

CHAPTER 7

WATER QUALITY AND AQUATIC ECOSYSTEMS

7.1 GENERAL

This chapter discusses general aspects of water quality sampling and specific aspects related to the sampling of rivers, streams, lakes, reservoirs and groundwaters. More detailed discussions can be found in the references (WMO, 1988; UNEP/WHO/UNESCO/WMO, 1992) and in more specialized publications related to biological water quality (American Public Health Association and American Water Works Association, 1999; Genin and others, 1997). Guidance on chemical or isotopic sampling and analytical techniques are provided in a long list of references by the International Atomic Energy Agency (IAEA).

7.2 SPECIFIC REQUIREMENTS FOR WATER-QUALITY MONITORING

There are several approaches to water quality monitoring. Monitoring can be accomplished through a network of strategically located long-term stations, by repeated short-term surveys, or by the most common approach, a combination of the two.

The location of stations and samplings should take into account the following factors:

- (a) Accessibility and travel time to the laboratory (for deteriorating samples);
- (b) Available staff, funding, field and laboratory data handling facilities;
- (c) Inter-jurisdictional considerations;
- (d) Population trends;
- (e) Climate, geography and geology;
- (f) Potential growth centres (industrial and municipal);
- (g) Safety of personnel.

Sampling frequency depends on the objectives of the network, the importance given to the sampling station, the levels of the measured values, the spacial variability of the studied parameters and, most importantly, on the available funding. Without sufficient previous information, an arbitrary frequency is chosen based on knowledge of the local conditions. This frequency may be adjusted after a sufficient number of samples have been taken and analysed and note has been taken of the

substances present, their concentrations and the observed variability.

The choice of sampling stations also depends on the present and planned water use, the stream or lake water quality objectives or standards, the accessibility of potential sampling sites (landowners, routes, airstrips), the existence of services such as electricity, and already existing water quality data. Figure I.7.1 shows the steps to follow for the choice of sampling sites.

7.2.1 Water-quality parameters

The parameters that characterize water quality may be classified in several ways, including:

- (a) Physical properties, for example, temperature, electrical conductivity, colour and turbidity;
- (b) Elements of water composition, such as pH, alkalinity, hardness, Eh or the partial pressure of carbon dioxide;
- (c) Inorganic chemical components, for example, dissolved oxygen, carbonate, bicarbonate, chloride, fluoride, sulfate, nitrate, ammonium, calcium, magnesium, sodium potassium, phosphate and heavy metals;
- (d) Organic chemicals, for example, phenols, chlorinated hydrocarbons, polycyclic aromatic hydrocarbons and pesticides;
- (e) Biological components, both microbiological, such as faecal coliforms, and macrobiotic, such as worms, plankton and fish, or vegetation.

7.2.2 Surface-water quality

The programme objectives will often precisely define the best locations for sampling in a river or lake system. For example, in order to determine the effect of an effluent discharge on a receiving stream, sampling locations upstream and downstream of the discharge would be required. In other cases, both location and frequency of sampling will be determined by anti-pollution laws or by a requirement for a specific use of a water body. For example, a permit to discharge surface waters may outline details of monitoring, such as location, number of samples, frequency and parameters to be analysed.

Sampling strategies are quite different for different kinds of water bodies and media, for example, water, sediment or biota. If the objective concerns

the impact of human activities on water quality in a given river basin, the basin can be separated into natural and altered regions. The latter can be further subdivided into agricultural, residential and industrial zones. In acid-deposition studies, an important factor is the terrain sensitivity to the deposition. Figures I.7.2 and I.7.3 give some examples as to how sampling stations could be located to meet specific objectives on river and lake systems.

Collecting relevant information on the region to be monitored is an essential step in water quality assessment. This information includes the geological, hydrological and climatic aspects. In addition, demographic conditions and planned water use

(water intakes, waste outlets, main drainage, irrigation schedules and flow regulation) are also relevant.

For surface waters, the distance downstream to the point of complete mixing is roughly proportional to the stream velocity and to the square of the width of the channel. For shallow rivers, waters attain homogeneity vertically below a source of pollution. Lateral mixing is usually attained much more slowly. Thus, wide swift-flowing rivers may not be completely mixed for many kilometres downstream from a pollution point source. Lakes can be vertically stratified owing to temperature or high-density saltwater intake.

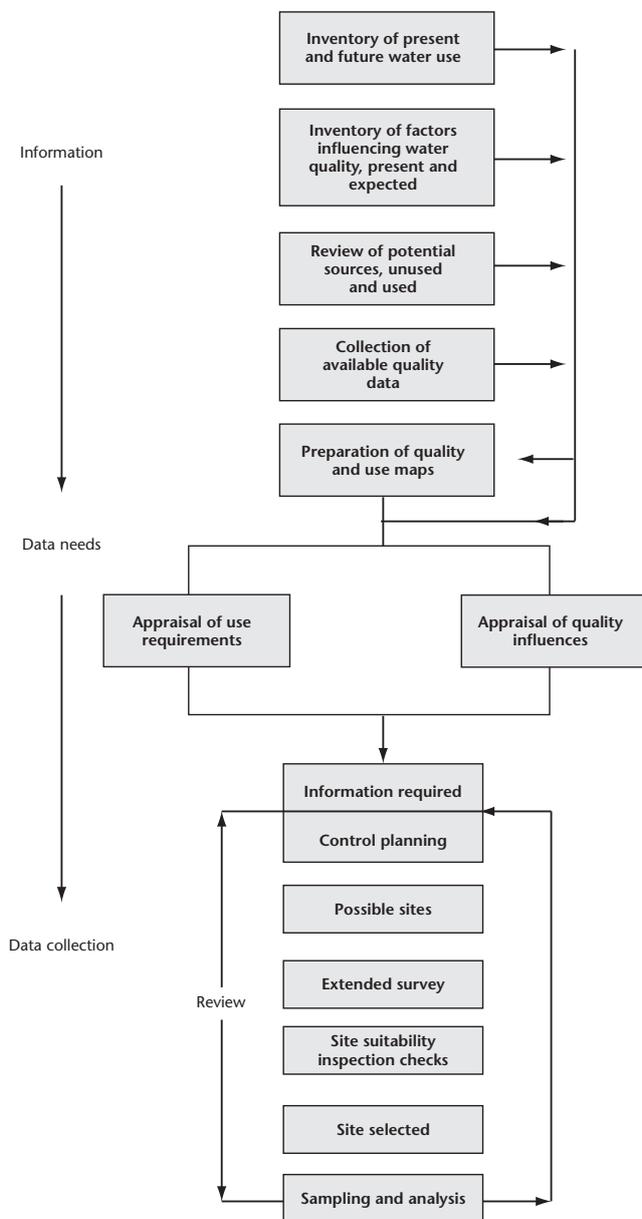
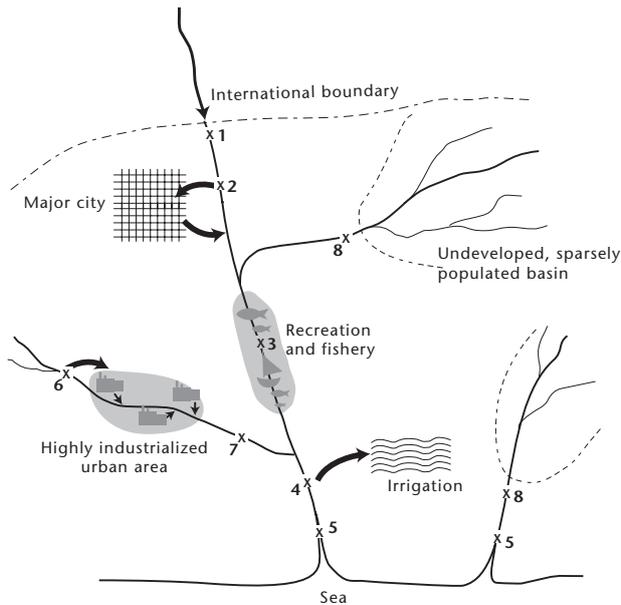
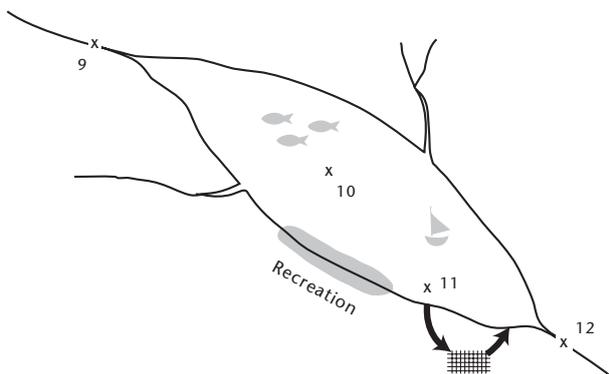


