts such as sodium chloride, magnesium, calcium sulphates and bicarbonates. The presence of salt can restrict abstraction of water for drinking purposes. If water abstraction is excessive, intruding saltwater can contaminate the groundwater. High salinity is a frequent problem in arid and coastal areas.

Salinity is the sum weight of many different elements within a given volume of water. It has always been the case that the conversion of a precise salinity as a concentration to an amount of substance (sodium chloride, for instance) requires knowing much more about the sample and the measurement than just the weight of the solids upon evaporation (one method of determining salinity). For example, volume is influenced by water temperature, while the composition of the salts is not a constant. Saline waters from inland seas can have a composition that differs from those of the ocean.

The salinity of lake waters depends primarily on the quality of the bedrock, the soil of the watershed, where the lake is situated and where its water source is. There are great differences in salinity between different geological areas. Freshwaters contain alkali and alkaline earth bicarbonate and carbonate, sulphate, chloride in dilutions and largely undissociated silicic acids. In smaller quantities, there are a great number of different elements (such as the important nutrients phosphorus and nitrogen, as well as aluminium, iron, manganese, copper, zinc, etc.), which can be measured everywhere in the world. Regarding groundwater, the formation of saline groundwater and the migration and/or mixing of these categories of groundwater are put into motion by certain natural drivers (deposition of marine sediments, sea-level variations, meteorological processes and the hydrological cycle, climate change), anthropogenic drivers (coastal protection, land reclamation and drainage; groundwater abstraction, irrigation, disposal of waste and pollution).

More information on this issue, see Section 4. Major ions.

## 2. Nutrients

Nitrogen and phosphorus are the major nutrients causing eutrophication of surface waters. These nutrients originate partially from natural sources but mostly from the anthropogenic sources in areas affected by various human activities. Nitrogen loading arises mainly from diffuse sources such as agriculture, while phosphorus loading is dominated by point sources, such as municipal sewerage waters or industrial effluents, but also by agriculture, in particular surface runoff. Both nutrients can infiltrate the soil and be transported by groundwater to discharge zones, for example baseflow in rivers or drainage pipes. When transported by the groundwater, chemical reactions, e.g. denitrification, can take place, depending on the reactivity of the subsurface and redox conditions.

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[42] Source: Wikipedia

[43] Salinity in Australian English and North American English may also refer to the salt content of soil.

Excessive loading of nitrogen and phosphorus may drastically change the biological structure of a water body leading to such undesirable phenomena as blue-green algal blooms, pronounced overgrowth of macrophytes or even fish kills caused by intensive decomposition of organic material and subsequent oxygen deficiency in the water column. Drinking-water contaminated with nitrate poses a health risk to infants. In most cases, phosphorus is the limiting nutrient for algal growth in lakes, especially in oligotrophic-mesotrophic conditions. The regulating role of nitrogen becomes more important in eutrophic or hypertrophic lakes and marine waters.

Most primary producers (e.g. phytoplankton, periphyton and macrophytes) can only utilize dissolved forms of nutrients such as ammonium, nitrite, nitrate, urea and phosphate. Hence, the total concentrations of nitrogen and phosphorus do not necessarily reveal the limiting nutrient of the lake ecosystem.

## 3. Organic matter

Organic matter, measured by DO, BOD and ammonium, constitute key indicators of the oxygen content of water bodies.

Concentrations of these parameters normally increase as a result of organic pollution caused by discharges from wastewater-treatment plants, industrial effluents and agricultural runoff. Severe organic pollution may lead to rapid de-oxygenation of river water, a high concentration of ammonia and the disappearance of fish and aquatic invertebrates.

The most important sources of organic waste load are: household wastewater; paper and food-processing industries (among others); and, occasionally, silage effluents and slurry from agriculture. Increased industrial and agricultural production, coupled with a greater percentage of the population being connected to sewerage systems, initially resulted in increases in the discharge of organic waste into surface water in most developed countries. Over the past 15-30 years, however, the biological treatment of wastewater has increased and organic discharges have consequently decreased.

Measurement of TOC or DOC is a much more rapid means of determining the organic content of water and wastewater than is the measurement of BOD. If the relative concentrations of organic compounds in the samples do not change greatly, empirical relationships can be established between TOC and BOD or COD to permit speedy and convenient estimations of the latter. Measurement of TOC can be used to monitor processes for the treatment or removal of organic contaminants without undue dependence on the oxidation states and is valid at low concentrations.

Humus is formed by the chemical and biochemical decomposition of vegetative residues and from the synthetic activity of microorganisms. Humus enters water bodies from the soil and from peat bogs or it can be formed directly within water bodies as a result of biochemical transformations. It is operationally separated into fulvic and humic acid fractions, each being an aggregate of many organic compounds of different masses. Natural organic compounds are not usually toxic but exert major controlling effects on the hydrochemical and biochemical processes in a water body. Some natural organic compounds significantly affect the quality of water for certain uses, especially those which depend on organoleptic properties (taste and smell). During chlorination for drinking-water disinfection, humic and fulvic acids act as precursor substances in the formation of tribalomethanes such as chloroform. In addition, substances included in aquatic humus determine the speciation of heavy metals and some other pollutants because of their high complexing ability. As a result, humic substances affect the toxicity and mobility of metal complexes. Measurement of the concentrations of these substances can, therefore, be important for determining anthropogenic impacts on water bodies.

Organic matter[44] in groundwater plays important roles in controlling geochemical processes by acting as proton donors/acceptors and as pH buffers, by affecting the transport and degradation of pollutants and by participating in mineral dissolution/ precipitation reactions.

## 4. Major ions

The most common elements which have been monitored from inland surface waters are sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), chloride (Cl) and sulphur (S). Sodium in water exists principally as the cation $Na^+$. Potassium does not exist in nature as a free element, it forms salts as chloride, bromide, sulphate, nitrate and aluminium silicates. Potassium is an essential element for plant growth. Calcium is the fifth most abundant element in rocks and soils on Earth. In surface waters, it is one of the most abundant cations because of the weathering of rocks and soils. It occurs mostly as the $Ca^{2+}$ ion but complexes can also occur. Magnesium is the eighth most abundant element on Earth. In water it exists largely as the $Mg^{2+}$ ion. It also forms complexes. Chloride (Cl) does not occur freely in nature. The chloride ion is the principal ion in seawater and is widely distributed in the environment as salts with sodium, potassium and calcium. Sulphur is the ninth most abundant element on Earth. Sulphur compounds are widely distributed in minerals and rocks. In water, sulphates occur mainly as free anion $SO_4^{2-}$, and form ion pairs with $Ca^{2+}$, $Mg^{2+}$, $Na^+$, $Fe^{2+}$, $Fe^{3+}$ and $Mn^{2+}$.

Sulphide formation in surface waters is principally through anaerobic, bacterial decay of organic substances in bottom sediments and stratified lakes and reservoirs. Traces of sulphide ion occur in unpolluted bottom sediments from the decay of vegetation but the presence of high concentrations often indicates the occurrence of sewage or industrial wastes. Under aerobic conditions, the sulphide ion converts rapidly to sulphur and sulphate ions. When appreciable concentrations of sulphide occur, toxicity and the strong odour of the sulphide ion make the water unsuitable for drinking-water supplies and other uses.

In connection with drinking-water supply, the variable water hardness is often used. Water hardness expresses the sum of all the metallic cations, except for alkali metals. The principal ions responsible for water hardness are calcium and magnesium. The following types of water hardness are commonly used:

- Total hardness is equivalent to the total concentration of $Ca^{2+}$ and $Mg^{2+}$, as well as the other bivalent ions, such as $Fe^{2+}$, $Mn^{2+}$, $Ba^{2+}$ and $Sr^{2+}$;
- Carbonate hardness;
- Non-carbonate hardness.

In the monitoring of lakes and groundwater, it is important to define the natural status of the salinity and the natural concentrations of the relevant elements. In the preparation of monitoring programmes, all possible sources of loading factors in this sense should be clarified.

## 5. Other inorganic variables

*Silica*: silica is widespread and always present in surface water and aquifers, existing in dissolved, suspended and colloidal states. Dissolved forms are represented mostly by silicic acid, products of its dissociation and association, and organo-silicon compounds.

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[44] http://water.usgs.gov/ogw/pubs/ofr0289/ga_organic.htm

Reactive silicon (principally silicic acid but usually recorded as dissolved silica ($SiO_2$) or sometimes as silicate ($H_4SiO_4$) results mainly from the chemical weathering of siliceous minerals. Silica may be discharged into water bodies with wastewater from industries using siliceous compounds in their processes such as potteries, glassworks and abrasive manufacture.

*Fluoride*: fluoride originates from hydrothermal/volcanic sources and the weathering of fluoride-containing minerals and enters surface waters with runoff and aquifers through direct contact. Liquid and gas emissions from certain industrial processes (such as metal- and chemical-based manufacturing) can also contribute fluoride ions (F-) to water bodies. Fluoride mobility in water depends, to a large extent, on the Ca2+ ion content, since fluoride forms low-solubility compounds with divalent cations. Other ions that determine water hardness can also increase F- solubility.

During weathering[45] and circulation of water in rocks and soils, fluoride can be leached out and dissolved in groundwater and thermal gases. The fluoride content of groundwater varies greatly, depending on the geological settings and type of rocks. The most common fluoride-bearing minerals are fluorite, apatite and micas. Fluoride problems tend, therefore, to occur in places where these minerals are most abundant in the host rocks. Aquifers from crystalline rocks, especially (alkaline) granites (deficient in Ca) are particularly sensitive to relatively high fluoride concentrations.

*Fluoride in groundwater*: the measurement of fluoride content is especially important when a water body is used for drinking-water supply. At high concentrations, fluoride is toxic to humans and animals and can cause bone disease. A slight increase in natural concentrations, however, can help prevent dental caries, although, at higher concentrations (above 1.5-2.0 mg $l^{-1}$), mottling of teeth can occur (WHO, 1984). Where fluoride is known to occur or can be anticipated, it is an essential variable in surveys where community water supplies are being planned but it is less important for long-term monitoring.