Figure I.7.1. Scheme for the selection of water quality sampling sites



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

Figure I.7.2. Monitoring site: rivers



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

Figure I.7.3. Monitoring site: lakes

Various protocols are recommended to determine representative sampling in the cross-section of the river. For example, six samples analysed in duplicate, taken from three positions across the river and at two depths or mid-depth samples at the quarter points, or other equal distance points across the width of the river. If a representative sample cannot be obtained, it is advisable to select another site, either immediately upstream or downstream. The other alternative is to obtain a flow-weighted composite sample from samples collected at verticals on the cross-section.

Longitudinal mixing of irregular or cyclic discharges into a river will have a secondary influence on the location of a sampling site. Their effects need to be taken into account in deciding the frequency of sampling and in interpreting the data.

For lake stations, the recommended practice is to sample for five consecutive days during the warmest part of the year and for five consecutive days every quarter. Alternatively, they should be sampled at least six times a year, together with the occasional random sample, to cover the periods such as open water prior to summer stratification, during mixing following summer stratification, under ice, and during the periods of snow melt and runoff.

Similarly, additional samples of rivers should be taken, if possible, after storm events and during snow melt and runoff. When parameters are plotted against time, some cyclic variation may be apparent amidst the random fluctuations.

The detection of cyclic events requires a sampling interval that is no longer than one third of the shortest cycle time and a sampling period at least ten times as long as the longest cycle. Therefore, long-period cycles will not be verified in the initial surveys, but become apparent during the operation of the network. In order to detect the cyclic variations, some random sampling is desirable, for example, on different days of the week or at different times of the day.

7.2.3 Precipitation quality

Specific aspects concerning the quality of precipitation, particularly sampling equipment, are discussed in 3.16. In general, sampling sites should be selected to give accurate and representative information concerning the temporal and spatial variation of chemical constituents of interest. Important factors to take into consideration are prevalent wind trajectories, sources for compounds of interest, frequency of precipitation events (rain, snow or hail), and

other meteorological processes that influence the deposition. The following criteria should be considered:

- (a) No moving sources of pollution, such as routine air, ground or water traffic, should be within 1 km of the site;
- (b) No surface storage of agricultural products, fuels or other foreign materials should be within 1 km of the site;
- (c) Samplers should be installed over flat undisturbed land, preferably grass-covered, surrounded by trees at distances greater than 5 m from the sampler. There should be no wind-activated sources of pollution nearby, such as cultivated fields or unpaved roads. Zones of strong vertical eddy currents, eddy zones leeward of a ridge, tops of wind-swept ridges and roofs of buildings, particularly, should be avoided because of strong turbulence;
- (d) No object taller than the sampler should be within 5 m of the site;
- (e) No object should be closer to the sampler than a distance of 2.5 times the height by which the object extends above the sampler. Particular attention must be given to overhead wires;
- (f) The collector intake should be located at least 1 m above the height of existing ground cover to minimize coarse materials or splashes from being blown into it;
- (g) Automatic samplers require power to operate lids and sensors and, in some cases, for refrigeration in the summer and thawing in the winter. If power lines are used, they must not be overhead. If generators are used, the exhaust must be located well away and downwind from the collector;
- (h) To address issues on a continental scale, sites should preferably be rural and remote, with no continuous sources of pollution within 50 km in the direction of the prevalent wind direction and 30 km in all other directions.

It may not be possible to meet all of these criteria in all cases. The station description should refer to these criteria and indicate the exact characteristics of each location chosen as a sampling site.

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

Precipitation sampling can be taken for each rain event or over a monthly period. In this case, rain is preserved for the same period before being analysed.

The analysis of event-precipitation samples enables pollutants associated with a particular storm to be determined, and a wind-trajectory analysis can determine probable sources. However, this sampling regime is very sensitive. The same statistical considerations concerning frequency of sampling apply here as for surface-water sampling.

7.2.4 Groundwater quality

The quality of groundwater is subject to change and deterioration as a result of human activity. Localized point sources of pollution include cesspools and septic tanks, leaks in municipal sewers and waste ponds, leaching from garbage dumps and sanitary landfills, seepage from animal feedlots, industrial waste discharges, cooling water returned to recharge wells, and leaks from oil tankers or pipelines. Larger geographical areas may suffer degradation of groundwater quality because of irrigation water returns, recharge into aquifers of treated sewage or industrial effluents, and intrusion of seawater in coastal zones or from other highly saline aquifers.

Water samples can be collected from free-flowing artesian wells or pumped wells. The wells should be pumped long enough to ensure that the sample is representative of the aquifer and not of the well. This is particularly necessary for open wells or where a well has a lining subject to corrosion. Portable pumps are needed in case of non-equipped wells. For sampling at different depths, mechanical or pneumatic equipment should be used to isolate specific sites. Sampling in shallow aquifers and saturated zones between impermeable layers can often be obtained by lowering a piezometer to the desired depth. The basic parameters used to define surface water quality can also be used for groundwater monitoring with the exception of turbidity, which is not usually a problem.

A good deal of hydrogeological information may be necessary to plan a groundwater sampling programme. Data on water levels, hydraulic gradients, velocity and direction of water movements should be available. The velocity of groundwater movement within the aquifers is highly variable. It can vary from 1 m y^{-1} in flat regions with low recharge to more than 1 m s^{-1} in karst aquifers. An inventory of wells, boreholes and springs fed by the aquifer should be drawn up and details of land use should be recorded.

For the collection of water samples (and water levels), an existing well is a low-cost choice, although they are not always at the best location or

made of non-contaminating materials. A well that is still in use and pumped occasionally is preferable to one that has been abandoned. Abandoned or unused wells are often in poor condition with damaged or leaky casings and corroded pumping equipment. It is often difficult to measure their water levels and there may be safety hazards.

Changes in groundwater can be very slow and are often adequately described by monthly, seasonal or even annual sampling schedules. In some cases, such as alluvial aquifers with large inputs from surface drainage, the temporal variation of water quality can be very relevant.

7.2.5 Sediment quality

Most of the selection criteria outlined in previous sections also apply to sampling for sediments (5.5.3 and 5.5.4). Therefore, only additional special recommendations will be described here.

For rivers where sediment-transport data are required, it is necessary to locate the sampling sites near a gauging station so that accurate stream-discharge information is available at all times. Sampling locations immediately upstream from confluences should be avoided because they may be subject to backwater effects. In streams too deep to wade, sampling sites should be located near bridges or cableways. When sampling from bridges, the upstream side is normally preferred. Sampling in areas of high turbulence, such as near piers, is often unrepresentative. Attention should also be paid to the accumulation of debris or trash on the piers, as this can seriously distort the flow and hence the sediment distribution. An integrated sample obtained by mixing water from several points in the water column according to their average sediment load can be considered as a representative sample as long as there is good lateral mixing.

The best places to sample bottom deposits in fast-flowing rivers are in shoals, at channel bends and at mid-channel bars or other sheltered areas where the water velocity is at its minimum.

Sampling sites should be accessible during floods, since sediment-transport rates are high during these times.