*Boron*: boron is a natural component of freshwaters (surface- and groundwater) arising from the weathering of rocks, soil leaching, volcanic action and other natural processes. Industries and municipal wastewaters also contribute boron to surface waters. In addition, agricultural runoff may contain boron, particularly in areas where it is used to improve crop yields or as a pesticide. Boric acid, which does not readily dissociate, is the predominant species in freshwaters.

*Cyanide*: compounds of cyanide enter freshwaters with wastewaters from industries such as electroplating. Cyanides occur in waters in ionic form or as weakly dissociated hydrocyanic acid. In addition, they may occur as complex compounds with metals. The toxicity of cyanides depends on their speciation; some ionic forms and hydrocyanic acid are highly toxic. The toxicity of complex compounds of cyanide depends on their stability. Cyanide also exists in the soils and groundwater near former gasworks.

Weak complexes formed with metals such as zinc, lead and cadmium are extremely toxic. Copper complexes are less toxic, while cobalt and ferrous complexes are only weak toxicants. Concentrations of cyanides in waters intended for human use, including complex forms, are strictly limited because of their high toxicity.

## 6. Metals

Metals[46] occur naturally and become integrated in aquatic organisms through food and water. Trace metals such as mercury, copper, selenium and zinc are essential metabolic components in low concentrations. Metals tend to bioaccumulate in tissues, however, and prolonged exposure or exposure at higher concentrations can lead to illness. Elevated

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[45] http://www.igrac.net/publications/150

[46] Verbatim, GEMS/Water 2008 p. 19

concentrations of trace metals can have negative consequences for both wildlife and humans. In particular, arsenic – a semi-metallic element which occurs naturally in some surface- and groundwater sources – may lead to development of skin lesions and cancer in people exposed to excess concentrations through drinking-water, bathing water or food. Human activities such as mining and heavy industry can result in higher concentrations than those that would be found naturally.

As a result of acid mine drainage – outflow of acidic water from, among others, metal mines – high concentrations of metals can be released into the environment.

Metals tend to be strongly associated with sediments in rivers, lakes and reservoirs and their release to the surrounding water is largely a function of pH, oxidation-reduction state and organic-matter content of the water (and the same is also true for nutrient and organic compounds). Thus, WQM for metals should also examine sediment concentrations, so as not to overlook a potential source of metal contamination to surface waters. The assessment of metal pollution is an important aspect of most WQ assessment programmes.

Regarding arsenic in groundwater[47], the physicochemical conditions favouring arsenic mobilization in aquifers are variable, complex and poorly understood, although some of the key factors leading to high groundwater arsenic concentrations are known. Mobilization can occur under strongly reducing conditions where arsenic, mainly as As(III), is released by desorption from, and/or dissolution of, iron oxides. Immobilization under reducing conditions is also possible. Some sulphate-reducing microorganisms can respire As(V), leading to the formation of an $As_2S_3$ precipitate. Some immobilization of arsenic may also occur if iron sulphides are formed.

## 7. Organic contaminants

Numerous hazardous substances deriving from the use of chemical substances are found in the aquatic environment. The most widespread contamination of the aquatic environment derives from pesticides and pesticide residues. Wastewater contains many hazardous substances derived from detergents and other substances flushed into sewers. In addition, many substances are used in industrial production and in the transport sector.

Numerous organic pollutants are found in groundwater, including pesticides and substances leaching from contaminated sites (for example, petroleum of chlorinated hydrocarbons). Pesticides also occur in watercourses. Concern is being expressed about hormone-like substances which can change the sexual characteristics of fish species, such as roach. In coastal waters, it has become apparent that hazardous substances, such as the antifouling agent tributyltin, can affect marine organisms.

Personal care products such as soaps, shampoos and different types of cosmetics contain substances that are not degraded in sewage-treatment systems and can therefore reach the environment. Many substances are persistent, lipophilic (capable of combining with or dissolving in fats) and bioaccumulating.

Triclosan is an antimicrobial active substance used for many purposes. such as disinfectants, preservatives and personal care products. Triclosan is transformed to methyltriclosan in the environment through a path which is not fully understood. This substance persists in the environment and accumulates in organisms. Methyltriclosan concentrations in fish are increasing at all sampling sites in Germany, but data about the toxicity and action of methyltriclosan are largely missing.

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47 http://www.igrac.net/publications/143

Many thousands of individual organic compounds enter water bodies as a result of human activities. These compounds have significantly different physical, chemical and toxicological properties. They are not monitored in all circumstances, however, because their determination requires sophisticated instrumentation and highly trained personnel. Much effort will be needed in monitoring these classes of compounds because they have become widespread and have adverse effects on humans and the aquatic environment. When selecting a list of variables for a survey of organic contaminants, the gross parameters of TOC, COD and BOD should be included. In intensive surveys, the following classes of organic pollutants should be identified: hydrocarbons (including aromatic and polyaromatic), purgeable halocarbons, chlorinated hydrocarbons, different pesticide groups, polychlorinated biphenyls (PCBs), phenols, phthalate esters, nitrosamines, nitroaromatics, haloethers, benzidine derivatives and dioxins.

## 8. Biological variables

The biological elements for classification of the ecological status of waters could be defined as follows:

- Composition, abundance and biomass of phytoplankton;
- Composition and abundance of other aquatic flora;
- Composition and abundance of benthic invertebrate fauna;
- Composition, abundance and age structure of fish fauna.

Groundwater-dependent ecosystems (GDE) are a diverse and important component of biological diversity. The term GDE takes into account ecosystems that use groundwater as part of survival and can potentially include wetlands, vegetation, mound springs, river base flows, cave ecosystems, playa lakes and saline discharges, springs, mangroves, river pools, billabongs and hanging swamps. The groundwater dependence of ecosystems will range from complete reliance to those that partially rely on groundwater, such as during droughts. The degree and nature of dependency will influence the extent to which ecosystems are affected by changes to the groundwater system, both in quality and quantity.

***Phytoplankton***: plankton algae are the most important group of primary producers in a lake. As planktic algae have very short generation times, they also react rapidly to shifts in the environment. Changes in the physical and/or chemical status of the water are traced after some weeks through alterations of the species and their abundances.

The amount and the species composition of algal biomass are significantly dependent on growth factors such as temperature and the concentrations of different nutrients. The minimum nutrient in freshwaters in most natural lakes is usually phosphorus. The highest density of algae can be found in the epilimnion.

In the classification of lakes, the phytoplankton is the most important factor, especially in deeper lakes with clear stratification. Phytoplankton can also be used in local pollution-control monitoring of recipient waters as an indicator of the toxic effects of sewage. In this case, samples are not preserved. The aim is to investigate if phytoplankton are alive or damaged by toxic substances.

Phytoplankton results can be used especially for assessment of the eutrophication status of lakes.

Besides the total amount of phytoplankton, an important characteristic is the species composition. Some species are typical in eutrophic waters, others indicate quite oligotrophic waters, etc. Several quotient systems based on phytoplankton species have therefore been developed and are used in the assessment of lakes. They are usually most suitable in smaller geographical areas – or even only in the same river basin.

Some algae species, however, are nearly always connected with eutrophy – the blue-green algae. The mass occurrence of cyanophytes is always a signal of severe eutrophication of a lake. These bloomings are usually found in late summer, when water temperature is high. A massive water bloom is not only an ecologically inferior phenomenon, it also has a negative impact on the use of water by restraining open-air activities and by decreasing the production of fish for consumption. It also affects drinking-water supplies.

***Macrophytes***: other biological quality elements for lakes are macrophytes and phytobenthos. There are many characteristics of aquatic macrophytes, which can be used as indicators in environmental monitoring. Due to local heterogeneity of habitats, generalizations of indicator values are difficult, however, and variation in responses should be interpreted carefully.

As the aquatic vegetation in a lake is influenced simultaneously by several factors, macrophytes have only rarely a good indicative value when evaluating some specific environmental variables. Instead, they give a good general estimation of the trophic state of the site. Their use as indicators is further motivated by their relative persistence in the site. Fluctuations in the population size of aquatic macrophytes are also usually minor in comparison with many other organisms.

***Periphyton***: Periphyton is a complex community of microbiota (algae, bacteria, fungi, animals, inorganic and organic detritus) that is attached to substrata. A distinct and unpleasant sliming of underwater surfaces, e.g. stones, fishing nets and piers, is the most visible nuisance effect caused by periphyton communities. Periphyton is often a major primary producer in rivers but also in lakes with an extensive littoral area. Periphyton has proved to be a good, useful indicator of WQ, responding to, and reflecting, conditions of the immediate past.

The measurement of periphyton growth on artificial substrata has been widely used when assessing the effect of point source loading (industrial effluents, municipal sewage waters, etc.) on the primary production of the recipient surface waters.

The analyses usually determined from the quantitative periphyton samples are chlorophyll-a content, fresh mass, dry mass, organic content and ash-free dry mass (AFDM). Chlorophyll a describes the algal mass of the periphyton. This parameter is most suitable for estimation of the eutrophication.

***Benthic invertebrate fauna***: benthic invertebrates (zoobenthos) have been increasingly used in freshwater monitoring programmes. Due to its large species richness, covering all types of freshwater habitats, and increased ecological knowledge of species' response to environmental conditions, zoobenthos can be used for different monitoring topics, such as eutrophication, acidification, changes in habitat structure and species' diversity and toxicity. Zoobenthos is relatively easy to sample and, as sedentary and rather long-lived organisms, they can reflect site-specific, long-term changes in nature.

***Fish***: fish are an important part of the biocoenosis in a lake. They have an important role in the food web of the lake but, additionally, are the most interesting part of biocoenosis for human consumption. It is quite natural, therefore, that fish faunae are also one of the biological quality elements for use in ecological classification.

Fish are at the top of the food webs of the lake ecosystem and therefore have a strong influence on other parts thereof. They feed on organisms belonging to other lower trophic levels but, at the same time, are also food for other fish and invertebrates and, finally, for birds and mammals, including human beings. Fish populations have also been found to have significant effects on WQ. For example, dense fish populations may inhibit the growth of phytoplankton and macrophytes through reducing the clarity of water.

At present, it is considered that the role of fish has changed and that fish populations are a part of the ecosystem. In particular, the reason for this has been, besides the implementation of the WFD, food-web manipulation for the purpose of WQ management. Manipulation of food webs has proved to be a very useful tool in the improvement of ecosystem health in lakes.

## 9. Microbiological indicators

The most common risk to human health associated with water stems from the presence of microorganisms. Microorganisms capable of causing disease in humans and animals are introduced into lake water in treated wastewater, runoff, contaminated brook and river water entering the lake and, occasionally, directly in animal droppings. Infectious agents are various bacteria, viruses and protozoa, together with other parasites. Today, it is not possible to monitor the occurrence of every pathogen possibly present in lake water. The main concerns are those pathogens transmitted through faeces and capable of causing epidemics via contaminated water.

The enumeration of bacteria normally occurring in high numbers in the faeces of humans and homoeothermic animals has been successfully used for more than a century for the detection of faecal contamination. This strategy has been of immense importance in protecting humans against infectious diseases transmitted via water that cause extensive epidemics through contaminated drinking-water and also contaminated water which is used for irrigation and recreational purposes.

When planning sampling programmes, it is important to assess the possible contamination sources and their temporal and spatial impacts. Pipelines conducting treated wastewater should be located and, ideally, the volume and quality of wastewater noted. Pipes bringing non-treated domestic wastewater and water from animal husbandry should be identified. Possible leakages in pipes causing groundwater contamination should also be taken into account. Pastures adjacent to lakeshores are probable sources of faecal contamination, especially during runoff episodes. Flocks of birds are known sources of direct contamination of lake water. Naturally, the hygienic state of a lake is affected by the hygienic quality of river and brook water entering it. Usually, surface water is most vulnerable to contamination, but the introduction or infiltration of wastewater to deeper water layers or re-suspension of sediment may also cause heavy contamination of subsurface- and groundwater.

## 10. Sedimentation

Sediment transport[48] into aquatic systems results from almost all human land use and industrial activities, including agriculture, forestry, urbanization and mining. Increases in sediment transport to aquatic systems are typically observed as bank-side vegetation is degraded or removed, rivers are canalized to enable development closer to stream-banks, and natural land cover is removed or replaced by human-built land cover (e.g. roads and buildings). The construction of impoundments also generates sediments and alters the natural sedimentation regime of many watercourses: sediments tend to accumulate in reservoirs and ecosystems downstream of reservoirs are often depleted of their natural sediment fluxes and riverbank scouring is increased.

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[48] Verbatim from GEMS/Water, 2008, 35-36

The transport of sediments into surface waters has both physical and chemical consequences for WQ and aquatic ecosystem health. High turbidity can decrease the amount of available sunlight, limiting the production of algae and macrophytes. Fish habitats can be degraded as spawning gravel becomes filled with fine particles, restricting the oxygen available for buried eggs. Turbid waters may also damage fish directly by irritating or scouring their gills or by reducing the success of visual predators. The scouring action of turbid waters may also harm some benthic macroinvertebrates.

Very fine sediment (less than 63 μm) is often chemically active. Phosphorus and metals tend to be highly attracted to the ionic exchange sites associated with iron and manganese coatings that occur on small particles. Many toxic organic contaminants, such as pesticides or their breakdown products, are strongly associated with silt, clay and organic carbon transported by rivers. Thus, sediments act as an agent in the process of eutrophication and toxicity in aquatic organisms. High sediment loads in surface waters can also increase thermal pollution by increasing the absorption of light, thereby increasing water temperatures. Finally, high-sediment loads can impair navigation and water-retention facilities by silting in watercourses and filling in reservoirs, thereby necessitating costly dredging or shortening their useful life. The dredging of reservoirs, watercourses, harbours and lakes also has serious implications for the ecology of these systems.

Due to dredging, toxic chemicals (heavy metals or PCBs) can be released from bottom sediments to the water column.

# Annex 2. Description of main water-quality monitoring methods and techniques

## 1. WQ monitoring equipment

In situ and portable WQM devices are often used as there is an increasing need to monitor large areas in short time intervals. The benefits associated with this type of technology include:

- Rapid results that can be sent immediately;
- Continuous monitoring;
- Automatic monitoring;
- Short-term management;
- Monitoring of decontamination processes;
- Early warning systems and applications;
- Reduction in error associated with sample preparation, transport and storage.

The development of novel, accurate and precise tests for the detection of physicochemical properties, biological conditions or pollutants in water has been rapid in the past decade, as new technologies have become available. One of the promising advances is a multi-parameter optical analyser based on lab-on-a-chip technology measuring up to 24 different physicochemical results in just a few minutes. Other recent technologies used for physicochemical detection include different kinds of immunoassays. Developing technologies for measuring microbial contaminants of waters include:

- New enzyme/substrate methods that incorporate high-sensitivity fluorescence detection instruments, including dual wavelength fluorometry simultaneously to assess both enzymatic hydrolysis and the loss of substrate;
- Quantitative polymerase chain reaction technology that relies on specific nucleic acid sequences, and antibody-antigen binding properties, which include evanescent wave fibre-optic biosensors;
- The rapid bacteria detection system, which is based on laser flow-through technology and capture of the antigen by antibodies on magnetic beads.

## 2. Optical monitoring

Optical absorption measurements – spectrophotometry – are used for measuring a range of analytes in aquatic environments, such as humic substances. Spectrophotometric sensors have the potential to offer superior stability and precision to electrode devices. Nutrients in water can be measured directly using UV absorption. The use of UV absorption for characterizing nitrates and other compounds in wastewater has been examined in several publications. Optodes for DO measurement are at an advanced stage of development. They have the advantages of simple construction, no analyte consumption, less sensitivity to fouling and good stability. A number of commercial instruments exist for chlorophyll measurement, using excitation in the UV (blue) and emission in the blue (red) parts of the spectrum (fluorometry).

The dependence of the refractive index of seawater on salinity is well known, including its temperature and pressure sensitivity. A fibre-optic refractive-index sensor based on surface-plasmon resonance has been developed for the purpose of salinity measurement. This kind of device has shown good sensitivity and correlation with a more traditional commercial conductivity-temperature-depth probe.

Another form of absorption spectroscopy is attenuated total reflection. Chlorinated hydrocarbons have been measured using this method. Optical backscatter can be used to measure suspended solids and turbidity. This has been used, for example, to measure phytoplankton production and total suspended matter concentrations.

Some optical instruments use thermal light sources, which could be made more compact, reliable and stable using light-emitting diodes (LEDs). Furthermore, the ever-expanding range of LEDs, at both ends of the optical spectrum, open up opportunities for new sensing techniques. LEDs are now available below 250 nm and up to 7 μm, with narrow enough bandwidths to avoid adjacent (e.g. $H_2O$) absorption bands. Additionally, tunable laser diodes allow fine spectral discrimination of, for example, narrow absorption lines. Another attractive technology is compact spectrometers, allowing nanometre spectral resolution in little more than the size of a matchbox. Fibre-optic sensors offer compactness, stability and high sensitivity and allow distributed measurements to be made.

Low-cost video/imaging technology applied to water bodies is a nascent field – opportunities exist for measuring flow and biota, for example. The latter would require image-processing techniques for recognizing and counting and could also be coupled with spectral information. Biofouling is a significant issue for optical sensors: some of the existing techniques are effective but there is scope for further work in this area. Simple techniques using standard digital cameras for water colour or transparency are also under development.

Different kinds of flow-through systems and profiling instruments using optical sensing (absorption, attenuation, fluorescence of light) have been developed for rapid monitoring of chlorophyll, suspended matter and humic substances. In conclusion: rapid developments in optical methods offer excellent solutions for better spatial resolution of sampling and cost-effective monitoring.

## 3. Simple field-measured variables

***Temperature***: temperature should be measured in situ, using a thermometer or thermistor. Some meters designed to measure oxygen or conductivity can also measure temperature. As temperature has an influence on so many other aquatic variables and processes, it is important always to include it in a sampling regime and to take and record it at the time of collecting water samples. For a detailed understanding of biological and chemical processes in water bodies, it is often necessary to take a series of temperature measurements throughout the depth of the water, particularly during periods of temperature stratification in lakes and reservoirs. There are also gauges for measuring water temperature in monitoring wells.

***pH measurement***: 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. Many portable pH meters are on the market today; investigators should select the one that best suits their needs.

***Conductivity measurement***: conductivity (specific conductance) is a numerical expression of water's ability to conduct an electric current. Conductivity depends on the concentration of ions in solution and in situ measurements are preferable. 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. Various conductivity meters are available which may also have temperature- and salinity-determining capabilities.

***Oxygen measurement***: DO should be measured in situ or in the field, as concentrations may show a large change in a short time if the sample is not adequately preserved. Even when it is preserved, as in a Winkler analysis, it is advisable to run the titrations within three to six hours from the time the sample was taken. DO concentrations may be determined directly with a DO meter, optode 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.

The samples for oxygen determinations are always taken as a vertical series starting from the uppermost layer in the epilimnion (usually one metre) and finishing in the hypolimnion at a depth that is one metre above the bottom sediment.

***Turbidity and transparency***: this is an optical measure of suspended sediment such as clay, silt, organic matter, plankton and microscopic organisms in a water sample. Whenever possible, turbidity should be measured in-field, since some of the particulate matter will settle or adhere to the container wall during transportation. Furthermore, changes in the pH of the sample may cause the precipitation of carbonates and humic acids, affecting the turbidity of the sample. Turbidity can be measured with turbidity meters that measure light-scattering by the suspended particles.

Although optical devices are available for measuring the intensity of solar radiation at depth in the water column, the simple procedure of determining transparency with a Secchi disc still retains its value. The method is to observe the depth at which a 30-cm-diameter disc, 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 disc is lowered, allow it to drop a little farther and then determine the point of re-emergence as the disc is raised. The mean of the two readings is known as the Secchi disc transparency.

## 4. Other important parameters that can be measured in situ

***Total suspended solids***: suspended particles affect water clarity and light penetration, temperature, the dissolved constituents of surface water, the adsorption 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. Analyses of solids 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.