For identification of peak pollution loads in rivers, two cases must be considered:

- (a) For pollution from point sources, sampling should be done during low-flow periods, when pollution inputs are less diluted;

- (b) When pollutants originate from diffuse sources, such as runoff of agricultural nutrients or pesticides, sampling must be focused on flood periods during which the pollutants are washed out of the soil.

If one of the objectives is to quantify the transport of sediment in the river system, it should be noted that peak concentrations of sediment do not necessarily correspond with times of peak flow. Also, a series of high flow rates will lead to progressively lower sediment peaks – an exhaustion effect arising from the depletion of material available for re-suspension. For lakes, the basic sampling site should be located at the geographic centre of the lake. If the lake is very large (area > 500 km²), several base stations may be needed. If various sediment types are to be sampled, then data from acoustic surveys (echo-sounders) can be used both to identify the type of surficial material (sand, gravel or mud) and to indicate the presence of layering below the surface.

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

Sampling frequency in lakes is influenced by the concentrations of suspended sediment which is generally low. Sediment traps should be operated during the periods of maximum and minimum algal productivity and at times of high input of sediment from rivers. Repeat sampling of bottom sediments in lakes needs to take into account the rates of sediment accumulation. Basins in cool, temperate climates often have accumulation rates in the order of 0.1–0.2 mm y⁻¹. A re-sampling period of five years would then be too soon to provide worthwhile new information, unless the presence of a new pollutant were to be tested.

7.3 SAMPLING METHODS [HOMS E05]

Sampling is the process of collecting a representative quantity of water from a river, lake or well. Sampling methods are determined by a number of factors, including the type of material being sampled, the type of sample and the quality parameter being analysed, which in turn determine the equipment and procedures to be used.

Sampling procedures should be adapted to different components such as the following:

- (a) Steady: the components do not change with time;
- (b) Nearly steady: the components change with time but can be stabilized during a period of 24 hours or less after appropriate treatment;
- (c) Unsteady: the components change rapidly and cannot be stabilized.

Groups (a) and (b) include components that are laboratory tested, whereas those included in group (c) must be measured in situ.

7.3.1 Types of water samples

7.3.1.1 Grab samples

Grab samples are appropriate when it is desired to characterize water quality in a particular location. They are also used to establish the water quality history based on relatively short time intervals. A discrete grab (or spot) sample is taken at a selected location and depth. A depth-integrated grab sample is collected over the depth of the water column at a selected location and time.

7.3.1.2 Composite samples

A composite sample is obtained by mixing several samples to obtain an average value of water quality over the sampling period. Discrete or continuous sampling can be used and the mixing proportion is calculated on a time or discharge basis. A portion of the composite sample is then analysed. An obvious advantage is in the economy of reducing the number of samples to be analysed. However, composite samples cannot detect changes in parameters occurring during the sampling period.

There are two main types of composite samples: sequential and flow-proportional.

A sequential composite is constituted by continuous, constant sample pumping, or by mixing equal water volumes collected at regular time intervals.

A flow-proportional composite is obtained by continuous pumping at a rate proportional to the flow, mixing equal volumes of water collected at time intervals that are inversely proportional to the rate of flow, or by mixing volumes of water proportional to the flow collected at regular time intervals.

7.3.2 Collecting a representative water sample

For sampling at sites located on a uniform, well-mixed reach of 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.

In other cases the number of samples taken will depend on the width, depth, discharge, amount of suspended sediment being transported and aquatic life present.

Three to five verticals are usually sufficient; fewer are necessary for narrow or shallow streams.

One common method is the equal-width-increment method, in which verticals are spaced at equal intervals across the stream. The equal-discharge-increment method requires detailed knowledge of the streamflow distribution in the cross-section to subdivide the cross-section into verticals spaced in proportion to the incremental discharges.

7.3.3 Sampling for the analysis of water stable isotopes

To complete the study of water quality, it is interesting to consider the stable isotopes of a water molecule (oxygen-18 and deuterium). For instance, in coastal areas, the analysis of water stable isotopes – both in surface and groundwater – is useful to detect whether the salinity of inland waters is due to anthropic pollution, agriculture activities or upstream saline water. Isotopes also permit the localization of aquifers, the study of surface and groundwater linkage or the detection of natural processes affecting waters such as mixing or evaporation. Detailed information on the use of stable isotopes relevant to this subject is provided in the references (Mook, 2000).

Isotopic analyses require specialized laboratories, but the required water samplings procedures are quite simple. Sampling procedures that take account of the specific protocol for isotope sampling and conditioning are as follows:

- (a) Use painted glass bottles or high-density plastic (10 to 60 ml), generally 50-ml containers and hermetic sealing caps (reinforced by an interior plastic plug);
- (b) Rinse the containers three times with the water to be sampled;
- (c) Fill the bottle to the brim; this avoids evaporation, which could enrich the residual water and vapour pressure. If transported by air, bottles

should not be filled and the cap should be insulated with a paraffin film;

- (d) Snow samples should be collected in clean plastic bags (using non-contaminating gloves), then gradually melted before being put into containers;
- (e) Ice samples are preserved in the frozen state to reach the laboratory;
- (f) Samples should not be filtered except when they have been in contact with oil (used for protection against the evaporation of collected precipitation);
- (g) Sample may be preserved for a long time (more than a year) in a cool, dark environment.

7.3.4 Radioactivity measurement

Detailed instructions for the analysis of radioisotopes associated with water quality together with recommended containers and preservation methods are provided in the references (United States Geological Survey, 1984; IAEA, 2004) and further reading at the end of this chapter

7.3.4.1 Sources of radioactivity in water

Sources of radioactivity in water may be natural or due to human activities. The main natural sources are derived from the weathering of rocks containing radioactive minerals and the fallout of cosmic-ray nuclides. The major sources of radioactivity due to human activities are: uranium mining, nuclear-power industries, nuclear weapons testing, and the peaceful applications of nuclear materials and devices, for example, energy production.

The principal radionuclides introduced naturally into surface water and groundwater are uranium, radium-226, radium-228, radon, potassium-40, tritium and carbon-14. All but the last two derive from radioactive minerals. In areas where radioactive minerals are abundant, natural uranium is the major radioactive constituent present in water. Tritium and carbon-14 are produced by the interaction of cosmic-ray neutrons with nitrogen in the upper atmosphere. The tritium (^3H) isotope, a constituent present in water, is eventually rained out as precipitation. Radioactive carbon is incorporated into atmospheric carbon dioxide.

Both tritium and radioactive carbon are also produced by thermonuclear power testing and are currently used for groundwater dating (time elapsed between aquifer recharge and water sampling). Since 1970 the nuclear power industry has probably been the larger source of tritium. Strontium-90 and

Cesium-137 are the major man-made radioisotopes of concern in water.

The geochemical behaviour of a daughter element may be grossly different from that of the radioactive parent element, although its occurrence, distribution and transport may be governed by those of the parent. The International Commission on Radiological Protection recommends the maximum permissible concentration values in water.

7.3.4.2 Collection and preservation of samples for radioactivity measurement

Acceptable containers (generally four-litre bottles) are made of polypropylene, polyethylene or Teflon. They should be pretreated in laboratory by filling them with concentrated nitric acid for a day, rinsing with detergent, and then rinsing several times with highly purified water.

For tritium, samples should be collected in high-density plastic bottles holding between 0.5 and 1.0 l.

For carbon-14, according to specialized laboratory requirements, one procedure is to take one litre of water in high precision bottles or to dissolve about 2.5 g of precipitate into more than 100 l of water in case of low carbon content.

The principal problem encountered in preserving these samples is adsorption on the walls of the container or on suspended matter. To analyse the total radio-element quantities and to minimize adsorption, 2 ml of concentrated HCl per litre of sample, or nitric acid to one per cent concentration, are added.

Generally, to minimize analysis cost, it is advisable to analyse an annual composite sample by mixing aliquots from each monthly sample.

If a significant level of radioactivity over environmental levels is found, the samples making up the composite are analysed individually to locate the sample(s) that has (have) the higher than expected radioactivity level.