TSS is a measure of the material collected on a glass fibre filter ($\phi$:0.45 µm and dried to a constant weight at 103°C–105°C. If the suspended matter clogs the filter and prolongs filtration, the weight difference between the total solids content (also dried at 103°C–105°C) and the total dissolved solids (filtrate dried to constant weight at 180°C) may be used to estimate the TSS. TSS can also be determined, using optical instruments (backscattering of light).

***Chlorophyll***: chlorophyll fluoresces red when excited by blue light and this property can be used to measure chlorophyll levels and indicate algal biomass. Direct and continuous measurement of chlorophyll fluorescence can be made with a fluorometer, which can be used in situ by pumping water through it or, for some specially designed instruments, by lowering it into the water. Chlorophyll can also be determined in situ by optical spectral instruments, using the reflectance spectra, and naturally from water samples in a laboratory.

***Carbon***: The principle of all methods for the determination of total carbon (TC) in water is oxidation of the carbon to $CO_2$. Oxidation may be carried out by combustion, chemical reaction by the wet method using appropriate oxidizing agents, UV irradiation or any other appropriate procedure. The $CO_2$ formed may be determined directly or indirectly following reduction to another component (methane, for example).

Various analytical methods have been suggested, some of which are:

- Infra-red spectrometry;
- Volumetric determination;
- Thermal conductivity;
- Conductimetric measurement;
- Coulometric measurement;
- Specific $CO_2$ electrode;
- Flame ionization, following methanization.

A water sample may contain variable amounts of dissolved and particulate organic carbon, organic carbon originating from more or less volatile substances and dissolved mineral carbon (carbonates, carbon dioxide) and particulate carbon (active charcoal). The different matrices of the specimens that result from the presence of these forms of carbon in variable proportions must be taken into consideration before the analysis, because they largely determine what apparatus and procedure to select. Total fulvic and humic acid content can be determined photometrically and their separate determination can be made with spectrophotometric methods.

***Alkalinity***: alkalinity is measured commonly by titration, using either a burette or the drop-count technique. A sample is titrated with an acid solution which neutralizes the alkaline species present. The endpoint is determined by observing a colour change or by titrating to a pH value of 4.5, using a pH electrode as an indicator. The volume of titrant required to change the colour to reach the endpoint is then used to calculate total alkalinity. Both methods have limitations: sample colour or turbidity affects the operator's ability to detect the colour change; use of a burette or dropper is tedious and time-consuming. Total alkalinity test kits, which simplify routine alkalinity measurement, are ideal for field use.

***Nutrients***: the measurement of nutrients (phosphates, nitrates) is a significant and widespread requirement that is currently met mostly by water-sampling or the deployment of expensive wet-chemical water analysers but there are also rapid developments in less expensive methods. Remote spectral sensing can be used to obtain information about large-scale distributions of nutrients in surface water but direct measurement methods are required for measurements on smaller scales (e.g. in creeks, rivers, wastewater, outfalls, etc.) for QA and evaluation of the remote-sensing data and for more accurate measurements. Optical spectral sensing techniques have been developed recently that provide reagent-free measurement of nutrients using UV absorption spectrophotometry.

In situ nutrient analysers are available for high-frequency time-series determination of nutrient concentrations in marine and freshwaters. Versions are available for the measurement of nitrate, phosphate, silicate and ammonia. Some analysers may be deployed unattended for periods of one to three months, although much longer deployments have been achieved.

***Microbiological indicators***: there is a strong need for the detection of pathogens, on-site and effectively in real-time (the "lab-to-sample" approach), to avoid the costs and delays associated with water-sampling and laboratory analysis. There is considerable interest in the development of toxicity sensing to overcome the problems associated with identification of individual target species from a large number of possibilities.

There are rapid screening technologies, from which results may be obtained within hours and there is an obvious push towards desktop and portable systems. They can detect, for example, the normal intestinal bacterium Escherichia coli as an "indicator" organism and total coliform bacteria for a wide variety of water-testing applications. In addition, the following bioagents may be detected: clostridium botulinum neurotoxin, staphylococcal enterotoxins (A and B), bacillus anthracis, yersinia pestis and also cholera toxin sub-units and tetanus toxin.

Methods for detecting the presence of faecal material have been developed which are based on the presence of "indicator" organisms, such as E-coli. Such methods are cheap and simple to perform and some have been developed into field kits, particularly for use in developing countries.

***Metals***: the low concentrations of metals in natural waters require determination by instrumental methods. Photometric methods, sometimes in combination with extraction, are the oldest and most inexpensive techniques (see various methods handbooks). Potentiometric methods, employing ion-selective electrodes, are also available for various methods for monitoring different metals in the field.

As these have high detection limits, however, they can only be used for the analysis of comparatively polluted waters. Atomic absorption methods are the most widely used for detecting lower levels of metals.

Inductively coupled plasma-mass spectrometry (ICP-MS) or inductively coupled plasma-optical emission spectroscopy (ICP-OES) are highly sensitive techniques that are capable of determining a range of metals and several non-metals.

## 5. Traditional water-sampling for laboratory chemical and biological analysis

The collection of water samples may seem a relatively simple task. More than the simple dipping of a container into water or the pumping of groundwater from the well is required, however, to obtain representative water samples and to preserve their integrity until they are analysed in the laboratory. The quality of the data collected depends first and foremost on how good the sample is, i.e. 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 making field measurements contributes to the good quality of the data, increases their precision and accuracy and contributes to the overall improvement of the WQ management process.

***Collecting surface water samples***: the type of surface-water sample to be collected is determined by a number of factors such as:

- The objectives of the study, including the parameters of interest and the precision and accuracy needed;
- The characteristics of the system being studied, including the flow regime, climatic conditions, industrial inputs, groundwater infusions, tributaries, the homogeneity of the body of water and the aquatic life present;
- The resources available, i.e. manpower, equipment and materials.

It is recommended that the design of the field-sampling programme be tested and assessed by a pilot projector in the initial rounds of sampling to ensure both its effectiveness and efficiency with respect to the objectives of the study.

***Groundwater samples***: these samples can be collected from wells and springs. Depending on the purpose of the monitoring, the depth or the resources available, automatic sampling and analysis can be done in situ by using water-quality sensors, thus avoiding atmospheric contamination of the groundwater sample.

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

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

The collection of grab samples is appropriate when it is desired to:

- Characterize WQ at a particular time and location;
- Provide information about minima and maxima;
- Allow collection of variable sample volumes;
- Deal with a stream which does not flow continuously;
- Analyse parameters which are likely to change;
- Establish the history of WQ, based on relatively short time intervals.

Grab samplers may be divided into two broad categories: those appropriate for taking samples in which only non-volatile constituents are of concern and those for taking samples in which dissolved gases and other volatile constituents must be analysed.

No simple technique is available for obtaining a representative sample of a surface film such as oil or grease. A grab sample can be taken with a solvent-cleaned glass bottle opened just below the surface but the sample will only be qualitative. A grab sample may be taken, using a "sampling iron" with an appropriate bottle, a Van Dorn bottle, a Kemmerer-style bottle or a pump-type sampler.

***Composite samples***: a composite sample is obtained by mixing several discrete samples of equal or weighted volumes in one container, an aliquot of which is then analysed for the constituents of interest or by continuously sampling the flow. There are two main types of composite sample:

- Sequential or time composite made up by:
  - Continuous constant sample pumping; or
  - Mixing equal water volumes collected at regular time intervals.
- Flow-proportional composite obtained by:
  - Continuous pumping at a rate proportional to the flow;
  - Mixing equal volumes of water collected at time intervals, which are inversely proportional to the volume of flow; or
  - Mixing volumes of water proportional to the flow collected during or at regular time intervals.

A composite sample provides an estimate of average WQ condition over the period of sampling. An obvious advantage is in the economy of reducing the number of samples to be analysed. On the other hand, composite samples cannot detect changes in parameters occurring during the sampling period.

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

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

These devices can sometimes be programmed to sample over extended periods of time. They reduce costly personnel requirements, if frequent sampling is required. If the site has automatic flow measurement, they can also provide flow-proportional samples. Both composite and individual sample models are available. Regular maintenance and scrupulous cleanliness are essential if the samples are to be representative. It is difficult to obtain representative samples of suspended solids because of gas release on pumping, which may also be a problem in sampling for dissolved gases.

## 6. Special sampling procedures

***Rivers***: sampling difficulties arise when the only acceptable sampling point lies in a non-homogenous – i.e. unmixed – length of a river. Individual samples will then not be representative of the 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 analysed 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 will ignore 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 – a time-consuming process, however.

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.

***Lakes***: many lakes exhibit seasonal thermal stratification. When stratification exists, a number of samples will be taken vertically, 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, 100-m 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 also be sampled in the neighbourhood of its upper boundary layer.

***Groundwater***: such samples will normally be taken at existing wells or boreholes. The water should be pumped for some 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 borehole and abstract at different levels. Probes to measure conductivity and other variables may be lowered into the well and their profile plotted.

As the groundwater 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 $CO_2$ 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 oxidized 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.

## 7. Biological assessment and fish tests

One of the oldest biological research methods of WQ is the examination of the biomass and composition of phytoplankton by microscopy. The considerable advantage of this method is that important information on species composition and dominant species is simultaneously achieved.

A good characteristic is the total volume (or total wet weight) of phytoplankton estimated by microscopy. Many classifications based on total amount have been presented. An indirect but practical method to obtain a relatively reliable estimation of the phytoplankton quantity is chemical chlorophyll analysis. These two characteristics are significantly correlated with each other. Different classifications have therefore been established, based on chlorophyll-a concentrations, which can also be determined by in situ optical methods.

Macroinvertebrates are the most commonly used group of organisms in biological monitoring in industrialized countries. In China, for example, biological assessment of water pollution in rivers and aquatic ecosystems has been carried out successfully with the use of plankton, benthos and fish as indicators. Algae are often selected as indicators of eutrophication and increases in turbidity. Bacteria are useful indicators for a range of pollutants and faecal coliform. They respond quickly to environmental changes.