7.3.5 Field sampling equipment and techniques

7.3.5.1 Grab samplers

Grab samplers may be classified as those appropriate only for volatile constituents, such as for

dissolved gases and others for non-volatile constituents. Both discrete (surface or specific depth) and depth-integrating types of samplers are available. Both may be used to collect water for the determination of non-volatile constituents.

To obtain an approximate depth-integrated sample, an open sampling apparatus should be lowered to the bottom of the water body and raised to the surface at a constant rate so that the bottle is just filled on reaching the surface. A sampling iron can be used for this purpose: it is a device, sometimes made of iron, used to hold sample bottles. The sample bottles are placed in the sample iron and are secured by the neck holder. In some cases, sampling irons may have provision for additional weights to ensure a vertical drop in strong currents.

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

Discrete samplers are used to collect water samples at a specific depth. An appropriate sampler is lowered to the desired depth, activated and then retrieved. Van Dorn, Kemmerer and pump samplers are frequently used for this purpose:

- Van Dorn bottle – The Van Dorn bottle (Figure I.7.4) is designed for sampling at a depth of 2 m. Its horizontal configuration should be used when samples are taken at the bottom, at the sediment-water interface;
- Kemmerer sampler – It is one of the oldest types of messenger-operated vertical samplers. It is commonly used in water bodies with a

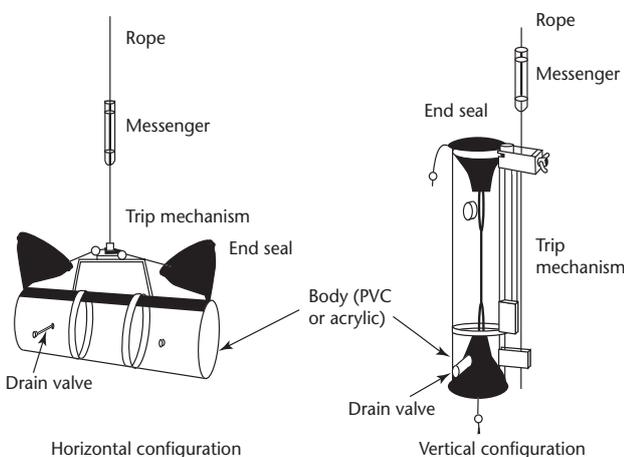


Figure I.7.4. Van Dorn bottle

depth of 1 m or greater. The Kemmerer sampler (Figure I.7.5) is available in volumes ranging from 0.5 to 8 l;

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

The Van Dorn samplers have an advantage over the Kemmerer bottle in that their lids do not lie in the path of the flow of water through the sampler, which can cause eddies and disturbance.

A multiple sampler (Figure I.7.6) permits the simultaneous collection of several samples of equal or different volumes at a site. Each sample is collected in an individual bottle. When the samples are of equal volume, information concerning the instantaneous variability between the replicate samples can be obtained. The sampler may be altered to accommodate different sizes and numbers of bottles according to the requirements of specific programmes. This may be done by changing cup

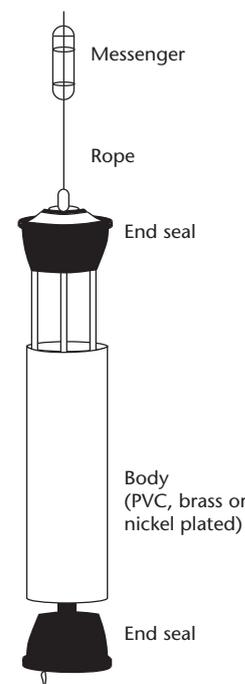


Figure I.7.5. Kemmerer sampler

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

7.3.5.2 Dissolved-oxygen sampler

A typical sampler for dissolved-oxygen concentration and Biochemical Oxygen Demand (BOD) is illustrated in Figure I.7.7. This sampler must be pulled up open, thus some mixture with the upper water layers is possible. If certain grab samplers are fitted with bottom drain tubes, they may be used by running the sample into the bottom of the analysis container. The samples should be collected in narrow-mouthed BOD bottles that have bevelled glass stoppers to avoid entrapment of air in the samples. Sampling of shallow streams is not advisable with this sampler. In this case, sample agitation (bubbling) should be minimized by gently tilting a BOD bottle downstream.

7.3.5.3 Automatic samplers

Automatic samplers range from elaborate instruments with flexible sampling programmes, which require external power and permanent housing, to simple, portable, self-contained devices, such as a submerged bottle with a rate of filling determined by a slow air bleed. These devices are often programmed to sample over a 24-hour period.

They reduce costly personnel requirements if frequent sampling is required. If the site has automatic flow-measurement capability, some automatic samplers can provide flow-proportional samples.

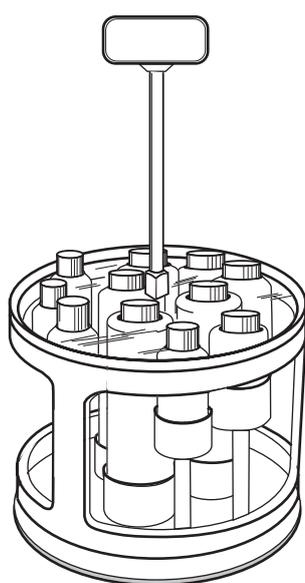


Figure I.7.6. Multiple sampler

Both composite- and individual-sample models are available.

7.3.5.4 Sampling procedures as influenced by station, location and season

In the field, the sampling situation determines which of several different sampling techniques is required. Some of the practical sampling considerations related to location and season of sampling are outlined below. Detailed procedures for sampling are given in the *Manual on Water Quality Monitoring: Planning and Implementation of Sampling and Field Testing* (WMO-No. 680).

Sampling from bridges is often preferred because of the ease of access and safety under most conditions of flow and weather. However, vehicular traffic is a potential hazard and should be considered.

Boats provide more flexibility and reduce the time of travel between sampling points. The sampling point must be identified by triangulation from landmarks, and here also the hazards of navigation, high flows and storms have to be considered (8.5). Aircraft, including helicopters, are expensive, but fast and flexible. Tests have shown that the disturbance of water under helicopters does not significantly affect even dissolved-oxygen water samples. Bank-side sampling should only be used when no alternative is possible. The sample should be taken in turbulent water or where the water is fast and deep. A sampling iron is often used when water samples are collected from shores, stream banks and wharves.

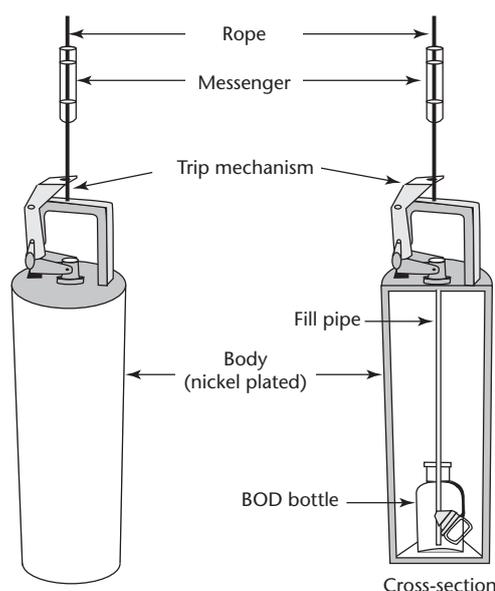


Figure I.7.7. Dissolved oxygen sampler

Sampling of ice and snow under winter conditions requires somewhat different techniques. The safety precautions outlined in 8.9 should be followed. Overlying snow should be removed from the ice surface to provide a suitable working area.

7.4 PREPARATION FOR FIELD TRIPS

7.4.1 General preparation

- (a) Obtain specific instructions on sampling procedures;
- (b) Prepare an itinerary according to the sampling schedule (also 2.4.3);
- (c) Prepare lists of required equipment and materials;
- (d) Ensure that all sample bottles have been cleaned in accordance with standard procedures;
- (e) Ensure that the laboratory has prepared the chemical reagents and standards needed for the trip;
- (f) Prepare a checklist (7.4.3 below).

7.4.2 Selection of sample volumes

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

- (a) When contact with air is to be avoided, the sample container should be completely filled;
- (b) When samples require vigorous shaking before taking aliquots for analysis, the container should not be completely filled;
- (c) Where both requirements must be met, the bottle should be completely filled, but pieces of clean, sterile inert solid such as beads should be added;
- (d) When the sample contains discrete particles, for example, undissolved materials, bacteria and algae, a volume of sample larger than usual may be needed to minimize errors.

7.4.3 Checklist prior to field trip

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

- (b) Replenish supplies of reagents for dissolved-oxygen determinations as well as reagents for chemical preservation;
- (c) Obtain fresh buffer solutions. The pH values for the buffers should be close to the values expected in the field;
- (d) Obtain KCl solution for pH probes;
- (e) Obtain road maps, station-location descriptions, field sampling sheets, sampling bottles, labels, samplers, preservation reagents, pipettes and equipment manuals;
- (f) Obtain writing materials, extra rope and a comprehensive toolbox;
- (g) Obtain electrical cables if the equipment has in-field charging capabilities;
- (h) Obtain ultrapure water (resistivity of 18.2 M Ω) and prepare clean beakers for pH, blanks and buffer measurements;
- (i) If field filtering is required, obtain filtering gauge and perfectly clean filters;
- (j) If microbiological sampling is to be done, obtain sterile bottles and ice chests. Ice chests are recommended for all sample storage;
- (k) Check the contents of the emergency first-aid kit.

7.5 FIELD MEASUREMENTS

7.5.1 Automatic monitoring

The use of one particular instrument requires that the water be pumped and that the measurements be made on shore. Other instruments use probes immersed in the water body and the measurements are made in situ. A more recent type is a self-contained, battery-operated instrument that can be operated as much as 300 m below the surface.

Currently, automatically measured parameters include pH, temperature, specific conductance, turbidity, dissolved oxygen, chloride, redox potential, stage, sunlight intensity and ultraviolet absorbance.

7.5.2 Field-measured parameters

Conductivity, pH, dissolved oxygen, temperature, turbidity, colour and transparency can change on storage of a sample, and should therefore be measured in the field as soon as possible after the sample collection.

The sample collector should also look out for any unusual features of the water body being sampled or any changes since previous sampling periods.

These qualitative observations might include unusual colour, odour, surface films and floating objects. Any special environmental conditions, such as rainfall, heavy winds, storm runoff, or ice break-up, should be noted.

7.5.2.1 pH measurement

In unpolluted natural waters, the pH is largely controlled by a balance between carbon dioxide, carbonate and bicarbonate ions. The concentration of carbon dioxide can be altered by exchanges at the air-water interface and by photosynthesis and decay processes. Changes in the pH are caused by acid rain, industrial wastes, mine drainage or leaching of minerals. The pH is an important criterion of the quality of water since it affects the viability of aquatic life and many uses of the water. Being temperature dependent, pH measurement must be strictly associated to the sample temperature at the sampling moment. Optimally, the pH is determined in situ, using a digital meter with a combined electrode permitting simultaneous temperature measurement.

The pH may also be determined colourimetrically by using pH indicators and buffer standards for visual or colourimeter comparison. This method is generally less accurate and is limited to waters with a low content of coloured substances and with little turbidity. In the field, the instrument should be recalibrated before each reading with appropriate buffer solutions and according to the instructions in the operating manual. The temperature of the buffer solutions and electrodes can be adjusted by submerging the bottles of buffer and electrodes in the water sample.

Extreme care must be taken to prevent the water from entering the buffer bottles. If the electrodes have not been used recently or have been allowed to dry for several days, they may require 10 to 20 minutes to stabilize. The meter should be protected from extreme temperature changes during measurement as these affect the stability of the electronic system and measurement accuracy.

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

If the pH meter shows a drift and the probe has been stored and correctly conditioned, the probe itself may require topping up with additional 3 mol/l KCl solution.

If there is persistent drifting, the electrode should be soaked in ammonium hydroxide. As with any piece of equipment, the probe should be protected from sludge, frost and rough handling at all times.

7.5.2.2 Conductivity measurement

Conductivity is an indicator of salt, acid and base non-organic concentration of ions dissolved in water. The relationship between conductivity and the concentration of dissolved solids is usually linear for most natural waters.

In situ conductivity measurement is preferable. Being temperature dependent, the conductivity meter should give a value for either a reference temperature (generally 20°C or 25°C) or the sample temperature, which must be recorded simultaneously. This is important to calculate and compare sample conductivity at a given reference time.

Before any measurements are taken, the sample containers and probe should be rinsed several times with the water sample. The water sample in which the pH was measured should not be used to measure the specific conductance, as KCl diffuses from the pH electrode.

The instrument should be recalibrated in the field before each reading. The KCl standard solutions, with the specific conductance closest to the values expected in the field, should be used. Equipment for measuring conductivity must receive the same care and maintenance required by all sensitive instruments. Accurate readings require that the meter be protected from sludge, shocks and frost.

The accuracy of measurement will depend upon the type of instrument, the way in which it has been calibrated and the actual conductivity value of the sample. If care is taken in selecting and calibrating the instrument, an uncertainty of ± 5 per cent of full scale should be possible over a temperature range of 0°C to 40°C with automatic temperature compensation.

7.5.2.3 Dissolved-oxygen measurement

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

There are two methods for dissolved-oxygen measurement: the first is in situ by using a polarographic or potentiometric (oxymeter) probe. The second is by using a Winckler chemical analysis. In the Winckler method the addition of reagents (Mn^{++} solution and basic iodure solution) in the sample at the moment of its grab permits its oxygen fixation. Analysis will then be performed in the laboratory on a sample preserved by light. There is also a field method based on the same principle, namely, the Hach method using pre-dosed reagents.

As concentrations may show large changes during the day, in situ time measurements are advisable.

For the chemical method, three water samples should be collect with the dissolved-oxygen sampler (7.3.5.2). Measurement of the dissolved-oxygen concentration of the samples is done by using a dissolved-oxygen meter or a Winkler chemical analysis. The recorded dissolved-oxygen value should be the average of at least two readings that are within 0.5 mg/l of each other.

In the electrochemical methods the probe responds to activity of oxygen, not concentration. Freshwater saturated with oxygen gives the same reading as saltwater saturated with oxygen at the same pressure and temperature, although the solubility of oxygen in saltwater is less. Thus, salinity, temperature and atmospheric pressure should be considered when sampling.

In the Winkler chemical method there are interferences when samples are highly coloured or turbid, or contain readily oxidizable or other interfering substances. This method is largely used in laboratories for its accuracy in measuring dissolved-oxygen concentration.

The probe method can be used when results are within ± 0.5 to 1.0 mg l^{-1} of the true value and are sufficient for the purposes of the study. If the sample has a relatively high dissolved-oxygen concentration, the accuracy is adequate, but in some cases the dissolved-oxygen concentration is shown to be very low; then it is important to use a new and carefully calibrated probe.

7.5.2.4 Temperature measurement

Temperature measurements may be taken with a great variety of thermometers. These include alcohol-toluene, mercury-filled, bimetallic strip or electrical thermometers. The last category includes thermocouples and less portable varieties, such as thermistors, quartz and resistance thermometers.

Some meters, such as those used to measure dissolved oxygen, pH, Eh and specific conductance, have temperature-measuring capabilities.

Before its use, the thermometer is rinsed with a portion of the water sample. The thermometer is immersed in the sample for approximately one minute or until the reading stabilizes. The thermometer must not be placed in any of the sample bottles being shipped to the laboratory. The value should be recorded in degrees Celsius on the field sheet.

In general, the accuracy of water-temperature measurements of 0.1°C will not be exceeded. However, in many circumstances, an uncertainty of 0.5°C can be tolerated and there are many instances where statistical temperature data are quoted to the nearest 1°C . Thus, it is important to specify the operational requirements so that the most suitable thermometer can be selected.