It is crucial to appreciate that ecosystems function as one entity in which feedback mechanisms regulate the stability between the various trophic levels: primary producers, decomposers, herbivores, etc. Natural fluctuations or point-pollution discharges can be considered at an ecosystem level. An impact at any trophic level is felt at every point within the food web and, if severe, leads to an imbalance in the entire ecosystem. Biodiversity studies are important for achieving an overall picture of the state of the ecosystem.

The choice of indicator must be carefully considered, as there is a wide range of sensitivities between organisms to stimuli and chemicals. Moreover, in view of the large number of samples required to obtain reliable results and the associated cost, it is advisable to limit the number of assays to only a few important species to ensure availability of funds for a satisfactory monitoring of temporal trends of some priority contaminants over time.

***Sampling for microbiological analysis***: the selection of microbiological parameters for monitoring depends on the aim. If this is to follow the level of faecal contamination in the lake or river water, enumeration of indicators of faecal contamination shall be monitored. If the identification of actual health risks is of concern, then pathogen detection is needed. In the selection of parameters, it is necessary to consider geographical, socio-economic and technological aspects. It is reasonable to set minimum requirements for the monitoring and to allow additional parameters to be selected on the basis of local circumstances.

Today, it is not possible to monitor the occurrence of every pathogen possibly present in lake or river water. The pathogens transmitted through faeces and capable of causing epidemics via contaminated water are the main concern. Direct, routine monitoring for the detection of these pathogens is still difficult but the rapid developments in molecular methods (e.g. microarrays or DNA chips) may, in the future, offer powerful methods for the direct monitoring of different pathogens simultaneously. The main emphasis in the protection of WQ and human health will, however, be on the restriction of faecal contamination.

Positive identification of the pathogenic bacteria Salmonella, Shigella or Vibrio spp. can be quite complex, requiring several different measurement methods. A special survey may be undertaken if a source of an epidemic is suspected or if a new drinking-water supply is being tested. As these organisms usually occur in very low numbers in water samples, it is necessary to concentrate the samples by a filtration technique prior to the analysis. Although methodologies for identification of viruses are constantly being improved and simplified, they require advanced and expensive laboratory facilities. Local or regional authorities responsible for WQ may be unable to provide such facilities. Suitably collected and prepared samples can easily be transported, however, making it feasible to have one national or regional laboratory capable of such analyses.

## 8. Kits

Partly due to resource and time constraints to establish well-equipped WQ testing laboratories in sufficient numbers, and partly due to the dynamic nature of water quality, there is a definite place for simplified field-test kits in an overall approach to WQM, especially in developing countries. Kits can accomplish the initial screening and periodical monitoring of waters. Such tests are relatively inexpensive and can be conducted at water-user level, thereby improving the potential for involvement of user communities. Results of kits can be supported by detailed analysis of problem sources in proper laboratories.

Several companies/agencies/NGOs/government laboratories have done a lot of work to produce kits which use titration principles but are light, can stand up to rough “travel” and still give fairly accurate results. These field test kits can be used anywhere and by anyone who can read the instructions. They consist of a sample bottle with a marking to indicate that the sample to be tested must be filled up to that mark. When the colour of the sample changes, the addition of the solution is stopped and the number of drops added is multiplied by a factor given in the instruction manual to arrive at the quantity of the parameter in mg/litre of water or parts per million.

Test kits used for testing the bacteriological content in water are slightly different. Some have a bottle in which the water sample to be tested is put and into which another solution is added. Another kit used for such tests is called a "dipslide": a slide made of an inert plastic material, coated with a nutrient kept inside a sealed container. Used in conjunction with an incubator, it avoids the need for lengthy laboratory-based procedures. Dipslides can be used to monitor microbial growth wherever the potential may exceed 1 000 organisms per millilitre of sample fluid. Tests for bacteriological contamination using such kits indicate only the presence or absence of contamination (also called a GO/NO GO result) and not its extent. UNICEF has also developed a simple kit using the $H_2S$ strip test, which is intended to detect or quantify hydrogen-sulphide-producing bacteria, considered to be associated with faecal or bacterial contamination.
In conclusion, there are field kits (discs, test strips, drop-test kits, dipslides) that allow qualitative testing for E-coli and bacterial contamination in general, DO, pH, electrical conductivity, temperature difference, turbidity and level of nitrite, nitrate and orthophosphate ions, arsenic, fluoride, iron, residual chlorine, chloride, alkalinity, hardness and aluminium and arsenic.

Using small samples (5-10 ml), these kits allow quick qualitative testing and recording of results anywhere. Results are taken by comparison with a colour chart if the sample turns a colour and are qualitative. The kits are useful for general water-testing. A choice can be made from a range of equipment and parameters to use individually or combine into a single test kit.

## 9. Remote-sensing (satellite, airborne or ground-based)

There are some unique challenges to the application of remote-sensing to WQ in inland and coastal regions:

- These waters are a complex mixture of constituents, the composition of which varies across water bodies, regions and globally. Unlike blue open-ocean surface waters, which are generally clear and typically contain only low concentrations of phytoplankton, inland and coastal waters contain a myriad of both dissolved and particulate matter reflected in their blue-green to green and brown colours;

- Inland and coastal waters may exhibit heterogeneous patterns of water quality. These patterns and associated processes and phenomena are dynamic, short-lived and small-scale and may be missed by satellites with inadequate spatial and/or temporal observing capabilities;

- Small water bodies (lakes) are irregularly distributed across the terrestrial landscape, often representing only a few pixels in a satellite image and confounded by a number of "edge" pixels;

- Remote-sensing generally only represents surface conditions down to the depth at which a white and black coloured (Secchi) disc can be seen;

- A translation is required from the observed colour in visible and nearby infra-red wavelengths to those WQ relevant properties primarily of interest to a manager or decision-maker (e.g. bacteria or eutrophication status).

Knowledge of the spatial distribution of different biological, chemical and physical variables is essential in environmental water studies, as well as for resource management. Coupled with advanced processing methods and improved sensor capabilities, recent years have therefore seen increasing interest and research in the remote-sensing of the quality of inland and coastal waters. Unless a water body is sufficiently instrumented by in situ sensors, remote-sensing is the only satisfactory method for detecting the quality of remote and large inland waters.

Waters, whose optical properties are influenced by more than just phytoplankton, are determined to be complex waters (unlike ocean waters). These additional non-algal optical properties may be composed of dissolved organic matter, dead particulate organic matter and particulate inorganic matter. The source can be allochthonous (via inflow from surrounding land) or autochthonous (produced within the water body by biological or chemical interactions). Many inland and coastal waters are significantly affected by anthropogenic influences such as nutrient enrichment or increased erosion-induced suspended material. In combination with the sometimes complex hydrological situation, highly contrasted structures evolve in time and space in these aquatic environments. It is obvious that a water system with different optically active substances with temporal and spatial variations is more complex and therefore requires more sophisticated analysis models for remote-sensing-based separation of the water constituents than the single optical component ocean waters. As many spectral bands as possible are therefore required across the visible and nearby infra-red spectrum, where light penetrates the water column. This is the reason for multispectral remote-sensing and, if available, imaging spectrometry is applied to coastal and inland water environments instead of a few bands in the blue-to-green spectral areas.

The colour of the water is caused by light-scattering and absorption processes, as well as light emission by substances in the water column and reflectance by the substrate (seagrass, macroalgae, corals, sand, mud, benthic microalgae, etc.). For the retrieval of different water constituents, as well as substrate type or cover from a remotely sensed multi- or hyperspectral signal within a remote-sensing image, a suite of inversion methods is available, ranging from the often used, but less precise regression methods, to physics-based inverse modelling or inversion methods. The water-colour data can be used to determine the concentrations of the water constituents and the substrate cover quantitatively. The range of optical WQ properties measurable in the water column that may be estimated by remote-sensing has increased from suspended matter to include properties such as vertical attenuation coefficients of downwelling and upwelling light, transparency, coloured dissolved organic matter, chlorophyll-a contents, blue-green algal pigments and even red tides and blue-green algal blooms. If the water column is sufficiently transparent, it has been demonstrated that maps may be made of seagrasses, macroalgae, sand and sandbanks, coral reefs, etc. Other applications and parameters are water clarity, macrophyte surveys, slick and spill detection and underlying geophysical parameters, such as surface temperature, winds, currents and waves, bathymetry and flood area.

Correct simulations of the reflectance spectrum (colour) from waters and suitable inversion methods drastically reduce the requirement for traditional in situ measurements in the long term. As in situ detection and monitoring become more expensive (due to rising labour costs) and is shown to be less exact, a remote-sensing based approach is beginning to make more and more economic sense. It will be necessary to have available local airborne multi- or imaging-spectrometry systems or similar types of data from space sensors. Imaging spectrometry seems to be the remote-sensing instrument of choice for the future for the accurate detection and monitoring of optical WQ and substrate variables. The increased sophistication and automation of in situ sensors, however, may prove to be a bonus for remote-sensing, as an integrated, automated in situ sensor with a dedicated, remote-sensing monitoring system could provide continuous data, even under unsuitable conditions.

Some countries and institutions have developed new operational products using satellite remote-sensing, such as the operational satellite-based WQ products of the Finnish Environment Institute. These are the surface-water temperature of the Baltic Sea and large lakes and surface algal blooms, turbidity and chlorophyll a of the northern Baltic Sea. The satellite images used are from NASA/Landsat, NOAA/AVHRR, Terra/MODIS and ENVISAT/MERIS and the operational products are available on their Websites. The use of satellite images requires reference measurements at the monitoring stations for algorithm calibration and validation. Remote-sensing includes also ground-based teledetection, which permits the characterization of the spatial and temporal changes obtainable by in situ methods.

Finally, some of the world's most advanced remote-sensing laboratories are now developing remote-sensing-based data-assimilation methods, where biogeochemical models, hydrodynamic models, in situ sensor data and quantitative remote-sensing methods are being integrated to provide hindcasting, nowcasting and forecasting of water quality.

## 10. Advanced instrumental analysis

***Atomic absorption spectrophotometry*** (***AAS***): AAS is commonly used in many analytical laboratories for determining trace elements in water samples and in acid digests of sediment or biological tissues.