7.5.2.5 Turbidity measurement

Turbidity is an optical measure of suspended sediment such as clay, silt, organic matter, plankton and microscopic organisms in a water sample. Turbidity virtually affects all uses of water and adds to the cost of water treatment. Whenever possible, turbidity should be measured in situ. Turbidity can be measured by visual methods (in Jackson turbidity units or JTU) or nephelometric methods (in nephelometric turbidity units or NTU). Using the Jackson Candle Turbidimeter, the distance through the suspension at which the outline of the standard candle becomes indistinct is compared with standard suspensions.

Nephelometric methods are preferred because of their greater precision, sensitivity and application over a wide turbidity range. They measure light scattering by the suspended particles. However, instruments of different design may give different results for the same sample. Colour in the sample as well as variations in the light source can cause errors. Both problems can be minimized by using an instrument that simultaneously measures the scattered and transmitted light, with both scattered and transmitted beams traversing the same path length.

To operate the turbidity meter, calibration curves for each range of the instrument should be prepared by using appropriate standards. At least one standard in each range to be used should be tested, making sure that the turbidity meter gives stable readings in all sensitivity ranges. The sample should

be shaken vigorously before analysis. Readings should always be made after the same time period following the homogenizing of the sample (for example, 10 seconds) to ensure uniform data. It is important to pour off the sample quickly and to measure the turbidity of the sample in triplicate.

The performance of a given turbidimeter will depend on the frequency of calibration with a formazin standard and the way that the sample is presented to the instrument. As a general guide, nephelometers used under laboratory conditions should be accurate to within ± 1 formazin turbidity unit (FTU) in the range 0 to 10 FTU, and to ± 5 FTU in the range 0 to 100 FTU at 95 per cent confidence level. The uncertainty of absorption meters will vary considerably, but should give at least ± 10 per cent of full scale for any given range of turbidity.

In practice, the performance of turbidimeters depends, to a large extent, on their optical configuration and, in the case of instruments that accept a flowing sample and give a continuous reading, on their ability to withstand fouling of optical surfaces by algal growth and sediment build-up, which would otherwise result in calibration drift and insensitivity.

7.5.2.6 Colour measurement

The true colour is observed after filtration or centrifugation. Colour results from the presence of metallic ions, humus and peat materials, plankton and industrial wastes. Colour is important for potable water supplies, washing or processing, or recreational purposes.

The hues ordinarily present in natural waters can be matched by mixtures of chloroplatinic acid and cobaltous chloride hexahydrate. Because this method is not convenient for field use, colour may be obtained by visually comparing standard glass colour discs with tubes filled with the sample.

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

7.5.2.7 Transparency measurement

Transparency of water is determined by its colour and turbidity. A measure of transparency can be obtained from depth in metres at which a 20- to 30-cm diameter disc – called a Secchi disc and

usually painted in black and white quadrants – disappears when lowered slowly and vertically into the water. Standard type on white paper is sometimes used instead of the disc. The measurement is usually made in lakes and other deep-water bodies and is useful in assessing biological conditions.

7.5.2.8 General summary of field procedures

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

- (a) Calibrate meters;
- (b) Standardize sodium thiosulphate when using Winkler analysis for dissolved oxygen;
- (c) Run field or in situ measurements for pH, conductivity, dissolved oxygen, temperature and turbidity;
- (d) Rinse all bottles with sampled water except for those that contain preservatives or those used for dissolved oxygen and bacteria analyses;
- (e) Collect and preserve samples according to the instruction manual;
- (f) Complete field sheet accurately according to the instruction manual;
- (g) Put bottles in appropriate shipping containers;
- (h) Label boxes and complete field sheets with all required information.

7.6 BIOMONITORING AND SAMPLING FOR BIOLOGICAL ANALYSIS

Environmental monitoring is mainly based on physical-chemical analysis techniques to evaluate the concentration of pollutants, sediments and living organisms in water. The major inconvenience of these methods may be their lack of information about the actual chemical impact on living organisms. Furthermore, certain groups of toxic pollutants are not detectable. This occurs because:

- (a) These molecules influence living organisms at a concentration below detection limits;
- (b) There may be completely new molecules;
- (c) The evolution of these toxic pollutants in the environment is little known (in this case the problem is to identify the by-products to be analysed).

Thus, the great variety of potential pollutants in the monitoring media makes these methods highly costly. Lastly, if chemical analyses inform about the existence or non-existence of a pollutant in different ecosystem compartments (water, soil, sediments or organisms), they are in any case insufficient to

predict the actual impact of the toxic substances on the organism, since the numerous interactions between pollutants and pollutants/organism have not been considered. Biological analyses can integrate the interactions between all the present pollutants and organisms and can diagnose the pollution impact on the organisms living in the ecosystem more realistically.

Biomonitoring is the study of the living response to all the degrees of biological organization (molecular, biochemical, cellular, physiological, histological, morphological and ecological) to pollutants. This definition (McCarthy and Shugart, 1990) identifies the following levels of observations:

- (a) At the intra-individual level a biomarker is the biological response detected at a level below the individual to a substance present in the environmental product (van Gestel and van Brummelen, 1996). This response measured in an organism or in its products shows a change in a normal state, for example, the modification of an enzymatic activity owing to a defence process in the organism. Biomarkers are also specific molecular, biochemical, physiological, histological and morphological changes in animal and vegetal populations observed after exposure to pollutants;
- (b) At the level of individuals or organisms a bio-indicator is performed by measuring the vital functions of a biological entity which, owing to its ecological specificity, reacts to a pollutant with a relevant specific modification of its vital functions (Kirschbaum and Wirth, 1997), for example, an alteration in the growth of a microinvertebrate organism;
- (c) At the level of populations and settlements, the hydrobiological analysis obtains integrative data on global water quality. There are biological indexes permitting the study of all or parts of the species settled in an ecosystem and the variations of their composition and structure owing to an anthropic factor. It is thus possible to define quality classes by the normalized inventory of certain species. For example, the Environmental Biological Index uses macroinvertebrate fauna as an environmental compartment integrator; a standardized sampling considering different types of settling habitats shows the ecosystem quality by the presence or absence of faunistic indicator groups.

In the current phase of biological monitoring, the studies using biomarkers concern the research of new methods to evaluate the health of organisms and practical applications to a larger amount of improved techniques of pollution monitoring.

Routine biomarker methods are still limited, but current studies show that it is already possible to detect polluted areas considering the health of organisms living there. The methods based on the studies at the organism or population level are used in biomonitoring network. Microbiological and macrobiota sampling will soon be developed.

Furthermore, there are also methods concerning the global evaluation of the environmental river self-epuration capacity. BOD, developed in this chapter, is the most widely used method.

7.6.1 Microbiological analysis

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

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

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

Whenever possible, water samples should be analysed immediately after collection. If immediate processing is impossible, then samples should be stored in the dark, in melting ice. Storage under these conditions minimizes multiplication and die-off problems up to 30 hours after collection. Samples should never be frozen. If samples are suspected of containing concentrations greater than 0.01 mg l⁻¹ of heavy metals, such as copper, nickel or zinc, their bacteriostatic or bactericidal effects should be minimized by the addition of 0.3 ml of a 15 per cent solution for each 125 ml of sample of ethylene

diamine tetra-acetic acid (EDTA) (Moser and Huijbregtse, 1976). Residual chlorine should be destroyed by the addition of 0.1 ml of a 10 per cent solution of sodium thiosulfate for each 125 ml of sample.

7.6.2 **Macrobiota**

There are several categories of multicellular species that may be monitored for a number of different reasons. Fish, as the top of the aquatic food chain, are indicative of a variety of water quality conditions, dependent on their type and age. Benthic macroinvertebrates (organisms living on or near the bottom that are retained by a standard sieve) are indicators of recent pollution events because of their low mobility and sensitivity to stress. Periphyton are sessile plants, growing attached to surfaces, and those that grow in the mat attached to it are some of the primary producers of aquatic organic matter, particularly in shallow areas. Macrophytes are large plants, often rooted, that cover large areas in shallow water and may interfere with both navigation and recreational uses of a water body. Plankton are small free-floating plants and animals. Phytoplankton are primarily algae whose growth is an indirect measure of, among other things, the concentration of nutrient chemical constituents. Zooplankton are found at all depths in both lentic and flowing waters.

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

Fish can be collected actively, with seines, trawls, electro-fishing, chemicals, and hook and line, or passively, with gill nets, trammel nets, hoop nets and traps. Macroinvertebrates may be sampled qualitatively by many methods, depending on their habitats and other parameters. In addition to nets, two methods are multiple-plate samplers and basket samplers. These are left suspended in place by floats for periods of four to eight weeks, and then are carefully raised to the surface with a net underneath for dislodgement of the specimens.

Plankton can be collected by using the water samplers described above in 7.3. There are also specially designed samplers, such as the Juday plankton trap, which encloses at least 5 l of sample at the desired depth and filters out the plankton. It is rather expensive and awkward to handle from a

boat. Zooplankton require large samples, and a metered nylon net can be employed. Periphyton can be sampled by exposing anchored or floating slides at the site for at least two weeks.

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

It is recommended that a suitable stain such as rose bengal be added before any fixatives. At a later date, the preserved animals can be picked out by personnel with less biological training because the colour causes them to stand out against the background. Tables recommending methods for the preservation of specimens of macrobiota are included in Table I.7.1. Some practitioners prefer the use of lugol solution rather than formaldehyde for periphyton and planktons.

7.6.3 **Biochemical oxygen demand**

The discharge of polluting organic matter into a water body instigates a natural purifying action through the process of biochemical oxidation. Biochemical oxidation is a microbial process that utilizes the polluting substances as a source of carbon, while consuming dissolved oxygen in the water for respiration. The rate of purification depends on many conditions, including the temperature and the nature of the organic matter. The amount of dissolved oxygen consumed by a certain volume of a sample of water for the process of biochemical oxidation during a period of five days at 20°C has been established as a method of measuring the quality of the sample, and is known as the biochemical oxygen demand test or BOD. Oxidation is by no means complete in five days and for some purposes longer periods of incubation may be used. The incubation period may be indicated by a suffix, for example, BOD₅ or BOD₂₀, and the results are expressed as mg of oxygen per litre of sample.

BOD is defined as the total amount of oxygen required by micro-organisms to oxidize decomposable organic material. The rate of biochemical oxidation is proportional to the remaining amount of unoxidized organic material. Thus, the BOD test is used to estimate the amount and rate of de-oxygenation that would occur in a watercourse or lake into which organic material is discharged. However, the predictions of the effects of such discharge are more complicated and may involve many other factors not involved in the

Table I.7.1. Techniques generally suitable for the preservation of samples

Biological analysis. The biological parameters to be determined are generally numerous and may sometimes vary from one biological species to another. For this reason, it is impossible to draw up an exhaustive checklist of all the precautions that should be taken to preserve samples for this type of analysis. The information below, therefore, only relates to certain parameters generally studied for various animal or vegetal groups. It should be noted that before carrying out any detailed study, it is essential to choose the parameters of interest.

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

determination of BOD. For example, suspended organic material can be deposited onto a stream bed in a slow moving stream just downstream from the source of discharge, where it may have a considerable effect on the local dissolved oxygen content. The presence of benthos, rooted plants and planktonic algae also influence the dissolved oxygen regime on a daily basis.

Serious complications in the BOD test can also occur as a result of the presence of nitrifying bacteria that will oxidize ammonia and organic nitrogen compounds to nitrite and nitrate.

Industrial effluents may also present problems because of potentially high concentrations of pollutants, which may suppress biochemical oxidation in the receiving water under natural conditions. In these circumstances, the sample may have to be diluted with pure water and "seeded" with sewage effluent that contains the active micro-organisms required to start the biochemical oxidation process. Special sample preparation techniques may have to be developed to suit the sample to be tested.

7.6.3.1 Methods of measurement

Several methods have been developed for the measurement of BOD. The one most commonly used is the dilution method, but manometric techniques, while still mainly used for research, may have advantages in some circumstances, for example the control of sewage effluent. Ideally, the sample should be analysed immediately after it has been taken from the effluent, watercourse or lake. If this is not possible, the sample must be kept at a temperature of 3° to 4°C to slow down the biochemical oxidation processes. If BOD of a sample is estimated to be greater than about 7 mg l⁻¹, appropriate dilution and/or seeding of the sample are necessary. An excess of dissolved oxygen must be present in the sample at the end of the test period for the BOD value to be valid.

BOD is calculated from the measurement of volumetric dilution of the sample and the difference between the dissolved-oxygen concentrations of the sample (7.5.2.3) before and after a five-day incubation period. During this period, a temperature of 20°C should be maintained, and atmospheric oxygen should be excluded from the sample, which should be kept in the dark to minimize the effect of photosynthetic action of green plants. However, the oxygen consumed by the respiration of algae is included in the test. For samples in which nitrification may occur during the test, allylthiourea (ATU) is added to the sample prior to incubation. In this

case, the resulting apparent BOD is indicative of carbonaceous polluting matter only. The rate of biochemical oxidation can be estimated on the basis of incubating five identical BOD samples and measuring the dissolved oxygen in the first bottle on day 1, the second bottle on day 2, the third bottle on day 3, the fourth bottle on day 4, and the fifth on day 5. The logarithm of BOD should plot against time as a straight line. Extrapolation of the straight line to ultimate time results directly in an estimate of the ultimate carbonaceous BOD, which is a measure of the total amount of oxygen required to oxidize decomposable organic material.

7.6.3.2 Accuracy of measurement

The BOD test is rather inexact. If statistical significance is to be made of the results, several samples must be diluted and incubated (and seeded, if necessary) under identical conditions, and an average BOD calculated. To achieve higher accuracies, it has been suggested that the manometric test should replace the dilution method. It should be borne in mind that the two methods are not always directly comparable (Montgomery, 1967). The manometric method can give an indication of the biological oxidizability of a sample in a period shorter than five days.

7.7 FIELD FILTRATION AND PRESERVATION PROCEDURES

7.7.1 Filtration

Sample filtration is recommended for separation of dissolved from particulate matter. Centrifuging requires more equipment, settling requires more time, and both cannot be easily calibrated and may increase contamination hazards. The filtration should be carried out in the field during or immediately after sample collection and must be followed by appropriate sample preservation procedures.

The total concentrations of metals may be determined by using a second unfiltered sample collected at the same time. This sample will undergo an acid digestion in the laboratory permitting particulate dissolution.

Samples requiring analysis for organic constituents are filtered immediately after collection by using a glass fibre filter or a metal membrane. The filtrate may be analysed for dissolved organic constituents, and the filtrate supporting the particulate fraction is available for particulate-organic analysis.

The adsorption of dissolved substances on the filter material can be a serious problem.

The best materials to be used for mineral substances are organic filters (polycarbonate, cellulose acetate or Teflon) and glass fibre filters for organic compounds.

The filter and filtration apparatus require laboratory pretreatment and should be rinsed with a portion of the collected sample before the filtrate is collected, by discarding the first 150 to 200 ml of filtrate. Either an electrical or a manual pump must be used to create the vacuum in the filtration apparatus. If an electrical pump is employed, filtration will require access to electrical services or the operation of a mobile power unit. Vacuum may cause changes in the pH due to loss of carbon dioxide, and result in the precipitation of some metals. For this reason and to reduce losses due to adsorption on the walls of the container, metal samples are often acidified.

7.7.2 Preservation techniques

Between the time that a sample is collected in the field and analysed in the laboratory, physical, chemical and biochemical changes may take place. Consequently, this time should be minimized as far as practicable, or sample preservation must be practised.