AAS is based on the principle that metallic elements in the ground state will absorb light of the same wavelength that 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, unionized "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. While the simplest analysis procedure is direct aspiration of a liquid sample into the atomizer-burner assembly, there may be limitations of detectability or interferences that make further sample processing necessary to increase concentration or isolate the element of interest from interfering species.

As already mentioned under the section on metals above, ICP-MS or ICP-OES are techniques that are highly sensitive and capable of determining a range of metals and several non-metals.

***Gas chromatography***: this is a highly sophisticated, analytical procedure. It should be used only by analysts who are experienced in the techniques required and competent to evaluate and interpret the data.

In gas chromatography, a carrier phase (a carrier gas) and a stationary phase (column-packing or capillary column-coating) are used to separate individual compounds. The carrier gas is nitrogen, argon/methane, helium or hydrogen. For packed columns, the stationary phase is a liquid that has been coated on an inert granular solid (the column packing) that is held in a length of borosilicate glass tubing. The column is installed in an oven with the inlet attached to a heated injector block and the outlet attached to a detector. Precise and constant temperature control of the injector block, oven and detector is maintained. Stationary-phase material and concentration, column length and diameter, oven temperature, carrier-gas flow and detector type (e.g. flame-ionization detection for polycyclic aromatic hydrocarbons, electron-capture detection for phenolics, organochlorinated insecticides and PCBs, thermionic specific detection for nitrogen-containing compounds or organophosphates, mass selective detection, etc.) are the controlled variables.

When the sample solution is introduced into the column, the organic compounds are vaporized and moved through the column by the carrier gas. They travel through the column at different rates, depending on differences in partition coefficients between the mobile and stationary phases.

***Flame photometry***: this makes possible the determination of trace amounts of lithium, potassium, sodium and strontium, although other methods of analysis for lithium and strontium are preferred.

The sample (after dilution, if necessary) is sprayed into a butane- or propane-air flame. The alkali metals absorb energy from the flame and become raised to an excited energy state in their atomic form. As these individual atoms “cool” they fall back into their original unexcited or ground state and re-emit their absorbed energy by the radiation of specific wavelengths, some of which are within the visible region of the electromagnetic spectrum.

This discrete emission is isolated by an optical filter and, for low concentrations, is proportional to the number of atoms returning to the ground state. This, in turn, is proportional to the number of atoms excited and, hence, to the concentration of the element in the solution.

The minimum detection level for both potassium and sodium is approximately 100 μg $l^{-1}$. The upper limit is approximately 10 mg $l^{-1}$, but this may be extended by diluting the samples.

## 11. Sampling procedures for isotopes in hydrological investigations

Detailed knowledge of hydrological systems forms an integral part of the sustainable resource development. Isotope techniques are effective tools for satisfying critical hydrological information needs like the origin of groundwater, recharge, residence time, impact of climate change on water resources and interconnections of water bodies, among others.

Applications of isotopes in hydrology are based on the general concept of “tracing”, in which either intentionally introduced isotopes or naturally occurring (environmental) isotopes are employed. Environmental isotopes (either radioactive or stable) have a distinct advantage over injected (artificial) tracers in that they facilitate the study of various hydrological processes on a much larger temporal and spatial scale through their natural distribution in a hydrological system. Thus, environmental isotope methodologies are unique in regional studies of water resources to obtain time- and space-integrated characteristics, whereas the artificial tracers are generally effective for site-specific, local applications.

In hydrological investigations, isotope techniques should be used routinely, together with hydrochemical and hydrogeological techniques. As all isotopic, hydrogeological, hydrochemical and hydrodynamic interpretations are space- and time-related, it is imperative to consider all the related aspects of water-sampling and prevailing hydrogeological conditions in a study area. More specific information on isotope applications in hydrological and environmental studies is available from the Isotope Hydrology Section of the International Atomic Energy Agency and WMO.

## Appendix 1. Summary of water-quality guidelines and standards by international organization or country

Source: GEMS/Water 2008, 111-112

| Geographic region | WHO (guidelines) | European Union (standards) | Canada (guidelines) | Australia (guidelines) | New Zealand (guidelines) | Japan (standards) | United States of America (standards) |
|---|---|---|---|---|---|---|---|
| **Parameters** | **mg/l** | **mg/l** | **mg/l** | **mg/l** | **mg/l** | **mg/l** | **mg/l** |
| Algae, blue-green | | | | | >1 toxic/ 10 ml | | |
| Alkalinity | | | | | | | |
| Aluminium | 0.2 | 0.2 | 0.2 | 0.2 | | 0.2 | 0.2 |
| Ammonia - unionized | * | 0.5 | 0.5 | 0.5 | | | |
| Ammonia - total | | | | | | | |
| Antimony | 0.005 | 0.005 | 0.006 | 0.003 | 0.003 | | 0.006 |
| Arsenic | 0.01 | 0.01 | 0.01 | 0.007 | 0.01 | 0.01 | 0 |
| Barium | 0.3 | # | | 0.7 | 0.7 | | 2 |
| Beryllium | * | # | | | 0.004 | | 0.004 |
| Bismuth | | | | | | | |
| Boron | 0.3 | 0.001 | 0.001 | 4 | 1.4 | 1 | |
| Bromate | * | 0.01 | 0.01 | 0.02 | 0.025 | 0.01 | 0 |
| Cadmium | 0.003 | 0.005 | 0.005 | 0.002 | 0.003 | 0.01 | 0.005 |
| Calcium | * | | | | | 300 | |
| Chloride | 250 | 250 | 250 | 250 | | 200 | 250 |
| Chlorophyll a | | | | | | | |
| Chromium | 0.05 | 0.05 | 0.05 | | 0.05 | 0.05 | 0.1 |
| Cobalt | | | | | | | |
| Coliform - faecal | # | | | | | | |
| Coliform - total | # | 0/100 ml | 0/100 ml | | | 0 | 0 |
| Colour | # | # | & | | | >5 degrees | 15 colour units |
| Conductivity | ^ | ^ | ^ | | | | |
| Copper | 2 | 2 | 2 | 1 | 2 | 1 | 1.3 |
| Cyanide | 0.07 | 0.05 | 0.05 | 0.08 | 0.08 | 0.01 | 0.2 |
| Enterococci | | 0/250 ml | 0/250 ml | | | | |
| Escherichia coli | | 0/250 ml | 0/250 ml | | >1/100 ml | | |
| Fluoride | 1.5 | 1.5 | 1.5 | 1.5 | 1.5 | 0.8 | 2 |
| Fluoride - inorganic | | | | | | | |
| DOC | | | | | | | |
| Hardness | * | # | | & | | 300 | |
| Iron | # | 0.2 | 0.2 | 0.3 | 0.01 | 0.3 | 0.3 |
| Lead | 0.01 | 0.01 | 0.01 | | 0.01 | 0.01 | 0 |
| Lithium | | | | | 0.9 | | |
| Magnesium | | | | | | 300 | |

Appendix 1 continued

| Geographic region | WHO (guidelines) | European Union (standards) | Canada (guidelines) | Australia (guidelines) | New Zealand (guidelines) | Japan (standards) | United States of America (standards) |
|---|---|---|---|---|---|---|---|
| **Parameters** | **mg/l** | **mg/l** | **mg/l** | **mg/l** | **mg/l** | **mg/l** | **mg/l** |
| Manganese | 0.5 | 0.05 | 0.05 | 0.5 | 0.5 | 0.05 | 0.05 |
| Mercury | 0.001 | 0.001 | 0.001 | 0.001 | 0.002 | 0.0005 | |
| Mercury - inorganic | | | | | | | 0.002 |
| Methylmercury | | | | | | | |
| Molybdenum | 0.07 | # | | 0.05 | 0.07 | | |
| Nickel | 0.02 | 0.02 | 0.02 | 0.02 | 0.02 | | |
| Nitrate | | 50 | 50 | | 50 | | 10 |
| Nitrate + Nitrite | 50 | | | | | 10 | |
| Nitrite | | 0.5 | 0.5 | | 3 | | 1 |
| Odour | | & | & | | | & | |
| Oil and grease | | | | | | | |
| Ortho-phosphorus | | | | | | | |
| Oxygen - dissolved | | | | | | | |
| Particulate matter <2.5 µm (PM<2.5) | | | | | | | |
| pH | * | # | | 6.5–8.5 | | 5.8–8.6 | 6.5–8.5 |
| Phosphorus - total | | | | | | | |
| Potassium | | | | | | | |
| Rubidium | | | | | | | |
| Salinity | | | | | | | |
| Selenium | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.05 |
| Silver | # | # | | 0.1 | 0.02 | | 0.1 |
| Sodium | 200 | 200 | 200 | 180 | | 200 | |
| Solids – total dissolved (TDS) | * | # | | & | | | 500 |
| Solids – total suspended (TSS) | * | # | | | | | |
| Strontium - 90 | | | | | | | |
| Sulphate | 500 | 250 | 250 | 500 | | | 250 |
| Temperature | | | | | | | |
| Thallium | | | | | | | |
| Tin | * | # | | | 1 | | 0.0005 |
| Total organic carbon | | | | | | | |
| Tritium | | 100 Bq/l | | | | | |
| Turbidity | * | # | & | | | >2 degrees | n/a |
| Uranium | * | # | 0.02 | 0.02 | 0.002 | | |
| Vanadium | 1.4 | # | | | | | |
| Zinc | 3 | # | | 3 | | 1 | 5 |