For several determinants, preservation is not possible and the measurements must be made in the field. Even when the constituent is reasonably stable, it is usually necessary to preserve the samples. This is done by various procedures, such as keeping the samples in the dark, adding chemical preservatives, lowering the temperature to retard reactions, freezing samples, extracting them with different solvents, or using field column chromatography.

7.7.2.1 Containers

The use of appropriate containers is very important in preserving the integrity of the sample especially when constituent concentration is low. Specifications are generally provided by laboratories. Many publications contain recommendations on which type of container should be used for particular cases (Clark and Fritz, 1997).

The major types of container materials are plastic and glass. Borosilicate glass is inert to most materials and is recommended when collecting samples to be analysed for organic compounds. Polyethylene is inexpensive and adsorbs fewer metal ions. It is

used for samples that will be analysed for inorganic constituents. Polyethylene containers should not be used to trace organic samples, such as pesticides and some volatile substances that can diffuse through plastic walls. Light-sensitive samples require opaque or non-actinic glass containers. Narrow-mouthed bottles with pointed glass stoppers are used for dissolved gases. Containers for microbiological samples must withstand sterilization.

For tracking elements, only low- or high-density polyethylene (LDPE and HDPE) should be used. Today disposable containers are available. Before use, they must be pre-decontaminated. They must be kept, for at least 24 hours, in an ultrapure 10 per cent solution of HNO₃, then rinsed in ultrapure (18.2 MΩ) water and preserved in polyethylene bags until their field use (Pearce, 1991).

Bottle caps are a potential source of problems. Glass stoppers may seize up, particularly with alkaline samples. Cap liners other than Teflon may introduce contaminants or absorb trace samples. The smaller the concentrations in the sample of the species to be determined, the more important these aspects become.

7.7.2.2 Chemical addition

This method is used for most dissolved metals and phenoxy acid herbicides. Some samples for biological analysis also require chemical preservation.

As a general rule, it is preferable to use relatively concentrated solutions of preserving agents. Corrections for the dilution of the sample by the small volume of preserving agent will then be small or negligible.

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

7.7.2.3 Freezing

When analysis is impossible in a reasonable period of time, freezing is recommended for the analysis of main anions, that is, chloride, sulfate and nitrates. However, this is not a general preservation technique because it can cause physical-chemical changes, for example, the formation of precipitates

and loss of dissolved gases that might affect the sample composition. In addition, solid components of the sample change with freezing and thawing, and a return to equilibrium followed by high-speed homogenization may be necessary before any analysis can be run. Water samples should never be frozen in glass bottles.

7.7.2.4 Refrigeration

Refrigeration at 4°C is a common preservation technique. In some cases it may affect the solubility of some constituents and cause them to precipitate. Refrigeration is often used in conjunction with chemical addition.

7.7.2.5 Practical aspects of preservation

An important aspect of preservation is adherence to a consistent routine to ensure that all samples requiring preservation receive immediate treatment. This is particularly important when a chemical preservative is added, as such additions may not produce an easily detectable change in the appearance of the sample. It may be advisable to mark or flag each preserved sample to ensure that none is forgotten or treated more than once.

Safe and accurate field addition of chemical preservatives also requires special precautions. Pre-calibrated and automatic pipettes ensure accurate field addition, as well as eliminating the safety hazard of pipetting acids by mouth. It is often convenient to add the preservative in the laboratory before the sample containers are taken to the field. Another alternative is to use colour-coded or labelled, sealed vials containing pre-measured preserving agents. Although more expensive, this method has the advantage of simplifying the field procedure and reducing the possibility of error and contamination.

7.8 REMOTE-SENSING AND SURFACE-QUALITY WATER

Teledetection permits the characterization of the spatial and temporal changes obtainable by other methods. However, it is not accurate in terms of local ground measures. Furthermore, it should be implemented with satellite image readings to interpret images in water quality and soil measurement terms. Remote-sensing application for suspended matter evaluation is discussed earlier in Chapter 5. More detailed information is provided on applications such as vegetation characterization, salinity and water temperature.

Satellites can be divided into two groups, depending on their energy source. Passive satellites need sunlight to capture object images on the Earth's surface. They generally operate in the visible and infra-red domain of EMS and supply the so-called "optic" images. Active satellites have their own energy source. They operate in the microwave domain of EMS and supply the so-called "radar" images.

Furthermore, satellite images can be differentiated according to four basic criteria:

- Range gating corresponding to pixel size. There are small sized (1 km or more, such as NOAA, SPOT vegetation or meteorological images), medium (20 m or more, such as Landsat MSS and TM or SPOT 1 to SPOT 4 images) or outsized range gating (10 m or less, such as in SPOT 5 or IKONOS);
- Spectrum gating corresponding to the wavelength in which images have been taken;
- Passage frequency of the satellite;
- Radiometric gating corresponding to the detector ability to catch the received radiant emittance.

The choice of satellite image is determined by many factors. First, the size of the studied area should be considered. It will not be possible to study a 20-km² marsh with a NOAA image based on low-range gating. Spectrum gating will be chosen according to the programme objectives. For example, an optical image is advisable to study water turbidity. Finally, the equalization between the time variables of the studied phenomenon and the satellite passage frequency over the studied area are required.

7.8.1 Water-quality study in the visible and infra-red domain

From the visible domain to the near IR, the radiometric response of pure water is like that of a black body absorbing the whole incident radiation. This well-known property is used to easily locate the presence of water on a satellite image.

Different factors, such as water salinity and turbidity, soil composition or vegetation presence, alter water radiometric response, which can therefore be used to inversely characterize these factors.

The best positive correlation between radiometric response and turbidity is in the green range (Bonn, 1993). This will indirectly provide indications on salinity. In fact, salinity and turbidity are generally inversely correlated. When salinity arises, it results in flocculation followed by sedimentation of

suspended matter and the lowering of the turbidity of the water.

Water radiometric response in the near IR may be perturbed by suspended matter and also by a shallow bottom (Chuvienco, 2000). For shallow waters, absorption is low and reflectance is large (due to high bottom reflectance). However this effect is complex, as soil radiometric behaviour is influenced by its chemical composition, texture, structure and humidity. Therefore, a clay soil, for example, will have quite a low reflectance, compared with a sand soil. The soil reflectance range is very large between light soils (sand, limestone or even gypsum), highly reflecting solar radiation, while dark soils (clay, rich in organic matter) absorb nearly the full amount of radiation (Bonn and Rochon, 1993).

In the radiometric domain, vegetation reflectance is reduced in the visible spectrum, but is very high in the near IR. As regards vegetation, low response in the visible range results from strong absorption of chlorophyll, especially in the red range, whereas the high response in the near IR is due to the internal cell structure of leaves. Thus, to study the presence of vegetation in shallow waters it is advisable to use optical images (Shutko, 1986, 1990; Gross and others, 1987).

The assessment of chlorophyll quantity in the ocean and estuaries has been carried out from different images, especially Coastal Zone Colour Scanner (CZCS) or AVHRR images (WMO, 1993). This assessment is limited to cases where suspended matter concentration is low enough not to mask the reflectance corresponding to that of chlorophyll (Ritchie and others, 1992). Macrophytes and aquatic vegetation can be generally studied following these basic principles (Ackleson and Klemas, 1987).

7.8.2 **Water-quality study in the microwave domain**

In waters, the microwave domain permits a certain penetration. Superficially it is possible to differentiate a rough from a smooth surface by a lambertian or symmetric response, respectively. For example, a radar image may be used if roughness is due to the presence of waves. These applications have also been exploited to detect surface anomalies such as those due to indiscriminate oil discharge. It has proved, both theoretically and practically, that microwave radiometry can be used to study salinity and general water mineralization (Shutko, 1985, 1986, 1987). In fact, microwave emissivity is sensitive to water conductivity variations, and thus to water composition.

Teledetection in the thermal IR domains and microwave radiation can be used to evaluate surface water temperature (examples in Engman and Gurney, 1991). Microwave radiation is less sensitive to atmospheric conditions and thus it will be more often used, but its resolution is rough compared with that of the IR (Shutko, 1985, 1986).

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