## Appendix 2. Key features of each chemical and physicochemical quality element (QE) for lakes

| Aspect/feature | Transparency | Thermal conditions | Oxygenation conditions | Salinity | Acidification |
|---|---|---|---|---|---|
| Measured parameters indicative of QE | Secchi depth, turbidity, colour, TSS | Temperature | DO,TOC, BOD, COD DOC | Conductivity | Alkalinity, pH, ANC |
| Relevance of QE | Eutrophication, acidification | Hydrological cycle, biological activity | Production, respiration, mineralization | | Buffering capacity, sensitivity to acidification |
| Pressures to which QE responds | Agricultural, domestic and industrial discharges | Thermal discharges, water management in reservoirs | Eutrophication, organic pollution, industrial discharges | Industrial discharges, runoff | Acid rain, industrial discharges |
| Level and sources of variability of QE | High, influenced by alloctonous and autochthonous material | High, influenced by climate conditions, topography, morphology and waterbody dimensions | Variable, diel changes due to respiration/ photosynthesis | Low-medium, influenced by climatic events | Low-medium, influenced by climatic events |
| Monitoring considerations | Seasonal variation | Seasonal variation (mixing and stratification) | Diel variation, high gradient in stratified lakes | Seasonal variation | Seasonal variation |
| Sampling methodology | In situ using Secchi disc TSS, field sample collection followed by laboratory analysis turbidity, in situ turbidimeters, nephelometers; colour: in situ comparison to Forel-Ule scale or in laboratory | In situ using thermistor probes or reversing type Hg thermometer | Online data acquisition; in situ submersible probes; field sample collection followed by laboratory Winkler titration | In situ using submersible probes | In situ measurement of pH with probe; sample collection followed by laboratory analysis |
| Typical sampling frequency | Monthly/ quarterly related to the biological elements sampling periodicity; fortnightly or monthly during growth season in Nordic countries | Monthly/ quarterly | Depends on morphological characteristics of lake: daily/monthly or at the end of stratification periods (late winter if ice cover or late) summer | Monthly/ quarterly, should be measured during snowmelt or heavy rainfall events | Monthly/ quarterly, should be measured during snowmelt or heavy rainfall events |
| Time of year of sampling | All seasons | All seasons | All seasons | All seasons | All seasons |

Appendix 2 continued

| Aspect/feature | Transparency | Thermal conditions | Oxygenation conditions | Salinity | Acidification |
|---|---|---|---|---|---|
| Typical "sample" size | In situ observations, sample collections for chemical analyses (turbidity, TSS) | Water-column profile | Single measurements, water column profiles. 100 ml for Winkler titration | In situ water column profile, integrated epilimnion or single sample from outlet (depending on monitoring purpose) | Single sample from outlet of lake or water column profile |
| Ease of sampling/ measurements | Simple, using in situ probes or surface water sample | Simple, using in situ probes or water samplers | Simple, using in situ submersible probes or sample collection followed by titration | Simple, using in situ probe | Simple |
| Basis of any comparison of results/quality/ stations, e.g. reference conditions/best quality | Historical data or data from comparable pristine lakes | Historical data or data from comparable pristine lakes | Historical data or data from comparable pristine lakes | Historical data or data from comparable pristine lakes | Historical data or data from comparable pristine lakes |
| Methodology consistent across EU? | No | No | No | No | No |
| Current use in monitoring programmes or for classification in EU | Yes | Finland, France, Italy, Norway | Finland, France, Italy, Norway, Sweden | Belgium, Finland, France, Italy | Belgium, Finland, France, Italy, Norway, Sweden, UK |
| Existing monitoring systems meet requirements of WFD? | No | No | No | No | No |
| Existing classification system meets requirements of WFD? | No | No | No | No | No |
| ISO/CEN standards | No | No | ISO 5813:1983 DO ISO 5815:1989 BOD5 | Yes | Yes, no standard for ANC |
| Applicability to lakes | High | High | High | Moderate | High |

Appendix 2 continued

| Aspect/feature | Transparency | Thermal conditions | Oxygenation conditions | Salinity | Acidification |
|---|---|---|---|---|---|
| Main advantages | Simple to sample, possibly the most universally used parameter in limnology, a simple and powerful tool for tracking long-term trends | Simple to measure, fundamental to understand the hydrological cycle and lake ecology | Simple to sample and to measure, extremely useful because it can act as an integrator of lake health. | Simple to measure, conductivity is little influenced by anthropogenic inputs. A good correlation was found with the MEI conditions and phosphorus (P) concentration, allowing the determination of natural background (reference) concentrations for P. | Simple to measure, provides long-term trends in acidification. Alkalinity is little influenced by anthropogenic inputs (except in acidified and limed lakes). A good correlation was found with MEI alkalinity and phosphorus (P) concentration, allowing the determination of natural background (reference) concentrations for P. |
| Main disadvantages | No disadvantages | May require intensive monitoring for appropriate description of thermal conditions. | May require intensive monitoring following depletion events in stratified lakes. | Does not provide long-term information on trends. | None |
| Conclusions/ recommendations | Easy to monitor: the Secchi disc is widely used in limnology for assessing the biological conditions of lakes. In humic lakes, Secchi disc is not useful for assessment of eutrophication. | Important supporting parameter for interpreting ecological conditions; seasonal variation, variation with depth; horizontal variation should be monitored in large lakes. | Recommended and particularly important in deep/ stratified lakes and lakes with ice cover. | Important for lake characterization, e.g. gives an indication of lake mixing processes and metabolic activity. | Important for lake characterization; acidity is important because it governs the chemical form in which metals occur in water body. Alkalinity and Its related variables, pH and conductivity are important classification parameters. |

## Appendix 3. Key features of each biological quality element (QE) for lakes

| Aspect/feature | Phytoplankton | Macrophytes | Phytobenthos | Benthic invertebrates | Fish |
|---|---|---|---|---|---|
| Measured parameters indicative of QE | Composition, abundance biomass (chlorophyll a), blooms | Composition and abundance | Composition and abundance | Composition, abundance, diversity and sensitive taxa | Composition, abundance, sensitive species and age structure |
| Supportive/ interpretative parameters often/typically measured or sampled at the same time | Nutrient concentrations (total/soluble), chlorophyll, DO, POC, TOC, pH, alkalinity, temperature, transparency, fluorometric in situ monitoring | Nutrient concentrations (total/soluble) in lake water, sediment and pore water, substrate type, pH, alkalinity, conductivity, transparency, Secchi disc, Ca concentration | Nutrient concentrations (total/soluble) in lake water, sediment and pore water, substrate type, pH, alkalinity, conductivity, transparency, Secchi disc, Ca concentration | Nutrient concentrations (total/soluble), DO, pH, alkalinity, sediment analysis, toxicity bioassays | Nutrient concentrations (total/soluble), DO, pH, alkalinity, temperature, toxicity bioassays, trophic condition, zooplankton dynamics, ANC, TOC |
| Pressures to which QE responds | Eutrophication, organic pollution, acidification, toxic contamination | Eutrophication, acidification, toxic contamination, siltation, river regulation, lake-water level, introduction of exotic species | Eutrophication, acidification, toxic contamination, siltation, river regulation, lake-water level, introduction of exotic species | Eutrophication, organic pollution, acidification, toxic contamination, siltation, river regulation, hydro-morphological alteration (littoral) | Eutrophication, acidification, toxic contamination, fisheries, hydro-morphological alteration, introduction of exotic species |
| Mobility of QE | Medium | Non-mobile | Non-mobile | Low to medium, high when hatching | High |
| Level and sources of variability of QE | High inter- and intraseasonal variation in community structure and biomass; medium-to-high spatial variability | Medium-high seasonal variability in community structure and biomass, high spatial variability | Medium-high seasonal variability in community structure and biomass, low interannual variability, high spatial variability | Medium-high seasonal variability in community structure and biomass, high spatial variability | High spatial and seasonal variability, populations clumped with respect to habitat variables |
| Presence in lakes | Abundant | Abundant, rare in reservoirs | Abundant, rare in reservoirs | Abundant | Abundant |

Appendix 3 continued

| Aspect/feature | Phytoplankton | Macrophytes | Phytobenthos | Benthic invertebrates | Fish |
|---|---|---|---|---|---|
| Sampling methodology | Integrated or discrete samples in the water column, 1-5 sites per lake. A number of sampling gear types are commonly used such as hand-held bottles or flexible hose. | Aerial photography and/or transect sampling perpendicular to the shoreline | In situ observations of occurrence of natural substrate in littoral zone and/or among macrophyte beds, as well as scraping of substrata | Qualitative or semi-quantitative hand net or kick-sampling; Ekman grab or core sampling. Gear type depends on type of substrate, e.g. submerged aquatic vegetation – dip net; sand and clay – Peterson, Van Veen grabs; mud – Ponar, Ekman grabs | Electrofishing net captures, several types (e.g. gillnets, trammel net), trawls, acoustic |
| Habitats sampled | Water column (i.e. epilimnion, euphotic zone, metalimnion) | Macrophytes: littoral zone | Benthic substrata/ artificial substrata | Littoral, sublittoral and profundal | Littoral, open waters |
| Typical sampling frequency | Monthly/ quarterly In Nordic countries, 6 times/ summer | Yearly (late summer in Nordic countries), in natural lakes every 3-6 years | Varies from several times during the growing season to once a year | Yearly in natural lakes every 3-6 years; twice a year in littoral waters | Depends on water-body physical characteristics and objective, yearly |
| Time of year of sampling | All seasons, at least twice a year during spring turnover of temperature-stratified water bodies and summer stratification; in Nordic countries, no sampling during ice cover; more stations are required where high spatial variations are expected. | Late summer, decided by expert judgement | Quarterly/ six-monthly/ several times during the growing season; in Nordic countries, no sampling during ice cover | Early spring and late summer | Late spring to early autumn |

Appendix 3 continued

| Aspect/feature | Phytoplankton | Macrophytes | Phytobenthos | Benthic invertebrates | Fish |
|---|---|---|---|---|---|
| Typical sample effort | Often 1 station located in centre of lake | 3-10 transects per lake with 2-3 quadrants on each transect should be sufficient for the majority of lakes. | Lake-wide, 3-10 transects, littoral to sublittoral | Lake-wide composite samples of 2/3 grabs at each of 3-5 sub-littoral sites (7-15 grabs total) | Depends on type of sampling gear: for electrofishing, multiple habitats are selected in littoral areas based on substrate and cover. In shallow lakes, fish can be sampled with multimesh gillnets and random sampling; sampling time 10-12 h overnight, time less in small lakes and where fish densities are high. In deeper lakes, stratification related to depth zones is recommended. |
| Ease of sampling | Relatively simple | Variable, requires specialized sampling equipment and relatively specialized personnel with diving qualifications. Alternative methods can be used such as drop cameras/ ROV/rakes. | Relatively simple, some difficulty in deep lakes, boat required and expert knowledge of potential hazards in specific lakes | Relatively simple, some difficulty in deep lakes, boat required and expert knowledge of potential hazards in specific lakes | Difficult, requires specialized sampling equipment. |
| Laboratory or field measurement | Laboratory sample preparation followed by identification, counting and biomass determination under microscopy; algal toxin determinations in laboratory, chlorophyll a | Field measurements through aerial photography; samples from transects, laboratory identification to species; analysis of chlorophyll-a content, fresh, dry and AFDM, organic content | | Sample processing in the laboratory, at least 100 organisms per subsample (if possible) are identified to the appropriated taxonomic level frequently to species. | Sampling duration and area or distance sampled are recorded in order to determine the level of effort. In the laboratory, the specimens are identified to species, enumerated, measured, weighted and examined for the incidence of external abnormalities. |

Appedix 3 continued

| Aspect/feature | Phytoplankton | Macrophytes | Phytobenthos | Benthic invertebrates | Fish |
|---|---|---|---|---|---|
| Ease and level of Identification | Relatively simple for measures based on high taxonomic levels (e.g. family), difficult for identification to lower taxonomic levels (i.e. genus and species), biomass evaluation difficult | Identification to species relatively easy with exception of vegetative stages of certain genera (e.g. Potamogeton) | Identification to species relatively easy for high taxonomic groups (e.g. family), difficult for genus or species and biomass evaluation | Relatively simple for measures based on high taxonomic levels, difficult for identification to lower taxonomic levels (i.e. species) | Relatively easy, some difficulties may appear with rare specimens and early fry. |
| Nature of reference for comparison of quality/samples/ stations | Estimates of phytoplankton indicators/ indices (e.g. cell density, biovolume) to be expected in the absence of significant anthropogenic pressures | Reference values refer to typical indicator values (trophic ranking score (TRS)) and species diversity of flora in lakes not significantly affected by human activities | Little knowledge of reference conditions for phytobenthos in lakes, no established methodology | Reference values for diversity, abundance and distribution indices indicate expected conditions if the lakes are not significantly affected by human activities. References set using the 25 percentile of sites considered unimpaired in Sweden | Difficult to determine because only impacts of the physicochemical and hydromorphological pressures are to be addressed, not fisheries/stocking/ species introductions. |
| Methodology consistent across EU? | No | No | No | No | No |
| Current use in biological monitoring or classification in EU | Denmark, Finland, Ireland, Netherlands, Norway, Sweden and UK | Denmark, Netherlands, Norway, Sweden, and UK for conservation | No | Finland, Netherlands, Norway and Sweden | Finland, Netherlands, Norway and Sweden |

Appendix 3 continued

| Aspect/feature | Phytoplankton | Macrophytes | Phytobenthos | Benthic invertebrates | Fish |
|---|---|---|---|---|---|
| Current use of biotic indicators and indices/ scores | Taxonomic analyses (e.g. diversity indices, taxa richness, indicators species), phytoplankton total volume, presence of spring diatom blooms, occurrence of harmful algae, number and proportion of toxin-producing cyanobacteria (blue-greens) | TRS: species with low TRS values occur primarily in waters poor in nutrients, while high values are associated with eutrophic waters), level of diversity; relative occurrence of functional groups, Macrophyte Trophic Index (TIM). | No | Shannon's diversity index (measure of variation and dominance within animal communities); Average Score Per Taxa index related to the occurrence of sensitive (high-index value) and tolerant (low value) species; Danish fauna index (evaluation of the effects of eutrophication and organic pollution in the exposed littoral zone of lakes); Benthic Quality Index (BQI) to evaluate eutrophication and organic pollution in the deep bottom areas); Organic Carbon Ratio (complementary or alternative to BQI); acidity index (reflects the presence of species with varying pH tolerances.) | Index of Biotic Integrity incorporates measurements of fish assemblage composition and relative abundance; percentage of piscivore/ zooplanktivore (surrogate for age structure of fish community); percentage of invertivore/omnivore |
| Existing monitoring system meets requirements of WFD? | No | No | No | No | No |
| ISO/CEN standards | Under development | Under development | Under development | Under development | Under development |
| Applicability to lakes | High | High (very low in reservoirs) | High (moderate in reservoirs, depending on water management) | Moderate | High (moderate to low in reservoirs) |

Appendix 3 continued

| Aspect/feature | Phytoplankton | Macrophytes | Phytobenthos | Benthic invertebrates | Fish |
|---|---|---|---|---|---|
| Main advantages | Easy to sample, relevant for water quality and trophic state, used in many countries to evaluate eutrophication, easy to standardize | Easy to sample and identify (especially in shallow water), good indicator of a broad range of impacts, especially eutrophication and siltation | Easy to identify at family level, good indicator of eutrophication | Easy to sample (particularly in shallow waters), relatively simple to analyse, combines chemical and biological features. | Possibility of adapting classification systems to incorporate the requirements of WFD |
| Main disadvantages | Requires taxonomic expertise for species identification, high temporal variability requires frequent sampling, vertical and horizontal sample profiles required due to spatial heterogeneity | Difficult to sample in deep waters, not commonly used in EU, lack of information for comparison to reference; methodology needs to be developed to incorporate requirements of WFD. | No standard methods, lack of information for comparison with reference conditions, not commonly used in EU; methodology needs to be developed to incorporate requirements of WFD. | Not commonly used in EU, lack of information for comparison with reference; methodology needs to be developed to incorporate the requirements of WFD, time-consuming and expensive to analyse. | Requires specialized sampling equipment; methodology needs to be developed to incorporate the requirements of WFD. |
| Conclusions/ recommendations | Responds rapidly to changes in phosphorus concentration levels, identification to order or genus levels is suitable/ recommended for monitoring phytoplankton taxonomic composition; at present, it is not clear that identification to species represents a substantial improvement of the information value of the data, more work required in this area. | Key parameter for evaluating other biological components in lakes. Macrophytes hold an important role in the metabolism of lakes but their monitoring is not frequently used in the assessment of ecological quality. | The phytobenthos holds an important role in the metabolism of lakes but there is very little experience and information on the use of phytobenthos. Further work is required in this area. | Important parameter for evaluating other biological components: their use is at an early stage of development. Meaningful methodologies must be developed. The drafting of a suitable guideline is part of the method development of CEN. The CEN group recommends that the identification of benthic invertebrate fauna should be carried out to the species level. | Key biological quality element, can be difficult to interpret (fishery, biomanipulation, etc.). integrates all anthropogenic and natural impacts. The composition, abundance and structure of fish communities can be very useful indicators of ecological quality. Fish are only included in monitoring systems of a few EU Member States. |

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## Acronyms

| | |
|---|---|
| AAS | atomic absorption spectrophotometry |
| AFDM | ash free dry mass |
| ANC | acid neutralizing capacity |
| APHA | American Public Health Association |
| AVHRR | Advanced Very High Resolution Radiometer |
| BOD | biochemical oxygen demand |
| BQI | benthic quality index |
| CEN | European Committee for Standardization |
| COD | chemical oxygen demand |
| CSO | combined sewer overflow |
| DAP | data analysis protocol |
| DIN | Deutsches Institut für Normung (German Institute for Standardization) |
| DO | dissolved oxygen |
| DOC | dissolved organic carbon |
| DPSIR | Drivers-Pressures-State-Impact-Responses |
| EDI | equal-discharge increment |
| EEA | European Environmental Agency |
| EC | electrical conductivity |
| Eh | redox potential |
| ENVISAT | Environmental Satellite |
| EQC | external quality control |
| EU | European Union |
| Eurostat | Statistical Office of the European Commission |
| EWI | equal-width increment |
| GDE | groundwater-dependent ecosystems |
| GEMS | Global Environment Monitoring System (UNEP) |
| GEMStat | global water quality database (UNEP-GEMS) |
| GGMN | Global Groundwater Monitoring Network |
| GIS | Geographic Information Systems |
| GRDC | Global Runoff Data Centre |
| GWD | Groundwater Daughter Directive (EU) |
| IAEA | International Atomic Energy Agency |
| ICP-MS | inductively coupled plasma-mass spectrometry |
| ICP-OES | inductively coupled plasma-optical emission spectroscopy |
| IEC | International Electrotechnical Commission |
| IGRAC | International Groundwater Resources Assessment Centre |
| INSPIRE | Infrastructure for Spatial Information in the European Community (EU) |
| IQC | internal quality control |
| ISARM | International Shared Aquifer Resources Management |
| ISO | International Organization for Standardization |

| | |
|---|---|
| IT | information technology |
| JMP | Joint Monitoring Programme (WHO-UNEP) |
| LANDSAT | Land Satellite |
| LC | liquid chromatography |
| LEDs | light-emitting diodes |
| MEI | Morphoedaphic Index |
| MERIS | Medium Resolution Imaging Spectrometer |
| MODIS | Moderate-resolution Imaging Spectroradiometer |
| MS | mass spectrometry |
| NASA | National Aeronautics and Space Administration (USA) |
| NGO | non-governmental organization |
| NOAA | National Oceanic and Atmospheric Administration (USA) |
| OECD | Organization for Economic Cooperation and Development |
| PCBs | polychlorinated biphenyls |
| PM | particuate matter |
| POC | particulate organic carbon |
| POPs | persistent organic pollutants |
| QA | quality assurance |
| QAO | quality assurance officer |
| QC | quality control |
| QE | quality element |
| QM | quality management |
| QMS | quality-management system |
| redox | reduction-oxidation |
| ROV | remotely operated vehicle |
| SOP | standard operating procedure |
| TC | total carbon |
| TDS | total dissolved solids |
| TERRA | NASA Earth Observation Satellite |
| TIM | Macrophyte Trophic Index |
| TOC | total organic carbon |
| TRS | trophic ranking score |
| TSS | total suspended solids |
| UNECE | United Nations Economic Commission for Europe |
| UNEP | United Nations Environment Programme |
| UNICEF | United Nations Children's Fund |
| US EPA | United States Environmental Protection Agency |
| UV | ultraviolet |
| VKI | Von Karman Institute for Fluid Dynamics |
| WQ | water quality |
| WQM | water-quality monitoring |
| WISE | Water Information System for Europe |
| WFD | Water Framework Directive (EU) |

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